THE CHEMICAL BEHAVIOUR OF SILVER IN THE PRESSURE OXIDATION OF COMPLEX SULPHIDE ORES AND CONCENTRATES

By

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ABSTRACT

As supplies of high-grade base metal concentrates diminish, the treatment of complex sulphide materials, which often contain a significant fraction of silver must be considered. Acid pressure oxidation is a promising process for these materials and silver recovery will play a major role in the economy of the process. However, in acid pressure oxidation processing, silver is incorporated into the jarosite specie and the cyanidation of the resulting residue yields very low recovery. Efforts to recover silver from complex sulphide concentrates therefore require an understanding of the chemical behaviour of silver in the pressure oxidation process. In the present work, pressure oxidation of various complex sulphides was investigated in the temperature range 110-150°C to shed new light on the deportment of silver from the source minerals to the residues with subsequent recovery by cyanidation.

Silver sulphide reacts in the autoclave under the conditions used for the oxidation of complex sulphide and silver ion is released into the solution. Once the silver is released, the sulphide ion (S^{2-}) at the surface of the mineral is oxidised to elemental sulphur by ferric ions. The rate-controlling step is the oxidation of the sulphide ions at the surface of the mineral and in the absence of ferric, the overall reaction is slow. The rate of reaction increases with increasing temperature and the concentration of ferric ions. However, the rate of reaction decreases with increasing silver sulfate concentration. The kinetics is controlled by chemical reaction with activation energy of 72.6 kJ/mol.

The aqueous silver released by the trace silver-bearing minerals can co-precipitate with iron and lead sulphate as a complex jarosite species. In this work, the precipitation kinetics of aqueous silver and ferric in the presence of a lead sulphate suspension were conducted at a temperature range of 110-150°C and under conditions that were relevant to zinc pressure oxidation. The major collector of silver on the oxidation residue was confirmed to be the plumbojarosite specie. The kinetics of the precipitation increases with increasing temperature and concentration of initial ferric sulphate and lead sulphate suspension. The initial acid level had a pronounced negative effect on the rate of formation of jarosite by reducing the rate of hydrolysis of ferric ion. The effect of temperature and seeding on the kinetics indicate that the reaction rate is controlled by a chemical reaction step, which is thought to be occurring at the surface of the
jarosite crystals with activation energy of 114.3 kJ/mol.

Silver precipitation is fast and finished before iron precipitation. The precipitation of iron continues. This usually leads to the zoning of the silver-rich jarosite in the core of the jarosite structures. During cyanidation of such a residue, only the silver ion in the outer crystal planes of the jarosite structures is thought to be accessible to the free cyanide ions in the pulp leading to low extraction of silver.

In this study, it was found that silver could also react with sulphur to form silver sulphide in an acid media containing ferrous and ferric sulphate. Under deoxygenated condition, the reaction apparently involves the reduction of aqueous silver to silvery white flakes (metallic silver) and the subsequent reaction of metallic silver with sulphur. The reduction of aqueous silver is very rapid under highly reducing conditions. The reaction of metallic silver with sulphur is believed to be the rate-determining step because of the positive effect of sulphur on the rate of reaction. Under the pressure oxidation condition, the presence of oxygen minimises the silver sulphide formation by oxidising ferrous to ferric. Also, any silver sulphide formed is oxidised to aqueous silver. Silver precipitation as silver sulphide, therefore does not occur under the pressure oxidation condition.

The addition of soluble iodide ion to low to medium temperature autoclave oxidation experiments confirmed that silver could be precipitated as silver iodide in the autoclave discharge residue. The reaction of aqueous silver ion and iodide to form silver iodide (AgI) is therefore an effective way of deporting silver into a recoverable form. Although silver iodide has a low solubility product, silver extraction by cyanidation from the autoclave precipitate which is formed at high temperature is not complete, which suggests that some silver ions are still captured by the jarosite phase during iron precipitation. The deportment of some silver ions to the jarosite phase is promoted by the decrease in stability of silver iodide at high temperature and the increase in the stability of jarosite specie at high temperature. Therefore, in the presence of iodide and under the optimal conditions that favour jarosite precipitation, some aqueous silver may react preferentially with hydrolysed ferric and sulphate to form jarosite. The resulting jarosite specie will impact the ability to recover silver from oxidation residues.

Three different complex sulphides were oxidised in the temperature range 110-150°C, and potassium iodide was added to the initial solution to promote AgI in the autoclave residue. High
zinc extraction into solution was achieved. The resulting residues were subjected to cyanidation for silver recovery. High recovery of silver (up to 98%) was achieved because its deportment into the lead-hydronium jarosite during the pressure oxidation was minimised, while its deportment into the cyanide-soluble silver iodide was promoted. Silver recovery decreased slightly at high temperatures (140 and 150°C) because of the enhanced stability and kinetics of lead-hydronium jarosite formation, but this could be overcome by increasing acidity and iodide concentration of the autoclave slurry.

It is believed that it is now possible to control the chemical behaviour of silver in the pressure oxidation of complex sulphide ores and concentrates at 110-150°C. Addition of small amounts of soluble iodide combined with careful control of temperature, oxidation kinetics and solution composition can ensure that most of the silver in the feed material forms silver iodide in the autoclave residue. Silver iodide in the residue can be quickly and completely leached in weak cyanide solution or perhaps in alternate silver lixiviant.
# TABLE OF CONTENTS

ABSTRACT ...................................................................................................................... ii
TABLE OF CONTENTS .................................................................................................. v
LIST OF TABLES .......................................................................................................... ix
LIST OF FIGURES ...................................................................................................... xi
LIST OF SYMBOLS ..................................................................................................... xvi
CHAPTER 1: INTRODUCTION ..................................................................................... 1
CHAPTER 2: LITERATURE REVIEW ........................................................................... 5
  2.1 Mineralogy of Silver and Cyanidation of Silver minerals ........................................ 6
  2.2 Significant of Silver to Zinc .................................................................................... 7
  2.3 Treatment of Complex Sulphides ........................................................................... 8
  2.4 Zinc and Silver Recoveries by Pressure Oxidation .................................................. 11
    2.4.1 Process Chemistry ......................................................................................... 11
    2.4.2 Silver Extraction in the Zinc Autoclave .......................................................... 15
    2.4.3 Silver Extraction by Cyanidation of Oxidised Residue ...................................... 15
    2.4.4 Modification of Oxidation conditions of Autoclave ........................................... 16
  2.5 Mechanism of Iron Precipitation and Phase Equilibria in Sulphate Media .............. 16
    2.5.1 Mechanism of Precipitation .......................................................................... 17
    2.5.2 Phase Equilibria ............................................................................................. 20
    2.5.3 Characteristics of Jarosite Species ................................................................... 23
  2.6 Relative Substitution of Silver in Jarosite Species .................................................. 25
    2.6.1 Effect of Silver Concentration ....................................................................... 28
    2.6.2 Effect of Lead Sulphate Suspense .................................................................. 29
    2.6.3 Simultaneous Incorporation of Copper and Zinc ............................................. 29
  2.7 Prevention of Lead Jarosite Formation ................................................................... 32
    2.7.1 Use of High Acidity ....................................................................................... 32
    2.7.2 Use of High Temperature ............................................................................... 33
    2.7.3 Use of Alkali .................................................................................................. 34
  2.8 Deportment of Silver during Acid Pressure Oxidation .......................................... 35
    2.8.1 Silver-Sulphur-Water System ....................................................................... 35
    2.8.2 Dissolution of Silver Sulphide ....................................................................... 39
    2.8.3 Mechanism of Acanthite Dissolution .............................................................. 41
    2.8.4 Other Deportment of Silver during Sulphide Oxidation .................................... 44
  2.9 Silver Recover by Sulphate-Iodide Process ............................................................ 46
    2.9.1 Silver-Water System ...................................................................................... 47
    2.9.2 Iodine-Water System ...................................................................................... 48
    2.9.3 Iodine Cycle ................................................................................................... 50
    2.9.4 Silver-Iodide-Water System .......................................................................... 52
    2.9.5 Silver Precipitation in Iodide-Sulphate media ................................................ 55
2.9.6 Other Metal-Iodide Precipitation reactions ...........................................57
2.9.7 Other Reactions of Iodide ........................................................................59
2.10 Comparisons of the various Department of Silver ......................................59
2.11 Kinetics Considerations of Iodide-Sulphate Media ......................................61
2.12 Summary of Literature Review and Objectives of the Present Study ..............63

CHAPTER 3: EXPERIMENTAL PROCEDURES .........................................................66
3.1 Experiments on the Pressure oxidation of silver sulphide ...............................70
  3.1.1 Reagents ..........................................................................................70
  3.1.2 Methodology ....................................................................................70
  3.1.3 Acanthite Mineral Samples .................................................................71
  3.1.4 Particle Size Analysis of the Acanthite Samples ...................................71
3.2 Experiments on Silver Department as Silver Jarosite Specie ..........................73
  3.2.1 Reagents ..........................................................................................73
  3.2.2 Methodology ....................................................................................73
3.3 Chemical Composition of Jarosite and Silver extraction by Cyanidation ..........73
  3.3.1 Reagents ..........................................................................................73
  3.3.2 Methodology ....................................................................................73
  3.3.3 Particle Size Analysis of the Jarosite Species .......................................74
3.4 Experiments on Silver Department as Silver Sulphide ..................................74
  3.4.1 Reagents ..........................................................................................74
  3.4.2 Methodology ....................................................................................74
3.5 Experiments on Silver Department as Silver Iodide .....................................75
  3.5.1 Reagents ..........................................................................................75
  3.5.2 Methodology ....................................................................................75
3.6 Pressure oxidation of complex sulphides in acid sulphate-iodide media .........76
  3.6.1 Reagents ..........................................................................................76
  3.6.2 Methodology ....................................................................................76
  3.6.3 Mineral Samples ................................................................................77
    3.6.3.1 Cannington Complex Sulphide Concentrate ...................................77
    3.6.3.2 Eskay Creek Complex Sulphide Concentrate ..................................78
    3.6.3.3 UBC Mixed Concentrate ..............................................................79
  3.6.4 Particle Size Analysis of the Complex Sulphide Samples .........................80
3.7 Determination of metal extractions and sulphide oxidation extents ...............80
3.8 Cyanidation ............................................................................................82
3.9 Analytical Methods and Characterization of Solid Samples .........................82

CHAPTER 4: RESULTS AND DISCUSSION ..........................................................84
4.1 Reaction of Acanthite during the Pressure oxidation ......................................84
  4.1.1 Effect of Temperature on the Reaction of Acanthite ...............................84
  4.1.2 Product of Acanthite Reaction in Autoclave ..........................................87
  4.1.3 Effect of Iron on the Reaction of Acanthite ............................................88
  4.1.4 Effect of Oxygen Partial Pressure on the Reaction of Acanthite ...............88
  4.1.5 Effect of Silver Sulphate concentration on the Reaction of Acanthite .........91
  4.1.6 Proposed Mechanisms for the Reaction of Acanthite .............................94
  4.1.7 Summary of the reaction of Acanthite during Pressure Oxidation ..........96
LIST OF TABLES

Table 2-1. Silver extraction from pure minerals ..............................................6
Table 2-2. Silver-zinc distribution matrix in zinc concentrates ..........................8
Table 2-3. Silver-lead distribution matrix in zinc concentrates ..........................8
Table 2-4. Names and Composition of jarosite-family end-member ....................23
Table 2-5. Possible replacement based on ionic radii ....................................25
Table 2-6. Gibbs free energies of formation of species in silver-iodide-water systems 52
Table 2-7. Free energy values for various species ...........................................60
Table 2-8. Free energies of the silver precipitation reactions ............................61
Table 2-9. Activation energy for various jarosite species .................................63
Table 3-1. Modifications carried out for different phases during the autoclaving ....69
Table 3-2. Results of Chemical analyses for the natural silver sulphide mineral ....71
Table 3-3. Results of chemical analyses for the reground Cannington Concentrate 78
Table 3-4. Results of chemical analyses for the Eskay Creek Concentrate ............78
Table 3-5. Results of chemical analyses for the natural zinc sulphide ...................79
Table 3-6. Results of chemical analyses for the UBC mixed concentrate .............80
Table 4-1. Summary of sulphide oxidation and oxidation to sulphur vs. sulphate ...87
Table 4-2. Lead distribution after the precipitation of jarosite at 140°C ...............104
Table 4-3. Effect of initial acidity on the rate of hydrolysis and precipitation ......110
Table 4-4. The resulting formula for the synthetic jarosites at different temperatures 122
Table 4-5. Size analyses of synthetic jarosites at different temperatures ...............123
Table 4-6. Summary of baseline cyanidation of various jarosites .......................124
Table 4-7. Summary of cyanidation of reground jarosites ................................125
Table 4-8. Distribution of silver and sulphur species after precipitation at 90°C ....128
Table 4-9. Silver recoveries by baseline cyanidation of complex sulphides ..........140
Table 4-10. Effect of temperature on the oxidation of Cannington Concentrate ....142
Table 4-11. Effect of temperature on the oxidation of Eskay Creek Concentrate ....144
Table 4-12. Effect of acidity on the oxidation of Cannington Concentrate at 110°C .147
Table 4-13. Effect of other conditions on the oxidation of Cannington Concentrate .150
Table 4-14. Effect of acidity on the oxidation of Cannington Concentrate at 150°C .153
Table 4-15. Effect of sulphur addition on the oxidation of Cannington concentrate .157
Table 4-16. Effect of other conditions at 150°C. .........................................................158
Table 4-17. Effect of temperature on the oxidation of UBC mixed sulphide ..........166
LIST OF FIGURES

Figure 2-1. Simplified BHP Cannington concentrator flowsheet ...........................................9
Figure 2-2. Areas of stability of various iron compounds in the Fe-S-O system ..................20
Figure 2-3. Phase equilibrium for Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O system; 0 to 40% SO$_4$ ......21
Figure 2-4. Phase equilibrium for Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O system; 30 to 70% SO$_4$ ......22
Figure 2-5. The structure of alunite .................................................................................24
Figure 2-6. Relative partitioning of silver and sodium between solution and jarosite ....26
Figure 2-7. Relative partitioning of silver and potassium between solution and jarosite at 97°C .................................................................27
Figure 2-8. Relative partitioning of silver and lead between solution and jarosite at 155°C ................................................................................27
Figure 2-9. Relative partitioning of silver and lead between solution and jarosite at 97°C ................................................................................28
Figure 2-10. Effect of silver sulphate concentration on lead, copper, silver and iron contents of jarosite. .................................................................30
Figure 2-11. Effect of lead sulphate suspense on the lead, copper, silver and iron contents of jarosite. ........................................................................30
Figure 2-12. Effect of zinc sulphate concentration on the lead, copper and zinc contents of jarosite specie .................................................................31
Figure 2-13. Effect of dissolved copper sulphate concentration on the lead, copper and zinc contents of jarosite specie .................................................................31
Figure 2-14. Effect of ferric ion concentration and initial acid concentration on the extent of iron precipitation as lead jarosite formed at 140°C. .........................33
Figure 2-15. Potential-pH diagram for the Ag-S-H$_2$O system, at 25°C, 1 atm. pressure and activity of 1.0 mol/l for all the dissolved sulphur species .......................36
Figure 2-16. Potential-pH diagram for the Ag-S-H$_2$O system, at 25°C, 1 atm. pressure, activity of 0.1 mol/l for Ag$^+$ and 1.0 mol/l for all the dissolved sulphur species .....................38
Figure 2-17. Potential-pH diagram for the silver-water system, at 25°C .................................................48

Figure 2-18. Potential-pH equilibrium diagram for the silver-water system, at 25°C......49

Figure 2-19. Speciation-pH diagram for an iodine water system at 25°C, total active iodine
mol/m^3 1 in 1.0 kmol/m^3 total iodide. ..................................................................................................................51

Figure 2-20. Potential-pH diagram for the Ag-I-H_2O system, at 25°C, 1 atm. pressure and
50 activity of 0.01 mol/l for Ag^+ and iodide species.................................................................................................53

Figure 2-21. Iodide activity-pH diagram for a silver-iodide-water system in equilibrium
with AgI at 25°C for a_{Ag} = 10^{-4} ......................................................................................................................54

Figure 3-1. Schematic representation of the autoclave set-up .................................................................68

Figure 3-2. Cumulative particle size distribution of the acanthite mineral samples as
determined by Elzone particle size counter ............................................................................................................72

Figure 3-3. Cumulative particle size distribution of the sulphide concentrates as
determined by Elzone particle size counter ............................................................................................................80

Figure 4-1. Effect of temperature on La Valenciana acanthite oxidation at 900 rpm, 100
psi, 0.5 g/l of acanthite at 4.62 g/l Fe^{3+} and 50 g/l H_2SO_4 ........................................................................84

Figure 4-2. Arrhenius plot of the acanthite oxidation rates .................................................................................86

Figure 4-3. Concentration-time profile of iron during pressure oxidation of acanthite .86

Figure 4-4. Effect of temperature on sulphur yield at different oxidation temperatures of
Ingleterra acanthite ................................................................................................................................................88

Figure 4-5. Effect of ferric ions on the oxidation of Ingleterra acanthite .................................................................89

Figure 4-6. Effect of oxygen partial pressure on the oxidation of Ingleterra acanthite ...89

Figure 4-7. Order of reaction with respect to dissolved oxygen concentration for the acid
pressure oxidation of Ingleterra acanthite .............................................................................................................90

Figure 4-8. Effect of silver ions on the oxidation of Ingleterra acanthite ..............................................................92

Figure 4-9. Effect of silver ions on the oxidation of Ingleterra acanthite in the presence of ferric ........................................................................................................................................93

Figure 4-10. Effect of initial ferric concentration on iron precipitation at 140°C ..........98
Figure 4-11. Effect of initial ferric concentration on silver precipitation at 140°C...........99

Figure 4-12. Effect of initial ferric concentration on acidity profile at 140°C..................99

Figure 4-13. Plot of natural logarithms of rate and initial ferric at 140°C..........................100

Figure 4-14. Effect of initial ferric on the level of iron complexes at 140°C.......................101

Figure 4-15. Effect of lead sulphate suspension on iron precipitation at 140°C................103

Figure 4-16a. Logarithm plot of reaction rate and concentration of lead, which participated in the reaction at 140°C.................................................................104

Figure 4-16b. Logarithm plot of reaction rate and initial concentration of lead sulphate at 140°C.................................................................105

Figure 4-17. Effect of initial lead sulphate suspension on silver precipitation at 140°C....106

Figure 4-18. Effect of initial acidity on iron precipitation at 140°C....................................108

Figure 4-19. Effect of initial acid on the acid-time profile during iron precipitation at 140°C ...........................................................................................................109

Figure 4-20. Effect of initial acidity on silver precipitation at 140°C.................................110

Figure 4-21. Effect of temperature on iron precipitation...................................................111

Figure 4-22. Arrhenius plot of the temperature effect on the initial rate of iron precipitation. ...........................................................................................................112

Figure 4-23. Effect of the operating temperature on silver precipitation .......................113

Figure 4-24. Effect of the seeding on the kinetics of iron precipitation at 125°C and 130°C ...........................................................................................................115

Figure 4-25. SEM micrograph of jarosite particles precipitated at 125°C after 4 hrs of reaction.................................................................118

Figure 4-26. SEM micrograph of jarosite particles precipitated at 125°C after 2 hrs of reaction.................................................................118

Figure 4-27. Molar partitioning of silver and sulphur specie at different initial silver and sulphur.........................................................................................127

Figure 4-28. Aqueous silver concentration-time profile at different initial level of silver and sulphur.........................................................................................128
Figure 4-29. Silver concentration-time profile at different temperatures and under the oxygenated conditions .......................................................... 130

Figure 4-30. Ferrous concentration-time profile at different temperatures under the oxygenated conditions ......................................................... 131

Figure 4-31. Effect of temperature on silver deportment from silver iodide .......... 134

Figure 4-32. Deportment of silver as iodide vs jarosite specie ........................................ 136

Figure 4-33. Deportment of silver from silver jarosite ............................................... 138

Figure 4-34. Effect of temperature on zinc extraction and total sulphide oxidation for the oxygen pressure oxidation of Cannington complex sulphide ....... 141

Figure 4-35. Effect of pressure oxidation temperature on the subsequent silver extraction by cyanidation of Cannington complex sulphide concentrate ................. 142

Figure 4-36. Effect of pressure oxidation temperature on the subsequent silver extraction by cyanidation of Eskay Creek complex sulphide concentrate ......................... 144

Figure 4-37. Silver extraction-time profile of the Cannington oxidized residues during cyanidation ........................................................................ 145

Figure 4-38. Effect of the pressure oxidation acidity on the subsequent silver recoveries of Cannington concentrates by cyanidation ........................................ 146

Figure 4-39. Effect of the iodide concentration on the subsequent silver recoveries of Cannington complex sulphide concentrates by cyanidation ........................................ 149

Figure 4-40. Effect of initial acidity on silver extraction from Cannington complex sulphide concentrate .............................................................. 152

Figure 4-41. Effect of initial acidity (in the absence of iodide) on silver extraction from Cannington mixed sulphide concentrate .............................................. 154

Figure 4-42. Effect of the iodide concentration on the subsequent silver recoveries of Cannington concentrates by cyanidation ............................................................. 155

Figure 4-43. Effect of temperature on zinc extraction from UBC mixed concentrate. 161

Figure 4-44. Acid–time profile of the pressure oxidation of UBC mixed concentrate. 162
Figure 4-45. Effect of temperature on the ferric and ferrous iron concentration of the pressure oxidation of UBC mixed concentrate ...........................................164

Figure 5-1. Conceptual flowsheet for the treatment of complex sulphide concentrate for silver........................................................................................................170
LIST OF SYMBOLS

$G_r^\circ$ Gibbs free energy at a temperature $(T)$, kJ/mol

$T$ temperature, (K)

$C$ heat capacity, J/mol-K

$a, b, c$ heat capacity coefficients for the non-ionic species

$\alpha_T, \beta_T$ Criss-Cobble heat capacity constants for the ionic species

$S$ entropy, J/mol-K

$\overline{S}$ absolute entropy, J/mol-K

$M_{E_{calc}}$ calculated head assay of metal, g.%

$m_{mol}^{Me}$ mass of metal solubilized, g,

$m_{Me}^{res}$ mass of metal in the oxidised residue, g

$m_t$ mass of the head sample, g

$m_{head}^{sulfide}$ mass of sulphide sulphur in the head sample, g

$m_{sulfide}^{res}$ mass of sulphide in the oxidised residue, g

$m_{sulfur}^{res}$ mass of elemental sulphur in the oxidised residue, g

$P_{80}$ 80% passing through
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Currently, the primary sources of zinc are zinc sulphide concentrates from high-grade ores, which are treated mainly by the roast-leach-electrowinning process. Many complex sulphide ore deposits remain undeveloped because of their poor responses to conventional single mineral flotation and the lack of alternative processes for their treatment. The individual mineral flotation is very difficult because of the fine-grained nature of these ores. Ultra-fine grinding may be required for adequate liberation of the inter-grown sphalerite, galena and chalcopyrite from the matrix of the host minerals (pyrite, pyrrhotite and arsenopyrite). Typical flotation plants produce copper, zinc and lead concentrates, which are sent to separate smelters. This approach suffers from poor economics due to losses of individual metals in other concentrates (such as zinc in copper concentrates and silver in zinc concentrates) and high smelting and refining charges. Penalties may also be exacted due to the presence of impurities and low grades of the concentrates. Finally, payment for the silver and gold in the concentrates may be poor. All of these reasons justify the development of an alternative approach. One approach is to recover a bulk concentrate of complex sulphides by flotation followed by recovery of metals. A hydrometallurgical process, which is capable of selectively extracting the base metals (zinc and copper) without the loss of precious metals (silver and gold), would be attractive for the treatment of these complex sulphide materials.

Some hydrometallurgical processes have been proposed for treating complex sulphide concentrates but most employ chloride media (Beyke, 1991; Harvey et al., 1992 and Dixon, 1997). The chloride-based processes have some disadvantages when compared to the sulphate in that the base metals are either dissolved simultaneously or are not dissolved efficiently and the metal product quality is low. Therefore, the sulphate-based processes with simpler leaching chemistry and established recovery technologies of base metal products are generally preferred.

The pressure oxidation process in a sulphate medium is preferred for the treatment of complex sulphides because of its comparative advantages over the roast-leach-electrowinning process such as higher zinc extraction and the production of elemental sulphur rather than sulphur dioxide, which necessitates acid by-product recovery and raises environmental concern. Also,
there has been a continuous improvement of this process over the last two decades and it is currently used for the processing of zinc concentrate and for the pre-treatment of gold bearing sulphide materials. However, there have been limited laboratory investigations on the pressure oxidation of complex sulphide concentrates and the commercial application is yet to be reported (Thompson et al., 1992). High acid pressure oxidation to reject lead as lead-silver residue has been proposed by Collins et al. (1990). In the work of Collins et al. (1990), solution from the high acid leach is treated with zinc concentrate in a low acid leach to decrease its acidity and iron content. The major limitation of this proposition is that the zinc concentrate must contain minimal quantities of silver, otherwise it will be lost to the jarosite species. Also, a two-stage pressure oxidation has been proposed by Harvey et al. to extract zinc and copper from zinc-copper lead concentrate at 210°C (Harvey et al., 1992 and Harvey and Yen, 1998). The previous studies have been conducted at temperatures higher than the range for the commercial zinc operation (110 to 150°C). A lower temperature range of 110°C to 150°C represents some cost savings and elemental sulphur formed can be recovered as a saleable or disposable product.

Although high zinc extraction is obtained by pressure oxidation and the precious minerals are liberated, cyanidation of the resulting residue yields almost all the gold, while silver extraction is typically less than 10%. The low extraction of silver from the oxidised residue is due to its incorporation into the jarosite specie during pressure oxidation. Enhancement of the silver extraction by digestion of the residue with lime at 90°C to render the silver amenable to cyanidation has been proposed (Berezowsky, 1986; Berezowsky et al., 1990). However, there is a high lime requirement, which also depends on the mineralogy of the residue or feed materials. 50% excess lime above the stoichiometric requirement has been reported in some investigations (Dreisinger, 1997). Another solution includes pressure oxidation at a temperature beyond the stability range of jarosite or to operate at very high acidity and with excess of K₂SO₄ (Bull et al., 1985). These conditions lead either to a hematite residue or to a potassium jarosite with very low silver content. The high pressure, high temperature and the high reagent costs, make these solutions unattractive for industrial application.

Efforts to recover silver from complex sulphides, which contain an economic fraction of silver require an understanding of the behaviour of the main silver mineral (acanthite) during the pressure oxidation. However, unlike the behaviours of silver alloys and silver chloride in ferric
chloride and ferric sulphate media, which are relatively well understood (Dutrizac, 1986; Dutrizac, 1987; Morrison, 1989), the study of oxidation of silver sulphide (Ag$_2$S) in sulphate medium has been complicated by the formation of argento-jarosite. Tourre (1984) investigated the sulphuric acid pressure oxidation of “make-up” mixed-sulphides, containing low-grade (~4% Ag) acanthite ore and substantial pyrite. At above 120°C, extensive dissolution of silver sulphide was reported with the sequestering of the dissolved silver into the jarosite phase. Longer residence time was required to achieve the same results at 100 and 110°C. The main limitation of this study was that the silver-extraction time was not provided and the form of silver prior to its encapsulation by jarosite specie was not obvious in this study. For example, it was not clear if the silver sulphide was covered by the jarosite specie (physical encapsulation) or if it was oxidized to aqueous silver prior to incorporation by jarosite specie (chemical encapsulation of silver).

A very low dissolution of silver sulphide in acidic ferric sulphate was observed at low temperature (85°C), when a disk of Ag$_2$S was leached with 0.3-3.0M Fe$^{3+}$ in de-oxygenated and oxygenated environments by Dutrizac (1994). However, possible formation of silver jarosite on the surface of the disk or silver sulphate precipitation could have hindered dissolution. Also, considerable uncertainties arise in the interpretation of chemical oxidation of sulphide minerals; when the experiments are carried out without controlling the redox potential, which is expected to fall drastically as ferric is consumed (Dixon and Bolorunduro, 2002). Obviously, a systematic approach is required to study silver deportment from the sulphide mineral before serious attempts can be made to recover silver from the complex sulphides.

The primary objective of this work was to investigate the chemical behaviour of silver during the acid pressure oxidation in the temperature range of 110-150°C and to deport silver into a residue suitable for high extraction by cyanidation. The secondary objective was to extract zinc into the solution suitable for recovery by electrowinning. The approach taken was divided into six sections. One, the oxidation kinetics of high grade natural acanthite (Ag$_2$S) over a temperature range of 110-150°C was investigated by following the silver extraction-time profile under the conditions, which avoided the precipitation of jarosite specie or silver sulphate. High acidity and low pulp density were employed to achieve this aim. Two, the kinetics and mechanisms of silver incorporation into the jarosite specie were investigated, over a temperature range of 110 –150°C to determine the challenges posed by the jarosite formation to alternative
silver deportment (for example, precipitation of silver iodide) and the conditions which could minimise silver loss to jarosite specie. Three, the chemical composition and the cyanidation of the jarosite species were investigated to study the extraction of silver from jarosite residues. Four, precipitation reaction was carried out to study the reaction chemistry and kinetics of silver deportment as silver sulphide in the presence of sulphur and under the pressure oxidation conditions. Five, precipitation reaction was carried out to investigate the deportment of silver ion as silver iodide and the stability of silver iodide in acid ferric media under the pressure oxidation. Six, the pressure oxidation of complex sulphide concentrates (obtained from different mines) was carried out in the temperature range of 110 and 150°C, while potassium iodide was added to the initial solution to precipitate silver as silver iodide (iodargyrite) before its incorporation into the jarosite specie. Three different sulphide materials were oxidised in the autoclave, under the conditions that were similar to the industrial zinc pressure oxidation. The oxidized residues were subjected to cyanidation for silver and gold recoveries. The various pressure oxidation conditions such as acidity, iodide concentration, sulphur and soluble iron concentration were investigated to identify process conditions that would improve subsequent silver extraction by cyanidation of the residue, without compromising the upstream zinc extraction in the autoclave.
CHAPTER 2
LITERATURE REVIEW

The primary sources of zinc are zinc sulphide concentrates (from high grade ores) which are treated mainly by the following hydrometallurgical routes:

1. Roast-Leach-Electrowinning (RLE) Process and
2. Zinc Pressure Leach (ZPL) Process

Over 75 percent of the world’s zinc is produced by the roast-leach-electrowinning process, which has advantages over pyrometallurgical alternative (smelting) such as lower capital, higher zinc extraction, and higher purity product. The disadvantage of the RLE process is that sulphur dioxide is generated during the roasting of the concentrate.

The direct pressure oxidation of zinc sulphide commenced commercially in October 1980 at Cominco’s operations in Trail, British Columbia. The zinc sulphide concentrates are oxidised under pressure to produce zinc sulphate solution and electrowinning of zinc metal is accompanied by conventional techniques. A particular advantage of the pressure oxidation is that sulphur is converted to the elemental form and without generation of sulphur dioxide.

In many instances, silver occurs in ores along with lead, zinc, copper, gold and other metals. In many mines the primary product is one of these metals as concentrates, with silver being a by-product. Out of the world mine production of 17,000 tons, the primary silver mines generated 23% of the total production of silver in 2001 while 77% was produced as a by-product. This is, in part, a consequence of the scarcity of large silver deposits, which can be economically exploited as the primary silver sources. The contributions from lead-zinc, copper and gold operations are 40%, 22% and 13% respectively (World Silver Institute, 2002).

The principal route of silver production from sulphide concentrate is smelting, which is expensive due to shipping costs, smelter charges and the penalties incurred on the low grade concentrates or at elevated level of impurities (arsenic, bismuth and antimony). An increase in the contribution of the hydrometallurgical processes theoretically, represents an attractive alternative in that hydrometallurgical processes are non-air polluting and potentially more cost effective on a small scale when compared to smelting processes.
2.1 Mineralogy of Silver and Cyanidation of Silver Minerals

Silver minerals are usually found in the oxidized zones of ore deposits, or in the hydrothermal veins associated with sulphides of base metals (Cu, Zn). Although several hundred silver-bearing minerals are known, only about ten are important for economic recovery of silver. The minerals may be divided into three main groups based on the solubility of their synthetic minerals in dilute cyanide solutions (Wyslouzil and Salter, 1990). The first group consists of the most leachable minerals, which are native silver, silver halide and sulphide, from which over 90% recoveries are possible. The second group is comprised of minerals with sulphur and arsenic or antimony from which cyanide leaching extracts about 60% of the silver and requires prior roasting to increase the extraction to 90%. The third group contains sulphide of base metals or complex minerals with iron and manganese and only 20% silver extraction can be extracted from these minerals. The summary of the groups and the silver recoveries are presented in Table 2-1.

Table 2-1. Silver extraction from pure minerals according to Wyslouzil and Salter (1990).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Extraction (Leaver and Woolf)</th>
<th>Extraction (Leaver, Woolf and Karchmer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorargyrite</td>
<td>AgCl</td>
<td>97.0%</td>
<td></td>
</tr>
<tr>
<td>Iodargyrite</td>
<td>AgI</td>
<td>99.3%</td>
<td>-</td>
</tr>
<tr>
<td>Argentite</td>
<td>Ag₂S</td>
<td>99.2%</td>
<td>87-93%</td>
</tr>
<tr>
<td>Proustite</td>
<td>Ag₃AsS₃</td>
<td>29.5-44%</td>
<td>42.55%</td>
</tr>
<tr>
<td>Pyrargyrite</td>
<td>Ag₃SbS₃</td>
<td>41.6-46%</td>
<td>67.00%</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>8(Cu₃SbS₃)</td>
<td>13.0-41%</td>
<td>25.00%</td>
</tr>
</tbody>
</table>

Silver sulphide (Ag₂S) is the main mineral for silver, which is associated mainly with silver bearing galena, and sometimes with sphalerite and chalcopyrite (Mottana et al., 1990 and Pellant, 1992). The cubic argentite is stable above 179°C but at normal temperatures, argentite is replaced pseudomorphically by acanthite.

The cyanidation of some silver minerals was investigated by Holt (1910) and it was reported that the halogen compounds of silver were the most soluble forms in cyanide solution and that no oxygen is required for their dissolution in potassium cyanide. Native silver is next in order of dissolution in an aerated solution, and it dissolves in accordance with Ellsner’s equation (Wyslouzil and Salter, 1990).

The silver sulphide, argentite, requires the removal of soluble sulphides to insure good
extraction and lead salts are applied for this purpose. It was reported by Holt (1910) that oxygen or an oxidizer is essential to the continued solution of silver sulphide in cyanide solution. The dissolution of the complex antimony and arsenic minerals in a cyanide solution was low and it was reported that the presence of lead salts decrease the solubility of the complex Sb and As silver minerals in a cyanide solution. The author (Holt, 1910) did not provide the mechanisms of dissolution of the silver minerals and explanation was not provided for the negative effect of the Pb salts on the dissolution.

The behaviour of the silver sulphide during cyanidation is relevant to this study because it has been speculated to form during the pressure oxidation and it is the main mineral of silver. Luna and Lapidus (2000) submitted the following net reaction for the redox reaction at the mineral-solution interface and the complex formation in the cyanide solution.

\[
Ag_2S + 4CN^- + O_2 + 1/2H_2O \rightarrow 2Ag(CN)_2^+ + 1/2S_2O_3^{2-} + OH^- \quad (2-1)
\]

The only sulphur specie detected in solution was the thiosulphate ion and on the basis of equilibrium calculations, Ag(CN)$_2^-$ was determined to be the most representative silver complex. The silver extraction from the concentrate increases as the cyanide concentration is elevated and that the silver extraction is kinetically controlled by a second order reaction relative to the local oxygen and sulphide ion concentrations (Luna and Lapidus, 2000). The process was thought to be a reaction-controlled regime, however, it was not obvious if the oxidation of the sulphide ion (S$^2$) to thiosulphate was the rate limiting step. The oxidation of S$^{2-}$ is believed to enhance the overall dissolution rate of sulphide minerals in cyanide solution (Zhang et al., 1997).

### 2.2 Significance of Silver to Zinc Industry

Silver is present in the zinc concentrate mainly as fine particles of metallic silver and in a variety of mineral forms including discrete finely divided silver minerals such as tetrahedrite, (CuAg)$_{12}$Sb$_4$S$_{13}$ or acanthite Ag$_2$S and silver-bearing impurity grains such as galena (Dutrizac, 1985; Petruk, 1985). Also, silver may be present in the solid solution of some sphalerite grains as sulphide (Dutrizac and Chen, 1990; Scott and Dienstbach, 1990). Analyses of the zinc, lead and silver grades of seventy randomly selected zinc concentrates by Rodier (1990) produced the following grids (Table 2-2 and 2-3).
Table 2-2. Silver-zinc distribution matrix in zinc concentrates selected by Rodier (1990).

<table>
<thead>
<tr>
<th>Zinc content</th>
<th>Low grade</th>
<th>Medium grade</th>
<th>High grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>High grade, &gt; 56%</td>
<td>10</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>52-56%</td>
<td>9</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Low grade, &lt; 52%</td>
<td>4</td>
<td>11</td>
<td>6</td>
</tr>
</tbody>
</table>

Silver content

Low-grade silver tends to be in the higher and cleaner grade of zinc concentrate.


<table>
<thead>
<tr>
<th>Lead content</th>
<th>Low grade</th>
<th>Medium grade</th>
<th>High grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 2%</td>
<td>3</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>1-2%</td>
<td>3</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>&lt;1%</td>
<td>15</td>
<td>19</td>
<td>9</td>
</tr>
</tbody>
</table>

Silver content

It is evident from Table 2-3 that the low-lead concentrates contain less silver, whereas the high lead concentrates have slight bias to high silver content. Therefore, there are opportunities to recover silver along with zinc during the pressure oxidation of zinc or zinc-lead concentrates. The recovery of a silver by-product will contribute to the economy of the process.

2.3 Treatment of Complex Sulphides

As supplies of the high-grade zinc concentrates diminish, the treatment of zinc-lead-iron complex sulphides containing significant fractions of copper and/or silver must be considered for zinc recovery. Complex sulphide ores can be broadly described as an association of inter-grown sphalerite, galena and chalcopyrite, which are generally very finely disseminated usually within a pyritic, pyrrhotitic or arsenopyritic matrix. Silicates and carbonates rock may also be major gangue constituents. The individual mineral flotation of these ores is very difficult because of the fine-grained nature of these ores. Ultra-fine grinding (with the associated cost) is required to produce adequate liberation. An alternative approach to separate concentrate production is to
recover a bulk concentrate of complex sulphides by flotation followed by recovery of individual metals. A hydrometallurgical process, which is capable of selectively extracting the base metals (zinc and copper) without the loss of precious metals (silver and gold), is attractive for the treatment of these complex sulphide materials. In a sulphate media, lead is lost to the final residue as lead sulphate. There are large numbers of complex sulphide deposits in Canada and throughout the world.

The BHP Cannington flotation plant, located in North West Queensland treats high-grade silver, lead and zinc sulphide ores producing a reject talc stream and two concentrate product streams. The two concentrates are silver rich-lead concentrate and zinc concentrate. The lead and zinc concentrate contains 3200 g/t and 500 g/t of silver respectively. The process flowsheet is presented in Figure 2-1 (Torrisi, 2001). The process plant comprises an autogenous mill, followed by the sequential floatation of talc, galena and sphalerite. The plant feed contains between 3 to 7 wt% fluoride in various fluoride-bearing silicates and minerals such as talc, chlorite, apatite, fluorite, amphibole and ferropyrosmalite.

![Simplified BHP Cannington concentrator flowsheet](image-url)
The BHP flotation circuit takes advantage of the natural flotability of talc to remove it from the feed stream prior to the addition of collector to promote the flotation of galena. The talc is sent to the tailing pond. The entrainment of some fluoride bearing silicates is avoided in the flotation circuits. The fluoride, silicates and some silver-bearing complex sulphides report to the tailings. Therefore, the tailing still contains materials, which can add to the economy of the mine. Acid leach processes at 50°C, pH 3.3 and in the presence of aluminium sulphate are incorporated for the lead and zinc concentrates to remove some fluoride bearing minerals. The fluorite, CaF₂ and apatite, Ca₅(PO₄)₃(F,Cl,OH) are readily removed by this patented acid leaching process, while chlorite, (Mn, Fe)₁₂(Si, Al)₈O₂₀(OH,F)₁₆ is slowly removed. However, the talc (Mg, Fe)₆Si₈O₂₀(OH, F)₄, and the ferropyrosmalite, (Fe, Mn)₈Si₆O₁₅(OH, F)₁₀ do not leach during the acid leaching process and may end up in the concentrates.

Other deposits of zinc-lead complex sulphides, which contain substantial silver are the Hellyer deposits in Australia, Brunswick and La Ronde deposits in Canada, Pering and Rosh Pinah in Namibia, etc. Direct acid pressure oxidation followed by cyanidation for silver/gold extraction will be attractive to these operations.

The pressure oxidation process will be appropriate for the complex sulphide materials because of its comparative advantages over the conventional methods (roast-leach-electrowinning and smelting) and its continuous improvement over the last two decades. Also, the handling of environmentally sensitive impurities such as arsenic and antimony are facilitated. Arsenic is fixed as ferric arsenate in the residue.

However, there have been limited laboratory investigations of the pressure oxidation of complex sulphide concentrates (Bull et al., 1985; Thompson et al., 1992; Harvey and Yen, 1998) or ores and the commercial application is yet to be reported. A two-stage pressure oxidation was proposed to extract zinc and copper from zinc-copper-lead concentrate at 210°C by Harvey et al. (1992). These studies have been conducted at temperatures higher than the operating range of the commercial zinc processes and the major drawbacks are the total oxidation of sulphur to sulphate and the loss of silver to the jarosite phase (Dreisinger, 1997). In the Comprex process, the lead jarosite phase can be avoided by operating at 210-220°C, but this oxidises all the sulphides to sulphate and the process requires high free acidity in the range of 30 to 50 g/l (Noguiera et al., 1980).
Also, a high acid pressure oxidation to reject lead as lead-silver residue has been proposed by Collins et al. (1990). In this proposal, solution from the high acid oxidation of complex sulphide is treated with zinc concentrate in a low acid oxidation to decrease its acidity and iron content. The major limitation of this proposition is that the zinc concentrate must contain minimal quantities of lead and silver, otherwise they will be lost as jarosite species. Also, data on the silver extraction from the complex sulphides was not presented in the study.

Unlike the previous studies, the current research represents the first systematic investigations of the path of silver from the mineral-source to the final residue and the recovery of silver along with the base metals by pressure oxidation (110-150°C) followed by cyanidation. Sulphur remains the predominant species at lower temperatures (110 to 130°C) and this can be floated for sales. However this may result into the loss of gold, which tends to follow sulphur/sulphide portion of the residue (Fair et al., 1991). The sulphide oxidation increases with increasing temperature. The low sulphide oxidation means high pyrite in the residue which may require a consideration for acid mine drainage (AMD), when the pyritic residue is exposed to oxygen and water. The oxidation of pyrite and the subsequent release of acid and iron sulphate can be minimised by preventing exposure to oxygen and/or water (Doyle, 1990). However, the treatment of the acid mine drainage is not the focus of this study.

2.4 Zinc and Silver Recoveries by Pressure Oxidation

The process is based upon the direct acid pressure oxidation of the high-grade zinc sulphide concentrate to produce zinc sulphate in solution and elemental sulphur and iron compounds in the residues. It has certain potential advantages over the conventional roast-leach such as higher zinc extraction (approximately 96 to 98% by weight) and the production of elemental sulphur (recovery more than 87%) rather than the production of sulphur dioxide. However, the cost of oxygen required for pressure oxidation, offsets some of these advantages.

2.4.1 Process Chemistry

The zinc pressure oxidation process depends upon the following reactions in which zinc sulphide, pyrrhotite or iron in sphalerite and chalcopyrite react with sulphuric acid and oxygen to produce metal sulphate and elemental sulphur (Buban et al., 1999).
\[ \text{ZnS} + H_2SO_4 + 0.5O_2 \rightarrow \text{ZnSO}_4 + H_2O + S^0 \]  \hspace{1cm} (2-2)

\[ \text{FeS} + H_2SO_4 + 0.5O_2 \rightarrow \text{FeSO}_4 + H_2O + S^0 \]  \hspace{1cm} (2-3)

\[ \text{CuFeS}_2 + 2H_2SO_4 + O_2 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2H_2O + 2S^0 \]  \hspace{1cm} (2-4)

Temperature increases the rates of these reactions, however, above the melting point of sulphur, the presence of a surface active agent (surfactants such as lignosol, quebracho) is necessary to prevent the occlusion of the sulphide particles by elemental sulphur and the consequent termination of the process. Owusu (1993 and 1995) measured the effect of the surfactants on the liquid sulphur-aqueous solution interfacial tensions and on the liquid sulphur-mineral contact angles and it was reported that most of the surfactants studied adsorbed at the liquid sulphur-aqueous solution interface, and all of them adsorbed at the solid mineral-aqueous solution interface. In most cases the liquid sulphur-aqueous solution interfacial tensions decreased substantially, from 54-55 mN/m in the absence of surfactant to as low as 20-22 mN/m in the presence of 0.1-0.3 g/l surfactant. Also, the liquid sulphur-mineral contact angles increased from 80° to as high as 155°. This resulted in a significant reduction in the work of adhesion between the liquid sulphur-mineral phase, which increased the tendency for the liquid sulphur to be dispersed. With a contact angle greater than 90°, the liquid sulphur should move freely about the surface and be easily removed as a result of slurry agitation and a zero contact angle is the condition for complete wetting of the mineral by liquid sulphur.

The commercialisation of zinc pressure oxidation was delayed until it was discovered that the addition of sulphur-dispersing surfactants to the leach greatly improved zinc extractions at temperatures above the sulphur melting point (Morikawa et al., 1972; Kawulka et al., 1975). The surfactants that were found to be beneficial are:

1. Lignin derivatives such as sodium and calcium lignosulphonate
2. Tannin compounds, particularly tree bark extracts such as quebracho
3. Alkylaryl sulphonates, particularly sodium alkylbenzene sulphonates

Results provided by Sherritt in their patent indicate that at surfactant dosages of 0.1-0.3 g/l, zinc extraction increased from 63% to 96-98%, when zinc sulphide concentrate was oxidised for 100 minutes at 150°C (Kawulka et al., 1975). INCO reported the use of tall oil pitch as surfactant for the processing of nickeliferous pyrrhotite concentrate at 130 to 150°C (Jones and Krause, 1976).
Different dosage of surfactant has been reported in the literature and its degradation, which necessitates high requirement in some sulphide oxidation. One possible degradation of the surfactant is its reaction with dissolved ferric iron (Dreisinger et al., 1990), which increases with increasing acidity.

\[ \text{Fe}^{3+} + \text{lig nosol} \rightarrow \text{Fe}^{2+} + \text{degraded lignosol} \]  

(2-5)

The surfactants may have a large number of anionic groups and most of them adsorb onto the sulphide surfaces, which are positively charged at high acidity. High levels of surfactants might have had negative effect on the mass transfer across the sulphide-solution interface, especially in a laboratory scale autoclave. Surfactants tend to produce rigid gas-liquid interfaces and suppress the surface renewal mode of mass transfer (Midoux and Charpentier, 1984), which may lead to the dependence of mass transfer on molecular diffusion alone. Also, adverse effect of surfactants on the homogenous ferrous oxidation reaction rate has been reported by Kimweri (2001) and this may have consequential effect on the sulphide oxidation. However, one would expect these adverse effects of surfactants to be less pronounced under the conditions used for commercial pressure oxidation and to be given less consideration than the adverse effect of molten sulphur on the mineral surface. The primary role of surfactant in this study was to prevent this effect of molten sulphur.

The zinc that is dissolved from reaction (2-1) is recovered by electrowinning following solution purification. Galena also reacts to form insoluble lead sulphate as follows:

\[ \text{PbS} + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} + \text{S}^0 \]  

(2-6)

These reactions (2-2) to (2-4) become fast in the presence of species that will facilitate oxygen transfer and one of such species is dissolved ferrous which is oxidized to ferric. The net reaction for oxidation of zinc sulphide, which is shown above as reaction (2-2) is the sum of the following two reactions:

\[ \text{ZnS} + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{ZnSO}_4 + 2\text{FeSO}_4 + \text{S}^0 \]  

(2-7)

\[ \text{FeSO}_4 + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \]  

(2-8)

There is sufficient acid soluble iron in the concentrate to supply the needs of the process. Pyrite is present in most zinc concentrates, and the extent of its oxidation depends on the oxidation parameters such as temperatures, oxidizing potentials and sulphide sulphur contents.
Under the zinc pressure oxidation conditions, some of the pyrite is oxidized directly to sulphate as shown below (2-9a), while some elemental sulphur is produced under high acidity, low temperature and oxidising conditions (2-9b).

\[
FeS_2 + H_2O + 3.5O_2 \rightarrow FeSO_4 + H_2SO_4 \quad (2-9a)
\]

\[
FeS_2 + H_2SO_4 + 0.5O_2 \rightarrow FeSO_4 + H_2O + 2S^0 \quad (2-9b)
\]

Since all zinc concentrates contain iron, and the iron minerals are oxidised in the autoclave, the behaviour of iron is controlled by the acid content of the pressure oxidation solution. The pressure oxidation of zinc concentrate is normally designated as a low-acid or a high acid pressure oxidation process.

In a low acid pressure oxidation process, the quantity of acid provided is slightly higher than that required to extract all the zinc present in the concentrate. Since the iron minerals, with the exception of pyrite, are in competition with the zinc minerals for the acids, acid concentration falls rapidly in the autoclave, and the hydrolysis and precipitation of iron is favoured. The following precipitation reactions, which regenerate sulphuric acid, are commonly observed during the pressure oxidation of zinc concentrates.

\[
Fe_2(SO_4)_3 + (x + 3)H_2O \rightarrow Fe_2O_3 \cdot xH_2O + 3H_2SO_4 \quad (2-10)
\]

\[
Fe_2(SO_4)_3 + 2H_2O \rightarrow 2FeOHSO_4 + H_2SO_4 \quad (2-11)
\]

\[
3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2H_3OFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad (2-12)
\]

\[
PbSO_4 + 3Fe_2(SO_4)_3 + 12H_2O \rightarrow 2PbO_2Fe_3(SO_4)_2(OH)_6 + 6H_2SO_4 \quad (2-13)
\]

\[
Ag_2SO_4 + 3Fe_2(SO_4)_3 + 12H_2O \rightarrow 2AgFe_3(SO_4)_2(OH)_6 + 6H_2SO_4 \quad (2-14)
\]

If sodium, potassium, ammonium ions are present in the autoclave solution, the corresponding jarosite species will be precipitated in the low-acid pressure oxidation. The precipitation of iron in the autoclave may be minimised by maintaining a relatively high residual acid concentration in the slurry. In situations where the lead and silver contents of the feed concentrates are significant, it may be desirable to limit the precipitation of iron during the zinc extraction process in order to separate a high-grade lead-silver product from the oxidised residue.
2.4.2 Silver Extraction in the Zinc Autoclave

According to Chalkley et al. (1995), silver is soluble in the zinc autoclave and in the presence of precipitating iron or molten sulphur, silver is removed from solution as either silver jarosite or silver sulphide. Silver precipitation as silver chloride may also be possible in the presence of chloride ions. The current net extraction of silver (into solution) in the autoclave is zero. The deportment of silver during the zinc pressure oxidation will depend on the type of process being used. In the single stage low acid pressure oxidation and the two stage countercurrent process (such as Hudson Bay Mining and Smelting Company, Ltd. Flin Flon), the majority of the silver present in the zinc concentrate reports to the oxidic fraction of the residue, presumably as jarosite specie. In a single stage high acid oxidation, the silver may split between the sulphidic and oxidic fractions of the residue.

2.4.3 Silver extraction by Cyanidation of Oxidised Residue

The treatment of zinc concentrate in the autoclave produces a residue containing elemental sulphur, residual sulphides and precipitated iron species (basic iron sulphates and jarosite). Flotation of the residue recovers most of the elemental sulphur and residual sulphides to the concentrate, leaving iron oxides and basic sulphate and jarosite in the tailings. The tailings also contain most of the silver and some gold. Direct cyanide leaching of the oxide tailings is capable of leaching most of the gold, but only a minor portion of the silver (about 20% extraction) at high consumption of reagent (Thompson et al., 1992).

2.4.4 Silver Enhancement Process

The silver enhancement process has been proposed prior to cyanide leaching of the oxidised residue (Berezowsky, 1986 and Berezowsky et al., 1990). The process consists basically of digestion of the residue with lime at 90°C to render the silver amenable to enhanced extraction by subsequent cyanidation. The batch tests showed that the treatment of the oxidised residue with 80 kg/t CaO at 90°C for 1 to 2 hours increased the silver extraction from less than 20% to 96%. The decomposition of jarosite by lime at elevated pulp temperatures of 85-90°C occurred according to the following proposed reactions:

\[ 2AgFe_3(SO_4)_2(OH)_6 + 3Ca(OH)_2 \rightarrow 6FeO(OH) + 3CaSO_4 \cdot 2H_2O + Ag_2SO_4 \]  

(2-15)
The silver released by this reaction is cyanide soluble. Silver and gold are subsequently extracted from the limed pulp by cyanidation, preferably without prior liquid-solid separation. Continuous testing of the process was carried out in a miniplant circuit, but the process has not been applied commercially. The process has the following disadvantages:

1. The process is uneconomical because of the high lime requirement, which also depends on the mineralogy of the residue or feed materials. 50% excess lime (beyond the stoichiometric requirement) has been reported in some investigations (Dreisinger, 1997),
2. The residue may be unsuitable for filtration because of the formation of a gelatinous precipitate consisting of iron oxide hydroxides and gypsum, and
3. Arsenic may also be released by destabilisation of the ferric arsenate precipitates in the autoclave residue.

2.4.4 Modification of the Autoclave Oxidation conditions

Currently, silver is not recovered from zinc pressure oxidation process and the following solutions proffered in the literature (Bull et al., 1985) are limited in that they involved extreme process conditions:

1. Pressure oxidation at temperature which is over 190°C to precipitate iron as hematite,
2. Acidity levels above 0.75 mol/L H₂SO₄ and
3. Addition of high levels of potassium sulphate, about 36 kg/tons of ore.

The latter condition will not prevent total silver losses because silver is incorporated into the potassium jarosite and subsequent cyanidation of the residue gives low extraction of silver.

2.5 Mechanism of Iron Precipitation and Phase Equilibria in Sulphate media

In the autoclave, the acid level declines as oxidation of metal sulphides progresses and this favours the formation of jarosite species. This is promoted in the presence of potassium and sodium, which are released by the dissolution of gangue components and in the presence of silver, if silver mineral is oxidised. Therefore, iron precipitation is the precursor for the loss of silver during the pressure oxidation of sulphides. In the roast leach electrowinning process of zinc, iron precipitation as jarosite specie is introduced deliberately to eliminate iron from zinc rich liquors (Arregui, 1979), and its acceptance by the zinc industry is due to the facts that the
jarosite process is effective, relatively inexpensive and easy to apply. However, its major drawbacks are its size (being a bulky material) and its stability under the weathering condition, which is creating environmental concern. Other iron phases, which are relevant to the zinc operations, are geothite and hematite.

2.5.1 Mechanism of Precipitation

The mechanism of iron precipitation has been presented in terms of ferric hydrolysis followed by the dimerization and subsequent polymerisation of the iron hydroxyl complexes, which leads to the eventual precipitation of some crystalline iron compound (Dutrizac, 1980). The iron removal is effected by hydrolysis and the hydrolysed ferric species subsequently precipitate. The simple ferric species exist in solution as hydroxyl ion and other polynuclear complexes such as Fe$_3$(OH)$_4^{5+}$ and Fe$_2$(OH)$_5^{5+}$ have also been advanced as minor species (Dutrizac, 1980). Regardless of the complex, the extent of hydrolysis increases with increasing temperature. In the region of concern to zinc processors (Fe$^{3+} = 0.01-1.0$ mol/l; pH =1-4), the predominant solution species are the dimer Fe$_2$(OH)$_2^{2+}$ and Fe$^{3+}$. In a strongly acidic sulphate solutions (i.e., in the comparative absence of OH), simple sulphate-iron (III) complexes (FeSO$_4^{+}$ and Fe(SO$_4$)$_2^{2-}$ are present and their stability constants increase with temperature (Nikolaeva and Tsvelodub, 1975).

Although the role played by bisulphate ion (HSO$_4^-$) in the precipitation of iron compounds is not clear, the high concentration of bisulphate ion in acidic solutions would likely override the lower stability of the Fe(III)-HSO$_4$ complexes with respect to their Fe(III)-SO$_4$ analogues (Nikolaeva and Tsvelodub, 1975). The net effect would be the presence of SO$_4^{2-}$, HSO$_4^-$, HSO$_4$.SO$_4$$^{3-}$ complexes of Fe(III) in solution. The iron complexes described above are solution species, which attain equilibrium with their surroundings in a matter of seconds. However, such species do not themselves appear to precipitate; they form polymers, which eventually lead to iron precipitation.

The addition of ferric ion to an aqueous sulphate system can result in the rapid formation of hydroxyl complexes:

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \hspace{1cm} (2-16)$$

$$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^+ \hspace{1cm} (2-17)$$

The hydroxyl species can also contain sulphate, bisulphate or sulphate-bisulphate ligand and such
iron solutions undergo slow reactions with the aqueous environment. During this period, the pH of the solution falls gradually and the colour changes from yellow to intense reddish-brown. The rate at which such changes occur depends on temperature, OH/Fe$^{3+}$ ratio, pH, iron concentration, ionic strength as well as the specific anions and cations present. The above changes seem to be associated with the formation of small iron polymers:

\[
2Fe_2(OH)_2^{4+} + 2H_2O \rightarrow Fe_4(OH)_6^{6+} + 2H^+ \quad (2-18)
\]

\[
2Fe_4(OH)_6^{6+} + 2nH_2O \rightarrow (Fe_2(OH)_4^{2+})_{2n} + 2nH^+ \quad (2-19)
\]

The critical step in the precipitation of crystalline iron compounds seems to be the growth of the small polymer Fe$_2$(OH)$_4^{2+}$ into a larger polymer, which becomes the immediate precursor of precipitation. If the pH of the solution is rapidly increased, thereby raising the OH/Fe$^{3+}$ ratio, continued growth of the Fe-OH chains occurs because the hydroxyl ions neutralise the acid produced (H$^+$) during polymerisation. This results in cross-linked polymer, which forms gel colloids and ferric hydroxide is precipitated.

\[
2[Fe_2(OH)_4^{2+}]_n + 2H_2O \rightarrow [Fe_2(OH)_2(OH^-)]_2[Fe_2(OH)_4^{2+}]_n + 2H^+ \quad (2-20)
\]

If the quantity of base is insufficient to cause immediate gel formation but is still moderately high, oxolation (formation of -O- bridges) can occur.

\[
2[Fe_2(OH)_4]_n \rightarrow [Fe_2(OH)_2(O)]_{2n} + 4nH^+ \quad (2-21)
\]

The oxolated structure is the precursor to goethite (FeOOH) and hematite (Fe$_2$O$_3$) precipitation with growth likely occurring by the addition of low molecular weight species such as Fe(OH)$_2^{2+}$ or Fe$_2$(OH)$_2^{4+}$ to the polymer unit. The tolerance of the oxolation reaction to acid increases with increasing temperature and therefore Fe$_2$O$_3$ can still be precipitated at 180°C in the presence of relatively large amounts of acid (Shang and Van Weert, 1992).

The precipitation of jarosite or other basic iron sulphates such as FeSO$_4$.OH occurs by reaction pathway, which is not well defined in the literature. If associated sulphates are considered, the small polymer chains (Equation 2-19) can be considered to consist of distorted Fe$^{3+}$ octahedra, which is shared at two edges. Such a structure could give rise to that of solid jarosite by the opening of the OH bonds such that all the octahedral would be shared at a corner.
instead of by edges. Since jarosites tend to be acidic species, it might be assumed that protons play an important role in the opening of the polymer chains. Sulphate or similar anions such as CrO$_4^{2-}$ (Powers et al., 1975) help stabilise the structure in some manner, which is not clear in the literature.

Margulis et al. (1976a) has attempted to explain the phenomena observed in the hydrolytic precipitation of iron by identifying the four stages, which are involved. When solutions of ferric sulphate and potassium hydroxide are mixed, the SO$_4^{2-}$ and H$_2$O ligands in the co-ordination sphere of iron are replaced by the OH$^-$ ions of the alkali as the first stage. The concentration and basic strength of the hydroxo-complexes of iron (Fe(OH)$_2^+$) are increased during this first stage. This is accompanied by partial neutralisation of the free acid; the pH increases sharply from its initial value of 1.2 to 1.7-2.7. The partial neutralisation of the acid by the alkali in the first stage displaces the system from the hydrolytic equilibrium and stimulates hydrolysis. This second stage is manifested by the decrease in the pH of the solution with time. The third stage involves the supersaturation of the solution by hydroxo-complexes of iron as a result of the exchange reactions with alkali, together with the hydroxo-complexes formed as a result of the gradual hydrolysis of iron, leads to the crystallization of the hydroxo-compound KFe$_3$(OH)$_6$(SO$_4$)$_2$, corresponding to the complex Fe(OH)$_2^+$. The equilibrium is apparently established between the ionic and colloidal forms of iron in the solution. Thus if the initial increase in the pH (first stage) is sufficient to bring about coagulation, the latter, being more rapid than crystallisation, leads to the removal of the colloidal particles from the iron sulphate solution in the form of an amorphous basic iron sulphate precipitate (2Fe$_2$O$_3$.SO$_3$.xH$_2$O). This suggests that the sulphate is bonded to the iron polymer before coagulation.

If the initial increase in pH (first stage) is insufficient for coagulation of the colloidal form of iron, jarosite is formed as the primary product of the hydrolytic precipitation. Margulis et al. (1976b), also observed the gradual conversion of the amorphous basic sulphate to jarosite and submitted that the attainment of a definite low pH value (during the second stage), brings about the peptisation of the amorphous basic sulphate from the precipitate. The accumulation of the colloidal particles leads to the transfer of iron from these particles to ionic complexes, and the accumulation of the latter leads to the precipitation of jarosite.
In the absence of potassium hydroxide, the hydrolysis of ferric takes place extremely slowly. The addition of potassium hydroxide causes the initial displacement of the hydrolysed state of iron in the solution, partial neutralisation of the free acid and the overcoming of the barriers to precipitate formation as a result of appreciable supersaturation and coagulation.

2.5.2 Phase Equilibria

The temperature-pH relationships for the synthesis of potassium jarosite were clarified by Babcan (1971) that hydrolysed 0.5 mol/l Fe$_2$(SO$_4$)$_3$-KOH solutions. The stability area of basic iron sulphate Fe(SO$_4$)(OH) has been neglected, but Figure 2-2 shows that jarosite is the predominant phase under the acid pressure oxidation conditions (110-150°C), which are relevant to this study. The jarosite stability zone is a band sloping to lower pH with increasing temperature. At 20°C, the region of jarosite formation extends from pH 2 to 3; at 100°C from pH 1 to 2.3 and at 200°C from pH 0-1.2. At pH values below the band, no precipitate is formed and at higher pH values, various other iron compounds are produced, mainly hematite above 100°C and goethite at lower temperatures.

![Figure 2-2. Areas of stability of various iron compounds in the Fe-S-O system. 0.5 mol/l Fe$_2$(SO$_4$)$_3$ solution at 20-200°C (Babcan, 1971).](image-url)
In sulphate systems, a host of ferric precipitates may form depending on ferric level, sulphate concentration, and pH (only two of these three factors are independent), temperature and the presence of alakalis. Posnjak and Merwin (1922) reported the chemical basis of the hydrolysis of iron from sulphate solution as polyfermers and these are represented in Figure 2-3 and Figure 2-4.

Precipitation will occur when compositions exceed the values of the "solubility planes" shown in Figure 2-3 for the Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O system. Figure 2-3 shows the data from about 0 to 40 wt% sulphate and Figure 2-4 from about 30% to 70%. The polyferm shows that, as the temperature rises, the solubility of iron at a given pH decreases. It is obvious from Figure 2-3, that high concentration of ferric sulphate can be stable at temperatures up to 140°C. Although, Figures 2-3 and 2-4 provide the phases at equilibrium, the phases that have been observed, depend on solution chemistry as well as temperature. For example, Sasaki et al., (1993) reported that at a temperature of 150°C, hydrolysis and precipitation of ferric oxide occurred up to the sulphuric acid concentration of 53.4 g/l, and above 53.4 g/l, basic iron sulphate was precipitated.
Brown (1971) has presented the equilibrium relationship between jarosite and goethite as follows:

$$3\text{FeOOH} + K^+ + 2\text{SO}_4^{2-} + 3\text{H}^+ \leftrightarrow K\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$$  \hspace{1cm} (2-22)

The free energy for this reaction is $-19.7$ kcal/mol and this shows that there is a sufficient driving force for the reaction. If goethite is formed at high pH, it can still form jarosite in the presence of sufficient potassium. This may be true for silver because the stability of silver jarosite is similar to that of potassium jarosite.
2.5.3 Characteristics of Jarosite Species

In theory, the jarosite family consists of nine end-members, which are shown in Table 2-4.

Table 2-4. Names and composition of jarosite-family end-members.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Mineral name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydronium jarosite</td>
<td>(H\textsubscript{3}O)Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)</td>
<td>Hydronium jarosite</td>
</tr>
<tr>
<td>Sodium jarosite</td>
<td>NaFe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>Natrojarosite</td>
</tr>
<tr>
<td>Potassium jarosite</td>
<td>KFe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>Jarosite</td>
</tr>
<tr>
<td>Silver jarosite</td>
<td>AgFe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>Argentojarosite</td>
</tr>
<tr>
<td>Lead jarosite</td>
<td>Pb\textsubscript{0.5}Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>Plumbojarosite</td>
</tr>
<tr>
<td>Mercury jarosite</td>
<td>Hg\textsubscript{0.5}Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>No mineral equivalent</td>
</tr>
<tr>
<td>Ammonium jarosite</td>
<td>(NH\textsubscript{4})Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>Ammoniojarosite</td>
</tr>
<tr>
<td>Thallium jarosite</td>
<td>TlFe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>No mineral equivalent</td>
</tr>
<tr>
<td>Rubidium jarosite</td>
<td>RbFe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}</td>
<td>No mineral equivalent</td>
</tr>
</tbody>
</table>

Although the end-members are presented in Table 2-4, none of them has ever been found in nature, nor synthesised in a laboratory. All synthetic jarosite species have hydronium (H\textsubscript{3}O\textsuperscript{+}) content and likewise some natural jarosite species. Another characteristic of jarosite species is that the alkali metals (Na, K, Ag) can be co-precipitated such as K\textsubscript{x}Na\textsubscript{y}H\textsubscript{3}O\textsubscript{(1-x-y)}Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}. The relative substitution of each metal depends on the concentration of the solution. Although, the end-member silver jarosite is rare during the pressure oxidation of silver bearing sulphides, under the conditions, which favour the formation of other jarosite species, silver is co-precipitated into these phases (Dutrizac and Jambor, 1987).

In terms of their crystallography, the jarosite species crystallise in the alunite structure, which itself is KAl\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}. The alunite crystal structure is shown in Figure 2-5 (Wills, 2001). This consists of sheets of hydroxyl- and sulphate-bridged Fe\textsuperscript{3+} distorted octahedra, wherein each Fe\textsuperscript{3+} is bonded to 4 OH\textsuperscript{-} groups and 2 SO\textsubscript{4}\textsuperscript{2-} groups, and each distorted octahedron is linked to its neighbours by 4 OH\textsuperscript{-} groups. Each SO\textsubscript{4}\textsuperscript{2-} group bonds three Fe(OH)\textsubscript{4} units, with one oxygen in the SO\textsubscript{4}\textsuperscript{2-} being “free” (Wang et al., 1965; Menchetti and Sabelli, 1976).

The layers of octahedron are stacked along C axis in such a way as to enclose a larger site in which a 12-coordination cation such as K, Na or NH\textsubscript{4} can be accommodated. Therefore, the substitution among the trivalent ions such as Fe\textsuperscript{3+} affects mainly the C axis. In the case of plumbojarosite, the general jarosite formula requires a modification because the alkali sites are occupied by divalent ions. In the previous studies of plumbojarosite by Hendrix (1937) and
Szymanski (1985), it was submitted that charge balance is attained because only one half of the alkali sites are occupied by Pb$^{2+}$, the C axis is doubled and that the formula becomes, Pb[Fe$_3$(SO$_4$_2)(OH)$_6$]$_2$. The beaverite (lead jarosite which contains copper) is different because charge balance is attained by substitution of Cu in the Fe position and the C axis is not doubled (Palache et al., 1944). Therefore, the Pb/Cu ratio must be maintained at 1/1 to retain charge balance.

![Figure 2-5. The structure of alunite (Wills, 2001).](image)

In addition to the presence of Cu in beaverite there is some substitution of Al for Fe. It has been shown that there is a complete Al-Fe solid solution between jarosite and alunite (Brophy et al., 1962). Theoretically, a number of possibilities exist for substitution in the jarosite lattice. The structure is composed of three main cation positions, which in ordinary jarosites are occupied by K, Fe and S. The possible replacements, based on ionic radii presented by Palache et al., (1944), are shown in Table 2-5. Although, the Table 2-5 does not include vanadium, its ion (V$^{3+}$) has been reported as a possible replacement for Fe and the compound (H$_3$O)V$_3$(SO$_4$_2)(OH)$_6$ has been synthesised by Wills (2001).
Table 2-5. Possible replacement based on ionic radii

<table>
<thead>
<tr>
<th>Potassium Position</th>
<th>Iron Position</th>
<th>Sulphur Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>Ionic Radii (Å)</td>
<td>Ion</td>
</tr>
<tr>
<td>Na$^1$</td>
<td>0.98</td>
<td>Fe (III)$^1$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.33</td>
<td>Al$^1$</td>
</tr>
<tr>
<td>Rb$^{2-}$</td>
<td>1.48</td>
<td>Cr</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>1.20</td>
<td>Co</td>
</tr>
<tr>
<td>Pb$^+$</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Hg$^{2-}$</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>Ce$^{2-}$</td>
<td>1.10</td>
<td></td>
</tr>
</tbody>
</table>

$^1$There are natural jarosite or alunite minerals of these ions.
$^2$There are synthetic jarosite compounds of these ions.

2.6 Relative Substitution of Silver in Jarosite Species

Silver is incorporated into other jarosites species, such as sodium jarosite, potassium jarosite and lead jarosite, which promotes the loss of silver in acid ferric media. At 97°C, there is a complete solid-solution series between argentojarosite and natrojarosite. The relative partitioning of the silver and sodium on a molar basis between the solution and jarosite phase is shown in Figure 2-6 (Dutrizac and Jambor, 1987). The dashed line in the figure represents the ideal behaviour, whereby the ratio in which silver and sodium are precipitated is that of their concentrations in solution.

Silver is precipitated as a jarosite-type compound in preference to sodium. In dilute silver solutions, which are those solutions of concern to pressure oxidation of complex sulphide, the limiting partitioning coefficient of silver is approximately 2. This indicates that silver losses to natrojarosite are significant and that there are solid-solution series between argentojarosite and natrojarosite.

The molar partitioning curve in Figure 2-7 (Dutrizac and Jambor, 1984) shows that silver and potassium are both precipitated in the same ratio as they are present in solution by forming approximate ideal solid solution. Although, potassium jarosite is known to be the most stable of all jarosite-specie minerals, Figure 2-7 indicates that argentojarosite is approximately as stable thermodynamically as the potassium jarosite.
The chemical molar partitioning in Figure 2-8 indicates that silver is highly concentrated into the lead jarosite phase (Dutrizac and Jambor, 1984). In silver-rich medium, which has $\text{Ag}/(\text{Ag} + \text{Pb})$ ratio, greater than 0.8, nearly lead-free argentojarosite is formed. For the dilute silver media, the chemical molar partitioning coefficient is about 3.0 and this shows that silver is concentrated substantially in the lead jarosite. At 97°C, the molar partitioning coefficient is 3.5 (Figure 2-9), which is similar to that of 155°C. The X-ray diffraction study of the precipitates formed at 155°C revealed mixtures of hydronium-bearing plumbojarosite and argentojarosite. It was submitted that the lead-poor argentojarosite was formed first because argentojarosite is more stable than plumbojarosite.

![Graph](image)

Figure 2-6. Relative partitioning of silver and sodium between solution and jarosite at 97°C.

(Dutrizac and Jambor, 1987)
Figure 2-7. Relative partitioning of silver and potassium between solution and jarosite at 97°C (Dutrizac and Jambor, 1984).

Figure 2-8. Relative partitioning of silver and lead between solution and jarosite at 155°C (Dutrizac and Jambor, 1984).
At 97°C, a homogenous single-phase was precipitated (only) from silver-rich (low lead) solution, while precipitation from moderate to high concentration of lead suspension solution produced two phases. The precipitation of a single phase, lead-poor argentjarosite indicates that the precipitation of plumbojarosite is delayed at low temperature and much more at low concentration of lead sulphate suspension.

![Figure 2-9. Relative partitioning of silver and lead between solution and jarosite at 97°C (Dutrizac and Jambor, 1984).](image)

2.6.1 Effect of Silver Concentration

The high molar partition of silver in lead jarosite means the behaviour of lead jarosite and the factors affecting the incorporation of silver are relevant to the pressure oxidation of complex sulphides. The effect of the concentration of silver sulphate on the lead, copper, silver and iron contents of jarosite specie is shown in Figure 2-10 (Dutrizac and Jambor, 1984). The silver
content of the precipitates increases with increase in the concentration of silver sulphate. The increase in silver is linear to about 0.03 mol/l Ag₂SO₄ but levels off thereafter. The lead content drops steadily with increase in Ag concentration, and an inverse relationship is obtained between silver and lead contents in the precipitate. This strongly suggests substitution of Ag⁺ for ½ Pb²⁺. The copper content falls as the lead content decreases with increase in the concentration of silver sulphate. Dutrizac and Jambor (1987) also suggested a coupled substitution of ½ Pb²⁺ and Cu²⁺ for Fe³⁺ in jarosite species and that the extra ½ Pb²⁺ occupied the vacant alkali site in plumbojarosite. Consequently, the iron content increases as lead and copper fall in Figure 2-10.

2.6.2 Effect of Lead Sulphate Suspension

The effect of lead sulphate suspension on the composition of the jarosite species is shown in Figure 2-11 (Dutrizac and Jambor, 1984). The mass of jarosite species increases with increase in the lead sulphate suspension, however, there was no appreciable decrease in the silver content of the jarosite species. In the absence of lead sulphate and at low concentration of copper sulphate, an argentojarosite containing very low concentration of copper is formed. As the lead sulphate suspension increases, the lead content of the jarosite species increases linearly. The extent of lead incorporation into the jarosite is fixed by the silver concentration of the solution used for precipitation. High concentration of silver sulphate was used by Dutrizac and Jambor (1984) for the precipitation of jarosite species and therefore, maximum increase in the lead sulphate suspension resulted in a precipitate containing only 4% weight of lead as shown in Figure 2-11. The copper content of the jarosite species increases with increase in the lead content, and this also shows the Pb-Cu substitutions in the jarosite species (Dutrizac and Jambor, 1987).

2.6.3 Simultaneous Incorporation of Copper and Zinc

Also, low concentrations of copper and/or zinc are incorporated into jarosite species by replacing the iron component of the jarosite, probably according to the following reaction:

\[ AgFe_3(SO_4)_2(OH)\_6 + xM^{2+} + xH^+ \rightarrow Ag(Fe_{3-x}M_x)(SO_4)_2(OH)_{6-x}(H_2O)_x + xFe^{3+} \]  \hspace{1cm} (2-23)

Where \( M = Cu, Zn \)

The end-member argentojarosite is used in equation (2-23) for the purpose of illustration. The charge neutrality in the molecule is maintained by conversion of some hydroxyl ions to water.
Figure 2-10. Effect of silver sulphate concentration on lead, copper, silver and iron contents of jarosite (Dutrizac and Jambor, 1984).

Figure 2-11. Effect of lead sulphate suspension on the lead, copper, silver and iron contents of jarosite (Dutrizac and Jambor, 1984).
When complex sulphide concentrate containing zinc, copper and lead is oxidised, a lead jarosite specie may be formed with copper and zinc incorporated. The effect of zinc sulphate concentration on the co-precipitation of copper and zinc is shown Figure 2-12. The zinc content of the lead jarosite increases with increasing concentration of zinc sulphate. The increase in the lead content is directly due to the increase in the copper and zinc contents. The copper content, which is higher than zinc indicates that copper is preferentially incorporated into the lead jarosite with respect to zinc.

The effect of copper sulphate concentration on the co-precipitation of copper and zinc is shown Figure 2-13. The concentration of copper sulphate has significant effect on the incorporation of zinc into the lead jarosite specie. The zinc content of the jarosite specie is at its highest level, when precipitation is carried out in the absence of copper. It is obvious that the lead content of the jarosite specie increases with increasing concentration of copper sulphate.

Figure 2-12. Effect of zinc sulphate concentration on the lead, copper and zinc contents of jarosite specie (Dutrizac and Dinardo, 1983).
2.7 Prevention of Lead Jarosite Formation

The high molar partition coefficient of silver in plumbojarosite (section 2.6) shows that, if silver dissolves during the oxidation of a lead bearing concentrate at 110-150°C, then it will be significantly concentrated in the plumbojarosite phase formed. It has been observed that lead jarosite is the major collector of silver during the pressure oxidation of silver-bearing zinc-lead concentrates (Parker, 1981; Dutrizac and Chen, 1984) and that end member argentojarosite is rare at low concentration of silver encountered in industrial autoclave. Therefore, the prevention of lead jarosite is considered as a precursor to silver extraction during pressure oxidation of complex sulphide. Various methods have been investigated to prevent lead jarosite formation during oxidation.

2.7.1 Use of High Acidity

It has been reported that if the terminal acid levels of the acid pressure oxidation of zinc-lead concentrates are moderate or low, lead jarosite and not lead sulphate is produced in the circuits.
Scott (1973) observed the use of 20-30% H₂SO₄ prevented lead jarosite formation and yielded lead sulphate. This is the basis of the Comprex process (section 2.3). Dutrizac et al. (1980) has quantified the effect of acid concentration on the composition and yield of lead jarosite; their results are presented in Figure 2-14 (Dutrizac, 1983). The yield of the jarosite product is dependent on both the iron concentration and the acidity. At high acidity, the yield of jarosite declines rapidly and no jarosite at all is produced above some critical acid concentration. The higher the iron concentration, the higher the critical acid concentration required to suppress jarosite formation. The use of high-level acid leaves substantial iron in solution, which must be neutralised and the neutralisation of the solid prior to cyanidation is an additional consideration.

![Figure 2-14. Effect of ferric ion concentration and initial acid concentration on the extent of iron precipitation as lead jarosite formed at 140°C from 1 l solution. Solid points are %Pb and open circles are product yield (Dutrizac, 1983).](image)

2.7.2 Use of High Temperature

Another procedure, which has been suggested to prevent lead jarosite formation, is to operate the autoclave above the jarosite stability temperature. Mumme and Scott (1966) identified this temperature as 190°C, and Dutrizac et al. (1980) noted the transition above 180°C. The
application of high temperature (200-220°C) to preclude lead jarosite is also a feature of the Comprex process (section 2.3). The transition temperature depends on the solution chemistry, therefore, the use of operating temperature and iron phases (section 2.5.2) to fix the problem of silver is not a reliable way of preventing the loss of silver during pressure oxidation of silver-bearing zinc-lead concentrates. For example, the formation of jarosite specie has been reported during the pressure oxidation of zinc leach residue at 170-190°C (Acharya et al., 1991). Also, the poor extraction of silver from the residue generated by pressure oxidation of complex sulphide has been attributed to the formation of jarosite specie at 210°C (Dreisinger, 1997).

2.7.3 Use of Alkali

Also the use of the alkali jarosite specie, which has higher stability than lead jarosite, has been suggested by Dutrizac et al., (1980). If alkali ions are present, then a low-lead alkali jarosite and lead sulphate will be the product of reaction (Bratt and Sinclair, 1971). Dutrizac et al., (1980), submitted that potassium, sodium and ammonium are effective ions and that the order of effectiveness was K > NH\textsubscript{4} > Na. The order of effectiveness of the various alkalis was shown to be consistent with the thermodynamics for the reaction:

\[
Pb_{0.5}Fe_3(SO_4)_2(OH)_6 + M^+ \rightarrow \text{MFe}_3(SO_4)_2(OH)_6 + 1/2\text{PbSO}_4 \quad (2-24)
\]

High concentration of alkali is required and if silver is present in solution, it will co-precipitate with the alkali jarosite and will be lost. This is based on the fact that argentojarosite is approximately as stable thermodynamically as the potassium jarosite (section 2.6). Tourre (1984) used alkali during pressure oxidation of sulphide ore to improve the silver extraction by cyanidation. The oxidation was carried out at 180°C; a high level of potassium sulphate (about 36 kg/ton of ore) was required. Sodium or ammonium sulphate additions were tested but did not improve the silver extraction. Considering the fact that the pressure oxidation was carried out at a high temperature, which favours transition from lead jarosite to hematite and the high acidity employed, it is unlikely this approach will contribute significantly to silver extraction from the silver-bearing sulphide concentrates. Moreover, the process is a function of the iron content of the feed material. In the work of Tourre (1984), iron content was only 1.3% of the ore and yet high concentration of alkali was required.
2.8 Deportment of Silver during Acid Pressure Oxidation

Efforts to recover silver from complex sulphides, which contain economic fraction of silver require the fundamental understanding of the behaviour of the main silver mineral (acanthite) during the pressure oxidation.

2.8.1 Silver-Sulphur-Water System

The potential-pH diagram for the Ag-S-H₂O system is shown in Figure 2-15 (Warren et al., 1984) for 25°C, 1 atmospheric pressure and activity of 1.0 for all the dissolved sulphur species. In Figure 2-16 (Warren et al., 1984), part of the predominance area for Ag⁺ is replaced by silver sulphate (Ag₂SO₄) because the solubility of silver is exceeded under these conditions. The solubility of silver sulphate at different temperatures has been investigated in sulphuric acid by Lietzke and Stoughton (1959) and in acidic ferric sulphate by Dutrizac et al. (1975). According to the data of Lietzke and Stoughton (1956 and 1959a), the solubility of silver sulphate increases with increasing temperature and sulphuric acid concentration. The solubility of silver sulphate increases from 0.0292 mol/l at 25°C to 0.100 mol/l at 150°C in a solution of 0.1 mol/l sulphuric acid. At 150°C, the solubility of silver sulphate is 0.100 mol/l in 0.1 mol/l sulphuric acid and it is 0.344 mol/l in 1.0 mol/l sulphuric acid. At a constant acid concentration, the solubility increases slightly with increasing ferric ion in the range of 0 to 0.3 mol/l. At 25°C, the silver sulphate solubility in 1 mol/l sulphuric acid is 0.036 mol/l (11.2 g/l), which is similar to that reported by Dutrizac et al. (1975) for the same solution containing 0.1 mol/l ferric addition.

Therefore, when the total dissolved sulphur is 1.0 mol/l, the solubility of silver sulphate is exceeded for any activity of Ag⁺ greater than 0.07 mol/l and the predominance area for Ag⁺ is replaced by silver sulphate, such as in Figure 2-16.

\[ 2\text{Ag}^+ + \text{HSO}_4^- \rightarrow \text{Ag}_2\text{SO}_4 + \text{H}^+ \]  

(2-25a)

The governing equations for the formation of the silver sulphate at low pH are (Lietzke et al., 1961; Warren et al., 1984):

\[ K = \frac{[\text{Ag}^+]^2[\text{HSO}_4^-]}{[\text{H}^+]} = 10^{-3.0} \]  

(2-25b)

\[ K = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 10^{-1.92} \]  

(2-25c)
Figure 2-15. Potential-pH diagram for the Ag-S-H2O system, at 25°C, 1 atm. pressure and activity of 1.0 mol/l for all the dissolved sulphur species (Warren et al., 1984).

The position of line (28) in Figure 2-16 depends on the concentrations of both dissolved sulphur species and silver. Also, an examination of equations (2-25b) and (2-25c) shows that [Ag+] is a function of dissolved sulphur and decreases as the concentration of sulphur species increases. If the numerator of equation 2-25b is increased, the equilibrium pH becomes lower resulting in a larger predominance area for silver sulphate. This is probably the basis of using high acidity to recover silver during the high acid leaching of ferrite. The equilibrium constant for the dissociation of bisulphate acid (2-25c) decreases with temperature (Lietzke et al., 1961), which is supposed to favour silver sulphate formation.

Warren et al., (1984) have listed the reactions, which are theoretically possible or impossible for each pair of electrode potential and pH values and these are included in Appendix 1 (Table A1-1). Anodic dissolution of Ag2S electrode in sulphuric acid solution under the applied constant
anodic current or overpotential has been proposed by Warren et al., (1984) as follows:

\[ Ag_2S \rightarrow 2Ag^+ + S^0 + 2e^- \]  

\hspace{1cm} (2-26)

Aqueous silver was detected in the solution. The reaction (2-26) is not favourable because silver wants to form Ag\(_2\)S from Ag\(^+\) and S. However reactions equivalent to this have been proposed for other sulphides (Dutrizac and MacDonald, 1978; Munoz et al., 1979; Warren et al., 1982). At large anodic overpotential, oxidation of the mineral to sulphate or bisulphate is expected to become important as has been observed for pyrite (Biegler and Swift, 1979) and chalcopyrite (Warren et al., 1982). Therefore, Warren et al. (1984) submitted that reaction (2-26) is substantially responsible for the production of silver in solution and that the balance of the silver sulphide is oxidised to bisulphate by the following reactions. The bisulphate reaction corresponds to line 26 in Figure 2-15 and line 37 in Figure 2-16 respectively on the E-pH diagrams:

\[ Ag_2S + 4H_2O \rightarrow 2Ag + HSO_4^- + 7H^+ + 6e^- \]  

\hspace{1cm} (2-27a)

\[ E = 0.408 - 0.069pH + 0.010 \log [HSO_4^-] \]  

\hspace{1cm} (2-27b)

\[ Ag_2S + 4H_2O \rightarrow 2Ag^+ + HSO_4^- + 7H^+ + 8e^- \]  

\hspace{1cm} (2-28a)

\[ E = 0.506 - 0.052pH + 0.007 \log ([Ag^+]^2 [HSO_4^-]) \]  

\hspace{1cm} (2-28b)

The reaction (2-27a) and (2-28a) are expected from the potential-pH diagrams for high and very low silver concentration respectively. For silver sulphide electrodes undergoing anodic dissolution in sulphuric acid, it is expected that once the solution near the surface becomes saturated, precipitation of silver sulphate would occur. The precipitation of silver sulphate on the silver sulphide surface during anodic potential sweeps has a passivating effect on the current. This effect is absent in the nitric acid medium because of the enhanced solubility of silver in nitric acid.

The reactions (2-27a) and (2-28a) were also proposed by Warren et al., (1984) to be responsible for the open circuit potential (0.51 V) across the silver sulphide electrode in acidic solutions of silver ion, although there was no evidence of metallic silver (in agreement with 2-27a) during the investigation.
Figure 2-16. Potential-pH diagram for the Ag-S-H₂O system, at 25°C, 1 atm. pressure, activity of 0.1 mol/l Ag⁺ and 1.0 mol/l dissolved sulphur species respectively (Warren et al., 1984).

The rest potential of the silver sulphide electrode has been observed to be dependent on silver ion concentration and dissolved sulphate. Although, the reaction (2-27a) is not expected from the thermodynamic standpoint, it agrees with the observed dependence on silver ion concentration. An equivalent reaction has been proposed for galena as the potential determining reaction for the rest potential, when the lead ion concentration is greater than 25 ppm (Peters, 1977).

At constant sulphate concentration, the rest potential observed by Warren et al., (1984) was independent of the pH, but at different concentrations of sulphate, the rest potential increased as concentration of hydrogen ion [H⁺] decreased. However, the reactions (2-27a) and (2-28a) indicate that the potential increase with the increase in [H⁺] and sulphate concentration, and that the potential is (more strongly) dependent on pH than on dissolved sulphate. Based on the dependence of the rest potential on the concentration of hydrogen ion [H⁺] or the total dissolved
sulphate provided by Warren et al., (1984), reactions (2-27a) and (2-28a) may not be responsible for the observed open circuit behaviour of the silver sulphide electrode.

Also, from the potential-pH diagram the following reaction, which corresponds to line 22 may be anticipated:

\[ Ag_2S + 2H^+ + 2e^- \rightarrow 2Ag + H_2S \]  \hspace{1cm} (2-29)

The reaction (2-29) has been proposed for the cathodic polarization of the silver sulphide electrode (in acidic solution) and this competes with the hydrogen evolution side reaction. Once the surface is substantially covered by the elemental silver, the side reaction becomes less important because of the large hydrogen overvoltage on silver.

Also, the anodic formation and cathodic reduction of Ag\(_2\)S films on metallic silver in basic sulphide solutions (pH~11 to 14) have been reported (Birss and Wright, 1981; Campbell et al., 1982) and the reaction which corresponds to line 23 on potential-pH diagram is as follows:

\[ Ag_2S + H^+ + 2e^- \rightarrow 2Ag + HS^- \]  \hspace{1cm} (2-30)

There is a possibility of direct cathodic reduction of Ag\(_2\)S to metallic silver by reactions 2-30 and 2-31, and the potential or driving force required could be provided by using an externally supplied voltage or by galvanic coupling with metals such as lead.

\[ 0.5Ag_2S + H^+ + 0.5Pb \rightarrow Ag + 0.5H_2S + 0.5Pb^{2+} \]  \hspace{1cm} (2-31)

2.8.2 Dissolution of Silver Sulphide

Although the behaviour of silver alloys and silver chloride in ferric chloride and ferric sulphate media is relatively well understood (Dutrizac, 1986; Durizac, 1987 and Morrison, 1989), the dissolution of Ag\(_2\)S has not been extensively studied. This may be attributed to the formation of argento-jarosite which complicates the dissolution kinetics. Tourre (1984) investigated the sulphuric acid pressure oxidation of "make-up" mixed-sulphides, containing low grade (~4% Ag) acanthite ore and substantial pyrite. The standard conditions were 15g/l sulphuric acid solution, 180 psi oxygen partial pressure and 2 hours retention time. At above 120°C, extensive dissolution of silver sulphide occurred with the consequent sequestering of the dissolved silver into the jarosite phase. Longer residence time was required to achieve the same
results at 90, 100 and 110°C. The main limitation of this study was that the silver extraction-time profile, before the sequestering of silver into jarosite was not provided.

Also, the dissolution of silver sulphide (Ag₂S) was confirmed by Van Weert and Tuinman (1993) at 160°C by pressure oxidation of this material in 30 g/l Fe₂(SO₄)₃.5 H₂O media and with 16 bar oxygen partial pressure. Although, the reaction and its mechanism have not been proposed in the literature, the dissolution of silver sulphide during the oxygen pressure leaching can be represented by the following chemistry:

\[
\begin{align*}
\text{Ag}_2\text{S} + 0.5\text{O}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{Ag}_2\text{SO}_4 + \text{S}^0 + \text{H}_2\text{O} & \Delta G^o = -50.54 \text{kJ/mol} \\
\text{Ag}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{Ag}_2\text{SO}_4 + \text{S}^0 + 2\text{FeSO}_4 & \Delta G^o = 43.47 \text{kJ/mol}
\end{align*}
\]

The reaction 2-33 is thermodynamically unfavourable, though the presence of ferric will assist sulphide oxidation. However, the following reaction is favourable:

\[
\begin{align*}
\text{Ag}_2\text{S} + 4\text{H}_2\text{O} + 8\text{Fe}^{3+} & \rightarrow 2\text{Ag}^+ + \text{HSO}_4^- + 8\text{Fe}^{2+} + 7\text{H}^+ & \Delta G^o = -206.63 \text{kJ/mol}
\end{align*}
\]

However, a very low dissolution of Ag₂S in sulphate medium was observed at low temperature (85°C), when a disk of Ag₂S was leached with 0.3-3.0 mol/l Fe³⁺ in de-oxygenated and oxygenated environment by Dutrizac (1994). Increasing the sulphuric acid concentration to 4.0 mol/l had no significant effect on the rate of silver dissolution. The low dissolution of silver sulphide in the work of Dutrizac (1994) contradicts that of Tourre (1984), although comparison of the two works is limited. Tourre used fine particle suspension for the oxidation tests under the oxygen partial pressure, while Dutrizac used disk of silver sulphide (massive) under the atmospheric pressure. Also, possible formation of silver jarosite on the surface of the disk or silver sulphate precipitation could have hindered the dissolution of the silver sulphide disk. In addition, considerable uncertainties arise in the interpretation of results, when ferric oxidation of sulphide mineral is carried out without controlling the redox potential, which is expected to fall drastically as ferric ion is consumed (Dixon and Bolorunduro, 2002). Obviously, a systematic approach is required to study silver deportment from the sulphide minerals into the final residue before serious attempts can be made to recover silver from the complex sulphides. This is one of the important contributions of the present work. An approach will be to conduct the tests under the conditions in which the silver extraction-time profile can be followed and these will preclude
the formation of jarosite specie and the silver sulphate precipitate.

2.8.3 Mechanisms of Acanthite Dissolution

The following mechanisms for the reaction of acanthite in acid ferric media can be considered based on the properties of the mineral and the general mechanisms known for other sulphides.

First, the ionic transfer mechanism, which involves the migration of silver ions and electron holes through the silver sulphide, the ionic conductivity of silver sulphide and the high mobility of silver ions in the crystal lattice make this possible. The solid state diffusivity of silver in Ag$_2$S has been described as the fastest solid state diffusional process known in inorganic chemistry (Peters and Doyle, 1988). Once the bond is broken, the sulphur specie is free to react. The self diffusion coefficients provided by Peschanski (1950) are $D_{S^2-} = 0.237e^{-24600/RT}$ and $D_{Ag^+} = 0.93 \times 10^{-2} e^{-9100/RT} \text{ cm}^2/\text{sec}$. According to Ishiguro et al. (1953), both Ag$^+$ and S$^{2-}$ take part in the ionic transport of current for Ag$_2$S, but S$^{2-}$ participates to a much lesser extent than Ag$^+$. The silver ion diffuses out and is released into the aqueous phase and S$^{2-}$ on the surface of the mineral is oxidised as follows:

$$Ag_2S \leftrightarrow 2Ag^+ + S^{2-} \quad (2-35)$$

The S$^{2-}$ is oxidized indirectly to elemental sulphur by oxygen through the help of the ferric iron and the oxidation of S$^{2-}$ may be stated as follows:

$$S^{2-} \rightarrow S^0 + 2e^- \quad (2-36)$$

The oxidation of the S$^{2-}$ pushes the equilibrium of equation (2-35) to the right. The equilibrium constant for the forward reaction in equation (2-35) is $6.196 \times 10^{-50}$, while the constant for the backward reaction is $1.61 \times 10^{49}$ (HSC program, 1999).

Second, the molecular mechanisms for the decomposition of some sulphides (excluding pyrite) can be considered for acanthite reaction. The equilibrium for this reaction can be expressed by the following (Peters and Doyle, 1988):

$$MS + 2H^+ \leftrightarrow H_2S + M^{2+} \quad (2-37a)$$
The dissolution of the mineral in weakly acidic thiourea solution has been investigated by Umetsu et al. (1991). It was submitted that the aqueous silver was dissolved by reaction (2-37a) and then complexed by thiourea. The removal of hydrogen sulphide was essential for the continual dissolution of silver sulphide and silver extraction up to 90% was obtained at 50°C, in a weak acid media (0.06 mol/l) and where the H₂S was eliminated by nitrogen gas. In the absence of hydrogen sulphide removal by ferric and nitrogen bubbling or flow, the reaction reached only 40% silver extraction. However, hydrogen sulphide formation was not confirmed and the direct complexation of the mineral by thiourea was not considered. It was observed that the rate of reaction increased with increasing concentration of thiourea and the direct proportionality of the rate to concentration should have suggested that the reaction is limited by the mass transfer of thiourea.

The transfer of sulphur with hydrogen sulphide as intermediate has been proposed by Jan et al. (1976) for the pressure oxidation of zinc sulphide. The first step involves the decomposition of the sulphide by H⁺ and the formation of hydrogen sulphide and the second step is the oxidation of hydrogen sulphide, which is assumed to be the rate controlling step. Van Weert et al., (1974) described a process for decomposing nickeliferous pyrrhotite, which is similar to that of zinc sulphide molecular mechanism. Also, Scott and Nicol (1977) studied the non-oxidative dissolution of natural galena (PbS), synthetic millerite (NiS), synthetic troilitre (FeS) and pyrrhotite (Fe₇S₈).

Peters and Doyle calculated equilibrium pH values for a number of minerals to determine, which of them will react according to reaction (2-37a). The equilibrium pH value for the generation of 1 atm H₂S from silver sulphide at 10⁻³ mol/l silver ion is -12.8, which is not achievable in the sulphate media because of the low activity of H⁺. Therefore, the acid decomposition mechanism, which involves hydrogen sulphide may not be applicable to the silver sulphide in sulphate media because the mineral is highly insoluble. The solubility product of silver sulphide at 25°C is 10⁻⁵⁰.⁵, while that of zinc sulphide is 10⁻²².².
The acid decomposition reaction was employed previously by boiling silver sulphides (containing some precious metals) with concentrated sulphuric acid in cast iron (containing high silicon) pots (Downie, 1937). The amount of acid used was 20 gallons of concentrated sulphuric acid (94% purity) per 130 lb. of sulphides. The silver dissolved into solution while the insoluble residue remaining from this acid treatment contains all the gold and any platinum which may be present in the initial feed. It was not clear if the process was catalysed by iron or iron hydroxide which was formed by the reaction of sulphuric acid with the iron pots in the presence of moisture. Iron addition was not reported for this operation and the extent of silver extraction was not mentioned. Also, the chemistry of the process was not reported. It is probable, the concentrated H$_2$SO$_4$ behaves as an oxidant.

$$\text{Ag}_2\text{S} + 4\text{H}_2\text{SO}_4 \rightarrow \text{Ag}_2\text{SO}_4 + 4\text{H}_2\text{O} + 4\text{SO}_2$$  \hspace{1cm} (2-37d)

Third, electrochemical mechanisms, which are promoted by high voltages as a result of high redox potentials in acidic ferric solution may be responsible for the oxidation of silver sulphide and this is represented as follows:

$$\text{Ag}_2\text{S} \rightarrow 2\text{Ag}^+ + \text{S}^0 + 2e$$  \hspace{1cm} (2-38)

Then:

$$2\text{Fe}^{3+} + 2e \rightarrow 2\text{Fe}^{2+}$$  \hspace{1cm} (2-39)

This oxidative dissolution of acanthite is based on the conductivity of the mineral. Therefore, in an aqueous solution, electrons can pass through the conducting solid phase from anodic to cathodic sites for the reduction of ferric. Then, the Fe$^{2+}$ and the Ag$^+$ are carried away from the reacting sites by the aqueous solution.

According to the Eh-pH diagram presented by Warren et al. (1984), acanthite may be oxidized at moderate potential (0.6V vs SHE) and at low pH values (section 2.8.1). Once acanthite is oxidized, silver reports to the aqueous phase as Ag$^+$, while sulphur may remain as elemental sulphur or form bisulphate or sulphate depending on the acidity.

Third, mechanism that generates sulphate as follows:

$$\text{Ag}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 2\text{Ag}^+ + \text{SO}_4^{2-} + 8\text{H}^+ + 8e$$  \hspace{1cm} (2-40)

$$8\text{Fe}^{3+} + 8e \rightarrow 8\text{Fe}^{2+}$$  \hspace{1cm} (2-41)

The mechanism which involves oxidation of sulphide sulphur to sulphate can be ruled out, if sulphur is found to be the predominant product as in the oxidation of pyrrhotite, sphalerite,
galena, etc.

The ionic transfer and the electrochemical mechanisms are tenable because the silver sulphide has been described effectively as a mixed conductor in which the current is carried by the silver ions and the electrons. The conductivity of the mineral increases with temperature and this increase has been shown to be greater for the electronic conductivity.

The difference between these reaction models is that in the ionic transfer case, $S^{2-}$ is an intermediate case, and it may react on the surface of the mineral or move out into the solution before it reacts further to elemental sulphur. In the electrochemical case, the intermediate is the electron pair, which may move from anodic site, where it is created, to a cathodic site where it is consumed. If neither the $S^{2-}$ nor the electrons move from their sites of origin before they react, there would be no way to clearly distinguish between a ionic and an electrochemical mechanism. Therefore, it may be difficult to know which of the mechanisms prevails during the oxidation of silver sulphide. However, the effect of silver ion concentration $[\text{Ag}^+]$ on the kinetics and the overall process should indicate ionic transfer mechanism (2-35). Equilibrium of reaction (2-35) is given as follows:

$$K_{\text{eq}} = [\text{Ag}^+]^2[S^{2-}]$$  \hspace{1cm} (2-42)

An increase in the silver ion concentration of the autoclave solution should shift the equilibrium state in such a way as to re-establish equilibrium according to equation (2-42). This will reduce the rate of either silver extraction or lower the activity of the $S^{2-}$ on the surface of the mineral, which will ultimately decrease the extent of silver extraction. The silver ion concentration will not have effect on the rate of extraction, if the electrochemical mechanism prevails during the oxidation of silver sulphide.

2.8.4 Other Department of Silver during Sulphide Oxidation

Another factor which can be attributed to the low concentration of silver during the hydrometallurgical treatment of silver bearing material is the possible cementation of dissolved silver on the surface of the reactive base metal sulphides such as (Rosato et al., 1990):

$$\text{Ag}_2\text{SO}_4 + \text{CuS} \rightarrow \text{Ag}_2\text{S}_{(surface)} + \text{CuSO}_4 \hspace{1cm} \Delta G^\circ = -79.90 \text{ kJ/mol}$$ \hspace{1cm} (2-43)

$$\text{Ag}_2\text{SO}_4 + \text{ZnS} \rightarrow \text{Ag}_2\text{S}_{(surface)} + \text{ZnSO}_4 \hspace{1cm} \Delta G^\circ = -144.90 \text{ kJ/mol}$$ \hspace{1cm} (2-44)
Scaini et al., (1995) used X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Scanning electron microscopy (SEM) to characterise the silver sulphide formed by the same reaction on the surface of galena, sphalerite and pyrite.

Similar reaction and subsequent oxidation of the Ag$_2$S have been observed to catalyse ferric sulphate oxidation of chalcopyrite (Millers et al., 1979, 1981). The enhanced rate of reaction has been attributed to the formation of intermediate silver sulphide films on the chalcopyrite surface by an exchange reaction:

$$CuFeS_2 + 4Ag^+ \rightarrow 2Ag_2S_{(surface)} + Cu^{2+} + Fe^{2+}$$  \hspace{1cm} (2-45)

The surface layer is porous and the original sulphide is still accessible to the leaching solution (either Ag$^+$ or Fe$^{3+}$). It was submitted that unlike uncatalysed ferric oxidation reaction, the rate is controlled by an electrochemical reaction of Ag$_2$S with Fe$^{3+}$:

$$Ag_2S_{(surface)} + 2Fe^{3+} \rightarrow 2Ag^+ + 2Fe^{2+} + S^0$$  \hspace{1cm} (2-46)

An alternative explanation for these observations is that silver sulphide provides a source of cathodic sites, enabling rapid transfer of electrons compared to a surface where a polysulphide or metal-deficient sulphur layer is present, as proposed by Parker et al. (1981).

The same catalytic effect of silver has been observed during the pressure oxidation of chalcopyrite by Pawlek (1976a and 1976b). The major limitation of the silver catalysed oxidation process is that the silver is lost to the jarosite specie and is difficult to recover by cyanidation. This indicates that the intermediate Ag$_2$S is oxidised to silver during the process rather than remaining as silver sulphide, which is cyanide soluble.

Peters and Doyle (1988) theorised that the reason silver is such an effective catalyst is that the solid state diffusivity of silver in sulphide minerals is very fast, so silver can easily enter into exchange reactions and silver sulphide can readily abstract electrons by ferric iron during its dissolution.

Also in the presence of elemental sulphur, silver sulphide may be formed (in an acid medium) through the following reaction.

$$Ag_2SO_4 + FeSO_4 + S^0 \rightarrow Ag_2S + Fe_2(SO_4)_3 \hspace{1cm} \Delta G^0 = -35.19 \text{ kJ/mol}$$  \hspace{1cm} (2-47)

The reaction may involve the following two steps:
The reaction (2-48) is reversible and has a well defined equilibrium constant (Tananaev, 1924). At 0°C, the constant for the reaction from left to right is 0.0019 and for the reverse reaction, it is 526.3. At 25°C, the constant for the reaction from left to right is 0.0060 and for the reverse reaction, it is 166.7. At 45°C, the constant for the reaction from left to right is 0.0110 and for the reverse reaction, it is 90.9. These show that the ferrous reduction of aqueous silver improves (thermodynamically) with temperature over range studied by Tananaev (1924). This is contrary to the previous conclusion (Cooke, 1913), that the increasing temperature favours the reaction to the left.

The reduction of aqueous silver through the first step (2-48) requires very low ferric/ferrous ratio and this depends on the concentration of aqueous silver as shown in the potential-pH diagram for silver-water system. At high concentration of ferric, the reaction tends to go in a reverse direction. The formation of silver sulphide through reaction (2-49) is based on the affinity of silver for sulphur. The precipitated silver combines with the sulphur, at ordinary temperature and pressure to form silver sulphide. The kinetics of the formation of silver sulphide from silver and sulphur has been investigated over the temperature range of 130 and 180°C by Reinhold and Seidel (1935). The rate determining factor is the rate of diffusion through the built-up layer and the rate of reaction is inversely proportional to the diameter of this layer. Similar mechanism has been reported at higher temperature (275°C) by Peters (1966).

Although the chemistry of the net reaction (2-47) is known, its contribution to the deportment of silver during the hydrometallurgical processes is not known from the literature.

2.9 Silver extraction by Sulphate-Iodide Process

The approach of this study to recover zinc and silver from zinc-lead-iron complex sulphide concentrates or ores is to oxidise the materials in the autoclave at a temperature range of 110 to 150°C and in the presence of low concentrations of potassium iodide. Zinc will be extracted into solution during the pressure oxidation without altering the iron phase, while silver will be precipitated as silver iodide (iodargyrite) in the acid sulphate-iodide medium. Iodargyrite (AgI)
has excellent leaching characteristics in cyanide solutions (Wyslouzil and Salter, 1990). The choice of iodide among halides is based on the solubility-product \( K_{sp}=1 \times 10^{-16.03} \) at 25°C of silver iodide, which is the least among the silver halides group (Sillen and Martell, 1964). The solubility product of AgCl is \( 1 \times 10^{-9.7} \) at 25°C.

The use of chloride will not be as effective as iodide because it is less stable and it has been shown previously by Dutrizac and Jambor (1987) that some AgCl dissolves in the acid ferric sulphate solution. Based on the concentration of chloride released into solution, a corresponding 10% silver loss can be calculated. The solubility of AgCl limits its application in the way iodide is applied in this work, despite the low reagent cost and the recent focus on the effects of chloride on refractory gold extraction. Other concerns on chloride application are the corrosion problem and its enhancement of the effects of preg-robbing carbon during cyanidation.

The two major considerations in hydrometallurgical process development are the extent to which a reaction will proceed and the rate at which the reaction will proceed. The first depends on the thermodynamic properties of the chemical system, which determine the overall reaction driving force. The second, which is the reaction kinetics depends on the combination of physical, chemical and mass transport factors which may be controlled to some extent by appropriate process selection and plant design.

### 2.9.1 Silver-Water System

Silver is a very noble metal, its domain of stability covers a very large portion of the domain of stability of water as shown in Figure 2-17 (Pourbaix, 1974). It is found in the native state in nature, often mixed with other metals (Au, Hg, Sb, Cu and Pt in particular). Silver is perfectly stable in the presence of water and aqueous solutions which are free from oxidising agents and complexing substances. It is not attacked appreciably by dry or moist air (provided that the air is free from ozone, sulphuric acid, halogens and ammonia).

Silver can be dissolved by acid oxidizing solutions (HNO₃ and concentrated H₂SO₄) to give colourless Ag⁺ ions. In natural water, Ag⁺ is stable under certain conditions and its existence in aqueous environments allows the formation of many silver-bearing minerals. Therefore, the silver ion can conceivably precipitate from the solutions to form sulphides, halogenides, jarosites, selenides, etc.
Hydriodic acid (HI) has no domain of predominance in Figure 2-18. It is a strong acid and it is completely dissociated to hydrogen ion and iodide. The iodides are stable in the presence of aqueous solutions free from oxidizing agents and it is generally in this form that iodine is found in nature. The reductions of tri-iodide (I$_3$), aqueous iodine, iodate (IO$_3^-$), iodic acid (HIO$_3$) and periodate (IO$_4^-$) lead to the formation of iodide.

\[
\begin{align*}
I_3^- + 2e^- &\rightarrow 3I^- \quad (E^\circ = 0.536\ V) \\
I_2 + 2e^- &\rightarrow 2I^- \quad (E^\circ = 0.621\ V) \\
IO_3^- + 6H^+ + 6e^- &\rightarrow I^- + 3H_2O \quad (E^\circ = 1.085\ V) \\
HIO_3 + 5H^+ + 6e^- &\rightarrow I^- + 3H_2O \quad (E^\circ = 1.077\ V) \\
IO_4^- + 8H^+ + 8e^- &\rightarrow I^- + 4H_2O \quad (E^\circ = 1.227\ V)
\end{align*}
\]

**Figure 2-17.** Potential-pH diagram for the silver-water system, at 25°C (Pourbaix, 1974).

### 2.9.2 Iodine-Water System

Hydriodic acid (HI) has no domain of predominance in Figure 2-18. It is a strong acid and it is completely dissociated to hydrogen ion and iodide. The iodides are stable in the presence of aqueous solutions free from oxidizing agents and it is generally in this form that iodine is found in nature. The reductions of tri-iodide (I$_3$), aqueous iodine, iodate (IO$_3^-$), iodic acid (HIO$_3$) and periodate (IO$_4^-$) lead to the formation of iodide.
Aqueous iodine is thermodynamically stable in a triangular region shown in Figure 2-18 (Pourbaix, 1974), which is situated in the upper left-hand region of the domain of stability of water. Iodine is therefore stable in oxidising acid solution. Although iodine is not a powerful oxidizing agent, its action (reaction 2-51) is generally rapid. It has been reported that the I$_2$/I$^-$ couple is only reversible at low iodide concentration of about 5.0 x 10$^{-4}$ mol/l (Desideri et al., 1973).

Iodic acid and iodate are strong oxidising agents and they are reduced to iodine as follows:

$$2HIO_3 + 10H^+ + 10e^- \rightarrow I_2 + 6H_2O \quad (E^o = 1.176\, V)$$

(2-55)
In acidic to slightly acidic media, iodic acid and iodate can be reduced to tri-iodide as follows:

$$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O \quad (E^\circ = 1.193 \text{V}) \quad (2-56)$$

Iodic acid (HIO₃) and the iodate are stable in the presence of water. Iodate is found in nature as saltpetres (sodium iodate) in Chile which is a leading producer of iodide and iodate salts. Iodic acid can be obtained by the action of water on the iodine pentoxide I₂O₅. The solubility of potassium iodide (KI) in water is 7.680 mol/l and 12.529 mol/l at 0 and 100°C respectively, while potassium tri-iodide (KI₃·1/2H₂O) is very soluble over a wide range of temperatures (Weast, 1977). Iodine dissolution in iodide gives rise to the I₃⁻ specie and in more concentrated iodide solutions, I₆²⁻ specie may be formed as shown below (Sillen and Martell, 1964):

$$I_2 + I^- \rightarrow I_3^- \quad (2-59a)$$
$$K_1 = 10^{2.8} \quad (2-59b)$$
$$2I_2 + 2I^- \rightarrow I_6^{2-} \quad (2-60a)$$
$$\beta_{22} = 10^{5.58} \quad (2-60b)$$

The speciation-pH diagram for iodine water system presented in Figure 2-19 (Ketsall et al., 1993), ignores I₆²⁻ because of lack of reliable thermodynamics data for this polyiodide ions. The predominant specie at low pH is triiodide ion for low activity of active iodine. The I₃⁻ ion does not adsorb onto mineral surfaces to any great extent (Jacobsen and Murphy, 1989) and does not complex with iron. I₃⁻ ion is reduced by metal sulphides at pH, less than 7 (Von Michaelis, 1987).

### 2.9.3 Iodine Cycle

In the acid sulphate-iodide media, the main iodine species which may be present are the free iodide ions (I⁻) ions, tri-iodide ions (I₃⁻), dissolved iodine (I₂), iodine vapour (I₂) and condensed (liquid) I₂ (I). At high concentration of iodide and high temperatures (above the boiling point of iodine; 185°C), the major part of the excess iodide is oxidised and would be expected to be lost.
to a physical "iodine cycle". The ability of iodide to form tri-iodide promotes the dissolution of molecular iodine in aqueous solutions. Any iodine vapour formed by the oxidation of tri-iodide ion will condense on the colder top of the autoclave. Iodine droplets may fall back into the autoclave slurry, where they may react with excess iodide ions to form anionic tri-iodide complex, which continues the cycle.

\[
I_2 + I^- \rightarrow I_3^- \quad (2-61)
\]

\[
2[I_3]^- \rightarrow 3I_2(g) + 2e^- \quad (2-62)
\]

\[
I_2(g) \rightarrow I_2(l) \quad (2-63)
\]

\[
I_2(l) \rightarrow I_2(aq) \quad (2-64)
\]

In this way a certain percentage of the total available iodide may be lost to physical "iodine cycle". This may become more important with increasing molar iodide to silver ratios. From the potential-pH diagrams, iodine vapour is of no direct importance to silver balance in the leach and no reactions between gaseous iodine and the leach slurry are expected (except for the re-dissolution of iodine vapour). Also, iodine vapour or condensed iodine may cause corrosion of metals in the autoclave freeboard.

Figure 2-19. Speciation-pH diagram for an iodine water system at 25°C, total active iodine 50 mol/m³ I in 1.0 kmol/m³ total iodide (Kelsall et al., 1993).
2.9.4 Silver-Iodide-Water System

The potential-pH diagram for the silver-iodide-water system has been presented previously by Welham et al. (1993), for high iodide concentration range. The iodide ions whose oxidation behaviours have been presented in section 2.9.2 were treated as complexants. The potential-pH diagram for the silver-iodide-water system is represented in Figure 2-20 for low iodide concentration, which is relevant to this research. Table 2-6 contains the Gibbs free energies of formation for the various species and phases considered in Figure 2-20.

Table 2.6. Gibbs free energies of formation of species in silver-iodide-water systems at 298K (Bard et al., 1985)

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G_f^\circ$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>77.16</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>-11.22</td>
</tr>
<tr>
<td>Ag$_2$O$_2$</td>
<td>27.63</td>
</tr>
<tr>
<td>Ag(OH)$_2^-$</td>
<td>-260.37</td>
</tr>
<tr>
<td>AgOH</td>
<td>-80.21</td>
</tr>
<tr>
<td>AgO</td>
<td>14.65</td>
</tr>
<tr>
<td>Ag$_2$O$_3$</td>
<td>121.39</td>
</tr>
<tr>
<td>Ag$_2$O$_2$</td>
<td>-10.99</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-237.178</td>
</tr>
<tr>
<td>I$^-$</td>
<td>-51.67</td>
</tr>
<tr>
<td>AgI</td>
<td>-66.22</td>
</tr>
<tr>
<td>AgI$_2^-$</td>
<td>-87.07</td>
</tr>
<tr>
<td>AgI$_3^{2-}$</td>
<td>-154.04</td>
</tr>
<tr>
<td>AgI$_4^{3-}$</td>
<td>-209.72</td>
</tr>
</tbody>
</table>

The silver iodide (iodargyrite) is very stable in the domain of stability of water. Figure 2-20 shows that elemental silver can be oxidised to silver iodide as follows:

$$\text{AgI} + e^- \rightarrow \text{Ag} + I^- \quad (2-65a)$$

The equilibrium line is represented by the following:

$$E = -0.1508 - 0.0592 \log [I^-] \quad (2-65b)$$

The comparison of Figure 2-20 with the corresponding diagram for the silver-water system at silver activity of 0.01 mol/l, indicates the addition of 0.01 mol/l of iodide decreases the required potential for silver oxidation from +0.7 V to -0.03 V. This shows that the metallic silver in the sulphide concentrates may be oxidised preferentially to silver iodide rather than being oxidised...
by ferric to aqueous silver (Ag⁺).

The formation of AgI on a silver anode has been reported to occur by a fast electron transfer step, at an iodide concentration of 2.5 mol/m³ of NaI, a highly porous film was formed at a rate limited by bulk diffusion of iodide to the surface. However, at 100 mol/m³ of NaI, the initial solution phase diffusion control switched to pore diffusion control, as the film thickened. In 1.0 kmol/m³, the solubility of silver is high; thick granular films of AgI formed at a rate limited by solid-state migration of ions in the bulk of the film.

Figure 2-20. Potential-pH diagram for the Ag-I-H₂O system, at 25°C, 1 atm. pressure and activity of 0.01 mol/L for Ag⁺ and iodide species.

The oxide of trivalent silver Ag₂O₃ has not been obtained in the pure state. The position of its domain of relative stability above the oxygen line characterises it as a substance that is very unstable in the presence of water and as a powerful oxidizing agent. It can be reduced to silver iodide as follows:

\[
Ag_2O_3 + 2I^- + 6H^+ + 6e^- \rightarrow AgI + 3H_2O
\]  
(2-66a)
The equilibrium for the above reaction is represented by the following expression:

\[ E = 2.2332 + 0.0296 \log [I^-] - 0.0887 \, pH \]  

(2-66b)

The silver iodide complexes (AgI\(_2\), AgI\(_3\)\(^-\) and AgI\(_4\)\(^-\)) are not stable at the concentration of iodide and silver considered in the potential-pH diagram. Silver iodides can exist in equilibrium with its complex and iodide in solution as shown below, but the stability constants of the following complexes are very low (Sillen and Martell, 1964):

\[
\begin{align*}
\text{AgI} + 2\text{I}^- & \rightarrow \text{AgI}_3^{2-} \quad \text{(2-67a)} \\
K_s_3 & = 10^{-2.52} \quad \text{(2-67b)} \\
\text{AgI} + 3\text{I}^- & \rightarrow \text{AgI}_4^{3-} \quad \text{(2-68a)} \\
K_s_4 & = 10^{-2.05} \quad \text{(2-68b)}
\end{align*}
\]

At high activity of iodide (1.0) and low activity of silver (10\(^{-4}\)), Welham et al. (1993) showed that silver iodide is replaced by triiodoargentate (I) ions as the predominant solution specie in the potential-pH diagram:

\[
\text{AgI}_4^{3-} + e^- \rightarrow \text{Ag} + 4\text{I}^- 
\]

(2-69)

The silver-iodide speciation presented by Welham et al. (1993) is shown in Figure 2-21.

![Figure 2-21. Iodide activity-pH diagram for a silver-iodide-water system in equilibrium with AgI at 25°C for a\(_{Ag} = 10^{-4}\) (Welham et al., 1993).](image)
In the presence of $10^{-4}$ Ag(I) activity, solid silver iodide (AgI) will form provided the activity of iodide is less than $10^{-0.7}$. The lower limit of the iodide activity, below which aqueous silver ($Ag^+$) becomes stable is not shown in Figure 2-21 by Welham et al. (1993) but this is calculated as $10^{-21.06}$ from the chemical reaction, which is represented as follows:

$$Ag^+ + I^- \rightarrow AgI$$ (2-70a)

$$\log(I^-) = -16.06 - \log(Ag^+)$$ (2-70b)

When the pH is above 6, the $Ag(OH)_{2}^-$ ion is formed:

$$Ag(OH)_{2}^- + I^- + 2H^+ \rightarrow AgI + H_2O$$ (2-71)

### 2.9.5 Silver Precipitation in Iodide-Sulphate media

In the presence of moderate concentration of iodide in the slurry, silver iodide is precipitated from the silver sulphate solution (formed during the pressure oxidation of silver-bearing complex sulphides) which is promoted by the low solubility product ($K_{sp}$) of silver iodide.

$$0.5Ag_2SO_4 + KI \rightarrow AgI + 0.5K_2SO_4 \quad \Delta G^o = -93.91 \text{ kJ/mol}$$ (2-72)

Silver iodide has very low solubility product as shown below at 25°C (Sillen and Martell, 1964):

$$AgI \rightarrow Ag^+ + I^-$$ (2-73a)

$$K_{sp} = [Ag^+][I^-] = 1.0 \times 10^{-16.03}$$ (2-73b)

The solubility product is $1.0 \times 10^{-13.80}$ at 421°K (Tien and Harrington, 1963) and this is lower than the solubility product at 298°K. Based on the data presented by Tien and Harrington (1963), the following expression can be deduced for the relationship between temperature (°K) and the solubility product over the temperature range of 421 and 467.5°K.

$$\log_{10} K_{sp} = 0.2239 - 59127^{-1}$$ (2-74)

The equation (2-74) indicates that there is a decrease in the solubility product of AgI as the temperature increases. Therefore, there is a need to investigate the stability of the silver iodide over the temperature range of 110° to 150°C (383° to 423°K), to ensure that the silver, which is deported into the iodide phase is not released subsequently to the jarosite specie during the pressure oxidation.
In the absence of any free iodide ions and at high potential, silver iodate may be precipitated from silver sulphate solution:

\[ 0.5 \text{Ag}_2\text{SO}_4 + K\text{IO}_3 \rightarrow \text{AgIO}_3 + 0.5K\text{SO}_4 \] \[ \Delta G = -26.32 \text{ kJ/mol} \] (2-75)

Even if iodate ions are present in substantial amounts in the autoclave, it can be calculated that on the basis of the difference in their solubility products, AgI will be formed more readily than AgIO₃ even if the ratio of iodate to iodide ions is up to 1.0 \times 10^9. The solubility product of silver iodate at 25°C is represented by the following expression (Sillen and Martell, 1964):

\[ \text{AgIO}_3 \rightarrow \text{Ag}^+ + \text{IO}_3^- \] (2-76a)

\[ K_{sp} = [\text{Ag}][\text{IO}_3^-] = 1.0 \times 10^{-7.45} \] (2-76b)

The oxidizing potential in the autoclave may be high enough for the formation of iodate and if this is formed, it will be reduced to iodide through the oxidation of sulphide which may enhance the silver extraction process from the silver sulphide.

Therefore, the presence of the substantial amount of AgI in the oxidised residue of the autoclave is expected based on the following reactions:

\[ 5\text{Ag}_2\text{S} + 4\text{O}_2 + 4\text{H}^+ + 4\text{IO}_3^- \rightarrow 3\text{Ag}_2\text{SO}_4 + 4\text{AgI} + 2\text{H}_2\text{SO}_4 \] \[ \Delta G^\circ = -2875.31 \text{ kJ/mol} \] (2-77)

\[ 3\text{Ag}_2\text{S} + 4\text{H}^+ + 4\text{IO}_3^- \rightarrow \text{Ag}_2\text{SO}_4 + 4\text{AgI} + 2\text{H}_2\text{SO}_4 \] \[ \Delta G^\circ = -1738.36 \text{ kJ/mol} \] (2-78)

Also, the oxidation of silver iodide by aqueous iodine and tri-iodide are possible according to the following equations:

\[ 0.5\text{Ag}_2\text{S} + 0.5\text{I}_2 \rightarrow \text{AgI} + 0.5\text{S}^0 \] \[ \Delta G^\circ = -45.98 \text{ kJ/mol} \] (2-79)

\[ \text{Ag}_2\text{S} + \text{I}_3^- \rightarrow 2\text{AgI} + \text{S}^0 + \text{I}^- \] \[ \Delta G^\circ = -92.09 \text{ kJ/mol} \] (2-80)

\[ 3\text{Ag}_2\text{S} + 2\text{I}_3^- + \text{I}_2 \rightarrow 6\text{AgI} + 3\text{S}^0 + 2\text{I}^- \] \[ \Delta G^\circ = -292.44 \text{ kJ/mol} \] (2-81)

Similarly, the reaction of the hydriodic acid on silver sulphide has been investigated by Noyes and Freed (1920) at 25°C. The reaction is stated as follows:

\[ \text{Ag}_2\text{S} + 2\text{HI} \rightarrow 2\text{AgI} + \text{H}_2\text{S} \] (2-82)
High equilibrium constant was obtained for the reaction, however the mechanism of the reaction is not known from the literature. The above reactions (2-77) to (2-82) show that the silver will be present in the residue, predominantly as silver iodide. In principle, any kind of leach for AgI can then be used to recover Ag from residue. Cyanidation is recommended. However, at low concentration of iodide, the role of iodine species on the pressure oxidation of silver sulphide is small, compared to that of ferric ion assisted oxidation (Van Weert and Tuinman, 1993; Van Weert and Van Lier, 1994).

2.9.6 Other Metal-Iodide Precipitation reactions

The iodides of Cu(I) and Hg(I) are insoluble and they will be precipitated by iodide in solution through the reductive precipitation:

\[
2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2
\]  

(2-83)

Cuprous iodide has very low solubility product as shown below (Sillen and Martell, 1964):

\[
\text{CuI} \rightarrow \text{Cu}^+ + \text{I}^- \quad (2-84a)
\]

\[
K_{sp} = [\text{Cu}^+][\text{I}^-] = 1.0 \times 10^{-12.03} \quad (2-84b)
\]

It has been demonstrated that metal surfaces accelerate the oxidation-reduction reaction of iodide. When exposed to the ferric and iodide reaction, mercury (metal) accelerated the electron transfer reaction and formed mercurous iodide, platinum also accelerated the reaction and was surrounded by iodine (Spiro, 1960). The reductant and oxidant ions are adsorbed on the metal surface, and electrons may be transferred between them through the metal. Therefore, the following reaction can be employed to remove excess iodide from the zinc solution.

\[
\text{CuSO}_4 + \text{ZnI}_2 + \text{Cu} \rightarrow 2\text{CuI} + \text{ZnSO}_4 \quad \Delta G^° = -100.99 \text{ kJ} \quad (2-85)
\]

In the absence of metallic copper, iodine is produced as follows:

\[
2\text{CuSO}_4 + 2\text{ZnI}_2 \rightarrow 2\text{CuI} + 2\text{ZnSO}_4 + \text{I}_2 \quad \Delta G^° = -46.92 \text{ kJ} \quad (2-86)
\]

The zinc diiodide is very soluble in aqueous media however there is no evidence of zinc iodide complexes in iodide solution, when the concentration is less than 4.0 mol/l of iodide (Sillen and Martell, 1964). The following low stability constants of the complexes confirm the non-stability of the zinc iodide.
Iron (II) iodide (FeI₂) is very soluble in cold and hot water, while the solubility of lead (II) iodide (PbI₂) is 0.63 and 4.1 g/l in cold and hot water respectively (Weast, 1973). Bismuth (III) iodide (BiI₃) and Thallium (I) iodide (TlI) have low solubility products, which are 10⁻¹⁸.⁰⁶ and 10⁻⁷.⁵¹ respectively. If they are present in solution, they will also precipitate along with silver iodide. Thallium (I) is known to form jarosite compounds and its deportment to this phase can be prevented.

2.10.7 Other Reactions of Iodide

Some strong oxidizing agents such as oxygen, ferric ions and iodates can liberate iodine from the acid solutions of iodides as shown below and these may become pronounced at high iodide concentration (Sidgwick, 1950).

\[
4KI + O_2 + 2H_2SO_4 \rightarrow 2I_2 + 2H_2O + 2K_2SO_4 \quad \Delta G^\circ = -245.60 \text{kJ} \quad (2-88)
\]

\[
Fe_2(SO_4)_3 + 2KI \rightarrow 2FeSO_4 + I_2 + K_2SO_4 \quad \Delta G^\circ = -9.03 \text{kJ} \quad (2-89)
\]

The kinetics of ferric reduction by iodide had been previously investigated (Morgan, 1954). The following mechanism is proposed by Fudge and Sykes (1952):

\[
\text{Fe}^{3+} + I^- \rightarrow \text{FeI}^{2+} \quad (2-90)
\]

\[
\text{FeI}^{2+} + I^- \rightarrow \text{Fe}^{2+} + I_2^- \quad (2-91)
\]

\[
\text{Fe}^{3+} + I_2^- \rightarrow \text{Fe}^{2+} + I_2 \quad (2-92)
\]

The net reaction for the oxidation of ferric ions by iodide ions is:

\[
2\text{Fe}^{3+} + 2I^- \rightarrow 2\text{Fe}^{2+} + I_2 \quad (2-93)
\]

The kinetics of the reaction may be written:
The retarding effect of ferrous ion is reflected in the denominator of the above expression and the strong influence of the iodide is shown by the second order dependence with respect to iodide concentration. The reaction can be minimised by using low concentration of iodide, this is desirable in this research.

Also, it has been demonstrated that the rate of reaction is also influenced by the anions (sulphate, chloride, nitrate and bromide) which can complex with ferric ions (Morgan, 1954 and Sykes, 1952). The anion affects the reaction by associating with the ferric (to form complexes) rather than with intermediary (FeI$_2^+$). Only the un-associated ferric ion reacts with iodide and there is a strong retardation caused by the strong complexing anions. However, the temperature effect on the kinetics of ferric reduction by iodide is not known from the literature.

2.10 Comparisons of the various Deporment of Silver

Silver precipitation as jarosite, sulphide and iodide phases can be represented as follows:

\[
\begin{align*}
\text{Ag}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} & \rightarrow \text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ \\
2\text{Ag}^+ + 2\text{Fe}^{2+} + \text{S}^- & \rightarrow \text{Ag}_2\text{S} + 2\text{Fe}^{3+} \\
2\text{Ag}^+ + \text{ZnS} & \rightarrow \text{Ag}_2\text{S} + \text{Zn}^{2+} \\
\text{Ag}^+ + \text{I}^- & \rightarrow \text{AgI}
\end{align*}
\]

Only one of the reactions, which is reaction 2-95 show the dependence on acidity and high acidity will reverse the reaction. The silver, which is precipitated as sulphides and iodides in reaction 2-96 to 2-98 are recoverable by cyanidation, while the silver in jarosite specie (2-95) is cyanide insoluble.

Dutrizac (1980) calculated the standard free energies of formation of various jarosite species from the solubility data of Kashkay et al., (1975) and these values are listed below together with the standard free energies of the corresponding alkali ions.
Table 2-7. Free energy values for various jarosite species (Dutrizac, 1980).

<table>
<thead>
<tr>
<th>Jarosite</th>
<th>kcal/mol</th>
<th>M⁺</th>
<th>For Cation, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>KFe₃(SO₄)₂(OH)₆</td>
<td>-788.6</td>
<td>K⁺</td>
<td>-67.5</td>
</tr>
<tr>
<td>NaFe₃(SO₄)₂(OH)₆</td>
<td>-778.4</td>
<td>Na⁺</td>
<td>-62.6</td>
</tr>
<tr>
<td>(H₂O)Fe₃(SO₄)₂(OH)₆</td>
<td>-772.5</td>
<td>H₂O⁺</td>
<td>0.0</td>
</tr>
<tr>
<td>(NH₄)Fe₃(SO₄)₂(OH)₆</td>
<td>-736.2</td>
<td>NH₄⁺</td>
<td>-19.0</td>
</tr>
<tr>
<td>AgFe₃(SO₄)₂(OH)₆</td>
<td>-701.3</td>
<td>Ag⁺</td>
<td>+18.4</td>
</tr>
<tr>
<td>Pb₀.₅Fe₃(SO₄)₂(OH)₆</td>
<td>-722.5</td>
<td>½ Pb⁺</td>
<td>-2.9</td>
</tr>
</tbody>
</table>

The data presented for potassium jarosite agreed with other values presented in the literature, for examples, Zotov et al., (1973) presented -790.1 kcal/mol and Brown (1970) presented -763 kcal/mol.

The use of the data in Table 2-7 confirms that potassium jarosite is more stable than sodium jarosite and this agrees with the literature (Brophy and Sheridan, 1965):

\[ \text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + K^+ \rightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + \text{Na}^+ \quad \Delta G^\circ = -5.3 \text{ kcal/mol} \quad (2-99) \]

The data also illustrates that the stability of silver jarosite is less than that of potassium jarosite and that silver jarosite is more stable than the lead jarosite.

\[ \text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6 + K^+ \rightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + \text{Ag}^+ \quad \Delta G^\circ = -1.4 \text{ kJ/mol} \quad (2-100) \]

\[ \text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + \text{Ag}^+ \rightarrow \text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6 + 0.5\text{Pb}^{2+} \quad \Delta G^\circ = -0.1 \text{ kJ/mol} \quad (2-101) \]

The free energy change is small for reactions 2-100 and 2-101, the course of the reaction can be reversed by unusual factors, such as activity difference caused by incorporation of foreign ions in the jarosite phases. Although the use of thermodynamics to predict the behaviour in such systems is limited by the variable ionic strength, extensive formation of solid solution compounds and by the kinetics of the process, the data are useful for predicting trends.

The standard free energy of formation for silver jarosite (in Table 2-7) was used in addition to the standard free energy values provided by Bard et al., (1985) to calculate the free energies of the reactions 2-95 to 2-98. The free energy values at high temperatures were estimated by using the method of Criss-cobble for the ionic species and by using heat capacity functions for the non-ionic species. The details are included in Appendix A1.2. The free energy values for the reactions 2-95 to 2-98 and the corresponding equilibrium constant (K) are shown in Table 2-8.
Table 2-8. Free energies of the silver precipitation reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_f$ kJ</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>100°C</td>
</tr>
<tr>
<td>2-95</td>
<td>-49.60</td>
<td>-112.9</td>
</tr>
<tr>
<td>2-96</td>
<td>-50.61</td>
<td>-21.32</td>
</tr>
<tr>
<td>2-97</td>
<td>-140.90</td>
<td>-128.0</td>
</tr>
<tr>
<td>2-98</td>
<td>-91.71</td>
<td>-87.63</td>
</tr>
</tbody>
</table>

Silver deportment as silver jarosite, sulphide or iodide depends on the depth of the thermodynamics "well" of each reaction, which depends on $\Delta G_f$. The comparison of the free energies of the reactions at 25°C indicates that reaction 2-97 is the most favourable followed by silver precipitation as iodide, reaction 2-98. The silver precipitation as jarosite specie by reaction 2-95 becomes much more favourable at high temperatures (100 and 150°C). This is consistent with the trend reported in the literature for jarosite species (Dutrizac et al., 1980; Dutrizac and Jambor, 1984). The slight decrease in the stability of silver iodide at high temperature has been reported previously and reviewed in section (2.9.5). At 150°C, the reaction 2-95 is the most favourable thermodynamically. If the silver sulphide formed by the reactions 2-96 and 2-97 is re-oxidised back to aqueous silver because of the high oxidation potential in the autoclave, then the two principal routes for silver are reaction 2-95 and 2-98. The trends in Table 2-8 show that at high temperature, the silver deportment to the jarosite phase has enough driving force to make it competes with the formation of silver iodide. The silver iodide formation is a precipitation reaction, which is expected to be fast. However, in the presence of both ferric sulphate and iodide, silver may react preferentially with ferric sulphate, and the resulting jarosite specie may prevent the rapid reaction of iodide with silver, provided the silver is encapsulated by the jarosite specie.

2.11 Kinetics Considerations of Iodide-Sulphate Media

The main steps which are involved during the oxidation of silver bearing complex sulphide and the subsequent precipitation of silver as iodide are as follows:

1. Oxidation of base metal sulphides and the chemical liberation of silver sulphide.
2. Oxidation of silver sulphide to aqueous silver.
3. Subsequent precipitation as silver iodide or jarosite.
The reactions of lead and zinc sulphides during the pressure oxidation are relatively fast at moderate temperature range (110 to 150°C). The silver sulphide phase is liberated for subsequent oxidation. At high temperature (above 160°C), the oxidation of silver sulphide is also fast but conclusions can not be drawn from the literature on the kinetics of silver sulphide.

The precipitation of silver iodide is a homogenous reaction, which is expected to be fast, however, prior investigations on the reaction of aqueous silver ion with iodide ion have been limited in the literature (Josien Marie Louise, 1936).

In the absence of iodide, silver is incorporated along with jarosite precipitation. The kinetics of jarosite precipitation is very complex and their elucidation has been complicated by the fact that the iron concentration and pH vary during the reaction. When a ferric sulphate-alkali sulphate solution is heated rapidly to 90-100°C, there is often an induction period before appreciable jarosite formation occurs. This effect is observed in laboratory studies and has been reported for industrial precipitation where induction time of about an hour has been observed (Steintveit, 1972). Such periods are presumably related to the formation of the right iron polymer species and probably not related to the final crystallization because they are observed commercially (at about 90°C) in the presence of seed.

If the silver sulphide oxidation is fast such that aqueous silver is available for further reaction, silver iodide precipitation may take place during this induction period and once silver iodide is formed it is stable enough to prevent the loss of silver to the jarosite phase (section 2.10). Once jarosite precipitation commences, rates are fairly rapid and complete reaction is achieved after 4 to 6 hours at 95°C; while complete reaction is achieved in less than 1 hour at 140°C (Dutrizac et al., 1991). It is unlikely, there will be a significant induction period at high temperature range (above 130°C) and when ferric is present in the initial solution used for oxidation.

Although little is known about the kinetics of silver-bearing lead jarosite precipitation at a temperature range of 110 to 150°C, the activation energies, which have been reported for the other jarosite species (in the range of 50 and 90°C) are fairly high (Table 2-9). According to Margulis et al. (1976b), the activation energy relates to the formation of jarosite crystallisation centres, which has been shown to be the limiting stage in the precipitation of iron as jarosite. This suggests that the rate of precipitation of jarosite specie is a strong function of temperature. For identical temperature and concentration conditions, the precipitation of iron by NaOH is
slower and the acid is less extensively neutralised. This has been attributed to the crystallization of sodium jarosite, which is slower than that of potassium jarosite and crystallization stage being the limiting step of the overall process (Margulis et al., 1975).

Table 2-9. Activation energy for various jarosite species.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Activation Energy (kJ/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KFe$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>74</td>
<td>Margulis et al. (1976b)</td>
</tr>
<tr>
<td>NaFe$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>101</td>
<td>Margulis et al. (1977a)</td>
</tr>
<tr>
<td>(NH$_4$)Fe$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>84.2</td>
<td>Margulis et al. (1977b)</td>
</tr>
</tbody>
</table>

Also, it has been reported that the rate of iron precipitation increases as the initial iron concentration increases such that the rate varies as $[\text{Fe}^{3+}]^{0.5}$ (Margulis et al., 1976a). The rate tends to be independent of the alkali concentration provided that above-stoichiometric amounts of alkali ion are present. The concentration of zinc sulphate has no effect on the rate of jarosite formation although high zinc sulphate levels retarded jarosite sedimentation or settling of the precipitate (Getskin et al., 1975). It appears that the rate (as well as the extent) of jarosite formation increases as the pH increases (Haigh, 1967; Margulis et al., 1977a; Margulis et al., 1977b and Das et al., 1996), although this conclusion is open to discussion given that most of the investigations have not been carried out at constant pH. Since jarosite precipitation appears to occur by a growth process, the presence of nuclei may be advantageous. In large vessels or under conditions where natural seeding is slow, the addition of seed is important (Getskin et al., 1975; Dutrizac et al., 1980). However, seeding under optimum conditions in small vessels does not significantly alter the rate of precipitation.

### 2.12 Summary of Literature Review and Objectives of the Present Study

There is impetus to recover zinc from complex sulphide concentrate because of the large number of complex sulphide deposits, which exists in Canada and throughout the world. Fortunately, many of the complex sulphides contain appreciable levels of silver and gold, which can be recovered along with the base metals (zinc and copper). The recoveries of precious metals, which are present in many complex sulphide deposits, will add to the economy of the process. Bulk concentrate of complex sulphides can be recovered by flotation followed by recovery of metals. A hydrometallurgical process which is capable of selectively extracting the
base metals without the loss of silver and gold is attractive for the treatment of the complex sulphide materials.

The pressure oxidation process in a sulphate medium will be appropriate for the treatment of the complex sulphides, however, silver is lost to the jarosite phase and cyanidation of the oxidised residue yields low extraction of silver. Currently, silver is not recovered from commercial acid pressure oxidation residues and the solutions proffered are limited in that they involved extreme process conditions:
1. leaching at temperature which is over 190°C to precipitate iron as hematite,
2. acidity levels above 0.75 mol/L H₂SO₄ and
3. Addition of high levels of potassium sulphate, about 36 kg/tons of ore.

The lead jarosite is the major collector of silver during the pressure oxidation of silver-bearing zinc-lead concentrates and an end member argentojarosite is rare at low concentration of silver encountered in industrial autoclaving. The high molar partition of silver in lead jarosite promotes the incorporation of silver into this phase. Silver extraction from high lead-iron-zinc complex sulphides by acidic pressure oxidation poses great challenges because of the high iron and lead contents which favour the formation of lead jarosite specie. The stability of lead jarosite also increases with temperature.

Efforts to recover silver from complex sulphides require a fundamental understanding of the behaviour of silver sulphide mineral during the pressure oxidation. However, the oxidation of silver sulphide in sulphate media is complicated by the formation of the jarosite specie, which has led some investigators to conclude that the silver sulphide mineral is not reactive in acid ferric sulphate. Where the extensive dissolution of silver sulphide has been reported with the sequestering of the dissolved silver into the jarosite phase, the silver-extraction time was not provided and the form of silver prior to its encapsulation by jarosite specie was not obvious in those studies.

The objective of the present study was to investigate the chemical behaviour of silver during the acid pressure oxidation in the temperature range of 110-150°C and to deport silver into a residue suitable for high extraction by cyanidation. The secondary objective was to extract zinc into the solution suitable for recovery by electrowinning. To accomplish these, the research focussed on six different areas. One, the pressure oxidation behaviour of high grade natural
acanthite (Ag₂S) in the temperature range of 110-150°C was investigated by following the silver extraction-time profile under the conditions, which avoided the precipitation of jarosite specie or silver sulphate. Two, the kinetics and mechanisms of silver incorporation into the jarosite specie were investigated, over a temperature range of 110-150°C to determine the challenges posed by the jarosite formation to alternative silver deportment (iodide) reactions and the conditions which could minimise silver loss to jarosite specie. Three, the chemical composition and the cyanidation of the jarosite species were investigated to study the extraction of silver from jarosite residues. Four, precipitation reaction was carried out to study the reaction chemistry and kinetics of silver deportment as silver sulphide in the presence of sulphur and under the pressure oxidation conditions. Five, precipitation reaction was carried out to investigate the deportment of silver ion as silver iodide and the stability of silver iodide in acid ferric media under the pressure oxidation. Six, the pressure oxidation of complex sulphide concentrates (obtained from different mines) were carried out in the temperature range of 110 and 150°C, potassium iodide was added to the initial solution to precipitate silver as silver iodide (iodargyrite) to prevent its incorporation into the jarosite specie.
CHAPTER 3
EXPERIMENTAL PROCEDURES

In order to achieve the objective of investigating the chemical behaviour of silver during the acid pressure oxidation of complex sulphides in the range of 110-150°C and to deport silver into a residue suitable for high extraction by cyanidation, the following experimental programs were developed.

1. Pressure oxidation experiments to study the kinetics of the natural silver sulphide mineral (Ag$_2$S) in acid ferric sulphate media;
2. Precipitation reactions to study the deportment of silver as silver jarosite specie in the presence of ferric and lead sulphate suspension, and under the pressure oxidation conditions;
3. Chemical composition and the cyanidation of the jarosite species formed under the pressure oxidation conditions;
4. Precipitation reactions to study the deportment (reaction chemistry and kinetics) of silver as silver sulphide in the presence of sulphur and under the pressure oxidation conditions;
5. Precipitation reactions to study the deportment of silver as iodide and the stability of silver iodide in acid ferric media under the pressure oxidation conditions;
6. Pressure oxidation of complex sulphide concentrates and ores with the stoichiometric iodide addition to deport silver into the cyanide soluble form (AgI) and to extract zinc into the solution. The extraction of zinc was monitored during the pressure oxidation and the oxidised residues were subjected to cyanidation for silver and gold extraction.

The pressure oxidation experiments and the precipitation reactions were carried out in a 2-litre autoclave. A schematic diagram of the autoclave setup and the controlling equipment used for all the pressure oxidation and precipitation experiments is shown in Figure 3-1. The autoclave was equipped with a temperature controller, internal vertical cooling tubes also acting as baffles, and a variable speed stirrer system. Agitation was provided by two 5.7 cm diameter 45° pitched blade impellers on a titanium shaft, the first one was positioned 2.5 cm off-bottom and the second was located 6.0 cm from the first impeller.

An electrically heated jacket assembly surrounding the autoclave bomb provided heating of
the autoclave contents. The temperature controller controlled both the heaters in the heating jacket and the cooling water flow. Also the same temperature controller had knob for manual adjustment of the stirrer speed and digital speed readout. The temperature of the solution could be controlled to within ±1°C. All the wetted parts and the magnetic stirrer were made of grade 4 titanium. The autoclave head and all valves were made of type 316 stainless steel. The thermocouple well, stirrer and cooling tubes are permanently fixed to the autoclave head. Oxygen input rates to the autoclave were measured by a mass flowmeter (Omega Instruments) and computerised data acquisition system.

In order to establish the minimum impeller rotation speed at which mineral particles are well suspended, preliminary tests were carried out in a transparent vessel which has the same dimensions as the autoclave bomb, the same cooling tubes, impeller, shaft and thermocouple well were utilised under ambient conditions. The effect of the stirring speed on particles suspension was carried out at the highest pulp density (15% w/v) used in this research and with sulphide concentrates. The head of the autoclave bomb was transferred into the transparent vessel, agitation was carried out with the autoclave stirring system by rotating the axis to one side of the fixed autoclave heating assembly. At an impeller rotation speed of about 750 rpm, the mineral particles were well suspended as observed visually in the transparent (acrylic) vessel. At this speed and in the absence of solid minerals, there was air bubble entrainment and the quantity increased with increase in rotation speed up to 1000 rpm. The rotation speed of 900 rpm was adopted in this work for the oxidation and precipitation reaction, it was expected that at this speed, oxygen in the autoclave would be dispersed sufficiently fast to ensure the reaction rate would not be limited by gas-liquid mass transfer.

Having established the hydrodynamic characteristics of the autoclave, the pressure oxidation tests were conducted on 1 litre scale in a standard 2 litre Parr titanium autoclave. Titanium is readily corroded at elevated temperatures under reducing conditions (Uhlig, 1971; Othmer, 1984). Ferric sulphate solution is usually added to provide oxidising conditions, which reduce corrosion of the titanium autoclave during the heating up period.

The reactants were charged into the bomb, the autoclave bomb was sealed and inserted into the heating assembly. In order to minimise the time required to reach the operating temperature, the jacket assembly was preheated for 15 minutes before inserting the autoclave bomb. Cooling
water tubes, oxygen supply and emergency solution discharge lines were connected. The thermocouple was put in place and the stirrer was connected to the driver system. Air and vapour were periodically vented up to a solution temperature approaching 100°C because at this temperature, the solubility of oxygen is minimum (Kimweri, 1990 and Hayduk, 1991). It is therefore, tenable to assume that most of the oxygen in the autoclave was in the gaseous phase and venting this gas took out most of the oxygen in the autoclave.

Figure 3-1. Schematic representation of the autoclave set-up.

When the system was approaching the desired temperature, stirring was increased to 900 rpm and when the operating temperature was reached, stirring was stopped for oxygen addition. Oxygen was admitted into the autoclave near the bottom through a dip tube which was also connected to an autoclave sampler. Once the required pressure was attained, the acquisition of the oxygen flow data was started. Then, the stirrer was switched on (at 900 rpm), which marked the commencement of the test.

A sampler, which can withdraw a 5-10 ml slurry sample during runs was developed and fitted to the reactor. The withdrawn slurry sample was weighed and filtered. After the reaction for the desired residence time, a test was terminated by cooling and de-pressurizing the autoclave. In
most cases, the autoclave contents were suction filtered and the residue was washed thoroughly with deionized water and the solids were dried overnight in an oven. The weight of the dried residue was measured and used for metal mass balance. All tests were carried out in duplicate and a third test was conducted in case of large difference (more than 5%) in results of the first two tests. Some modifications were made to the autoclave procedures to achieve the different objectives of each phase. These modifications are summarised in the following Table 3.1.

Table 3.1. Modifications carried out for different phases during the autoclave experiments

<table>
<thead>
<tr>
<th>Experimental Phase</th>
<th>Addition of reagents</th>
<th>Stirring and Oxygen addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver sulphide Oxidation</td>
<td>When ferric was present in the initial solution. Acanthite was sealed in an ampoule to avoid any oxidation of acanthite during heating. The solution and the ampoule were charged into the bomb.</td>
<td>Stirring delayed until temperature was reached and ampoule was broken by the impellers. Then oxygen was added.</td>
</tr>
<tr>
<td></td>
<td>In the absence of ferric, concentrated sulphuric acid was sealed in ampoule to avoid the corrosion of titanium during heating and prior to oxygen injection.</td>
<td></td>
</tr>
<tr>
<td>Deportment of silver as silver jarosite</td>
<td>Chemical reagents were dissolved in deionized water and charged into the bomb.</td>
<td>Slow stirring speed (180 rpm) to minimise reaction during the heating. Oxygen was not used.</td>
</tr>
<tr>
<td></td>
<td>Reagents charged into the bomb. Non interruptive tests in which samples were not taken during the reaction.</td>
<td>Slow stirring speed (180 rpm) to minimise reaction during the heating. Oxygen was not used.</td>
</tr>
<tr>
<td>Chemical composition of silver jarosite</td>
<td>Initial solution was highly reducing (high ferrous/ferric ratio), therefore, sulphuric acid and silver sulphate were sealed in an ampoule. Sulphur and surfactant were added to the solution.</td>
<td>No stirring until the temperature was reached and the ampoule was broken by the impellers. Then, oxygen was admitted into the bomb.</td>
</tr>
<tr>
<td>Deportment of silver as silver sulphide</td>
<td>To minimise reaction during heating, silver sulphate solution was sealed in one ampoule and potassium iodide solution was sealed in another ampoule.</td>
<td>No stirring until the temperature was reached and the ampoules were broken by the impellers. Oxygen was not used.</td>
</tr>
<tr>
<td>Deportment of silver as silver iodide</td>
<td>Chemical reagents were dissolved in deionized water and made up to 1 litre. Slurry of the concentrates and solution were charged into the bomb.</td>
<td>Slow stirring speed (180 rpm) to minimise reaction during the heating. Oxygen was admitted when the operating temperature was reached.</td>
</tr>
</tbody>
</table>
3.1 Experiments on the Pressure oxidation of silver sulphide

3.1.1 Reagents

The reagent used in the pressure oxidation experiments were: ferric sulphate \((\text{Fe}_2(\text{SO}_4)_3\cdot 5\text{H}_2\text{O}, 97\% \text{ purity})\), sulphuric acid \((\text{H}_2\text{SO}_4, 95-98\% \text{ concentration})\) and cylinder grade pressurised oxygen \((\text{minimum 99.5}\% \text{ purity})\).

3.1.2 Methodology

Pressure oxidation of natural acanthite \((\text{Ag}_2\text{S})\) was investigated under the conditions of high acidity and low pulp density to prevent the precipitation of jarosite specie and silver sulphate. Surfactants \((0.05 \text{ g/l lignosol and 0.05 g/l quebracho})\) were added to the acanthite. Samples were taken during the reaction, the weight of each slurry was assumed to be equal to the weight of the solution (because the percentage of the solid was very low) and from the initial density of the solution, the volume of the solution sample was determined. In order to present extraction-time profile, silver extraction was calculated from the total weight of silver in solution divided by the weight of silver in the head. This included correction factor which was applied to adjust for the changing volume due to sampling.

\[
X = \frac{V_j C_j + \beta_j}{m \frac{\alpha}{100}} \times 100\%
\]  

(3-1)

Where:

- \(X\) Percentage extraction of silver, %;
- \(C_j\) Silver concentration of the \(j\)th sample, g/L;
- \(V_j\) Volume of solution prior to taking the \(j\)th sample, L;
- \(\beta_j\) Total amount of silver withdrawn prior to the \(j\)th samples, g;
- \(m\) Initial mass of the solid, g;
- \(\alpha\) Percentage composition of silver in the initial solid;
3.1.3 Acanthite Mineral Samples

Two sets of high grade natural acanthite specimen originating from La Valenciana and Ingleterra mines were obtained through the Metallurgical Research Laboratory, Inc., San Jose. The two sets were supplied in small quantity and at different time because of the scarcity of the mineral. Each set was crushed and wet ground in a ceramic mortar to a $P_{80}$ of 25 $\mu$m (Figure 3-2.). The information on the particle size distribution of the acanthite mineral samples is given in section 3.1.4. Certificate of composition from Metallurgical Research Laboratory indicates that the constituent minerals were acanthite with traces of pyrite, barite and silica. Table 3-2 compares the chemical composition of the La Valenciana and Ingleterra mines silver sulphide minerals to the composition expected for pure $Ag_2S$.

Table 3-2. Results of chemical analyses for the natural silver sulphide mineral.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ag  (%)</th>
<th>Fe  (%)</th>
<th>Zn  (%)</th>
<th>Cu  (%)</th>
<th>Pb  (%)</th>
<th>$S_T$ (%)</th>
<th>$S^{2-}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Valenciana mineral$^1$</td>
<td>70.01</td>
<td>3.20</td>
<td></td>
<td></td>
<td>1.75</td>
<td>14.21</td>
<td>14.20</td>
</tr>
<tr>
<td>Ingleterra mineral$^1$</td>
<td>80.01</td>
<td>1.27</td>
<td>1.57</td>
<td>1.15</td>
<td></td>
<td>13.04</td>
<td>13.02</td>
</tr>
<tr>
<td>$Ag_2S$(theoretical)</td>
<td>87.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>12.92</td>
<td>12.92</td>
</tr>
</tbody>
</table>

$^1$Assay results are average values obtained from duplicate analyses.

3.1.4 Particle Size Analysis of the Acanthite Samples

The sieving method was not a very satisfactory technique for determining the particle size distribution of the acanthite samples used for pressure oxidation, because a large proportion of the particles were finer than the finest available sieve (25 $\mu$m). The cumulative particle size distributions of the acanthite samples are plotted in Figure 3-1. Therefore, the Elzone particle size counter from Micrometrics (formerly Particle Data, Inc.), which is capable of measuring finer particles (~2.0 $\mu$m) was used. The technique involves passing particles suspended in an electrolyte through a small orifice, having an immersed electrode on either side (Berg, 1958). As each particle passes through the orifice, it interrupts a small current between the electrodes. The size of the interruption or 'resistance blip' is directly proportional to the volume of the particle passing through. The instrument counts and measures particle volumes and reports the equivalent spherical diameter. The magnitude of the size increment is set by the operator. For homogenous
materials where all the particles have essentially the same density, as was the case with the samples tested here, the volume fraction is equivalent to the weight fraction.

The dilute slurries of samples were made up in a 100 ml beaker using a dispersant solution consisting of 10% w/v Triton in deionized water and later introduced to the equipment. Ultrasonic probe was applied to break up particles which had agglomerated and to disperse the solids. Further dilution of the slurry was carried out with an electrolyte solution. Two electrolytes were used depending on the size range being measured. For the coarse size range (10-200 μm), determined using a 300 μm orifice tube, the electrolyte consisted of 1% w/v NaCl and 0.5% w/v triton. The fine size range (~2.0-25 μm), was analyzed by using a 48 μm orifice tube, the electrolyte consisted of 4% w/v NaCl and 0.5% w/v triton. Overhead stirring was employed during measurement to suspend the particles. A computer attached to the instrument acts as a multi-channel analyser and software which blends the two data sets to obtain the overall particle size distribution.

Figure 3-2. Cumulative particle size distribution of the acanthite mineral samples as determined by Elzone particle size counter.
The Elzone instrument has the advantage of being able to measure particle diameters over a wide range, from ~2.0-1000 μm. The maximum size measurable in this range depends on the ability to keep the particles in uniform suspension.

3.2 Experiments on Silver Deposition as Silver Jarosite Specie

3.2.1 Reagents

The reagents used in the silver and iron precipitation reactions were: silver sulphate (Ag₂SO₄, 99% purity), cupric sulphate (CuSO₄, 99% purity), ferric sulphate (Fe₂(SO₄)₃·5H₂O, 97% purity), sulphuric acid (H₂SO₄, 95-98% concentration) and lead sulphate (PbSO₄, 99% purity).

3.2.2 Methodology

Precipitation reactions were carried out to investigate the reaction chemistry and kinetics involved in the reaction of aqueous silver with ferric sulphate. Cupric was added to the initial solution to provide additional oxidizing conditions required because ferric was depleted during the precipitation reaction. At low concentration, cupric would not interfere with the precipitation of jarosite specie (Dutrizac and Jambor, 1987). The solutions were analyzed for iron, silver and free H₂SO₄, concentration-time profiles for iron and silver were provided. In some tests, lead and copper in the solution were analyzed.

3.3 Chemical Composition of Jarosite and Silver extraction by Cyanidation

3.3.1 Reagents

The reagents used for the precipitation of jarosite specie were: silver sulphate (Ag₂SO₄, 99% purity) magnesium sulphate (MgSO₄, 99% purity), ferric sulphate (Fe₂(SO₄)₃·5H₂O, 97% purity), sulphuric acid (H₂SO₄, 95-98% concentration) and lead sulphate (PbSO₄, 99% purity).

3.3.2 Methodology of the Experiments

Precipitation reactions were carried out and the precipitates were subjected to cyanidation.
Where the microscopic, particle size and chemical analysis of the jarosite specie were required, the dried solids which contain synthetic jarosite and lead sulphate were slurried 4 times in 1 L solution of 10% ammonium acetate at room temperature as described by Dutrizac et al. (1980). This method was used to remove lead sulphate from the precipitates. After filtration, the solids were washed and dried, and then analyses for iron, silver, lead and sulphate were carried out. The method used for precipitation of jarosite specie was employed previously by Dutrizac and Kaiman (1976) and by Dutrizac and Jambor (1987). However in this work, the initial solution used for precipitation was not neutralised with any base and in this way, the approach differed from the previous studies. The exclusion of neutralisation step was done to prevent the possible formation of geothite or basic iron sulphate (section 2.5.1).

Where the synthetic jarosite specie was required for subsequent cyanidation studies, only one sample was taken at the end of the test and prior to cooling of the autoclave. The washing of the jarosite precipitates (jarosite and lead sulphate) with ammonium acetate was excluded when, the residue was required for cyanidation.

3.3.3 Particle Size Analysis of the Jarosite Specie

The size analyses of the jarosite samples were carried out by using Malvern Mastersizer 2000. This equipment is capable of measuring wet and dry samples in the range of 0.02–2000 μm. The sizes of jarosites, which had been prepared previously in the absence of seeding range from 0.2 to 1.5 μm (Roca et al., 1993; Patino et al., 1998 and Cruells et al., 2000). Therefore, Elzone equipment (Section 3.1.4) could not be used for the size analysis of jarosite specie.

3.4 Experiments on Silver Deportion as Silver Sulphide

3.4.1 Reagents

The reagents used in the silver-sulphur precipitation reactions were: silver sulphate (Ag₂SO₄, 99% purity), ferrous sulphate (FeSO₄·7H₂O, 97% purity), ferric sulphate (Fe₂(SO₄)₃·5H₂O, 97% purity), sulphuric acid (H₂SO₄, 95-98% concentration) and sulphur (S, 98% purity).
3.4.2 Methodology

Precipitation reactions were carried out under the conditions required to prevent the formation of jarosite specie and the oxidation of silver sulphide. The initial solution used for this set of experiments contained very low concentration of ferric and high concentration of ferrous. Sample solutions were withdrawn from the autoclave and were filtered. The solutions were analyzed for silver, ferric, ferrous and total iron.

Some tests were carried out at atmospheric pressure in the absence of oxygen in a glass reactor at 90°C. The glass reactor has water jacket and hot water was circulated through this jacket from a water bath. The initial solution of ferric/ferrous sulphate was made up to 1 litre with deionized water and then, charged into the glass reactor. The glass reactor was sealed, the thermo-circulator turned on and the agitation started. The solution was flushed with nitrogen prior to reaching the operating temperature in order to de-oxygenate the unit. Once the desired temperature was reached, elemental sulphur and silver sulphate crystals were added through one of the ports on the cover and the test commenced. The space above the solution was flushed with nitrogen. Sample solutions were withdrawn from the autoclave and were filtered to remove the precipitates. The solutions were analyzed for silver and iron after the determination of the sample density.

3.5 Experiments on Silver Deposition as Silver Iodide

3.5.1 Reagents

The reagents used in the silver and iodide precipitation reactions were: silver sulphate (Ag₂SO₄, 99% purity) or silver iodide (AgI, 99%), ferric sulphate (Fe₂(SO₄)₃·5H₂O, 97% purity), sulphuric acid (H₂SO₄, 95-98% concentration), lead sulphate (PbSO₄, 99% purity) and potassium iodide (KI, 99% purity).

3.5.1 Methodology

Precipitation reactions were carried out to investigate the reaction of aqueous silver with iodide in the presence of ferric sulphate. The stability of silver iodide in acid ferric sulphate was also investigated by substituting silver iodide suspension for aqueous silver. The resulting
precipitates were subjected to cyanidation for silver recoveries. The filtrate and wash water were analysed for silver. Each test was repeated without introducing potassium iodide during precipitation reaction.

3.6 Pressure oxidation of complex sulphides in acid sulphate-iodide media

3.6.1 Reagents

The reagent used in the pressure oxidation experiments were: ferric sulphate (Fe$_2$(SO$_4$)$_3$.5H$_2$O, 97% purity), ferrous sulphate (FeSO$_4$.7H$_2$O, 99% purity), sulphuric acid (H$_2$SO$_4$, 95-98% concentration), potassium iodide (KI, 99.9% purity), sulphur (99.99% purity) and cylinder grade pressurised oxygen (minimum 99.5% purity).

3.6.2 Methodology

Potassium iodide was added to the pressure oxidation slurry in order to precipitate silver as silver iodide (iodargyrite) before it was incorporated into the jarosite specie. Surfactants, lignosol and quebracho were added, whenever the experiment was conducted at a temperature, which was higher than the melting point of sulphur (~119°C). 2.63 kg/t (0.25 g/l) each of lignosol and quebracho were used. Preliminary investigation at this level of combination revealed that sulphide occlusion was prevented, but at lower level of surfactants, occluded particles were observed in the residues after drying. At high levels of initial acid such as 75 g/l sulphuric acid, the 2.63 kg/t lignosol and 2.63 kg/t quebracho combination was not sufficient. However, 4.21 kg/t (0.4 g/l) each of the surfactants were found to be effective.

The withdrawn slurry sample was weighed, and then suction filtered and the density of the filtrate also determined by weighing the known volume. After drying the solid sample, it was weighed and its mass was deducted from the mass of the slurry sample to obtain the mass of the solution sample. The volume of the solution sample was then obtained from its mass and density. The solution was analysed for zinc, iron and free acid.

Non-interruptive tests were carried out (without periodical sampling), when the residues were required for cyanidation. Also, in some cases, non-interruptive tests were carried out to determine the sulphide oxidation to sulphur and sulphate.
Where the calculation of sulphide oxidation to sulphur and sulphate were required, the dried residues were repulped, 4 times in 1 litre solution of 10% ammonium acetate to remove lead sulphate. The chemical analysis of the wash solution was carried out to ensure that only lead was dissolved. These procedures have been used in prior investigations to reduce the effect of lead on the analyses, which introduces errors into the calculation of total sulphur and the resulting sulphate calculation (Tourre, 1984; Doyle and Arauco, 1984). (Additional information on the chemical analyses of total sulphur and the sulphate deduction is provided in Section 3.7). The residue was washed with deionized water and air dried for solid analysis.

Where the residue was required for silver/gold recoveries by cyanidation, washing with ammonium acetate was omitted, unlike the previous study (Tourre, 1984).

3.6.3 Mineral Samples

Three different sulphides materials were used in this investigation.

3.6.3.1 Cannington Complex Sulphide Concentrate

A bulk sample of zinc-lead-iron sulphide material was obtained from the tailing pond of Cannington underground mine in North West Queensland, Australia. BHP Cannington process plant treats high grade silver, lead and zinc sulphide ores by rejecting talc \((\text{Mg, Fe})_5\text{Si}_8\text{O}_{20}(\text{OH, F})_4\) into the tailing pond, followed by successive flotation of lead and zinc concentrates, which contain silver (section 2.3). The tailings from the flotation circuits contain complex sulphides of iron, lead and zinc, and fluoride-bearing silicate minerals. Therefore, the major economic sulphides associated with Cannington material are galena and sphalerite (Torrisi, 2001). The principal iron mineral is pyrite. The silver content is principally in the form of freibergite \((\text{Ag, Cu, Fe})_{12}(\text{Sb, As})_4\text{S}_{13}\), but may also present in a solid solution within the galena (as \(\text{Ag}_2\text{S}\)) and as a native silver (BHP web site, 2001).

Before the concentrate was used for the pressure oxidation tests, 15-kg samples were wet-ground in a rodmill to reduce the particle size to a \(P_{80}\) of 70 \(\mu\)m and bulk flotation was carried out by Process Research Associates Laboratory (PRA), B.C., to produce bulk sulphide concentrate. The re-ground and floated samples from PRA were filtered, washed and dried at room temperature. The chemical analyses performed in duplicates by Chem Met Consultants Inc., B.C., on the re-ground Cannington concentrate are summarized in Table 3-3.
Table 3-3. Results of chemical analyses for the reground Cannington concentrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (%)</th>
<th>Zn (%)</th>
<th>Pb (%)</th>
<th>S&lt;sub&gt;T&lt;/sub&gt; (%)</th>
<th>S&lt;sup&gt;2-&lt;/sup&gt; (%)</th>
<th>Ag (g/t)</th>
<th>Au (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; 7-kg grinds</td>
<td>17.22</td>
<td>4.80</td>
<td>7.40</td>
<td>9.52</td>
<td>9.49</td>
<td>422</td>
<td>0.30</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; 7-kg grinds</td>
<td>19.20</td>
<td>4.80</td>
<td>7.40</td>
<td>10.70</td>
<td>10.60</td>
<td>462</td>
<td>0.30</td>
</tr>
</tbody>
</table>

<sup>1</sup>Assay results are average values obtained from duplicate analyses.

3.6.3.2 Eskay Creek low grade Ore

Low sulphide material originating from Eskay Creek mine, which is a high-grade precious and base metal-rich sulphide and sulphosalt deposit located 80 km Northwest of Stewart, British Columbia. The ore minerals are dominantly sphalerite, tetrahedrite and lead-sulphosalts with lesser freibergite (Ag, Cu, Fe)<sub>12</sub>(Sb, As)<sub>4</sub>S<sub>13</sub>, galena, pyrite, electrum, amalgam and minor arsenopyrite (Homestake web-site, 2001).

The material was obtained by the Mining Department of the University of British Columbia and subjected to grinding and gravity concentration tests to upgrade the gold content of the material (Klein, 2001). The dense materials (tailing) at the bottom of the gravity concentration tank were collected, combined, filtered, washed and dried at room temperature. The dried materials were wet-ground in a rodmill by Process Research Associates Laboratory, B.C., to reduce the particle size to a P<sub>80</sub> of 30 μm and to produce about 2 kg of feed for the pressure oxidation tests. The re-ground samples were filtered, washed and dried at room temperature. The chemical analyses performed in duplicates by Chem Met Consultants Inc., B.C., on the as-received and re-ground Eskay Creek low grade ore in Table 3-4.

Table 3-4. Results of chemical analyses for the as-received and reground Eskay Creek ore.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (%)</th>
<th>Zn (%)</th>
<th>Pb (%)</th>
<th>Cu (%)</th>
<th>S&lt;sub&gt;T&lt;/sub&gt; (%)</th>
<th>S&lt;sup&gt;2-&lt;/sup&gt; (%)</th>
<th>Ag (g/t)</th>
<th>Au (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ore</td>
<td>1.65</td>
<td>0.09</td>
<td>0.02</td>
<td>0.03</td>
<td>1.64</td>
<td>1.48</td>
<td>290.0</td>
<td>52.80</td>
</tr>
<tr>
<td>Reground ore</td>
<td>2.00</td>
<td>0.09</td>
<td>0.02</td>
<td>0.03</td>
<td>1.61</td>
<td>1.55</td>
<td>263.0</td>
<td>47.60</td>
</tr>
</tbody>
</table>

<sup>1</sup>Assay results are average values obtained from duplicate analyses.
3.6.3.3 UBC Mixed Concentrate

The materials from Cannington and Eskay Creek mines have low concentration of zinc. Therefore, in order to produce a feed which contained high concentration of zinc, the Cannington concentrate was mixed with a high grade natural sphalerite. The natural sphalerite of unknown origin had earlier been obtained from Wards Natural Science Ltd., Ontario, by the Hydrometallurgical group of the University of British Columbia. The sphalerite samples were washed and dried in the air. To prepare the sample for leaching, a 1-kg sample was crushed and rod milled, then filtered and allowed to air dry at room temperature. The re-ground sphalerite samples were dry-screened for 1 hour on a Rotap shaker by using Tyler sieves #150 (105 μm aperture size), #200 (74 μm), #270 (53 μm), #400 (38 μm) and #500 (25 μm). The chemical analyses performed in duplicates by Chem Met Consultants Inc., B.C., on the -74 +53 μm size fraction are summarized in Table 3-5.

Table 3-5. Results of chemical analyses for the zinc sulphide mineral.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (%)</th>
<th>Zn (%)</th>
<th>Pb (%)</th>
<th>ST (%)</th>
<th>S² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc sulphide mineral¹</td>
<td>2.38</td>
<td>66.00</td>
<td>0.02</td>
<td>31.60</td>
<td>31.60</td>
</tr>
<tr>
<td>ZnS(theoretical)</td>
<td>0.00</td>
<td>67.14</td>
<td>0.00</td>
<td>32.86</td>
<td>32.86</td>
</tr>
</tbody>
</table>

¹Assay results are average values obtained from duplicate analyses.

The -74 +53 μm size fraction was selected (arbitrarily) for mixing with Cannington concentrate. 70 g of the Cannington concentrate was mixed with 25 g of high grade natural sphalerite to produce a batch of UBC mixed concentrate for some pressure oxidation tests. 10 batches of the mixed concentrates were produced and each of them was stored in a sealed polythene bag. The chemical analyses performed in duplicates by the Chem Met Consultants Inc., B.C., on the UBC mixed concentrate are summarized in Table 3-6. Calculations were made based on the individual chemical composition of the materials and the mixing ratio. The differences between the chemical analyses and calculated compositions were within the 5% experimental error limit.
Table 3-6. Results of chemical analyses for the UBC mixed concentrate.

<table>
<thead>
<tr>
<th></th>
<th>Fe (%)</th>
<th>Zn (%)</th>
<th>Pb (%)</th>
<th>S (%)</th>
<th>S^2- (%)</th>
<th>Ag (g/t)</th>
<th>Au (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyses^1</td>
<td>15.80</td>
<td>20.20</td>
<td>5.50</td>
<td>15.8</td>
<td>15.60</td>
<td>341</td>
<td>0.21</td>
</tr>
<tr>
<td>Computational^2</td>
<td>14.94</td>
<td>20.77</td>
<td>5.45</td>
<td>16.2</td>
<td>16.13</td>
<td>340.4</td>
<td>0.22</td>
</tr>
</tbody>
</table>

^1 Assay results are average values obtained from duplicate analyses.
^2 Based individual chemical composition of the materials and the mixing ratio.

3.6.4 Particle Size Analysis of the Complex Sulphide Samples

The Elzone counter (section 3.1.4) was used for the particle size analyses of the mixed sulphides. The cumulative particle size distributions of the Cannington and Eskay Creek complex sulphide concentrates are plotted in Figure 3-3.

![Particle Size Distribution](image)

Figure 3-3. Cumulative particle size distribution of the sulphide concentrates as determined by Elzone particle size counter.

3.7 Determination of metal extractions and sulphide oxidation extents

For the interruptive tests, where samples were taking during the pressure oxidation, the metal extraction was calculated from the total weight of metal in solution divided by the weight of
metal in the head. This included correction factor which was applied to adjust for the changing volume due to sampling. The expression (equation 3-1) given in section 3.1.2 was also used for this purpose.

For the non-interruptive pressure oxidation of mixed sulphides, zinc and iron balances were carried out to ensure that the calculated zinc and iron were reliable. If the metal out / metal in mass ratio did not fall within the target variation of 0.95 to 1.05, the solution and / or residue analyses were repeated to check for any analytical error, and in some cases the tests were repeated. The mass balance yielded a calculated head assay, $M_{\text{calc}} (Me = \text{Zn or Fe})$, defined by:

$$M_{\text{calc}} = \left( \frac{m_{\text{Me}}^{\text{sol}} + m_{\text{Me}}^{\text{res}}}{m_i} \right) \times 100\% \quad (3-2)$$

Where $m_{\text{Me}}^{\text{sol}}$ is the mass of metal (Zn or Fe) in solution, $m_{\text{Me}}^{\text{res}}$ is the mass of metal in the oxidized residue and $m_i$ is the total starting mass of the head sample. The percent metal extraction was based on the calculated head assay:

$$\text{Percent metal extraction} = \frac{m_{\text{Me}}^{\text{sol}}}{(M_{\text{calc}}/100)(m_i)} \times 100\% \quad (3-3)$$

Where the calculation of sulphide oxidation to sulphur and sulphate were required, the sulphur species analyses of the head sample and that of the oxidized residue (which had been washed with ammonium acetate) were used in the following formulas:

Total $S^{2-}$ oxidation (to $S^0 + SO_4^{2-}$) = \left( \frac{m_{\text{sulfide}}^{\text{head}} - m_{\text{sulfide}}^{\text{res}}}{m_{\text{sulfide}}^{\text{head}}} \right) \times 100\% \quad (3-4)

$S^{2-}$ oxidation to $S^0 = \left( \frac{m_{\text{sulfur}}^{\text{res}}}{m_{\text{sulfide}}^{\text{head}}} \right) \times 100\% \quad (3-5)$

$S^{2-}$ oxidation to $SO_4^{2-} = (\text{total sulfide oxidation}) - (S^{2-} \text{oxidation to } S^0) \quad (3-6)$

Where $m_{\text{sulfide}}^{\text{head}}$ is the mass of sulphide sulphur in the head sample, $m_{\text{sulfide}}^{\text{res}}$ is the mass of sulphide in the oxidized residue and $m_{\text{sulfur}}^{\text{res}}$ is the mass of elemental sulphur in the oxidized residue.
3.8 Cyanidation

The cyanidation tests of the oxidized residues and synthetic jarosite species were carried out in 500 ml glass reactors, placed in a fume hood and at ambient temperature (about 23°C). Agitation was provided by one 5.7 cm diameter 45° pitched blade impeller on a stainless steel shaft, the impeller being positioned 2.5 cm off-bottom. The slurry for the cyanidation of oxidised residues contained 40 g of solids in 200 ml deionized water. In the case of jarosite, the whole solids generated by synthesis were used for cyanidation tests. Generally, the slurry was agitated with an overhead stirrer at a rate of 400 rpm. Prior to the addition of sodium cyanide, the pH of the slurry was raised to about 10.75 by the addition of calcium oxide powder. The pH was measured periodically, and restored back to its initial level by the addition of calcium oxide powder. Cyanidation test was usually carried out for 24 hours.

The concentration of free cyanide in the slurry was determined by titration with silver nitrate using p-dimethylaminobenzal-rhodamine as the indicator. This was performed after 2-8 hours of leaching and the cyanide strength was brought back to the initial level to sustain the 24 hour leaching. After 24 hours of reaction, the slurry was filtered and the residual free CN⁻ concentration in the filtrate was determined by the same titration method. The purity of calcium oxide used in pH control and alkaline pre-treatment was checked regularly by titration with hydrochloric acid. After cyanidation, the slurry was filtered and the solids air-dried. The weight of the filtrate was obtained from the difference between the weight of the slurry and that of the dry solids. The density of the filtrate was measured by weighing 20 ml solution so that the volume of filtrate could be determined. The cyanide consumption and the metals in solution were then calculated based on this measured volume. Both the solids and the filtrate were retained for analyses.

3.9 Analytical Methods and Characterization of Solid Samples

The solid from the precipitation reactions was examined by SEM/EDX for elemental composition analysis and the individual phases were identified by XRD. The details have been included in the Appendix B.

The soluble iron, the dissolved zinc and silver in the solution were analyzed by atomic absorption spectrophotometry (AAS), while the solid samples and gold in solution were analysed by Chem Met Consultants, Inc. (CMC) and International Plasma Laboratory (IPL), Vancouver,
B.C. The dissolved ferrous iron was determined by redox titration with a standard (0.1 N) ceric sulphate solution using ferroin indicator. This was complemented by potentiometric titration, which was carried out on some solution samples with high concentration of iodide.

The acid content of the solution was determined by first reducing the ferric with copper shot after deaeration using nitrogen gas. Mg-EDTA was used to complex the metals in solution and the resulting solution was then titrated with a standard (1 N) sodium hydroxide under a nitrogen atmosphere to a preset pH value. Details of the analytical methods have been documented in the literature (Pribil, 1982; Vogel, 1989 and Harris, 1990).

The solids were analyzed for zinc and iron by AAS after digesting in aqua regia/bromine solution (wet analyses). Silver and gold in the solid samples were determined by fire assay/AAS technique. The same fire assay/AAS technique was used to analyse gold in solution. The detailed procedures for gold and silver analyses by fire assay/AAS are included in Appendix B (chemical analyses). The total sulphur was determined gravimetrically as BaSO₄ after digesting in a KBr-Br₂/HNO₃ solution. HCl was added to keep the pH low and BaCl₂ was added to precipitate BaSO₄. If the lead concentration was low compared to the total sulphur, lead would stay in solution. If the lead content was high, lead would end up in the solids as PbSO₄, then, this would lead to a high total sulphur determination, because lead has an atomic wt. of 207, while barium has an atomic wt. of 137. In order to minimize this error, oxidized residue was washed with ammonium acetate prior to sulphur analysis, for the removal of lead sulphate and the reduction of the ratio of lead to total-sulphur. The elemental and sulphide sulphur species were determined gravimetrically after carrying out the following procedure. The sulphur species were determined by a sequential leach/digestion procedure. Initially, elemental sulphur was dissolved in boiling perchloroethylene (the boiling point is 121°C), then the perchloroethylene leach residue was boiled with 10% Na₂CO₃ solution to selectively dissolve sulphate. Finally, the Na₂CO₃ leach residue was digested in a KBr-Br₂/HNO₃ solution to dissolve the remaining sulphur, which was assumed to be sulphide. Then, the elemental sulphur and sulphide-sulphur were determined gravimetrically as BaSO₄. In this work, the difference between the total sulphur and the sum of elemental sulphur and sulphide sulphur is taken as sulphate-sulphur as follows.

\[ S_{SO_4} = S_T - S^o - S^{2-} \]  

(3-7)
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Reaction of Acanthite during the Pressure oxidation

There has been no previous information on the extraction-time profile of acanthite (Ag₂S) during aqueous oxidation in acid ferric solution. One of the contributions of this work is the first systematic study of the reaction of acanthite during the acid pressure oxidation.

4.1.1 Effect of Temperature on the Reaction of Acanthite

La Valenciana acanthite (section 3.1.3) was oxidised at temperatures varying from 110-150°C to ascertain the effect of temperature on reaction rate for this particular feed. Test conditions were 0.5 g/l pulp density, 0.05 g/l lignosol and 0.05 g/l quebracho, 100 psi oxygen pressure and 2-3 hour residence time. The initial solution contained 4.62 g/l Fe³⁺ and 50 g/l H₂SO₄. The results are presented in Figure 4-1.

![Figure 4-1. Effect of temperature on La Valenciana acanthite oxidation at 900 rpm, 100 psi Oxygen partial pressure, 0.5 g/l of La Valenciana at 4.62 g/l Fe³⁺ and 50 g/l H₂SO₄.](image)
At low temperatures, 120°C, the rate of reaction was slow, as indicated by the long residence time (2-3 hour) required to attain 70% silver extraction. At relatively high temperatures, 130-150°C, the rate of reaction was fast, high silver extraction (70-90%) was achieved within 1 hour reaction time. It is obvious from Figure 4-1, that the rate of oxidation of acanthite is a function of temperature. Tourre (1984) observed a similar trend during the acid pressure oxidation of "make-up" sulphides, containing low-grade (~4% Ag) acanthite ore and substantial pyrite; at above 120°C, extensive sequestering of the silver into the jarosite phase was reported after 1 hour. Longer residence time was required to achieve the same results, when temperature was below 120°C.

Equations for the extraction-time curves were obtained by using fifth-order polynomial regression fits, which gave correlation factor of 0.999, 0.998, 0.999 and 0.996 at 120, 130, 140 and 150°C respectively. These equations were differentiated and the values at time zero were taken as the initial reaction rates (Laidler, 1965). The Arrhenius rate law normally estimates the dependence of reaction rate constant on temperature:

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

(4-1)

Where:

- \( k \) Rate constant
- \( A \) Pre-exponential factor
- \( E_a \) Activation energy, J/mol;
- \( R \) Gas constant, which is 8.314 J/mol/K
- \( T \) Temperature, K.

This equation can be used to obtain the activation energy if the kinetic rate constant is known. The Arrhenius relation gives a straight line in a plot of log rate versus \( 1/T \times 10^3 \) and from the slope, the value of \( E_a \) (kJ/mol) can be deduced. An Arrhenius plot of the initial rate data for the oxidation of acanthite is presented in Figure 4-2. The activation energy of 72.6 kJ/mol (17.5 kcal/mol) was obtained with a correlation factor of 0.993, which indicates that the kinetics is controlled by chemical reaction and that the oxidation of acanthite is a strong function of temperature.

The concentration of iron in solution is plotted in Figure 4-3.
Figure 4-2. Arrhenius plot of the acanthite oxidation rate.

Figure 4-3. Concentration-time profile of iron during pressure oxidation of acanthite at 900 rpm, 100 psi, 0.5 g/l of La Valenciana acanthite, 4.62 g/l Fe$^{3+}$, 50 g/l H$_2$SO$_4$ and 150°C.
The total soluble iron was obtained by analysing the solution sample and adjusting for change in volume of solution as a result of sampling. The concentration profile of iron confirmed that there was no iron precipitation during the reaction.

4.1.2 Product of Acanthite Reaction in Autoclave

The reaction products were determined by analysing solution and residues from non-interruptive pressure oxidation reaction tests carried out on Ingleterra acanthite mineral. Test conditions were 1 g/l pulp density, 0.05 g/l lignosol and 0.05 g/l quebracho, 100 psi oxygen pressure and 90 minute residence time. Higher pulp density was used to generate some residues for analysis. The initial solution contained 4.62 g/l Fe$^{3+}$ and 50 g/l H$_2$SO$_4$. Each test was repeated to generate enough residues for analyses and tests were taken to be identical when the silver extraction (based on the calculated head assay) was the same (within the experimental error of 5%). The effects of temperature on the total sulphide oxidation and on the oxidation to sulphur or sulphate are presented in Table 4-1. At low temperature, i.e. 120-125°C, the rate of reaction was low, as indicated by low silver extraction and low total sulphide oxidation.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Time minute</th>
<th>Total S$^{2-}$ oxidation (%)</th>
<th>S$^{2-}$ oxidation to Sulphur (%)</th>
<th>S$^{2-}$ oxidation to Sulphate (%)</th>
<th>Ag Extraction$^1$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>90</td>
<td>31.12</td>
<td>29.02</td>
<td>2.10</td>
<td>34.91</td>
</tr>
<tr>
<td>125</td>
<td>90</td>
<td>42.44</td>
<td>39.01</td>
<td>3.69</td>
<td>46.16</td>
</tr>
<tr>
<td>130</td>
<td>90</td>
<td>53.76</td>
<td>48.48</td>
<td>5.28</td>
<td>57.40</td>
</tr>
<tr>
<td>135</td>
<td>90</td>
<td>69.95</td>
<td>62.26</td>
<td>7.69</td>
<td>72.21</td>
</tr>
</tbody>
</table>

$^1$Assay results are average extraction values obtained from calculated head assay.

The sulphur yield is the proportion of sulphide sulphur oxidized to elemental sulphur and is obtained by dividing the oxidation to sulphur by the total sulphide oxidation. The sulphur yields at different temperatures are presented in Figure 4-4. At 120°C, the sulphur yield was 93%, this decreased slightly with increasing temperature and at 135°C, the sulphur yield was 89%. The sulphur yield of silver sulphide (Ag$_2$S) in this work was similar to the high sulphur yields reported for ZnS, PbS, CuS and CuFeS$_2$ autoclave oxidation, which were nearly 100% (Peters, 1986).
4.1.3 Effect of Iron on the Reaction of Acanthite

Pressure oxidation tests of Ingleterra acanthite were carried out at 120°C, 250 psi oxygen partial pressure, 10 g/l sulphuric acid and in the presence of surfactant to investigate the catalytic role of ferric ions. The results of these tests are presented in Figure 4-5. After two hour of oxidation in the absence of ferric ions, the oxidation yielded only 32% silver extraction while the presence of 100 mg/l of ferric in the initial solution resulted in 52% silver extraction under the same conditions (Figure 4-5). The rate and extent of reaction increased with increasing concentration of initial ferric ion in solution.

4.1.4 Effect of Oxygen Partial Pressure on the Reaction of Acanthite

The effect of oxygen partial pressure on the reaction of acanthite was investigated in the range of 150-250 psi. The pressure oxidation tests were carried out in the absence of ferric ion and at 120°C. Figure 4-6 shows the silver extraction - time profile at different oxygen partial pressure.
Figure 4-5. Effect of ferric ions on acanthite oxidation at 120°C, 900 rpm, 250 psi oxygen partial pressure, 0.5 g/l of Ingleterra acanthite, 10 g/l H$_2$SO$_4$.

Figure 4-6. Effect of oxygen partial pressure on acanthite oxidation at 120°C, 900 rpm and 0.5 g/l of Ingleterra acanthite in 10 g/L H$_2$SO$_4$, no ferric.
There was no significant effect of partial pressure on the rate of oxidation of acanthite in the range 150 to 250 psi. The effect of partial pressure of oxygen also suggests that the direct cathodic reaction of oxygen with the mineral plays a minimum role in the pressure oxidation of acanthite.

The dissolved oxygen concentration was calculated by using the technique and the equation presented by Tromans (1998). The equation for oxygen solubility covers the temperature range from 273 to 616 K and up to 6.08 MPa (60 atm) pressure. The molal oxygen solubility is presented as a function of the operating temperature and pressure, and this can be converted to molar units by using the density of the solution. The dissolved oxygen concentrations at 150, 200 and 250 psi oxygen partial pressures were calculated to be 0.0083, 0.0110 and 0.0138 mol/l respectively. According to the following reaction (4-2), the concentrations of dissolved oxygen exceeded the stoichiometric requirement for the acanthite oxidation.

\[ \text{Ag}_2\text{S} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ag}^+ + \text{S}^0 + \text{H}_2\text{O} \]  

(4-2)

The rate of reaction was determined from the extraction-time curves similar to section 4.1.1 and plotted against the dissolved concentration on natural logarithms basis (Figure 4-7).

Figure 4-7. Order of reaction with respect to dissolved oxygen concentration of acid pressure oxidation of Ingleterra acanthite at 120°C, 900 rpm and 0.5 g/l of acanthite in 10 g/L H$_2$SO$_4$. 

90
The order of reaction with respect to the dissolved oxygen concentration was 0.18 as shown in Figure 4-7, however half order dependence with respect to oxygen concentration was expected for the mechanisms involving migration of silver ions (ionic transfer mechanism) and electron transfer (electrochemical mechanism). These mechanisms have been reviewed in section 2.8.3. The lower order of reaction can be attributed to the reversible adsorption of some of the oxygen molecules on the surface of the mineral, while some oxygen molecules react with the mineral.

The slow oxidation of acanthite in the absence of ferric (section 4.1.3) and small effect of oxygen partial pressure on the reaction (section 4.1.4) suggest that the acanthite oxidation is catalysed by dissolved iron through the following sequence of reactions:

1. Gas-liquid mass transfer of oxygen
   \[ O_{2(gas)} \rightarrow O_{2(aq)} \]  
   \[ (4-3) \]

2. Homogeneous oxidation of ferrous iron
   \[ 2Fe^{2+} + 1/2O_{2(aq)} + 2H^+ \rightarrow 2Fe^{3+} + H_2O \]  
   \[ (4-4) \]

3. Ferric ion oxidation of silver sulphide
   \[ 2Fe^{3+} + Ag_2S \rightarrow 2Ag^+ + S^0 + 2Fe^{2+} \]  
   \[ (4-5) \]

There is cyclic regeneration of ferric by reaction (4-4). In the pressure oxidation of complex sulphide, there is sufficient acid-soluble iron in the complex sulphide concentrate in the form of pyrite or pyrrhotite to satisfy the iron requirements for acanthite reaction.

### 4.1.5 Effect of Silver Sulphate concentration on the Reaction of Acanthite

Pressure oxidation tests of acanthite mineral were carried out at 120°C and at different initial concentration of silver ions to investigate the effect of silver ions on the rate of reaction. Other test conditions were 0.5 g/l Ingleterra acanthite, 0.05 g/l lignosol and 0.05 g/l quebrachro, 250 psi oxygen pressure, 2 hour residence time and the absence of ferric ions. The results of the effect of initial silver ions in the autoclave solution are shown in Figure 4-8.

The rate of reaction and the extent of silver extraction decreased with increasing silver ions concentration of the initial solution. At high concentration of initial silver ions (640 mg/l), the reaction almost did not proceed and only about 5% silver extraction was obtained. These tests were carried out in the absence of ferric, the result obtained could be attributed to the combined effect of the slow oxidation of the sulphide ions (S$^{2-}$) by oxygen and the reduction of the activity
of sulphide ions \((S^{2-})\) at the surface of the mineral. The reduction of the sulphide ion activity is caused by the presence of silver ions in the initial solution and according to the following equilibrium reaction:

\[
2Ag^+ + S^{2-} \leftrightarrow Ag_2S \quad \Delta G^o = -280.85 \text{ kJ} \tag{4-6}
\]

The equilibrium of reaction (4-6) is given as follows:

\[
K_{eq} = \frac{1}{[Ag^+]^2[S^{2-}]} \tag{4-7}
\]

An increase in the silver ion concentration of the autoclave solution shifts the equilibrium state in such a way as to re-establish equilibrium according to equation (4-7) and this suppresses the activity of sulphide ions \((S^{2-})\) at the surface of the mineral. According to reaction (4-6), the presence of silver decreases the extent of silver extraction and the rate of reaction.

Also, a parallel reaction of the \(S^{2-}\) is its oxidation to elemental sulphur by oxygen:

\[
S^{2-} + 2H^+ + \frac{1}{2}O_2 \rightarrow S^o + H_2O \quad \Delta G^o = -331.30 \text{ kJ} \tag{4-8}
\]

The oxidation of the \(S^{2-}\) pushes the equilibrium of reaction (4-6) to the left and the fast oxidation by ferric ions will minimise the retarding effect of initial silver ions on the rate and extent of reaction.

![Figure 4-8](image-url)

Figure 4-8. Effect of silver ions on acanthite oxidation at 900 rpm, 250 psi oxygen partial pressure, 0.5 g/l Ingleterra acanthite at 120°C, 0 g/l Fe\(^{3+}\) and 10 g/l H\(_2\)SO\(_4\).
The effect of silver ions on the rate of reaction in the presence of ferric ions was investigated. The conditions were the same as that of Figure 4-8, except that ferric ions (1 g/l) were present in the autoclave solution and higher acidity (15 g/l of H₂SO₄) was employed to avoid iron precipitation. The effect of initial silver ions in the presence of ferric is shown in Figure 4-9.

![Graph showing the effect of silver ions on acanthite oxidation](image)

Figure 4-9. Effect of silver ions on acanthite oxidation at 900 rpm, 250 psi oxygen partial pressure, 0.5 g/l Ingleterra acanthite at 120°C, 1 g/l Fe³⁺ and 15 g/l H₂SO₄.

The rate of reaction and the extent of silver extraction decreased because of the presence of silver ions in the initial autoclave solution. However, the effect of silver ions on the oxidation in the presence of ferric ions (Figure 4-9) was less significant than its effect in the absence of ferric ions (Figure 4-8). It is believed that ferric ion oxidises the silver sulphide, which is formed by the reaction of sulphide ion and silver (reaction 4-6) or the ferric ion oxidises the S²⁻. Either of these will cause the silver extraction to proceed until the mineral or the ferric is used up and since ferric is regenerated continuously by ferrous oxidation, the reaction continues until the mineral is completely oxidised. The results show the catalytic role of soluble iron and that the oxidation of the sulphide ions is very important in the overall oxidation of silver sulphide. Once the oxidation of sulphide ion is fast, the overall oxidation of silver sulphide is fast.
4.1.6 Proposed Mechanisms for the Reaction of Acanthite

The rate of reaction of silver sulphide increases with increasing temperature and ferric ion concentration, however, the rate of reaction decreases with the initial silver ion concentration. The ionic transfer mechanism (section 2.8.3) which involves the migration of silver ions through the silver sulphide is proposed for the extraction of silver and the formation of sulphur. This is based on the ionic conductivity of silver sulphide (acanthite) and the high mobility of the silver ions in the crystal lattice. The solid-state diffusivity of silver in Ag$_2$S has been described as the fastest solid-state diffusional process known in inorganic chemistry (Peters and Doyle, 1988). Previous investigation by Ishiguro et al. (1953) indicates that Ag$^+$ and S$^{2-}$ take part in the ionic transport of current for Ag$_2$S, but S$^{2-}$ participates to a much lesser extent than Ag$^+$. Once the Ag-S bond is broken, the sulphur species is free to move or react. The silver ion diffuses out to the surface and is released into the aqueous phase and S$^{2-}$ on the surface of the mineral is oxidised and this sequence can be represented as follows:

\[
\begin{align*}
Ag_2S & \rightarrow 2Ag^+ + S^{2-} \\
S^{2-} + 2Fe^{3+} & \rightarrow 2Fe^{2+} + S^0
\end{align*}
\] (4-9) (4-10)

Also, the presence of ferric ions plays a catalytic role in the oxidation of silver sulphide and is regenerated through the following reaction:

\[
2Fe^{2+} + 2H^+ + 1/2O_2 \rightarrow 2Fe^{3+} + H_2O
\] (4-11)

The overall reaction is represented as follows:

\[
Ag_2S + 2H^+ + 1/2O_2 \rightarrow 2Ag^+ + S^0 + H_2O
\] (4-12)

In the absence of ferric, reaction (4-10) is replaced by the oxygen reaction, which is represented as follows:

\[
S^{2-} + 1/2O_2 + 2H^+ \rightarrow S^0 + H_2O
\] (4-13)

The proposed mechanism is based on the following observations:

1. In the absence of ferric, the slow oxidation of acanthite was observed in this work (Figure 4-5 and Figure 4-6). The low rate of reaction is attributed to the low rate of oxidation of sulphide.
ions in reaction (4-13). The increase in the oxygen partial pressure had little effect on the kinetics of silver extraction as shown in Figure 4-7. According to Wadsworth (1972), in the absence of any iron species the oxygen reacts at the mineral surface to form intermediates such as H$_2$O$_2$ and HO$_2^-$ in a series of single-electron charge-transfer steps. This results in a relatively slow discharge of oxygen due to the strength of the oxygen-oxygen double bond.

2. In the presence of ferric, the reaction of acanthite becomes fast. The increase in the rate of reaction can be attributed to the fast oxidation of sulphide ions by ferric. The higher the ferric ions in the solution, the faster the oxidation of the sulphide ion (S$^{2-}$) at the surface of the mineral (reaction 4-10) and this suggests that the rate limiting step is the oxidation of sulphide ions to elemental sulphur.

3. The presence of silver sulphate in the initial solution increases the surface concentration of silver ions. The reduction of the overall rate can be attributed to the suppression of sulphide ion activity by the following reaction:

$$2Ag^+ + S^{2-} \rightleftharpoons Ag_2S$$  \hspace{1cm} (4-14)

The equilibrium of reaction (4-14) is given as follows:

$$K_{eq} = \frac{1}{[Ag^+]^2[S^{2-}]}$$  \hspace{1cm} (4-15)

The rate of disappearance of S$^{2-}$ is the sum of the rates of formation of silver sulphide (reaction 4-14) and that of elemental sulphur (reaction 4-13). The presence of initial silver ions shifts the equilibrium state in such a way as to re-establish equilibrium according to reaction (4-15). This will reduce the concentration or activity of sulphide ions (S$^{2-}$) at the surface of the mineral. The effect of the concentration of S$^{2-}$ on the overall reaction depends on the order of reaction with respect to sulphide ions in the two parallel reactions (Fogler, 1992). In this work, the low concentration of S$^{2-}$ as a result of the initial silver ions, decreases the overall rate of reaction, which suggests that the reaction order for the sulphur formation (reaction 4-13) is greater than the reaction order for the silver sulphide formation (reaction 4-14). The effect of the initial silver ions on the rate was observed in the presence and absence
of ferric ions, but its adverse effect on the rate was minimised in the presence of ferric ions. The presence of ferric ions promotes the sulphide oxidation to elemental sulphur and pushes the equilibrium of reaction (4-14) to the left. Also, this suggests that the rate-limiting step is the reaction of the sulphide ions \(S^2\).  

4.1.7 Summary of the reaction of Acanthite during Pressure Oxidation

Silver sulphide reacts in the autoclave under the conditions similar to that of the treatment of complex sulphide and silver ion is released into the solution. These observations reported in sections (4.1.1 to 4.1.5) represent the deportment of silver from the sulphides during the acid pressure oxidation. The predominant product of reaction is elemental sulphur. The process is described by an ionic transfer mechanism, which is based on the ionic conductivity of silver sulphide (acanthite) and the high mobility of the silver ions in the crystal lattice.

Once the silver is released, the sulphide ion \(S^2\) at the surface of the mineral is oxidised to elemental sulphur by ferric ions. The rate of reaction increases with increasing temperature and with the presence of ferric ions. However, the rate of reaction decreases with increasing silver concentration. The kinetics is controlled by chemical reaction with activation energy of 72.6 kJ/mol. The oxidation of the sulphide ions \(S^2\) is the rate-determining step and in the absence of ferric, the overall oxidation reaction is slow.

There is an incentive to recover the silver that is released into solution in addition to the base metals (copper and zinc) by deporting the aqueous silver into a cyanide soluble form such as silver iodide. This will provide the opportunity to treat the large number of complex sulphide deposits containing silver, milling of which may not be viable, however acid pressure oxidation followed by silver/gold leaching may well be attractive.

High acidity, low pulp density and low ferric concentration were used in this work to prevent the complication of the reaction by jarosite specie, normally, acidity decreases due to reaction with base metal sulphides and the conditions in the commercial autoclave favour the formation of jarosite specie and the incorporation of silver.

Therefore, the kinetics and mechanisms of silver incorporation into the jarosite specie are important to determine the effect of the operating conditions on silver loss to jarosite specie and the challenges posed to achieve alternative silver reaction.
4.2 Deportment of Silver as Jarosite Specie

The iron / silver concentration-time profiles are provided during the reaction of aqueous silver and ferric ions in the temperature range of 110°-150°C. The kinetic data were evaluated by the method of initial rates. The initial rates of iron precipitation were obtained by polynomial regression analysis on the iron-time profile obtained for each run. Adequate fittings of the data were obtained with a second degree polynomial of the form:

\[
[Fe]_t = [Fe]_0 - r_0 t + r_1 t^2
\]

Where \([Fe]_t\) is the iron concentration at time \(t\), \([Fe]_0\) is the ferric concentration at time 0, \(r_0\) is the initial rate of precipitation and \(r_1\) is a positive parameter. The fit of the polynomial was judged by the squared correlation coefficient, which was usually better than 0.990. A typical iron precipitation profile (data) together with the fitted polynomial curve is shown in Figure 4-10.

4.2.1 Effect of initial ferric concentration

The tests on the effect of the initial concentrations of ferric were carried out in the range of about 3.24 to 6.04 g/l ferric. In some preliminary tests, it was observed that at high initial concentration of ferric ions, acid generation by jarosite precipitation was high and that the rate of ferric precipitation declined significantly after the initial accumulation of acid. Therefore, to separate the effects of ferric and acid concentration on the precipitation kinetics, low initial ferric concentration was used to study the effect of ferric, while high ferric concentration was used to study the effect of acidity. The \(-74 +53 \mu m\) size fraction of the lead sulphate was selected (arbitrarily) for all the tests and from the same batch. The initial solution used for this set of experiments contained lead sulphate (in suspension), copper sulphate and silver sulphate with concentration of 10.31, 5.16 and 0.19 g/l, respectively. The following conditions were fixed: temperature 140°C; stirring speed 900 rpm; reaction time 120 minutes; initial acidity 15 g/l H₂SO₄. The results of the effect of initial ferric concentration are presented in Figure 4-10 and 4-11. The rate of iron precipitation increased with increasing concentration of initial ferric ion from 4.64 to 6.04 g/l, but with a corresponding higher final ferric in solution. Also, the rate of silver precipitation increased with increasing concentration of initial ferric ions in Figure 4-11 and at high concentration of initial ferric ion (6.04 g/l), silver precipitation was completed within 15 minutes. This suggests that under the industrial oxidation conditions, silver precipitation as
jarosite specie is very rapid once the silver is released into the aqueous phase under the similar conditions.

The results of the titration for free acid are presented in Figure 4-12. Acid generation increases with increasing initial ferric concentration because of the increase in the rate of hydrolysis of ferric ion and the resulting formation of the iron polymer (section 2.5.1). In the absence of alkali, the hydrolysis stage and the accompanied increase in acidity were reported to be slow at low temperature range of 50°-90°C (Margulis et al., 1976a). Therefore, the general high level of acid obtained in this work could be attributed to the high temperature (140°C) used in this set of experiments. This suggests that the hydrolysis step is fast at high temperature and is not the rate-determining step. The plot of the natural logarithm of the initial rate (in mol l⁻¹ min⁻¹) against the concentration of ferric in Figure 4-13 shows the response of rate to initial ferric concentration. The reaction order obtained in this work was 0.49, which confirmed a 0.5-order dependence on the initial ferric concentration, previously reported at low temperature (90°C) by Margulis et al. (1976a).

Figure 4-10. Effect of initial ferric concentration on iron precipitation at 140°C.
Figure 4-11. Effect of initial ferric concentration on silver precipitation at 140°C.

Figure 4-12. Effect of initial ferric concentration on acidity profile at 140°C.
Figure 4-13. Plot of natural logarithms of rate and initial ferric at 140°C.

The effect of the initial ferric concentration on the rate of precipitation can be attributed to the formation of the dinuclear right iron complex $\text{Fe}_2(\text{OH})_2^{4+}$, which undergoes reaction with the aqueous environment and grows into a polymer $(\text{Fe}_2(\text{OH})_4^{2+})_{2n}$. The growth of the latter into larger polymer is a precursor of jarosite precipitation according to the reaction pathway already reviewed in section 2.5.1. The concentrations of the iron hydroxyl complexes at different concentrations of ferric were obtained by speciation calculation routine (Appendix A1.3). From the results of the calculation, when the initial ferric concentration was double, the concentration of the iron complex $\text{Fe}_2(\text{OH})_4^{2+}$ was also more than double. Similar effect of ferric concentration on the iron complex has been demonstrated by Limpo et al. (1976). The concentration of $\text{Fe}_2(\text{OH})_4^{2+}$ is given by the following expression:

$$[\text{Fe}_2(\text{OH})_4^{2+}] = \frac{K[\text{Fe}_2(\text{OH})_4^{4+}]}{a_i^2n_i} \quad (4-17)$$
The results of the calculation are shown in logarithmic scales for the different initial ferric concentration in Figure 4-14. The iron complexes participate as reactants in the precipitation (Dousma and DeBruyn, 1978; Fryer et al., 1974) and it is possible that an increase in the total ferric may cause a corresponding increase in the rate of adsorption of these complexes on the jarosite surface. Since the effect of the increase in the initial ferric ions on the rate of precipitation was positive in this work, it could be deduced that the iron complexes did not adsorb so strongly so as to block the reaction sites and reduce the rate of iron precipitation. The iron complexes are thought to adsorb and become part of the lattice, which causes crystal growth and the generation of the new adsorption sites that reduces the blocking effect (Teixeira and Tavares, 1986).

![Figure 4-14. Theoretical effect of initial ferric on the level of iron complexes at 140°C.](image)

**4.2.2 Effect of initial lead sulphate concentration**

The tests on the effect of the initial concentrations of lead were carried out at 140°C. The initial concentrations of lead sulphate (in suspension) were 2.58, 5.16, 7.73 and 10.31 g/l, which corresponded to 1.76, 3.52, 5.28 and 7.04 g/l of lead respectively. The −74 +53 μm size fraction
of the lead sulphate was selected (arbitrarily) for the tests. Initial solution used for the tests contained ferric, copper and silver sulphate with concentrations of 24.39, 7.98 and 0.19 g/l respectively, which were fixed in this set of experiments. The following conditions were also fixed: stirring speed 900 rpm; reaction time 120 minutes; initial acidity 15 g/l H₂SO₄. After the completion of each experiment, the solids were filtered and washed with deionized water and then with ammonium acetate solution. The filtrate, wash solution and acetate wash solution were analysed for lead by AAS.

The effects of initial lead concentration on the rate of precipitation are presented in Figure 4-15. The rate of iron precipitation increased with increasing concentration of lead from 1.76 to 7.04 g/l, with a corresponding higher final lead as lead sulphate (solid) in the residues. In the absence of lead sulphate, the reaction did not proceed within the 120 minutes reaction time used in this set of experiments. At the low concentration of silver used in these experiments, silver jarosite was not formed, however, one would have expected the formation of hydronium jarosite to promote the precipitation of iron. Hydronium jarosite has low stability, sufficient time (more than 2 hours) may be required for its formation in the absence of alkali (Posnjak and Mervin, 1922) and it requires low acidity and very high initial ferric level to improve its kinetics of precipitation (Qian-kun et al., 1985). In the absence of lead, the rate of iron precipitation is very low because of the low kinetics of hydronium jarosite formation under the conditions used in these experiments (Figure 4-15).

In the presence of lead, the kinetics of iron precipitation increases with increasing slurry concentration of lead sulphate. This indicates that at low concentration of silver ion and moderate to high concentration of lead sulphate (in suspension), the primary phase is plumbojarosite like the small addition of alkali produces an alkali jarosite containing only limited hydronium ion substitution (Brophy and Sheridan, 1965). The presence of alkali increases the iron precipitation and promotes the rate of jarosite formation. The addition of alkali ions is thought to stimulate the crystallisation stage of the formation of the jarosite precipitate i.e., the removal of the hydroxo complexes of iron from the solution, and this accelerates the hydrolysis reaction (Getskin et al., 1975). The results presented in Figure 4-15 for the effect of lead on the kinetics of iron precipitation at 140°C are similar to the results previously reported for the effects of potassium and sodium sulphate at 90°C (Getskin et al., 1975). The increase in the concentration of initial
lead sulphate suspension reduced the induction period (i.e. the period before appreciable jarosite formation). Since such period is related to the formation of the iron polymer species (Dutrizac, 1980), it can be deduced that lead accelerates the hydrolysis reaction.

Figure 4-15. Effect of suspended lead sulphate on iron precipitation at 140°C.

The soluble lead ($\text{Pb}^{2+}$) in the autoclave discharge was analysed after filtration of the precipitates. The dried residue contained both jarosite specie and unreacted lead sulphate. The lead in the jarosite specie was determined by analysing the jarosite after washing the dried residue with acetate. Lead as lead sulphate was obtained by analysing the acetate wash solution (acetate filtrate) and a mass balance was carried out on the lead in each experiment. The lead, which participated in the reaction, was taken as the sum of the lead in the precipitation filtrate and that in the jarosite specie (solid).

The summary of the lead distribution is presented in Table 4-2. The plot of the natural logarithm of initial rate (in g l$^{-1}$ min$^{-1}$) against the concentration of lead (which participated) in the reaction is shown in Figure 4-16a. The reaction order obtained in this work approached a
0.25-order dependence on the lead concentration, which participated in the reaction. Similar fractional reaction order (0.50) dependence on alkali concentration has been reported at low temperature (98°C) for potassium, ammonium and sodium jarosite (Qian-kun et al., 1985). The low order of dependence with respect to lead may be attributed to the low solubility of lead sulphate unlike potassium, ammonium and sodium sulphate.

Table 4-2. Lead distribution after the precipitation of jarosite specie at 140°C.

<table>
<thead>
<tr>
<th>Initial Pb$^{2+}$ g</th>
<th>Lead distribution after precipitation</th>
<th>Pb$^{2+}$, which participated$^2$ g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb$^{2+}$ in filtrate$^1$, g</td>
<td>Pb$^{2+}$ in jarosite, g</td>
</tr>
<tr>
<td>7.04</td>
<td>0.123</td>
<td>1.57</td>
</tr>
<tr>
<td>5.28</td>
<td>0.128</td>
<td>1.03</td>
</tr>
<tr>
<td>3.52</td>
<td>0.123</td>
<td>0.84</td>
</tr>
<tr>
<td>1.76</td>
<td>0.119</td>
<td>0.35</td>
</tr>
</tbody>
</table>

$^1$soluble lead (Pb$^{2+}$) in the autoclave discharge, after precipitation reaction.

$^2$sum of lead in acetate filtrate and in jarosite specie.

Figure 4-16a. Logarithm plot of reaction rate and concentration of lead that participated in the reaction at 140°C.

For the purpose of explanation, the jarosite specie may be presented as an end-member lead
jarosite as shown below and its formation requires prior dissolution of lead sulphate.

\[
PbSO_4(s) \leftrightarrow Pb^{2+} + SO_4^{2-} \quad (4-17)
\]

\[
Pb^{2+} + 6Fe^{3+} + 4SO_4^{2-} + 12H_2O \rightarrow PbFe_6(SO_4)_4(OH)_{12} + 12H^+ \quad (4-18)
\]

According to the solubility data presented for lead sulphate (Linke, 1958), only \(-150\) mg/l of lead would be soluble. Therefore the concentration of lead that participated in the precipitation reaction (Table 4-2) could be attributed to reaction (4-18), which drives reaction (4-17) to the right.

Although, the lead sulphate used in these experiments were from the same size fraction (-74 +53 µm), the surface area of PbSO_4 (solid) should have increased with increasing concentration, which could affect the reaction rate by promoting the crystallisation stage. This should also be the case for the solid-to-solid transformation of lead sulphate to lead jarosite, but (theoretically) the activation energy associated with this would be very high. The plot of the natural logarithm of initial rate against the initial concentration of lead sulphate (PbSO_4) is shown in Figure 4-16b. The reaction order dependence on the initial lead sulphate (PbSO_4) concentration is approximately equal to the response obtained in Figure 4-16a.

![Figure 4-16b. Logarithm plot of reaction rate and initial concentration of lead sulphate (PbSO_4) at 140°C.](image-url)
However, previous microscopic study of the commercial autoclave residue by Dutrizac and Chen (1984) indicated that the plumbojarosite specie formed as discrete crystals and there was no evidence of it forming on the lead sulphate, which would have been the case for the solid-to-solid transformation of PbSO₄ into lead jarosite. Therefore, plumbojarosite seems to form via dissolved PbSO₄ even though the solubility of the lead sulphate is low.

The rate of silver precipitation also increases with increasing concentration of initial lead sulphate (in suspension) from 1.76 to 7.04 g/l (Figure 4-17). In the absence of lead sulphate, the reaction did not proceed within the 120 minutes reaction time used in these experiments and silver remained in solution. However the rate of silver precipitation increased with increasing lead sulphate.

![Figure 4-17. Effect of initial suspended lead sulphate on silver precipitation at 140°C](image)

Figure 4-17 suggests that at low concentration of silver ions, the major collector of silver is plumbojarosite and it is the precipitation of this phase that drives silver deportment into the jarosite specie for the test condition (in which there is no Na⁺, K⁺ or NH₄⁺). It has been observed
that during the acid pressure oxidation of silver-bearing zinc-lead concentrates, silver reports into
the plumbojarosite (Parker, 1981; Dutrizac and Chen, 1984) and that the end member
argentojarosite is rare at the low concentration of silver encountered in the industrial autoclave.
In Figure 4-17, at high level of initial lead sulphate, silver precipitation was completed within 20
minutes while iron precipitation continued (Figure 4-15). Therefore, one would expect the
formation of the silver-rich plumbojarosite specie at the initial stage and the hydronium-bearing
plumbojarosite at the latter stage of the precipitation. The mixture of silver-rich jarosite and
hydronium-bearing plumbojarosite has been reported by Dutrizac and Jambor (1984), during the
X-ray diffraction study of the precipitates formed at 155°C from and it was submitted that the
lead-poor argentojarosite was formed first because argentojarosite is more stable than the
plumbojarosite.

4.2.3 Effect of initial acidity

In order to investigate the effect of the initial acidity on the rate of reaction, further
experiments were conducted at 140°C. The lead sulphate used for this set of experiments was
from the same batch of chemical and from the -74+53 μm size fraction. Initial solution contained
lead sulphate suspension, copper sulphate and silver sulphate with concentration of 5.16, 7.98
and 0.19 g/l respectively, which were fixed in this set of experiments. The following conditions
were also fixed: stirring speed 900 rpm; reaction time 240 minutes; initial ferric concentration
13.95 g/l and the total volume of initial solution 1 litre. After precipitation, the solids were
filtered and washed with deionized water and then with ammonium acetate solution. The filtrate,
wash solution and acetate wash solution were analysed for lead by AAS.

The results of the effect of initial acid concentration are presented in Figure 4-18 and 4-19. At
high initial acid level of 45 g/l H₂SO₄, the iron precipitation barely proceeded within the 240
minutes residence time. Similar result was reported by Dutrizac et al. (1980) at 140°C and over a
longer residence time of 24 hours and at this level of acidity, the yield of the jarosite declined
rapidly and no jarosite was produced above this critical acid concentration. However, it was
observed that the higher the initial iron concentration, the higher the critical acid concentration
required for the suppression of jarosite formation. When the initial acidity was in the range of 15-
35 g/l H₂SO₄, where the jarosite reaction could proceed, the rate of iron precipitation decreased
with increasing initial acidity or hydronium ions ($\text{H}_3\text{O}^+$) concentration (Figure 4-18). Hydronium participates as product of the hydrolysis reaction as follows (Getskin et al., 1975):

$$\text{Fe}(\text{H}_3\text{O})_3^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{FeOH}(\text{H}_2\text{O})_5^{2+} + \text{H}_3\text{O}^+$$ \hspace{1cm} (4-19)

The acidity then gradually increases as a result of slowly occurring hydrolysis (reaction 4-19), which leads to the formation of various hydroxo complexes of iron (Margulis et al., 1976a). Therefore, high initial acid level or high concentration of $\text{H}_3\text{O}^+$ makes the reaction (4-19) shift towards the left and becomes slow, which ultimately affects the crystallisation stage of the formation of precipitates.

Figure 4-18. Effect of initial acidity on iron precipitation at 140°C.

Since the jarosite precipitation is autocatalytic, the jarosite crystal formed during the early stage of the precipitation may act as a surface for the subsequent reaction such that reaction (4-19) takes place at the surface of the crystal. An increase in the initial concentration of $\text{H}_3\text{O}^+$ reduces the rate of desorption of the adsorbed $\text{H}_3\text{O}^+$ ions produced by reaction (4-19) at the
surface of the crystals and retards the overall rate. If the \( \text{H}_3\text{O}^+ \) adsorbs and becomes part of the lattice, the level of hydronium-substitution will increase with increasing concentration of initial acid. However, Dutrizac et al. (1980) has demonstrated that the hydronium-substitution decreases with increasing concentration of initial acid. This suggests that the hydronium reacts to a lesser extent and adsorbs strongly to retard the overall rate of reaction. The acidity of the initial solution plays a major role on the extent of jarosite precipitation.

The results of the titration for the free sulphuric acid (acidity-time profile) are presented in Figure 4-19. At 15 g/l, the initial rate of iron precipitation was high and there was a significant increase in the acidity at the early stage (up to 30 minutes) by reaction (4-19), but the increase in acidity became less pronounced as the solution approached equilibrium. At 25 g/l initial acid, the initial rate of iron precipitation was lower than that of 20 g/l, there was a gradual increase in the acidity over a longer period of time because equilibrium was delayed at high level of initial acid. At 35 g/l initial acid, the initial rate of precipitation was very low and there was a small increase in the acidity.

Figure 4-19. Effect of initial acid on the acid-time profile during iron precipitation at 140°C.
The hydrolysis rates were determined from the linear parts of the various acidity-time profile curves having the steepest slopes. The comparison of the rate of hydrolysis with the rate of iron precipitation (during the crystallisation) is summarised in Table 4-3. The experiments were carried out at the same temperature, therefore the contribution from the temperature factor could be ignored and the rate of hydrolysis could be attributed to the concentration factor. The effect of initial acidity on the rate of hydrolysis is much more pronounced than its effect on the rate of iron precipitation.

Table 4-3. Effect of initial acidity on the rate of hydrolysis and iron precipitation at 140°C.

<table>
<thead>
<tr>
<th>Initial Acidity, g/l</th>
<th>Rate of Hydrolysis, g/l-min</th>
<th>Rate of Precipitation, g/l-min</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.208</td>
<td>0.053</td>
</tr>
<tr>
<td>20</td>
<td>0.142</td>
<td>0.044</td>
</tr>
<tr>
<td>25</td>
<td>0.060</td>
<td>0.036</td>
</tr>
<tr>
<td>35</td>
<td>0.021</td>
<td>0.006</td>
</tr>
</tbody>
</table>

The rate of silver precipitation is high at low initial acid levels and becomes low at high initial acid as shown in Figure 4-20.

Figure 4-20. Effect of initial acidity on silver precipitation at 140°C.
At 45 g/l initial acid, 9% of the initial silver was precipitated after 180 minutes, while at 25 g/l and below, silver precipitation was completed within 20 minutes of the reaction time. The low rate of silver precipitation as jarosite at higher acidity also indicates that acidity plays significant role on the extent of silver precipitation.

### 4.2.4 Effect of Temperature

The effect of temperature on the kinetics was investigated in the temperature range of 110 to 150°C. The lead sulphate used for this set of experiments was again from the same batch and comprised the -74 +53 μm size fraction. The initial solution contained lead sulphate suspension, copper sulphate and silver sulphate with concentration of 5.16, 7.98 and 0.19 g/l respectively. The following conditions were also fixed: stirring speed 900 rpm (section 3.1); reaction time 120-240 minutes; initial ferric concentration 4.64 g/l; initial acidity 15 g/l H₂SO₄ and total volume of initial solution 1 litre. The results of the effect of temperature on the kinetics of precipitation are presented in Figure 4-21.

![Figure 4-21. Effect of temperature on iron precipitation.](image-url)
There was no appreciable precipitation of iron at 110°C and there was a long induction period before minor iron precipitation commenced. At low temperature range (110-125°C), the initial rate of reaction was low and less than 30% of the initial ferric was precipitated after 240 minutes. The rate of iron precipitation increases with increasing temperature and substantial iron is precipitated in the temperature range of 130-150°C. At 150°C, more than 80% of the initial iron was precipitated after 120 minutes. The previous investigation of the effect of temperature on lead jarosite stability revealed that the stability increased with temperature (Dutrizac et al., 1980).

The result of the effect of temperature is shown in Figure 4-22 as ln $r_0$ versus $1/T \times 1000$ diagram (T is absolute temperature). The data of the 110°C experiment were not included because the iron precipitation was less than 6%.

![Figure 4-22. Arrhenius plot of the temperature effect on the initial rate of iron precipitation.](image)

The apparent activation energy of the reaction was calculated by using the Arrhenius equation, and this gave a value of 114.3 kJ/mol (27.6 kcal/mol). In the temperature range of 50-90°C, the values reported by Margulis et al. (1976a; 1976b) for the end members potassium, sodium and
ammonium jarosites were 17.7, 21.7 and 20.1 kcal/mol respectively. In another study and in the same temperature range, Limpo et al. (1976) reported an activation energy value of 29.8 kcal/mol for the end member ammonium jarosite. End member jarosite specie is not formed under the conditions used in this work and that of industrial autoclave operations because of the low concentration of silver and the high availability of lead.

The activation energy reported in this work and the previous work indicates that the kinetics of iron precipitation is a strong function of temperature and it relates to the crystallization stage. Activation energy (24.15 kJ/mol) of the hydrolysis stage has been reported to be higher than the activation energy (17.9 kJ/mol) of the crystallisation stage for the precipitation of potassium jarosite (Margulis et al., 1976b), which suggests the marked influence of temperature on the rate of hydrolysis and the formation of hydroxo complexes of ferric. Temperature has an effect on the induction period as shown in Figure 4-22 and since this is related to the formation of the hydroxo complexes of ferric (Dutrizac, 1980), this suggests that temperature affects the kinetics of jarosite formation by promoting iron hydrolysis.

The effect of temperature on the silver precipitation is shown in Figure 4-23.

![Figure 4-23](image)

**Figure 4-23.** Effect of the operating temperature on silver precipitation.
At 110°C, silver remains substantially in solution after 240 minutes. At low temperature range, the rate of precipitation of silver is low and at above 130°C, silver precipitation becomes very fast.

4.2.5 Effect of Seeding

The effect of jarosite seed on the kinetics was investigated at 125° and 130°C. The lead sulphate from the same batch of chemical and from the –74 +53 μm size fraction was used for this set of experiments. The initial solution contained lead sulphate suspension, copper sulphate and silver sulphate with concentration of 5.16, 7.98 and 0.19 g/l respectively. The following conditions were also fixed: stirring speed 900 rpm; reaction time 240 minutes; initial ferric concentration 4.64 g/l; initial acidity 15 g/l H₂SO₄; various level of seeds and total volume of initial solution 1 litre. Prior seed syntheses were carried out at the same temperatures being investigated and by using the same composition of silver, lead and ferric sulphate during each synthesis. These were repeated several times in the absence of seed to generate enough jarosite seeds required for this set of experiments. The unreacted lead sulphate was removed in each case by dissolving the residue in ammonium acetate solution. The results of the effect of seeding on the rate of iron precipitation are presented in Figure 4-24. Seeding had an effect on the kinetics of jarosite precipitation at both 125° and 130°C. In the absence of seed, there is an induction period before appreciable precipitation takes place, this induction period is pronounced at low temperature, low ferric and high acidity.

At 125°C, the addition of 25g seed reduced the induction period and increased the rate of iron precipitation. Since the induction period is associated with the formation of iron polymer by hydrolysis, the reduction of this period by seeding suggests that the hydrolysis reaction and the subsequent growth of the hydroxo complex of iron occur at the surface, once the crystal is formed. The rate and the extent of iron precipitated increased with increasing seed addition of 50g. Therefore, the role of the seed may be interpreted as that of a catalyst, accelerating the reaction. At 130°C, the effect of seeding on the rate of iron precipitation was less than its effect at 125°C, however, the presence of seed caused an increase in the rate. Previously, a small effect of seeding on jarosite formation has been reported at 90°C by Getskin et al., 1975 and Zapuskalova et al., 1978. However, Parmmenter and Haigh (1981) reported a significant effect of
seeding on the rate of precipitation by using large quantities of seed at 100°C.

The positive effect of seeding shows that the crystallisation of jarosite specie is heterogeneous and like other heterogeneous crystallisation, the slowest step is assumed to be the crystal-growth step and competitive homogeneous nucleation becomes comparatively less significant and therefore not directly relevant to the overall kinetics of precipitation. At 125°C and in the absence of seed, the primary nucleation is slow, heterogeneous precipitation, obviously requires the presence of active solid surfaces to catalyse the reaction and the initial rate of reaction is directly proportional to the weight and hence the area of solid surface available. At 130°C, the primary nucleation is fast and once the nuclei are formed, they act in an autocatalytic way to promote precipitation. Although it is small, the positive effect of seeding on the rate at 130°C shows that the self-nucleating precipitation is not sufficient to change the mechanism from heterogeneous to homogeneous precipitation.

![Figure 4-24. Effect of the seeding on the kinetics of iron precipitation at 125°C and 130°C.](image-url)
4.2.6 Mechanism of Jarosite formation

The formation of jarosite species consists of two stages, which are the formation of the jarosite complex in an aqueous phase and its crystallization. It can be expressed as follows:

$$3Fe_2(SO_4)_3 + M_2SO_4 + 12H_2O \leftrightarrow 2MFe_3(SO_4)_2(OH)_3(aq) + 6H_2SO_4$$  \hspace{1cm} (4-20a)

$$\downarrow$$

$$2MFe_3(SO_4)_2(OH)_6(s)$$  \hspace{1cm} (4-20b)

Where M = Ag^+, 1/2Pb^{2+} and H_3O^+

As discussed in the sections on the precipitation kinetics, silver precipitation is completed first and much earlier under the conditions, which enhances kinetics of precipitation. The rate of silver precipitation is linear up to about 85% precipitation, which suggests a surface chemical process of silver incorporation. Although the precipitation of silver precipitation is fast, end member silver jarosite is not formed because of the low concentration of silver (120 mg/l) used in this work. Lead and hydronium ions are co-precipitated and this is also expected during the industrial oxidation of sulphides, which contain trace amount of silver. Subsequent to complete silver precipitation, iron precipitation continued, but the concentration of silver remained almost at zero level, which ruled out the ion exchange reaction of silver jarosite specie with lead or hydronium ion. The following two stages can be considered (Getskin et al., 1975):

1. The formation of hydroxo complexes of ferric in solution by slow hydrolysis reaction and this is accompanied by the increase in acidity of the solution,
2. The formation of jarosite (crystallisation stage) as a result of the participation of hydroxo complexes of ferric in crystallisation.

The concentration of the hydroxo complexes of ferric increases with the initial concentration of ferric and the hydrolysis stage is promoted by temperature. The supersaturation of the solution by hydroxo-complexes of iron as a result of the gradual hydrolysis of ferric, leads to the crystallisation of the hydroxo compound (jarosite specie). The additions of monovalent cations and lead ions stimulate the crystallisation stage i.e., the removal of the hydroxo complexes of iron from solution, and this accelerates the hydrolysis reaction. Based on this, Getskin et al., (1975) submitted that the crystallisation step is the rate-controlling step of the process. The accelerating effect of the seeds on the precipitation of jarosite specie (in section 4.2.5) suggests that the crystallisation is limited by the linear growth of the crystals and not by the formation of...
crystallisation centres.

The possible participations of hydroxo complexes of ferric in crystallisation have been examined by Dutrizac (1980) and reviewed in section 2.5.1. These principally involve the growth of the small polymers $\left(\text{Fe}_2(\text{OH})_{4}^{2+}\right)_{2n}$ into larger polymer units which become the immediate precursors of precipitation. If associated sulphates are considered, the small polymer chain can be considered to consist of distorted $\text{Fe}^{3+}$ octahedra shared at two edges. Such a structure could give rise to that of solid jarosite by opening of OH bonds such that all octahedra would be shared at a corner instead of by edges. It is thought that protons play an important role in the opening of the polymer chains (Dutrizac et al., 1980). Since the structure is stabilised by jarosite forming cation ($\text{NH}_4^+$, $\text{Na}^+$, $\text{K}^+$, 1/2$\text{Pb}^{2+}$, etc), it is possible these cations also play a role in the opening of the polymer chains. Sulphate helps to stabilise the structure and it is bonded to the iron in the polymer before crystallisation (Margulis et al., 1976b).

For heterogeneous precipitation, the slowest step (in most cases) is assumed to be the crystal-growth step and the size of the crystal increases with the extent of iron precipitation. The scanning electron micrograph of the jarosite specie formed at 125°C after 120 and 240 minutes (section 4.2.4) are presented in Figure 4-25 and 4-26 respectively. The agglomeration of some particles might have occurred during the acetate washing of the resulting solids.

Although, silver precipitation was substantially completed after 120 minutes, 10% of the iron was precipitated after 120 minutes and 25% of iron was precipitated after 240 minutes. The particle size increased slightly with the extent of iron precipitation as shown in Figure 4-25 and 4-26. In Figure 4-26, zoning of the jarosite particle was observed and elemental analysis of the spot by EDS analysis (Appendix C) revealed that this core is silver-rich lead-hydronium jarosite and the shell is mainly lead-hydronium jarosite. Generally, two phases are present after 4 hours of precipitation in Figure 4.26, which are mainly lead-hydronium jarosite and some zoned silver-lead-hydronium jarosite phases, and Dutrizac and Jambor (1987), have reported similar observations. A possible mechanism to explain the existence of lead-hydronium jarosite distinct phase is to consider a parent particle with a number of nuclei, which has formed on its surface. Some of these remain attached to the parent particle while others become detached and produce new particles. This mechanism is supported by the appearance of the particles in Figure 4-26, where a number of surface outgrowths are seen.
Figure 4-25. SEM micrograph of jarosite particles precipitated at 125°C after 2 hrs of reaction

Figure 4-26. SEM micrograph of jarosite particles precipitated at 125°C after 4 hrs of reaction
Under the optimal conditions of precipitation such as high temperature (130-150°C) and high ferric such as that of industrial zinc pressure oxidation, the chemical reaction process represented by reaction (4-20a) is fast. This is promoted by the low acidity resulting from the proton consumption by the sulphides. In the absence of seed, the reaction starts homogeneously and nuclei are generated, which act as seeds to accelerate the precipitation in an autocatalytic manner. Therefore, the process of jarosite formation can be considered to be occurring at the surface of the jarosite particles.

The first step involves the diffusion of the right jarosite-forming complexes to the surface of the nuclei and the second step involves the adsorption of these complexes onto the surface to occupy selected active sites. The species adsorb differently, those that are strongly adsorbed may block a site and slow down the rate. Generally, the complexes (participating and non-participating) may compete for the adsorbed sites. The third step is the chemical reaction between the adsorbed species to produce adsorbed products. The inference is that the adsorbed jarosite "complexes" produced fit perfectly on to the surface lattice, causing the crystal to grow and the generation of new adsorption sites. The fourth step is the desorption of the co-produced ions (H\(^+\) or H\(_3\)O\(^+\)), which is affected by the initial concentration of the acid. The fifth step is the diffusion of the co-produced ions out to the bulk solution.

The high activation energy of jarosite precipitation obtained in section 4.2.4 supports the chemical adsorption, chemical reaction and the desorption in the second, third and fourth step respectively. The results obtained on the effect of seeding and temperatures suggest that the precipitation reaction rate is controlled by a chemical reaction step occurring at the surface of the jarosite crystals.

4.2.7 Summary of the Kinetics of Silver and Iron Precipitation as Jarosite Specie

The reaction of aqueous silver and iron in the presence of lead sulphate suspension revealed the kinetics and stability of jarosite formation under the conditions that are similar to that of industrial autoclaving. Unlike previous studies, the investigations on the reaction kinetics were conducted at a temperature range (110-150°C) that was relevant to zinc pressure oxidation. Neutralisation of the solution prior to precipitation was avoided.

In the absence of lead sulphate, the reaction did not proceed and silver and iron remained in
solution after 120 minutes reaction time and under the conditions used in this work. However, the precipitation of silver and iron increased with the concentration of lead sulphate suspension. This indicates that at low concentration of silver ions, the major collector of silver is plumbojarosite and it is the precipitation of this jarosite specie, which drives the silver deportment into the jarosite specie. The use of lead sulphate in this work was based on the association of silver with lead sulphide minerals and the high content of lead in the zinc-lead-iron complex sulphides. Also, the assumption that alkali (\(\text{Na}^+, \text{K}^+, \text{etc}\)) may only be present as trace elements in the zinc-lead-iron complex sulphide was made. The addition of alkali (\(\text{Na}^+, \text{K}^+, \text{etc}\)) to precipitate iron as alkali jarosites and to preclude lead jarosite in the presence of lead sulphate requires high concentration of the alkali (Dutrizac et al., 1980; Bull et al., 1985).

The series of tests conducted on the effects of initial ferric, lead, acidity and temperature revealed that the kinetics of iron and silver precipitation increased with increasing temperature and concentration of initial ferric and lead, but the kinetics decreased with increasing concentration of acid. The initial acid level has pronounced effect on the rate of formation and the stability of jarosite by reducing the rate of hydrolysis and the formation of the right hydroxo complex of ferric, these result into the reduction of the rate of crystallisation.

The significant effect of temperature and the slight effect of seeding indicate that the precipitation reaction rate is controlled by a chemical reaction step (possibly) occurring at the surface of the jarosite crystals. The stability and the rate of reaction are enhanced at high temperature (above 130°C), low initial acid (about 15 g/l), high initial ferric and the presence of lead sulphate suspension. Such optimal conditions exist during the pressure oxidation of sulphides. Although the precipitation of silver was fast under the optimal conditions, end member silver jarosite was not formed because of the low concentration of silver (120 mg/l) used in this work, with the presence of silver as trace element in the sulphides. Lead and hydronium ions are co-precipitated during the formation of jarosite and this is also expected during the industrial oxidation of sulphides.

The silver precipitation was completed first and much earlier under the optimal conditions, which enhanced the kinetics of precipitation. Subsequent to complete silver precipitation, iron precipitation continued, but the concentration of silver remained almost at zero level, which ruled out the ion exchange reaction of silver jarosite with lead or hydronium ions.
4.3 **Chemical Composition and Cyanidation of Synthetic jarosite**

Under the conditions which are similar to the commercial pressure oxidation of silver-bearing sulphides, the silver which is released into solution by silver sulphide oxidation (section 4.1) is thought to be subsequently incorporated into the jarosites species (section 4.2). Therefore, it is important to investigate the extent of silver extraction by cyanidation of the jarosite species formed in the temperature range of 110°-150°C.

In this set of experiments, synthetic jarosites, which contain silver, were precipitated at different temperatures (110-150°) and attempts were made to recover silver by cyanidation. This investigation revealed the effect of temperature on the compositions and phases of jarosite formed. Also, the effect of grinding (i.e. physical alteration) on the silver extraction from cyanidation of jarosites was investigated.

4.3.1 **Chemical Composition of Jarosite specie at different Temperatures**

The initial solution contained 60.02 g/l Fe₂(SO₄)₃.5H₂O, 15 g/l H₂SO₄, 0.19 g/l Ag₂SO₄, 10.31 g/l PbSO₄, 160.21 g/l Mg₃(SO₄)₂.7H₂O in a total volume of 1 litre. Lead sulphate was highly insoluble in the sulphate medium; therefore the initial solution contained lead sulphate suspension. High concentrations of ferric, lead (in suspension) and sulphate were used in these experiments to enhance the rate and the extent of precipitation. The experiments were carried out at 110, 120, 130 and 150°C in a 2-liter Parr autoclave for 2 h. The stirring speed was maintained at 900 rpm.

The product of each experiment was filtered and washed with warm water; the solids were dried overnight in an oven. Silver was not detected in the solutions (final and wash solutions), and this indicated that the silver was precipitated under the conditions investigated. The solids (jarosite species and lead sulphate) were subjected to cyanidation for silver extraction. In some experiments, the dried solids (synthetic jarosite and lead sulphate) were slurred (4 times) in 10% ammonium acetate solution at room temperature. The solids were washed and dried; the solids and solutions (acetate and wash solution) were analyzed. Chemical analysis of the acetate wash solution did not indicate the presence of dissolved silver or ferric from solids, which indicated that the jarosite specie did not dissolve during the acetate wash.

The precipitation of silver as jarosite specie was completed at 110, 130 and 150°C and the
resulting chemical formula at different temperatures are summarised in Table 4-4. The hydronium content increased with temperatures as previously observed by Dutrizac et al. (1980) because hydronium jarosite stability is favoured at elevated temperatures (Dutrizac and Kaiman, 1976). Also, the increase in hydronium substitution with increasing temperature in the low temperature range (50-90°C) has been reported previously in the literature (Margulis et al., 1976a; 1977a; 1977b). However, the opposite trend on the hydronium substitution has been reported in other works (Brophy and Sheridan, 1965; Dutrizac, 1982). Obviously, there is some uncertainty concerning the effect of temperature on the extent of hydronium substitution and this requires further clarification.

The chemical formula of the end member plumbojarosite is Pb$_{0.5}$Fe$_3$(SO$_4$)$_2$(OH)$_6$, but in this work, compositions at 150° and 110°C correspond to 66 and 74 mole % Pb respectively. The increase in the stability of hydronium jarosite increases the hydronium substitution and decreases the lead composition. Also, the initial slurry concentration of lead sulphate affects (positively) the level of lead in the lead jarosite specie. When precipitation was carried out at different initial concentration of lead sulphate, Mumme and Scott (1966) observed solid solution of Pb-H$_3$O jarosites with the molar percentage of the lead member ranging from 27 to 89 mole % Pb. In the previous work conducted by Dutrizac et al. (1980), the compositions extended from 0 to 89 mole % Pb.

Also, the silver content decreased with temperatures in the same trend as observed by Arauco and Doyle (1986) during pressure oxidation of silver-bearing mixed sulphide. Silver precipitation was complete at all the temperatures investigated in this work, but the jarosite yield was high at high temperature. At high temperature, silver is concentrated over a large mass of jarosite product and therefore, there is a decrease in the concentration of silver with increase in temperature.

Table 4-4. The resulting formula for the synthetic jarosites at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>Pb$<em>{0.37}$Ag$</em>{0.05}$H$<em>3$O$</em>{0.21}$Fe$_3$(SO$_4$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>130</td>
<td>Pb$<em>{0.35}$Ag$</em>{0.02}$H$<em>3$O$</em>{0.28}$Fe$_3$(SO$_4$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>150</td>
<td>Pb$<em>{0.33}$Ag$</em>{0.02}$H$<em>3$O$</em>{0.32}$Fe$_3$(SO$_4$)$_2$(OH)$_6$</td>
</tr>
</tbody>
</table>
Under the conditions similar to pressure oxidation of sulphides, silver is precipitated from the aqueous phase to form a mixture of zoned silver-hydronium-lead jarosite and lead-hydronium jarosite phases (section 4.2.6). The composition of silver in each phase depends on the concentration of silver in the initial solution used for precipitation. Dutrizac and Jambor (1984) revealed that a series of lead-silver-hydronium jarosite solid solutions were formed when jarosite was precipitated from the solution of lead and iron sulphate, which contain low or moderate concentration of silver. The maximum solubility of silver corresponds to $\text{Ag}_{0.07}$ in the chemical formula of the phase when precipitation was made from initial solution containing low concentration of silver. At higher concentration of silver in the initial solution, the mixtures consist of argentojarosite and silver-bearing lead jarosite solid solution with the maximum solubility of lead that corresponds to $\text{Pb}_{0.25}$ in the silver-bearing-lead jarosite phase.

Although, heterogeneous phases are formed when the jarosite species are precipitated at high temperature (section 4.2.6), a homogenous phase is formed at low temperature (Patino et al., 1994). At a temperature, which is below 100°C, the silver precipitation is slow and both silver and lead are co-precipitated and this results into a solid solution of silver-hydronium-lead jarosite single phase (Dutrizac and Jambor, 1984). It is expected that the silver ion will be present in both the inner and the outer crystal planes of the single-phase jarosite specie (formed at low temperature) and the end member argentojarosite formed in the absence of lead and at high initial concentration of silver.

The size analyses of the various jarosites formed in this work at different temperatures are summarized in Table 4-5. The size of the synthetic jarosite decreased slightly with increase in temperatures, which suggested that super-saturation (or concentration difference) decreased slightly with increase in temperature (Nielsen, 1964; Demopoulos et al., 1995; Cheng and Demopoulos, 1997). In addition to temperature, other factors such as hydrodynamics and the presence of impurities or seeds may affect the crystal size.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Weighted Mean Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C</td>
<td>4.91</td>
</tr>
<tr>
<td>130°C</td>
<td>4.50</td>
</tr>
<tr>
<td>150°C</td>
<td>4.01</td>
</tr>
</tbody>
</table>

Table 4-5. Size analyses of synthetic jarosites at different temperatures
4.3.2 Cyanidation of Synthetic Jarosites

Baseline direct cyanidation tests were performed on the precipitation products (resulting jarosite and the lead sulphate) in a glass reactor. All the cyanidation tests were carried out with 20g of solids (precipitation products) in 200 ml solution at room temperature for 24 hours with NaCN at a stirring speed of 300 rpm. The cyanidation process was carried out at high concentration of NaCN (5g/l). The solids used were not subjected to prior acetate wash, in order to have condition that was similar to the cyanidation of oxidised residue of sulphides. After 24 hours of leaching, the solution samples were analyzed for silver. The residue was washed with distilled water and dried at 110°C. The dried residue was weighed, rolled and analyzed for Ag by fire assay.

The results of the baseline cyanidation of the synthetic jarosites are summarized in Table 4-6. The silver extraction into the cyanide solution (in 24 hour) from silver-lead-hydronium jarosite is very low and such low extraction of silver from the oxidised residue has been reported previously in the literature (Berezowsky, 1986; Berezowsky et al., 1990). The mass balance of the silver revealed that silver remained in the solid jarosite specie after cyanidation.

Table 4-6. Summary of baseline cyanidation of various jarosites

<table>
<thead>
<tr>
<th>Temperature of Synthesis</th>
<th>Test I.D</th>
<th>Silver Extraction %</th>
<th>NaCN Consumption, kg/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C</td>
<td>AT1</td>
<td>0.17</td>
<td>1.75</td>
</tr>
<tr>
<td>130°C</td>
<td>AT2</td>
<td>0.71</td>
<td>1.88</td>
</tr>
<tr>
<td>150°C</td>
<td>AT3</td>
<td>1.25</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Low silver was recovered from the cyanidation of the jarosite species formed at a temperature range of 110°-150°C because only the silver ion in the outer crystal planes of the jarosite structures would be accessible to and could react with free cyanide ions in the pulp. This explains the difference between the cyanidation of the jarosite species formed in this work and that of the end-member argentojarosite (Roca et al., 1993; Van Weert and Tuinman, 1993; Tuiman, 1992). This also explains the difference between the reactivity of the jarosite species formed in this work and that of the single phase silver-lead jarosite formed at low temperature (97°C) and from high concentration of aqueous silver (Patino et al., 1994). The end member argentojarosite is rarely, if ever, formed under the condition, which is similar to the autoclaving of high-lead
complex sulphides, which contain low concentration of silver. High temperatures and low concentration of silver were used in this work to precipitate the silver-lead hydronium jarosite species, silver precipitation was fast and completed first, however, the precipitation of iron continued leading to the zoning of the silver-rich jarosite in the core (section 4.2.6) of the lead-hydronium jarosite.

The jarosites formed at different temperatures (110 to 150°C) were ground in the ceramic mortar with pester to prevent contamination. After grinding, the cyanidation procedures were repeated on the various reground precipitates to determine the effect of grinding on silver extraction from the synthetic jarosites. The silver recoveries by cyanidation of the reground jarosites are summarised in Table 4-7. One would have thought that grinding of the jarosite species prior to cyanidation would help the silver extraction by exposing the silver-rich core and by increasing the surface area or defects of the jarosite species. The results revealed minimal improvement on the silver extraction by prior grinding. This suggests that grinding of the oxidised residues after autoclaving may not improve the silver extraction and that the silver-rich jarosite may be concentrated at sub-micron level such that additional grinding (or ultra fine grinding) is required to expose the silver prior to cyanidation. The consumption of cyanide could be attributed to the reaction of CN⁻ with Fe³⁺ on the jarosite surface or partial loss to the gas phase as HCN in the fume hood.

Table 4-7. Summary of cyanidation of reground jarosites

<table>
<thead>
<tr>
<th>Temperature of Synthesis</th>
<th>Test L.D</th>
<th>Grinding Time, hr</th>
<th>Weighted Mean Diameter (μm)</th>
<th>Silver Extraction %</th>
<th>NaCN Consumption, kg/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C</td>
<td>AT1-1</td>
<td>2</td>
<td>3.50</td>
<td>0.17</td>
<td>1.44</td>
</tr>
<tr>
<td>110°C</td>
<td>AT1-2</td>
<td>5</td>
<td>2.50</td>
<td>0.24</td>
<td>1.87</td>
</tr>
<tr>
<td>150°C</td>
<td>AT3-1</td>
<td>2</td>
<td>3.31</td>
<td>1.31</td>
<td>2.26</td>
</tr>
<tr>
<td>150°C</td>
<td>AT3-2</td>
<td>5</td>
<td>3.11</td>
<td>1.57</td>
<td>2.42</td>
</tr>
</tbody>
</table>

4.3.3 Summary of the Chemical Composition and Cyanidation of Synthetic Jarosite

Aqueous silver is incorporated into the jarosite species under the conditions which are similar to pressure oxidation of sulphide minerals and in the temperature range of 110-150°C. There is no significant difference in the chemical formula of the resulting silver-hydronium-lead jarosite
species formed at different temperatures. However, they differ from the end member lead jarosite because of the incorporation of silver and hydronium ions. The hydronium content increases with temperatures as previously observed by Dutrizac et al. (1980) because hydronium jarosite stability is favoured at elevated temperatures (Dutrizac and Kaiman, 1976). Also, the silver content decreases with temperature in the same trend as observed by Arauco and Doyle (1986) during the pressure oxidation of silver-bearing mixed sulphide.

Under the conditions such as high temperatures (110°-150°C) and low concentration of silver in the initial solution, silver precipitation is fast and completed first, however, the precipitation of iron continues after the completion of silver. This leads to the zoning of the silver-rich jarosite in the core (section 4.2.6) of the jarosite structures. During cyanidation, only the silver ion in the outer crystal planes of the jarosite structures is accessible to and can react with free cyanide ions in the pulp leading to low extraction of silver where the silver ion is concentrated in the core rather than the outer plane. Prior grinding of the jarosite specie does not improve the subsequent silver extraction (by cyanidation), which suggests that the silver-rich jarosite may be concentrated at sub-micron level such that additional grinding (at high cost) may be required to expose the silver prior to cyanidation.

In order to recover silver from sulphide minerals by pressure oxidation and subsequent cyanidation, there is need to deport silver into a cyanide soluble form such as silver sulphide (Zhang et al., 1997; Taylor et al., 1989) or silver iodide (Van Weert and Tuinman, 1993).
4.4 Deportment of Silver as Silver Sulphide

The deportment of aqueous silver as silver sulphide was investigated in the presence and absence of oxygen. The results are presented in the following sections.

4.4.1 Deportment of Silver as Silver Sulphide under the Deoxygenated condition

The experiments were carried out at different ratios of silver to sulphur under the deoxygenated conditions (section 3.3). The $-38 \pm 25 \mu m$ size fraction of the elemental sulphur was selected (arbitrarily) for all the tests and from the same batch of chemical reagent. The initial solution contained ferrous and ferric with concentration of 5.0 and 0.1 g/l respectively (as sulphate). This corresponds to the ferrous/ferric ratio of 50 to 1 and the solution was sparged (with nitrogen) during the period of heating and reaction. The following conditions were also fixed: temperature 90°C; stirring speed 900 rpm; reaction time 180 minutes; initial acidity 50 g/l $H_2SO_4$ and initial total moles of silver and sulphur 0.048 moles and at atmospheric pressure.

The results of the silver precipitation at the different initial molar ratios of silver to sulphur are presented in Figure 4-27 and Table 4-8.

Figure 4-27. Molar partitioning of silver and sulphur specie at different initial silver and sulphur. Conditions: 90°C, 900 rpm, 180 minutes, 50 g/l $H_2SO_4$, 0.048 mol/l initial total concentration of silver and sulphur.
Table 4-8. Distribution of silver and sulphur species at the initial and final stage of silver sulphide precipitation at 90°C under the deoxygenated condition.

<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>Residue, after 3 hours precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag, mol/l</td>
<td>S, mol/l</td>
</tr>
<tr>
<td>0.012</td>
<td>0.036</td>
</tr>
<tr>
<td>0.016</td>
<td>0.032</td>
</tr>
<tr>
<td>0.024</td>
<td>0.024</td>
</tr>
<tr>
<td>0.032</td>
<td>0.016</td>
</tr>
</tbody>
</table>

The molar partitioning of silver and sulphur in the silver sulphide precipitate was (almost) the same, irrespective of the molar ratio of silver to sulphur at the beginning of the experiment (Figure 4-27). This suggests that once the aqueous silver is reduced to metallic silver by the high reducing conditions, the precipitated silver combines with elemental sulphur at atmospheric pressure to form silver sulphide. The aqueous silver concentration-time profile is presented in Figure 4-28.

Figure 4-28. Aqueous silver concentration-time profile at different initial level of silver and sulphur. Conditions: 90°C, 900 rpm, 180 minutes, 50 g/l H₂SO₄, 0.048 mol/l initial total concentration of silver and sulphur. Initial iron: 5.0 g/l Fe²⁺ and 0.1 g/l Fe³⁺.
The precipitation of silver was observed as silvery white flakes in the solution sample that was taken during the early stage of the reaction. The silver precipitation can be represented as follows:

$$Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag^0$$ (4-21)

The reaction (4-21) has been reported to be an equilibrium reaction in the literature (Tananaev, 1924) and that it proceeds to the left with increasing temperature. Under the high reducing condition employed in this work, the reaction proceeds to the right and it is relatively fast. Also, some black precipitates were observed in the solution samples that were taken towards the end of the reaction.

The reaction of the precipitated silver and sulphur can be represented as follows:

$$2Ag^0 + S \rightarrow Ag_2S$$

$$\Delta G^o = -40.52 \text{ kJ/mol}$$ (4-22)

The rate of reaction (Figure 4-28) increases with decreasing initial silver/sulphur ratio or with increasing initial sulphur. The effect of the initial level of sulphur (or silver/sulphur ratio) on the rate of reaction suggests that the reaction of metallic silver and sulphur affects the equilibrium of reaction (4-21) and that reaction (4-22) is the rate-determining step. The kinetics of formation of silver sulphide from silver and sulphur had been described by Reinhold and Seidel (1935) to be controlled by the rate of diffusion through the built-up layer (of silver sulphide) and the rate was reported to be inversely proportional to the diameter of the layer.

It is expected that the completeness of the reaction (4-22) will depend on the amount of sulphur. At the end of the reaction, it was observed that the silvery white flakes had turned to black precipitates. In order to ascertain that the black mass did not include iron sulphide (such as marcasite), comparison between the final iron concentration in solution and the initial iron concentration was made. There was no change in the concentration of total iron during the reactions, which suggested that the black mass was silver sulphide alone. Also, high acidity and the reducing conditions used for the silver sulphide precipitation in this work precluded silver deportment as jarosite specie and only silver sulphide formation could account for the decrease in silver concentration (section 4.2).
4.4.2 Department of Silver as Silver Sulphide under Oxygenated condition

The experiments were carried out at different temperatures under the pressure oxidation conditions (section 3.4). The -38 +25 μm size fraction of the elemental sulphur was selected (arbitrarily) for all the tests and from the same batch of chemical reagent. The initial solution used for all the experiments contained ferrous and ferric with concentration of 5.0 and 0.1 g/l respectively (as sulphate). This corresponds to the ferrous/ferric ratio of 50 to 1. The following conditions were also fixed: stirring speed 900 rpm; reaction time 60 minutes; initial acidity 50 g/l H₂SO₄; oxygen partial pressure 100psi; initial concentration of silver and sulphur are 0.012 and 0.036 mol/l respectively. The initial silver / sulphur ratio corresponds to 0.33 in section 4.4.1 and at 120°C, 0.05 g of lignosol and quebracho surfactants were added. The low temperature range of 90°-120°C was used to provide comparison with the deoxygenated experiments, which were carried out at 90°C.

The results of the silver precipitation at different temperatures are presented in Figure 4-29.

![Figure 4-29. Silver concentration-time profile at different temperatures. Conditions: 900 rpm, 60 minutes reaction time, 50 g/l H₂SO₄, 100 psi oxygen partial pressure, initial silver and sulphur are 0.012 and 0.036 mol/l respectively. Initial iron in solution: 5.0 g/l Fe²⁺ and 0.1 g/l Fe³⁺.](image-url)
There was initial silver precipitation because the high reducing condition created by the initial high ferrous/ferric ratio favoured the reaction (4-21). The silvery white flakes were observed in the samples taken after 1 and 3 minutes.

There was high rate of ferrous oxidation during the early stage of the reaction (Figure 4-30) and this stage corresponded to an increase in the concentration of aqueous silver after the initial precipitation of the silver (Figure 4-29). The metallic silver, which was initially precipitated was oxidised to aqueous silver by reaction (4-21) in a reverse direction, which can be represented as follows:

\[
Fe^{3+} + Ag^- \rightarrow Fe^{2+} + Ag^+ \quad \Delta G^\circ = 2.90 \text{ kJ/mol} \quad (4-23)
\]

The reaction (4-23) has been investigated previously by Morrison (1989), it is said to be fast with an activation energy of 28 kJ/mol and that sulphate and ferrous ions have retarding effects on the rate of reaction.

![Figure 4-30. Ferrous concentration-time profile at different temperatures. Conditions: 900 rpm, 60 minutes reaction time, 50 g/l H2SO4, 100psi oxygen partial pressure, initial concentration of silver and sulphur are 0.012 and 0.036 mol/l respectively. Initial iron: 5.0 g/l Fe^{2+} and 0.1 g/l Fe^{3+}.](image-url)
After 10 minutes, there was a significant change in the rate of ferrous oxidation (Figure 4-30) and there was corresponding decrease in the aqueous silver concentration (Figure 4-29). Some black precipitates were observed in the solution samples of the 90°C experiment, which suggested that there was silver sulphide precipitation. There was no change in the concentration of total iron during the reactions, which suggested that the iron was not precipitated as sulphide.

The low rate of silver precipitation could be attributed to the reaction (4-21), which became slow under the oxidising condition (low ferrous/ferric ratio). It is probable that the reaction (4-21) became as slow as reaction (4-22) or slower than reaction (4-22) under the oxidising conditions. The silver precipitation was not completed as shown in Figure 4-29, despite the high initial concentration of sulphur used in these experiments. Also, the silver precipitation seems to reach equilibrium after 30 minutes of reaction. It was probable that the silver sulphide oxidation to aqueous silver (section 4.1) under oxidising condition also played a role in minimising the rate and the extent of silver precipitation. The silver sulphide precipitation became less favourable at high temperature, leaving high concentration of aqueous silver in the final solution.

A comparison of the silver sulphide precipitation under the deoxygenated condition with the precipitation under the oxygen pressure shows that silver precipitation as sulphide is completed under the deoxygenated condition. This suggests that the presence of oxygen minimises the silver sulphide formation under the pressure oxidation condition.

4.4.3 Summary of the Deportment of Silver as Silver Sulphide

Under the deoxygenated condition, silver precipitation as silver sulphide is promoted by the presence of sulphur. The reaction involves the reduction of aqueous silver to metallic silver and the subsequent reaction of metallic silver with sulphur. The reduction of aqueous silver is very rapid under the high reducing conditions (high ferrous/ferric ratio). The rate of silver precipitation (as silver sulphide) increases with decreasing initial silver/sulphur ratio or with increasing initial sulphur concentration. The effect of the initial level of sulphur (or silver/sulphur ratio) on the rate of reaction suggests that the reaction of metallic silver with sulphur may be the rate-determining step.

Under the pressure oxidation condition, the presence of oxygen minimises the silver sulphide formation by oxidising ferrous to ferric. The silver precipitation was not completed under the
pressure oxidation condition and in addition, the silver precipitation reaction seems to reach equilibrium quickly and leaving high concentration of aqueous silver. The reaction became less favourable at high temperature, leaving high final concentration of silver in the solution at the end of the reaction. In addition to the fact that the silver precipitation as silver sulphide is minimal in the presence of oxygen, it is unlikely that this plays a prominent role in the loss of silver because the silver sulphide is soluble in cyanide solution (Zhang et al., 1997; Taylor et al., 1989).
4.5  Deportment of Silver as Silver Iodide

The deportment of silver as silver iodide and the stability of silver iodide in acid ferric media were investigated. The results are presented in the following sections.

4.5.1 Stability of Silver Iodide at different temperatures

Silver iodide from the same batch of chemical reagent and $-74 \pm 53 \mu m$ size fraction was selected for stability tests. Preliminary cyanidation of the silver iodide yielded 99% silver extraction. The iron precipitation experiments were carried out at different temperatures with silver iodide as a source of silver. The initial solution contained 9.30 g/l ferric and 7 g/l lead (in suspension) as sulphate. The following conditions were also fixed: stirring speed 900 rpm; reaction time 360 minutes; initial acidity 15 g/l $H_2SO_4$ and initial concentration of silver iodide 56.30 mg/l, which contained 25.90 mg/l of silver. The results of the silver extraction from the precipitates formed at different temperatures are presented in Figure 4-31.

![Figure 4-31](image)

Figure 4-31. Effect of temperature on silver deportment from silver iodide. Condition for precipitation: 900 rpm, 6 hours, 15 g/l $H_2SO_4$, 9.30 g/l ferric, 7 g/l lead (in suspension) and initial concentration of silver iodide 56.30 mg/l. Cyanidation: all precipitate in 200 ml water with 3 g/l NaCN and at room temperature.
The silver extraction by cyanidation of the jarosite precipitates was below 99% which suggested that some silver iodide dissolved and precipitated as jarosite specie during the iron precipitation. The extent of silver iodide dissolution and the subsequent incorporation into the jarosite phase increased with increasing temperature. The migration of the silver to the jarosite phase is promoted by the solubility of the silver iodide, which increases with temperature (Gavrich and Galinker, 1955) and the enhanced stability of jarosite specie, which increases with temperature (section 4.2). This suggested that the loss of silver (about 10% at 150°C) involved the dissolution and subsequent crystallisation as follows:

\[ \text{AgI} \rightarrow \text{Ag}^+ + I^- \]  
\[ \text{Ag}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ \]

The jarosite precipitation is presented (simply) as an end member silver jarosite in reaction for the purpose of explanation. The silver-hydronium-lead jarosite specie is formed under these conditions and the silver, which is incorporated into the jarosite phase, is not recoverable by cyanidation (section 4.2 and 4.3). In addition to the temperature, other factors such as the volume of solution, the reaction time, the particle size of the silver iodide and the concentration of silver iodide may affect the solubility of the silver iodide in the autoclave.

### 4.5.2 Competition between Iodide and Jarosite specie for Aqueous Silver

Attempts were made to investigate the effect of temperature and initial acidity on the deportment of silver under the condition, which favour both silver iodide and silver jarosite formation. 10 ml solution containing 0.19 g of silver sulfate was sealed in an ampoule and another 10 ml solution containing 0.20 g of potassium iodide was sealed in another ampoule. The iodide concentration corresponded to 100% stoichiometric of iodide to silver. The initial solution, which was 980 ml contained 61.25 g of ferric sulfate, 5.16 g of lead sulfate (in suspension) and 15 g of sulphuric acid. The reaction time was 120 minutes and the experiments were carried out at 110°C, 130°C and 150°C. At the operating temperature, the ampoules were broken by the impeller blades when the agitator was switched on. The precipitates formed were subjected to cyanidation experiments.

The results of the silver extraction from the precipitates formed at different temperatures are
presented in Figure 4-32. Under the conditions of high ferric and lead concentration, the jarosite specie formation is promoted (section 4.2) and once silver is incorporated into the jarosite phase, it cannot be recovered by cyanidation (section 4.3). Also, under the conditions used for the experiments, silver iodide formation is promoted and the iodide precipitation does not depend on the acidity of the solution. Analysis of the filtrate revealed that all the aqueous silver was precipitated from the solution during the reaction. The silver extraction from the precipitate in Figure 4-32 can be attributed substantially to the silver in the iodide phase, which dissolves in cyanide solution.

![Graph showing silver extraction by cyanidation vs temperature](image)

Figure 4-32. Department of silver as iodide vs jarosite specie. Initial condition for precipitation: 0.129 g/l Ag⁺, 13.95 g/l Fe³⁺, 0.150 g/l I⁻ and 3.52 g/l Pb²⁺ (in suspension). Cyanidation: all precipitate in 200 ml deionized water with 3 g/l NaCN and at room temperature.

At low temperature (110°C), silver deportment as silver iodide is almost completed and subsequent silver extraction by cyanidation is very high. 75% of silver was recovered by cyanidation of the precipitates, which was formed at 150°C and 25 g/l initial acidity. At high temperature, silver deportment as iodide is not completed and part of the silver reports to jarosite
specie. This is pronounced when low initial acid was used during the precipitation. The deportment of some silver as jarosite specie may be attributed to the fact that silver iodide becomes less stable at high temperature (Tien and Harrington, 1963), while jarosite specie becomes more stable at high temperature (section 4.5.2). Therefore, it is probable that the silver precipitation as jarosite specie by reaction (4-24) helps in shifting the equilibrium of reaction (4-25) to the right and promotes silver loss under the conditions, which favour jarosite formation. High initial acid maximized the silver deportment into the iodide phase by minimizing the stability and kinetics of jarosite specie. When high initial acidity of 30g/l was used for precipitation at 140°C, the silver extraction by cyanidation of the precipitate increased to 96%. Also, 89% of silver was recovered from the precipitates formed at 150°C, when high initial acidity was used for the experiment.

The silver iodide formation is a precipitation reaction that is expected to be fast, however in the presence of both hydrolysed ferric, sulphate and iodide, some aqueous silver may react preferentially with hydrolysed ferric and sulphate to form jarosite. The resulting jarosite specie has very high stability at high temperature (section 4.2) and therefore, it may prevent the rapid and total deportment of silver as silver iodide especially when the silver is incorporated into the core of jarosite.

4.5.3 Deportment of Silver iodide from Silver jarosite

The experiments were carried out in an autoclave at different iodide concentrations and the source of silver was synthetic silver jarosite which had a chemical composition of \((\text{Ag})_{0.9} (\text{H}_3\text{O})_{0.1} \text{Fe}_3(\text{SO}_4)_2(\text{OH})_6\). The initial solution used for precipitation contained 13.95 g/l ferric as sulphate and 0.76 g/l synthetic silver jarosite. The initial concentration of potassium iodide were 0.20 g/l, 0.40 g/l, 0.60 g/l and 0.80 g/l which corresponded to 100%, 200%, 300% and 400% stoichiometric of iodide to silver respectively. The following conditions were also fixed: stirring speed 900 rpm; reaction time 120 minutes; initial acidity 30 g/l \(\text{H}_2\text{SO}_4\) and temperature 140°C. Precipitation was followed by the cyanidation of the whole precipitates.

The results of the silver extraction from the precipitates formed at different concentration of iodide are presented in Figure 4-33. There was no silver present in the autoclave solution after the precipitation reaction. The silver extraction from the precipitate increased with the
concentration of iodide used for the autoclave reaction.

The increase in the silver extraction can be attributed to the formation of silver iodide from silver jarosite during the precipitation reaction. This suggests that some silver jarosite recrystallises to form hydronium jarosite, thus freeing the silver to form silver iodide. The displacement of silver ion was not observed during the precipitation of silver-hydronium-lead jarosite in section 4.2. It is possible the iodide species adsorbs on the silver jarosite to promote the dissolution of silver jarosite or that the silver ions in the outer crystal planes of the silver jarosite are accessible. The silver jarosite decomposition did not go to completion within the reaction time used, or at the stoichiometric level of iodide to silver chosen for these experiments. However, there was about 15% increase in the silver extraction, when the iodide concentration was increased from 100% to 400% stoichiometric of silver. Van Weert and Tuinman (1993) reported a similar observation.

Figure 4-33. Deportment of silver from silver jarosite. Initial condition for precipitation: 13.95 g/l ferric, 0.76 g/l synthetic silver jarosite, 900 rpm, 2 hour, 30 g/l H₂SO₄ and 140°C. Cyanidation: all precipitate in 200 ml deionized water with 3 g/l NaCN and at room temperature.
The assumption that the trend on the silver extraction (Figure 4-33) is due to the formation of silver iodide in the autoclave may be valid because the cyanidation of 0.76g of silver jarosite (without re-crystallisation in iodide solution) gave only 30.50% silver extraction. Also, the addition of iodide to the silver jarosite suspension during the cyanidation reaction (24 hours) did not result in the increase in silver extraction. This suggests that the re-crystallisation of the silver jarosite and the release of silver to form silver iodide are temperature dependent and could be surface dependent.

4.5.4 Summary of the Silver Deposition as Silver Iodide

The deposition of silver as silver iodide is an effective way of recovering silver during the pressure oxidation. However, silver extraction from the autoclave precipitates was below 100%, which suggested that some silver iodide dissolved under a long residence time and precipitated as jarosite specie during the iron precipitation. The extent of silver iodide dissolution and the subsequent incorporation into the jarosite phase increased with increasing temperature. The migration of some silver ions to the jarosite phase is promoted by the decrease in stability of silver iodide at high temperature and the increase in the stability of jarosite specie at high temperature.

Although, the silver iodide formation is a precipitation reaction that is expected to be fast, but in the presence of both hydrolysed ferric, sulphate and iodide, some aqueous silver may react preferentially with hydrolysed ferric and sulphate. The resulting jarosite specie may prevent the rapid and total deposition of silver as silver iodide especially when the silver is incorporated into the core of the jarosite. If the silver jarosite is formed along with the silver iodide, some of the silver jarosite may re-crystallise to form hydronium jarosite, thus freeing the silver to form silver iodide. However, the silver jarosite decomposition does not go to completion within the reaction time used, or at the stoichiometric level of iodide to silver chosen for these experiments.
4.6 Pressure Oxidation of Complex Sulphides for Silver and Zinc

Pressure oxidation tests on three complex sulphide feed materials were conducted followed by cyanidation of the resulting residues. The results are presented in the following sections.

4.6.1 Silver Extraction from Complex Sulphides by Baseline Cyanidation

The baseline cyanidation tests were carried out on the Cannington and Eskay Creek complex sulphides without prior pressure oxidation and the results are presented in Table 4-9. The results suggest that the Cannington complex sulphide concentrate (as received) requires the liberation of the silver mineral phase (e.g. by pressure oxidation) to make the silver accessible to cyanide. The Eskay Creek sulphide ore, which was finer (as discussed in section 3.6.3.2) and silver extraction was higher than the extraction from Cannington material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Au Extraction</th>
<th>Ag Extraction</th>
<th>Initial concentration of NaCN, g/l</th>
<th>NaCN Consumption kg/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cannington sulphide</td>
<td>N/A¹</td>
<td>36.60</td>
<td>7.5</td>
<td>24.17</td>
</tr>
<tr>
<td>Eskay Creek sulphide</td>
<td>60.19</td>
<td>51.85</td>
<td>3</td>
<td>3.36</td>
</tr>
</tbody>
</table>

¹ Not available. The feed contains very low level of gold (section 3.6.3.1).

4.6.2 Pressure Oxidation at different Temperatures and Silver Extraction

Pressure oxidation of the Cannington concentrate was carried out at different temperatures in the range of 110-150°C and the resulting residues were subjected to cyanidation for silver extraction. Initial solution used for the tests contained ferric, ferrous and zinc with concentration of 5 g/l, 5g/l and 20g/l respectively as sulphate. Other conditions were: oxygen partial pressure 100 psi; autoclave residence time 60 minute; pulp density 8%; initial acidity 50 g/l; agitation 900 rpm; initial solution 1000 ml; stoichiometric iodide addition 200% of silver. The same pressure oxidation conditions were used for Eskay Creek ore, except that lower stoichiometric iodide addition was used (100% of silver). Lignosol and quebracho (2.53 kg/t each) were used at 120 to 150°C and these were added at the beginning of each test. The results of the effect of temperature on the zinc extraction and sulphide oxidation of Cannington complex sulphide are presented in Figure 4-34.
After the pressure oxidation, sulphur remains the predominant species at lower temperatures (110 to 130°C) as shown in Table 4-9 and this can be floated for sales or discarded. The total sulphide oxidation increases with increasing temperature of pressure oxidation. The increase in the extent of sulphide oxidation to sulphate with increasing temperature is a characteristic of pressure oxidation in which jarosite specie is the main iron precipitate.

Figure 4-34. Effect of temperature on zinc extraction and total sulphide oxidation for the oxygen pressure oxidation of Cannington complex sulphide concentrate. Oxidation conditions: 95 g/l pulp density, 1 hour retention time and 100 psi oxygen pressure. Initial solution contained 5 g/l Fe$_3^+$, 5 g/l Fe$_2^+$, 20 g/l Zn$^{2+}$, 50 g/l H$_2$SO$_4$ and stoichiometric iodide addition at 200% silver.

The silver recoveries by cyanidation of the oxidised Cannington residues are presented in Figure 4-35. High silver recoveries were obtained by cyanidation of the residues, when the prior pressure oxidation was carried out at lower temperature range of 110°C to 130°C. The silver recoveries from the residues were less than 90%, when the pressure oxidation tests were carried out at 140° and 150°C.
Table 4-10. Effect of temperature on the pressure oxidation of Cannington complex sulphide concentrates.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Zinc Extraction %</th>
<th>S\text{oxid.} To Sulphur %</th>
<th>S\text{oxid.} To Sulphate %</th>
<th>Sulphur Yield %</th>
<th>Net Iron dissolution / Precipitation (-)(^1)</th>
<th>Final Acidity g/l H\text{2}SO\text{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>89.93</td>
<td>57.19</td>
<td>12.99</td>
<td>81.49</td>
<td>+5.20</td>
<td>15.69</td>
</tr>
<tr>
<td>120</td>
<td>90.19</td>
<td>53.05</td>
<td>16.96</td>
<td>75.77</td>
<td>-0.03</td>
<td>21.35</td>
</tr>
<tr>
<td>130</td>
<td>90.64</td>
<td>52.63</td>
<td>18.71</td>
<td>73.77</td>
<td>-1.65</td>
<td>21.62</td>
</tr>
<tr>
<td>140</td>
<td>91.58</td>
<td>47.67</td>
<td>25.83</td>
<td>64.86</td>
<td>-4.37</td>
<td>22.70</td>
</tr>
<tr>
<td>150</td>
<td>93.42</td>
<td>49.09</td>
<td>29.46</td>
<td>62.50</td>
<td>-7.04</td>
<td>23.08</td>
</tr>
</tbody>
</table>

\(^1\)Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of initial total iron (solid +solution); where this is -ve this indicates net iron precipitation and where this is +ve it indicates net iron dissolution.

Figure 4-35. Effect of pressure oxidation temperature on the subsequent silver extraction by cyanidation of Cannington complex sulphide concentrate. Prior pressure oxidation condition as for Figure 4-34. Cyanidation test conditions: 200 g/l pulp density in 200 ml deionized water with initial 3 g/l NaCN and at room temperature.

Silver deportment is affected by the composition (mainly iron and lead) of the feed materials which are released during the sulphide oxidation and which take part in the silver jarosite reaction. At 110°C, iron dissolution was greater than the iron precipitation and at 140° and
150°C, the iron precipitation was more than the iron dissolution (Table 4-10). The precipitation kinetics of the jarosite specie is promoted by the high iron dissolution from the Cannington complex sulphide, low acid level and the high temperatures (section 4.2; Dutrizac et al., 1980). This leads to the competition for silver ion by the jarosite precipitation reaction.

The stability of jarosite specie increases with increasing temperature, while the stability of silver iodide decreases with increasing temperature (sections 4.5.1 and 4.5.2; Tien and Harrington, 1963). The silver ions, which are released by the silver iodide (at high temperatures), will re-precipitate as jarosite species. The net reaction for the migration of silver ion from silver iodide to the jarosite phase can be represented as follows:

\[
AgI + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow AgFe_3(SO_4)_2(OH)_6 + 6H^+ + I^-
\] (4-26)

The jarosite is presented as an end member silver jarosite in reaction (4-26) for the purpose of explanation, however, in the presence of lead sulphate, silver-hydronium-lead jarosite species are formed (section 4.2; Parker, 1981; Dutrizac and Chen, 1984). If the silver ions are incorporated into the core of the jarosite crystals, the silver will not be extracted during cyanidation because only the silver ions in the outer crystal planes of the jarosite can react with free cyanide ions (section 4.3; Van Weert and Tuinman, 1993).

The silver recoveries from the cyanidation of the oxidised Eskay Creek residues are presented in Figure 4-36. High silver recoveries (~ 95%) were obtained irrespective of the temperature used for the pressure oxidation of Eskay Creek complex sulphide. Also, the gold (47 ppm) which was present in the Eskay Creek complex was recovered (up 95%) alongside with silver by cyanidation of the pressure oxidised residue. The gold extraction will contribute to the economy of the process.

Although the stoichiometric iodide addition was 100% of silver, which was lower than the iodide concentration used during the pressure oxidation of Cannington complex sulphide, silver extraction from the residues of Eskay Creek sulphide were almost complete in all the cases unlike the Cannington complex sulphide. The iron and lead compositions of the Eskay Creek complex sulphide were less than that of the Cannington complex sulphide and the extent of iron precipitation during the pressure oxidation of Eskay Creek complex sulphide was less accordingly. In Table 4-11, the final acid was above 45 g/l H₂SO₄ after the oxidation of Eskay Creek sulphide and the high free acid suppressed jarosite precipitation during the oxidation.
Figure 4-36. Effect of pressure oxidation temperature on the subsequent silver extraction by cyanidation of Eskay Creek complex sulphide ore. Prior pressure oxidation condition as for Figure 4-34 except stoichiometric iodide addition 100% of silver. Cyanidation: 200 g/l pulp density in 200 ml deionized water with 3 g/l NaCN and at room temperature.

Table 4-11. Effect of temperature on the pressure oxidation of Eskay Creek complex sulphide.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Total Sulphide Oxidation, %</th>
<th>S_{Oxid.} To Sulphur, %</th>
<th>S_{Oxid.} To Sulphate, %</th>
<th>Sulphur Yield %</th>
<th>Net Iron dissolution / Precipitation (-)^1, %</th>
<th>Final Acidity g/l H_2SO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>55.94</td>
<td>44.75</td>
<td>11.19</td>
<td>79.99</td>
<td>+8.10</td>
<td>48.57</td>
</tr>
<tr>
<td>120</td>
<td>62.48</td>
<td>43.74</td>
<td>18.74</td>
<td>70.01</td>
<td>+8.21</td>
<td>48.03</td>
</tr>
<tr>
<td>150</td>
<td>94.15</td>
<td>56.49</td>
<td>37.66</td>
<td>60.10</td>
<td>+8.54</td>
<td>46.47</td>
</tr>
</tbody>
</table>

^1Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of initial total iron (solid +solution); where this is -ve this indicates net iron precipitation and where this is +ve it indicates net iron dissolution.

The silver extraction-time profile during the cyanidation of Cannington oxidized residues are presented in Figure 4-37. Silver extraction from the oxidized residue into cyanide solution was very fast and was completed within 2 hours because of the solubility of silver iodide in cyanide and the strong complexation of silver by cyanide. Other reasons which have been presented for
the fast dissolution of silver iodide by cyanide are its fine nature and high surface area (Van Weert, 1999). Jarosite specie is speculated to form iron hydroxide coating, only silver ions in the outer crystal planes of the jarosite structure are exposed to and can react with free cyanide ions in the pulp and resulting into low dissolution of silver (Van Weert and Tuinman, 1993). The fast dissolution of silver iodide may offer added advantages such as reduction of residence time and cyanide consumption by side reactions (such as competing cyanicides). These process factors are beyond the scope of this investigation.

![Figure 4-37. Silver extraction-time profile of the Cannington oxidized residues during cyanidation.](image)

From the above investigations, low temperature (110°C) pressure oxidation followed by cyanidation gives high silver extraction in addition to energy/cost saving. At low temperatures, i.e. temperatures below the melting point of sulphur (119°C), pressure oxidation of sulphide results in a high yield of elemental sulphur, a potentially saleable by-product, instead of sulphate, which is probably not saleable. High temperature oxidation requires high reagent consumption such as oxygen for sulphide oxidation and alkali for neutralisation of the residues. Also,
increasing the operating temperature moderately (120-150°C) in an attempt to accelerate the kinetics may be counter-productive because oxidation becomes stifled by molten sulphur, which wets and agglomerates the sulphide particles. Therefore, further investigation at low temperature was conducted to improve sulphide oxidation and zinc extraction without compromising high silver extraction.

4.6.3 Low Temperature Pressure Oxidation and Silver Extraction

The pressure oxidation tests of Cannington complex sulphide were carried out at 110°C without surfactant followed by cyanidation.

4.6.3.1 Effect of Initial Acidity

Pressure oxidation tests of Cannington complex sulphide were carried out at 110°C and at different acid concentrations followed by cyanidation of the residues. The initial solution used for the tests contained ferric, ferrous and zinc with concentration of 5 g/l, 5g/l and 20g/l respectively as sulphate. Other fixed conditions were: oxygen partial pressure 100 psi; autoclave residence time 60 minute; pulp density 8%; agitation 900 rpm; initial solution 1000 ml; stoichiometric iodide addition 200% of silver. Effect of initial acidity on the subsequent silver extraction is presented in Figure 4-38.

When the pressure oxidation was conducted at high initial acidity (75 g/l H₂SO₄), the deportment of silver into the iodide phase was almost complete because jarosite precipitation was minimised and subsequent leaching of the residue yielded almost 100% silver extraction. The use of 25 g/l H₂SO₄ as initial acid level for the pressure oxidation reduced significantly, the silver extraction by cyanidation of the residue because the kinetics of jarosite precipitation became fast enough to compete with the iodide reaction:

\[
\text{Ag}^+ + I^- \rightarrow \text{AgI} 
\]

\[
\text{Ag}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ 
\]

The jarosite precipitation reaction (4-28) is promoted by low acidity which is created as a result of the following acid consuming sulphide reaction:

\[
\text{MS} + \text{H}_2\text{SO}_4 + 1/2\text{O}_2 \rightarrow \text{MSO}_4 + \text{H}_2\text{O} + S^0
\]

Where M can be Zn, Fe (in pyrrhotite), Pb, etc
Figure 4-38. Effect of the pressure oxidation acidity on the subsequent silver recoveries of Cannington concentrates by cyanidation. Oxidation conditions: 95 g/l pulp density, 1 hour retention time and 100 psi oxygen pressure. Initial solution contained 5 g/l Fe$^{3+}$, 5 g/l Fe$^{2+}$, 20 g/l Zn$^{2+}$, 50 g/l H$_2$SO$_4$ and stoichiometric iodide addition at 200% silver. Cyanidation test conditions: 200 g/l pulp density in 200 ml deionized water with initial 3 g/l NaCN.

Other results obtained from the tests on the effect of initial acidity summarized in Table 4-12.

Table 4-12. Effect of initial acidity on the pressure oxidation of Cannington complex sulphide concentrates at 110°C.

<table>
<thead>
<tr>
<th>Initial acidity g/l</th>
<th>Final acidity g/l</th>
<th>Zinc Extraction %</th>
<th>$S_{\text{oxid.}}$ to Sulphur %</th>
<th>$S_{\text{oxid.}}$ to Sulphate %</th>
<th>Sulphur Yield %</th>
<th>Net Iron dissolution / Precipitation (-) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.12</td>
<td>81.43</td>
<td>56.28</td>
<td>13.83</td>
<td>80.27</td>
<td>-10.28</td>
</tr>
<tr>
<td>50</td>
<td>12.69</td>
<td>89.93</td>
<td>57.19</td>
<td>12.99</td>
<td>81.49</td>
<td>+5.20</td>
</tr>
<tr>
<td>75</td>
<td>23.19</td>
<td>95.50</td>
<td>62.41</td>
<td>12.67</td>
<td>83.12</td>
<td>+49.14</td>
</tr>
</tbody>
</table>

1Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of initial total iron (solid +solution); where this is −ve this indicates net iron precipitation and where this is +ve it indicates net iron dissolution.
The zinc extraction in the autoclave increases with increasing initial acidity. Sulphide oxidation to sulphur and the total sulphide oxidation increase slightly with acidity because of the following reactions, which are favoured under mildly oxidizing conditions and in the presence of large amounts of sulphuric acid and ferric sulphate (McKay and Halpern, 1958; Bailey L.K. and Peters, 1976):

\[ FeS_2 + 2O_2 \rightarrow FeSO_4 + S^0 \]  
\[ FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^0 \]  

(4-30)  
(4-31)

High initial acidity left substantial iron and final acid in solution as shown in Table 4-12, since the total sulphide oxidation did not increase significantly, the high iron dissolution could be attributed to the dissolution of the iron-manganese silicate minerals which are present in Cannington complex sulphide (section 2.3). Where the pregnant solution of zinc is sent to the electrowinning circuit, the iron must be removed. This may not be a problem in the commercial operations where zinc pressure oxidation has been integrated with existing roast-leach process, but would be important in a stand-alone pressure oxidation plant. Also, the high final acid level will necessitate substantial neutralisation of the residue prior to cyanidation. The final acid level is a net result of reaction (4-29) and the following reaction:

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

(4-32)

4.6.3.2 Effect of Iodide Concentration

Pressure oxidation tests for Cannington complex sulphide were carried out at 110°C and at different iodide concentrations followed by cyanidation of the residue. Other autoclave conditions were the same as those used in study of acidity effect except the initial acidity which was fixed at 50 g/l H₂SO₄. Also, the subsequent cyanidation conditions were the same as that of acidity effect.

Silver extraction from the residue increases with increasing level of iodide employed during pressure oxidation, up to 100% stoichiometric of iodide to silver. Subsequent increase in iodide concentration results into a slight increase in the silver extraction. In Figure 4-39, 91% silver extraction was obtained at 100% stoichiometric of iodide to silver and this increased slightly to about 94%, when the iodide was increased to 200% of silver. This suggests that the near stoichiometric concentration of iodide is adequate to recover silver and such low concentration
prevents (corrosive) iodine displacement to the autoclave freeboard and losses in the vent gases. In addition to the energy/cost saving associated with low temperature operations, the use of a stoichiometric quantity of iodide is also a distinct benefit.

Figure 4-39. Effect of the iodide concentration on the subsequent silver recoveries of Cannington complex sulphide concentrates by cyanidation. Pressure oxidation conditions: 110°C and 50 g/l initial acidity, others as in Figure 4-38 except iodide. Cyanidation condition: same as in Figure 4-38.

4.6.3.3 Effect of other Pressure Oxidation Conditions on Silver Extraction

Effects of other test conditions on the pressure oxidation of Cannington complex sulphide concentrate at 110°C and the subsequent silver extraction are summarized in Table 4-13. Standard conditions were: ferric, ferrous and zinc 5 g/l, 5g/l and 20g/l respectively as sulphate; oxygen partial pressure 100 psi; residence time 60 minutes; pulp density 8%; initial acidity 50 g/l; agitation 900 rpm; initial solution 1000 ml and stoichiometric iodide addition 200% of silver (except in test BT1).
At 110°C, sulphide oxidation is incomplete in all the tests (Table 4-13), high acidity and total iron (ferric and ferrous) are required to increase the sulphide oxidation and zinc extraction slightly. High initial acidity and low iron leave substantial iron in solution after the pressure oxidation. Elemental sulphur is the main product of the sulphide oxidation at low temperature. Chloride, which may exist in the feeds or process water, does not affect the subsequent silver extraction (Test ET1), over and beyond the effect of iodide. The presence of iodide did not affect zinc extraction or sulphide oxidation, when comparing AT1 and BT1.

Table 4-13. Effect of other test conditions on the pressure oxidation of Cannington complex sulphide concentrates at 110°C and the subsequent silver extraction by cyanidation.

<table>
<thead>
<tr>
<th>Test ID.</th>
<th>Conditions</th>
<th>Zinc Extraction %</th>
<th>S\textsubscript{oxid.} To Sulphur %</th>
<th>S\textsubscript{oxid.} To Sulphate %</th>
<th>Net Iron Dissolution %</th>
<th>Silver Extraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT1</td>
<td>Standard conditions</td>
<td>89.93</td>
<td>57.19</td>
<td>12.99</td>
<td>5.20</td>
<td>95.57</td>
</tr>
<tr>
<td>BT1</td>
<td>Absence of iodide</td>
<td>90.07</td>
<td>57.30</td>
<td>14.10</td>
<td>6.58</td>
<td>11.01</td>
</tr>
<tr>
<td>CT1</td>
<td>Acidity at 75 g/l</td>
<td>95.50</td>
<td>57.41</td>
<td>17.67</td>
<td>49.13</td>
<td>98.50</td>
</tr>
<tr>
<td>DT1</td>
<td>Ferric at 7.5 g/l</td>
<td>90.41</td>
<td>56.78</td>
<td>13.28</td>
<td>6.83</td>
<td>90.75</td>
</tr>
<tr>
<td>ET1</td>
<td>Addition of 2 g/l CaCl\textsubscript{2}</td>
<td>90.47</td>
<td>46.83</td>
<td>13.47</td>
<td>9.97</td>
<td>90.75</td>
</tr>
<tr>
<td>FT1</td>
<td>150 psi oxygen pressure</td>
<td>89.82</td>
<td>56.22</td>
<td>14.46</td>
<td>2.89</td>
<td>90.12</td>
</tr>
<tr>
<td>GT1</td>
<td>H\textsubscript{2}SO\textsubscript{4} at 75 g/l, 2.5 g/l Fe\textsuperscript{3+} and 2.5 g/l Fe\textsuperscript{2+}</td>
<td>94.32</td>
<td>54.38</td>
<td>10.81</td>
<td>64.43</td>
<td>98.61</td>
</tr>
<tr>
<td>HT1</td>
<td>Surfactant: 0.1 g each of lignosol and quebracho</td>
<td>90.21</td>
<td>57.21</td>
<td>12.01</td>
<td>5.70</td>
<td>93.78</td>
</tr>
</tbody>
</table>

¹Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of total iron (solid + solution).

It is worth noting that all the oxidation conducted at 110°C in this work were carried out in the absence of surfactant, search for molten sulphide particles were conducted physically after drying and none was observed. It has been submitted that two forms of liquid sulphur, S\textsubscript{x} and S\textsubscript{μ} exist in equilibrium, the presence of iodine (Smith and Carson, 1907) or iodide (Smith and Carson, 1908) favours the latter and S\textsubscript{μ} lowers the freezing point of sulphur. Although, sulphur and iodide do not form compounds or solid solution, eutectic mixture has been reported with a freezing point of 65.6°C (Smith and Carson, 1908). Additional test was carried out with surfactant (HT1), the sulphide oxidation was not different from that of the oxidation carried out in the absence of
surfactant and both were the same with the results obtained, when oxidation was carried out without iodide addition.

High silver recoveries (more than 90%) were obtained when the residues produced by pressure oxidation (in the presence of iodide) were subjected to cyanidation (Table 4-13). One could think that the high recoveries of silver were due to the fact that the silver minerals remained unreacted during the autoclaving at low temperature. However, the cyanidation of the residue produced by pressure oxidation in the absence of iodide (BT1) yielded silver which was lower than that of baseline cyanidation of the Cannington complex sulphide (Table 4-9). This comparison indicates that silver is rendered insoluble in a cyanide solution by prior pressure oxidation at low temperature and the need to prevent this can be achieved by stoichiometric addition of iodide. This correlates with other work done on refractory argento-pyrite at 180°C by Van Weert and Van Lier (1994).

Increase in initial acidity did not increase substantially the extent of sulphide oxidation at low temperature (110°C), however the 68-75% sulphide oxidation of Cannington concentrates was sufficient to liberate the precious metals (Au and Ag) that were previously locked up in the refractory feeds. The extent of sulphide oxidation required varies from one sulphide to another depending on the mineralogy and the size of the materials. The silver bearing minerals may well oxidise prior to galena or sphalerite, but such investigation was outside the scope of this study.

4.6.3.4 Summary of the Low Temperature Pressure Oxidation and Silver Extraction

The stoichiometric iodide addition to the low temperature pressure oxidation of complex sulphide prevented silver deportment into the jarosite phase. The deportment of silver into the silver iodide phase is completed because of the fast kinetics of silver iodide and its stability at low temperature (sections 4.5.1 and 4.5.2). The cyanidation of the resulting residue gives high silver extraction (above 90%). Low initial acidity and acid consumption by sulphides create a very low level of acid in the autoclave, which promotes the stability and the kinetics of jarosite formation. Under such conditions, some silver ions are incorporated into the jarosite specie, which results into low silver extraction (75%) by cyanidation of the residue.
4.6.4 High Temperature Pressure Oxidation and Silver Extraction

At high temperature (150°C), the kinetics of oxidation becomes fast, iron precipitation is improved and pressure oxidation yields less elemental sulphur, which consumes cyanide during cyanidation. However, silver extraction poses additional challenges (section 4.6.2) because of the enhanced kinetics and stability of jarosite species. Therefore, further pressure oxidation was carried out at 150°C, with the objective of improving the subsequent silver extraction.

4.6.4.1 Effect of Initial Acidity

Pressure oxidation tests of Cannington complex sulphide concentrate were carried out at 150°C and at different levels of initial acid. These were followed by cyanidation and the results are presented in Figure 4-40;

![Graph showing effect of initial acidity on silver extraction from Cannington complex sulphide concentrate. Test conditions: 150°C, 95g/l pulp density and 100 psi oxygen pressure. Initial solution: 5 g/l Fe³⁺, 5 g/l Fe²⁺, 20 g/l Zn²⁺ and stoichiometric iodide addition was 200% of silver. Cyanidation: 200 g/l pulp density in 200 ml deionized water with 3.0 g/l initial NaCN and at room temperature.]

Figure 4-40. Effect of initial acidity on silver extraction from Cannington complex sulphide concentrate. Test conditions: 150°C, 95g/l pulp density and 100 psi oxygen pressure. Initial solution: 5 g/l Fe³⁺, 5 g/l Fe²⁺, 20 g/l Zn²⁺ and stoichiometric iodide addition was 200% of silver. Cyanidation: 200 g/l pulp density in 200 ml deionized water with 3.0 g/l initial NaCN and at room temperature.
Solution used for the tests contained ferric, ferrous and zinc with concentration of 5 g/l, 5g/l and 20g/l respectively as sulfate. Other conditions were: oxygen partial pressure 100 psi; autoclave residence time 60 minute; pulp density 8%; agitation 900 rpm; initial solution 1000 ml; stoichiometric iodide addition 200% of silver. 4.21 kg/t each of lignosol and quebracho surfactants were added at the beginning of each experiment.

Silver extraction increases with increasing initial acidity of the pressure oxidation. The increase in silver extraction is attributed to high acidity, which reduces the kinetics of precipitation of jarosite specie (reaction 4-28) and minimises its competition for silver ions (section 4.5.2). The silver extraction from the residue increased from 70% to 95%, when the initial acidity of the oxidation slurry was increased from 50 g/l to 100 g/l.

The results of the pressure oxidation are summarized in Table 4-14. The high initial acid leaves substantial iron in solution after the oxidation, however the final free acid concentration shows substantial consumption of acid by sulphide oxidation during pressure oxidation. The final acid level is a net result of reactions (4-26) and (4-29), and this is higher than that of the low temperature experiment (section 4.6.3) because of the substantial iron precipitation at higher temperature. High acidity can be used at high temperature (150°C) to improve silver extraction without compromising the iron precipitation.

Table 4-14. Effect of initial acidity on the pressure oxidation of Cannington mixed sulphide concentrates at 150°C.

<table>
<thead>
<tr>
<th>Initial Acidity g/l</th>
<th>Final Acidity g/l</th>
<th>Zinc Extraction %</th>
<th>S_{\text{oxid. to Sulphur}} %</th>
<th>S_{\text{oxid. to Sulphate}} %</th>
<th>Sulphur Yield %</th>
<th>Net Iron dissolution / Precipitation (-) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>14.65</td>
<td>93.37</td>
<td>45.03</td>
<td>19.75</td>
<td>69.51</td>
<td>-5.65</td>
</tr>
<tr>
<td>60</td>
<td>19.55</td>
<td>93.93</td>
<td>47.12</td>
<td>19.76</td>
<td>70.45</td>
<td>-0.55</td>
</tr>
<tr>
<td>75</td>
<td>29.30</td>
<td>95.50</td>
<td>49.44</td>
<td>19.42</td>
<td>71.80</td>
<td>8.00</td>
</tr>
<tr>
<td>100</td>
<td>36.75</td>
<td>96.86</td>
<td>57.74</td>
<td>22.69</td>
<td>71.78</td>
<td>20.31</td>
</tr>
</tbody>
</table>

1Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of initial total iron (solid +solution); where this is -ve this indicates net iron precipitation and where this is +ve it indicates net iron dissolution.

The pressure oxidation tests were carried out in the absence of iodide, while other conditions remained the same. The filtrate and the wash solution obtained after pressure oxidation tests were analysed for silver, which showed almost zero concentration in all the tests. The results of the
cyanidation are presented in Figure 4-41. In the absence of iodide, high initial acid alone is not sufficient to prevent silver encapsulation because of the enhanced stability of lead-hydronium jarosite, especially at high ferric concentration, temperature and sulphate. Free acid concentration above 45 g/l is required to suppress lead-hydronium jarosite precipitation at 140°C from solution containing 4.60 g/l Fe$^{3+}$ and 5.30 g/l PbSO$_4$ suspension (section 4.2). Once the jarosite species are formed, the silver is co-precipitated and remains insoluble during the cyanidation. It is obvious from Figure 4-41 that the high acidity proffered by Tourre (1984) will not help silver extraction in the temperature range of 110-150°C.

![Figure 4-41](image)

Figure 4-41. Effect of initial acidity (in the absence of iodide) on silver extraction from Cannington mixed sulphide concentrate. Test conditions: same as Figure 4-40 except the absence of iodide. Cyanidation: same as Figure 4-40.

4.6.4.2 Effect of Iodide Concentration

Pressure oxidation tests of Cannington complex sulphide were carried out at 150°C and at different iodide concentrations followed by cyanidation of the residue. Other autoclave conditions were the same as that of acidity effect except the initial acidity, which was 75 g/l, and
the cyanidation conditions were the same as that of acidity effect. The results of the cyanidation are presented in Figure 4-42.

![Graph showing effect of iodide concentration on silver extraction](image)

Figure 4-42. Effect of the iodide concentration on the subsequent silver extraction from Cannington concentrate by cyanidation. Pressure Oxidation condition: 150°C, 95g/l pulp density and 100 psi oxygen pressure. Initial solution: 5 g/l Fe³⁺, 5 g/L Fe²⁺, 20 g/L Zn²⁺, 75 g/l H₂SO₄ and stoichiometric iodide addition varied from 0 to 400% of silver. Cyanidation: same as in Figure 4-40.

Silver extraction from the residue increases linearly with increasing level of iodide employed during pressure oxidation, up to 100% stoichiometric of iodide to silver. At 100% stoichiometric of iodide to silver, the silver extraction from the resulting residue was not complete, which suggested that some silver ions were deported into the jarosite phase. The deportment of some silver as jarosite specie may be attributed partly to the solubility of silver iodide, which increases at high temperature (Gavrich and Galinker, 1955) and partly to the stability and kinetics of jarosite, which increase at high temperature.

\[
AgI \rightarrow Ag^+ + I^-
\]  

(4-33)
The silver ions which are released by reaction (4-33), are incorporated into the jarosite phase by reaction (4-28).

If the silver jarosite is formed along with the silver iodide, some of the silver jarosite may recrystallize to form hydronium jarosite, thus freeing the silver to form silver iodide.

\[ \text{AgFe}_3(SO_4)_2(OH)_6 + H_3O^+ \rightarrow (H_3O)_3Fe_3(SO_4)_2(OH)_6 + Ag^+ \] (4-34)

The positive effect of the iodide on the silver extraction suggests the iodide species may adsorb on silver jarosite to promote the dissolution of the jarosite (section 4.5.3). The silver jarosite decomposition did not go to completion within the reaction time used, or at the stoichiometric level of iodide to silver chosen for these experiments.

An increase in iodide concentration from 100% to 200% resulted in an increase in the silver extraction from 73.39% to 84.86%. Subsequent increase in iodide causes slight increase in the silver extraction to 91.92% at 400% of iodide to silver. This correlates with other work done on silver sulphide at 160°C (Van Weert and Tuinman, 1993). It is unlikely that iodide concentration higher than 100% stoichiometric of silver will be employed in practice because excess iodide will form volatile iodine in the autoclave gas phase.

4.6.4.3 Effect of Sulphur

Oxidised residue produced at low temperature (110°C) contained substantially more sulphur than the residue (section 4.6.2) produced at high temperature (150°C). Effect of elemental sulphur on silver extraction was investigated at 150°C by adding elemental sulphur to the initial solution. The initial solution used for the tests contained ferric, ferrous and zinc with concentration of 5 g/l, 5g/l and 20g/l respectively as sulphate. Other conditions were: oxygen partial pressure 100 psi; residence time 60 minute; pulp density 8%; agitation 900 rpm; initial volume of solution 1000 ml; acidity 50 g/l H₂SO₄; stoichiometric iodide addition 200% of silver. 2.53 kg/t of lignosol and 2.53 kg/t of quebracho surfactants were added to the initial solution at the beginning of the pressure oxidation tests. The results are presented in Table 4-15.

The 1.00 g of sulphur corresponded to the 10% of the sulphide in the feed and at this level of addition, it was expected that the sulphur in the resulting residue would be more than the sulphur in the oxidised residue produced at 110°C (section 4.6.2). 6.07g of sulphur was obtained in the
resulting residue, when 1.00 g of sulphur was added to the initial slurry used for oxidation at 150°C, while 5.15 g of sulphur was obtained at 110°C without prior addition of sulphur to the slurry. One would have thought that elemental sulphur helped the silver extraction from the oxidised residue by forming the cyanide soluble silver sulphide as follows:

$$2Ag^+ + 2Fe^{2+} + S^0 \rightarrow Ag_2S + 2Fe^{3+}$$  \hspace{1cm} (4-35)

As shown in Table 4-15, there was no effect on the subsequent silver extraction, when sulphur was added to the initial slurry of the autoclave. In the presence of oxygen, high ferric/ferrous ratio is established which minimises the aqueous silver reduction to metallic silver and the subsequent precipitation of the silver sulphide (section 4.4). Also, if some silver sulphide is formed as a result of silver reaction with sulphur, it will be oxidised back to aqueous silver especially at high temperature (section 4.1).

Table 4-15. Effect of elemental sulphur addition on the pressure oxidation of Cannington complex sulphide concentrates at 150°C and subsequent silver extraction by cyanidation.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Sulphur Added g</th>
<th>Zinc Extraction %</th>
<th>$S_{\text{oxid. to Sulphur}}$ %</th>
<th>$S_{\text{oxid. to Sulphate}}$ %</th>
<th>Total Oxidation %</th>
<th>Silver Extraction by Cyanidation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT2R-1</td>
<td>0.00</td>
<td>93.37</td>
<td>49.09</td>
<td>29.46</td>
<td>78.55</td>
<td>70.01</td>
</tr>
<tr>
<td>FAT2-1</td>
<td>0.50</td>
<td>94.11</td>
<td>49.31^1</td>
<td>35.92</td>
<td>85.23</td>
<td>70.10</td>
</tr>
<tr>
<td>FAT2-2</td>
<td>1.00</td>
<td>95.52</td>
<td>50.25^1</td>
<td>40.21</td>
<td>90.46</td>
<td>69.10</td>
</tr>
</tbody>
</table>

^1The amount of sulphur added at the beginning of the experiment was deducted from the resulting sulphur before calculation was made.

Although addition of elemental sulphur did not help silver deportment into a recoverable form, its presence improved the total sulphide oxidation as shown in Table 4-15. Alternatively, pyrite may be effective and can be investigated in future work. This may be relevant in the autoclaving of sulphur deficient concentrates, in which low concentration of sulphur (in the feed) could results in heat “sink” since sulphur oxidation is required to sustain the heat needed.

4.6.4.4 Effect of other conditions

Effects of other test conditions on the pressure oxidation of Cannington complex sulphide concentrate at 150°C and the subsequent silver extraction are summarized in Table 4-16. The standard conditions were: ferric, ferrous and zinc 5 g/l, 5g/l and 20g/l respectively as sulphate;
oxygen partial pressure 100 psi; residence time 60 minute; pulp density 8%; initial acidity 50 g/l; agitation 900 rpm; initial solution 1000 ml and stoichiometric iodide addition 200% of silver. 2.53 kg/t of lignosol and 2.53 kg/t of quebracho surfactants were added at the beginning of the pressure oxidation. The different conditions which are shown in Table 4-16 were investigated and unless as stated, other conditions of each test remained the same as that of standard condition. When the initial acidity was higher than 50 g/l, 4.21 kg/t of lignosol and 4.21 kg/t of quebracho surfactants were added.

Table 4-16. Effect of other test conditions on the pressure oxidation of Cannington mixed sulphide concentrates at 150°C and subsequent silver extraction by cyanidation.

<table>
<thead>
<tr>
<th>Test ID.</th>
<th>Initial Conditions</th>
<th>Zinc Extraction %</th>
<th>$S_{\text{oxid. to Sulphur}}$ %</th>
<th>$S_{\text{oxid. to Sulphate}}$ %</th>
<th>Net Fe dissolution / Precipitation (%)</th>
<th>Silver Extraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT2R-1</td>
<td>Standard conditions</td>
<td>93.37</td>
<td>49.09</td>
<td>29.46</td>
<td>-7.04</td>
<td>70.01</td>
</tr>
<tr>
<td>CT2</td>
<td>Acidity at 75 g/l</td>
<td>95.72</td>
<td>49.44</td>
<td>19.42</td>
<td>7.60</td>
<td>84.86</td>
</tr>
<tr>
<td>CT2R</td>
<td>Acidity at 75 g/l</td>
<td>95.77</td>
<td>46.06</td>
<td>20.68</td>
<td>11.47</td>
<td>92.33</td>
</tr>
<tr>
<td>DT2</td>
<td>Ferric at 7.5 g/l</td>
<td>93.61</td>
<td>48.32</td>
<td>28.73</td>
<td>-5.44</td>
<td>66.30</td>
</tr>
<tr>
<td>ET2</td>
<td>Addition of 2 g/l</td>
<td>92.74</td>
<td>55.61</td>
<td>6.16</td>
<td>-7.77</td>
<td>70.11</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GT2</td>
<td>Acidity at 75 g/l, 2.5 g/l Fe$^{3+}$ and 2.5 g/l Fe$^{2+}$</td>
<td>95.28</td>
<td>46.61</td>
<td>23.69</td>
<td>10.42</td>
<td>88.20</td>
</tr>
<tr>
<td>GT2R</td>
<td>Acidity at 75 g/l, 1.61 g/l Fe$^{3+}$ and 2.5 g/l Fe$^{2+}$</td>
<td>94.97</td>
<td>44.53</td>
<td>21.92</td>
<td>14.04</td>
<td>93.39</td>
</tr>
<tr>
<td>VT2-1</td>
<td>Acidity at 75 g/l 15% pulp density</td>
<td>84.72</td>
<td>51.06</td>
<td>10.11</td>
<td>-5.34</td>
<td>70.28</td>
</tr>
<tr>
<td>VT2-2</td>
<td>Acidity at 75 g/l 11% pulp density</td>
<td>92.18</td>
<td>51.44</td>
<td>12.46</td>
<td>-4.82</td>
<td>75.57</td>
</tr>
</tbody>
</table>

*Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of total iron (solid + solution); where this is –ve this indicates net iron precipitation and where this is +ve, it indicates net iron dissolution.*

At 150°C, elemental sulfur remains the main product of the sulfide oxidation although the sulphur yield is generally lower than that at lower temperature oxidation (110°C).
High initial acidity and low initial iron leaves substantial iron in solution after pressure oxidation (Test CT2, CT2R, GT2 and GT2R), however, this improves silver extraction from the residues (Table 4-16). The process tolerates high initial ferric during pressure oxidation with slight reduction in subsequent silver extraction (Test DT2). Chloride, which may exist in the feeds or process stream water, has negligible impact on sulphide oxidation and the subsequent silver extraction (Test ET2).

The sulphide oxidation to sulphate was minimal in the presence of chloride; it may be necessary for a future study to explore this effect further. The molar ratio of chloride to silver was 97 to 1 and therefore, it was unlikely that silver chloride which has less stability than its iodide counterpart would be predominant in the presence of iodide. Analysis of the final solution did not reveal any silver in solution, which indicated that silver was still deported into the solid phase in the presence of chloride.

The net iron precipitation increases with increasing pulp density (CT2, VT2-1 and VT2-2) as shown in Table 4-16. This is attributed to the increase in acid consumption during the autoclaving of the sulphide and the resulting low acid levels, which promotes iron hydrolysis and precipitation of jarosite specie. The increase in the stability of jarosite specie and its kinetics of precipitation enhances competition for silver with iodide.

4.6.4.5 Summary of High Temperature Pressure Oxidation and Silver Extraction

Silver extraction from the residue decreases when the pressure oxidation is conducted at high temperature because of the enhanced stability and the kinetics of the jarosite specie. The enhanced kinetics of lead-hydronium jarosite precipitation poses challenge by competing for silver, however, this can be minimised by using moderately high initial acid and low initial ferric during the pressure oxidation. At high temperature, the stability of silver iodide decreases which also, contributes to the decrease in the silver extraction from the oxidised residue.

The presence of the low concentration of chloride during the pressure oxidation does not affect the silver extraction by iodide addition. The use of chloride as a silver-sequestering agent will not be as effective as iodide because the solubility of silver chloride limits its application in the way iodide is applied in this work, despite the low reagent cost and the recent focus on the effects of chloride on refractory gold extraction.
4.6.5 Zinc Extraction from Complex Sulphide by Pressure Oxidation

The Cannington sulphide concentrate contains sphalerite, galena and pyrite. Three different responses were selected to follow the overall behaviour during pressure oxidation and these were:

1. Zinc concentration in solution as a function of time, which were expressed as a percentage of the total zinc present in the concentrate. In order to have substantial zinc for profiling, Cannington complex sulphide concentrate was mixed with high grade zinc sulphide mineral in ratio 14 to 5 respectively and "surnamed" UBC mixed concentrate (section 3.6.3.3),

2. Iron concentration in solution, which would be determined by iron dissolution and precipitation, and

3. Free acid (H$_2$SO$_4$), which would be decreased by sulphide oxidation and increased by iron hydrolysis.

4.6.5.1 Concentration – Time Profile of the Zinc, Acid and Iron

Pressure oxidation of UBC mixed concentrate was investigated at temperatures range of 120°-150°C; above the melting point of sulphur and in the presence of iodide. Samples were withdrawn during the reaction for analysis. The response–time profiles at different temperatures are presented in Figure 4-43 to Figure 4-45.

Initial solution used contained ferric, ferrous and zinc with concentration of 5 g/l, 5g/l and 20g/l respectively, added as sulphate. Other standard conditions were: oxygen partial pressure 100 psi; residence time 90 minute; pulp density 8%; agitation 900 rpm; initial volume of solution 1000 ml; acidity 50 g/l H$_2$SO$_4$; stoichiometric iodide addition was 100% of silver. 2.53 kg/t of lignosol and 2.53 kg/t of quebracho surfactants were added at the beginning of the pressure oxidation. A sample was withdrawn when the system reached the operating temperature, prior to the admission of oxygen into the bomb and this was considered as time zero. The rate of zinc extraction increases with increasing temperature in Figure 4-43 because the oxidation of zinc sulphide is a strong function of the temperature with an activation energy value which varies from 25.88 kJ/mol (Jan et al., 1976) to 79 kJ/mol (Dobrakhotov and Onuchkina, 1964; Verban and Crundwell, 1987).
Figure 4-43. Effect of temperature on zinc extraction from UBC mixed concentrate. Test conditions: 95 g/l pulp density and 100 psi oxygen pressure. Initial solution 5 g/l Fe$^{3+}$, 5 g/l Fe$^{2+}$, 20 g/l Zn$^{2+}$, 50 g/l H$_2$SO$_4$ and stoichiometric iodide addition was 100% of silver.

There was ferric oxidation of the sphalerite (Crundwell, 1987) and galena (Dutrizac and Chen, 1995) during the heating period according to the following reactions:

\[
\text{ZnS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{ZnSO}_4 + 2\text{FeSO}_4 + S^0 \quad (4-36)
\]
\[
\text{PbS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{PbSO}_4 + 2\text{FeSO}_4 + S^0 \quad (4-37)
\]

There was also some iron dissolution during the heating period according to the following reactions:

\[
\text{FeS} + H_2\text{SO}_4 \rightarrow \text{FeSO}_4 + H_2\text{S} \quad (4-38)
\]
\[
\text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 \rightarrow 3\text{FeSO}_4 + 2S^0 \quad (4-39)
\]

Other direct acid reaction involving galena has been reported to be predominant at high acid concentrations greater than 0.3 mol/l (Dutrizac and Chen, 1995) and this can be represented as follows:

\[
\text{PbS} + H_2\text{SO}_4 \rightarrow \text{PbSO}_4 + H_2\text{S} \quad (4-40)
\]
The hydrogen sulphide from reactions (4-38) and (4-40) is oxidised by ferric sulphate.

\[ H_2S + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4 + S^0 \]  (4-41)

In this work (Figure 4-44), initial acidity was 50 g/l H₂SO₄ and it decreased during the heating period to 38 and 35 g/l at 120 and 150°C, respectively, most likely because of the sulphide reactions and the reaction with the acid consuming gangue minerals (section 3.6.3.1).

![Acid-time profile of the pressure oxidation of UBC mixed concentrate](image)

**Figure 4-44.** Acid–time profile of the pressure oxidation of UBC mixed concentrate. Test conditions: 95g/l pulp density and 100 psi oxygen pressure. Initial solution 5 g/l Fe³⁺, 5 g/l Fe²⁺, 20 g/l Zn²⁺, 50 g/l H₂SO₄ and stoichiometric iodide addition was 100% of silver.

Once oxygen is admitted into the bomb, the following zinc sulphide reaction proceeds:

\[ ZnS + H_2SO_4 + 1/2O_2 \rightarrow ZnSO_4 + H_2O + S^0 \]  (4-42)

At higher oxidation potentials the following reaction may occur through bisulphate formation at high acidity or sulphate at low acidity i.e. at pH ~2 (Doyle and Arauco, 1986).

\[ ZnS + 2O_2 \rightarrow ZnSO_4 \]  (4-43)

In many of the reported studies on the acid pressure oxidation of zinc sulphide, acidity is very high (pH < 1.0) with consequent high yields of sulphur. Therefore, the contribution by the
sulphate formation route in this work is minimal because of the high acidity used in this work and hence will not be part of these discussions.

The acid data in Figure 4-44 were compared with theoretical acid profile that were calculated based on the zinc extracted into solution by reaction (4-42). The actual acid data were below the theoretical values for the entire extraction-time profile. This confirms that other gangue minerals (section 2.3) also take part in the acid consumption during autoclaving of UBC mixed sulphide (made from Cannington complex sulphide).

Previous qualitative observations on the reaction of the galena contained in zinc concentrates during acid pressure oxidation at about 150°C suggest that galena reacts rapidly to form PbSO$_4$ and elemental sulphur (Collins et al., 1990).

\[ \text{PbS} + H_2SO_4 + 1/2O_2 \rightarrow \text{PbSO}_4 + S^0 + H_2O \]  

(4-44)

At higher temperatures, the lead sulphate is sufficiently soluble to re-precipitate as lead jarosite (Scott, 1973).

\[ \text{PbSO}_4 \leftrightarrow Pb^{2+} + SO_4^{2-} \]  

(4-45)

\[ \text{PbSO}_4 + 3Fe_2(SO_4)_3 + 12H_2O \rightarrow \text{PbFe}_6(SO_4)_4(OH)_{12} + 6H_2SO_4 \]  

(4-46)

Although the product of reaction (4-46) is written as end member lead jarosite, in practice hydronium ion is co-precipitated.

For very finely ground material such as that derived from fine-grained complex sulphide, some oxidation of pyrite may be expected as follows:

\[ \text{FeS}_2 + 2O_2 \rightarrow \text{FeSO}_4 + S^0 \]  

(4-47)

At low acidity, pyrite oxidation can proceed through the sulfate route as follows:

\[ \text{FeS}_2 + 7O_2 + 2H_2O \rightarrow 2\text{FeSO}_4 + 2H_2SO_4 \]  

(4-48)

The iron dissolution reactions, which occurred during the heating were responsible for the increase in the initial ferrous iron from 5 g/l to ~10 g/l and decrease in ferric iron from 5g/l to 2.5 g/l. The total iron, therefore increased from the initial concentration of 10 g/l to ~ 12.5 g/l at time zero (Figure 4-45).
Figure 4-45. Effect of temperature on the ferric and ferrous iron concentration of the pressure oxidation of UBC mixed concentrate. Test conditions: 95g/l pulp density and 100 psi oxygen pressure. Initial solution 5 g/l Fe$^{3+}$, 5 g/L Fe$^{2+}$, 20 g/L Zn$^{2+}$, 50 g/l H$_2$SO$_4$ and stoichiometric iodide addition was 100% of silver.

Also, once oxygen is admitted into the slurry, ferrous oxidation causes a Fe$^{2+}$ decline with time as shown in Figure 4-45, because of the following reaction:

$$2FeSO_4 + H_2SO_4 + 1/2O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (4-49)$$

The net effect of ferrous oxidation reaction (4-49) and the precipitation reaction (4-46) is thought to be responsible for the ferric profile shown in Figure 4-45. At 150°C and after 90 minutes, the ferric concentration declined to ~ 2.5 g/l and ferrous declined to ~ 0.75 g/l. The UBC mixed sulphide was made by mixing the Cannington complex sulphide with high-grade zinc sulphide mineral. The resulting composition of the mix has been presented in section 3.6.3.3 and the gangue minerals have been presented in section 2.3. The high composition of lead in the UBC mixed sulphide feed (5.50%) and the low level of acid, which results from the acid consumption by zinc sulphide and other gangue minerals (section 2.3) were responsible for the substantial precipitation of iron.
At the early stage of oxidation (first 30 minutes), the net ferric concentration increases because the ferric precipitation reaction “lags” behind the ferrous oxidation until low acid level is reached. The ferric precipitation is delayed further at low temperature (120°C) because of the low rate of jarosite precipitation at low temperature. At high temperature (150°C), a very low level of ferric remains in the final solution because of the increase in the stability and the precipitation rate of jarosite.

Also, one would have expected a significant difference in the acid profiles of the low and high temperatures oxidation based on the zinc extraction. The difference is minimised by the iron precipitation reaction at high temperature, which produces acid according to reaction (4-46). At high temperature, the effect of the acid generation by ferric precipitation became obvious towards the end of the reaction and this was manifested as increase in acidity (Figure 4-44).

4.6.5.2 Non interruptive Zinc Extraction and Sulphide Oxidation

Non-interruptive pressure oxidation tests, in which samples were not taken during the experiments, were carried out on the UBC mixed concentrate. The conditions for the pressure oxidation were the same as that of Figure 4-43. The results are presented in Table 4-17.

The extents of sulphide oxidation and iron precipitation of UBC mixed sulphide were more than those of Cannington complex sulphide concentrate (4.6.4). The UBC mixed concentrate contains more sulphide than the Cannington complex sulphide concentrate but its pyrite content is less than that of the latter. Therefore, the high iron precipitation during UBC mixed sulphide oxidation could be attributed to the significant consumption of acid by zinc sulphide oxidation, which resulted into a low level of acid. This promoted the subsequent iron hydrolysis and jarosite precipitation. At high temperature, the kinetic of iron precipitation is enhanced and this may promote competition for silver by the jarosite specie (sections 4.6.2 and 4.6.3). The sulphate formation observed (Table 4-17) could have formed from the oxidation of some pyrite at very low acid level, when the slurry would have been sufficiently neutralised by the acid consuming sulphide oxidation. In their study on the pressure oxidation of pyrite, McKay and Halpern (1958) reported that the use of 0.15 mol/l initial acid yielded 50% elemental sulphur and 50% sulphate in the same temperature range.
Table 4-17. Effect of temperature on the pressure oxidation of UBC mixed sulphide concentrates. Conditions: non-interruptive tests and other conditions were the same as in Figure 4-43.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Zinc Extraction %</th>
<th>S\textsubscript{oxid.} to Sulphur %</th>
<th>S\textsubscript{oxid.} to Sulphate %</th>
<th>Sulphur Yield, %</th>
<th>Net Iron dissolution / Precipitation ((^{-1}))%</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>92.56</td>
<td>67.30</td>
<td>26.09</td>
<td>72.06</td>
<td>-24.52</td>
</tr>
<tr>
<td>135</td>
<td>84.95</td>
<td>62.41</td>
<td>25.85</td>
<td>70.71</td>
<td>-11.01</td>
</tr>
<tr>
<td>120</td>
<td>75.90</td>
<td>57.41</td>
<td>25.31</td>
<td>69.40</td>
<td>-3.31</td>
</tr>
</tbody>
</table>

\(^1\)Net iron is calculated by subtracting the iron of the initial solution from the final iron of the pregnant solution and adding iron in wash. This is expressed as a percentage of initial total iron (solid + solution), where this is \(-ve\), this indicates net iron precipitation and where this is \(+ve\), it indicates net iron dissolution.

4.6.5.3 Summary of Zinc Extraction from Complex Sulphide by Pressure Oxidation

High zinc extraction can be obtained by the pressure oxidation of complex sulphides, when a stoichiometric amount of iodide (to silver) is added to the slurry. The product of the oxidation can be separated into an impure zinc rich solution and a washed residue. The pregnant solution can be sent to zinc recovery and the residue can be leached in the cyanide for silver extraction. The effects of iodide on the zinc electrolyte purification and electrowinning have not been reported in the literature. Low level of chloride is desired in the zinc plant because of the chlorine gas evolution at high levels (~300 ppm) when anodes are new and its effect on the corrosion of aluminium starting sheets and silver lead anode during the electrowinning of the zinc (Krauss, 1985). Similarly, a low level of iodide may be required prior to electrowinning and one possible approach is to precipitate the iodide from the solution by adding copper sulphate (CuSO\(_4\)) and copper scraps (section 2.10.6). This approach will require the recovery of the copper. Carbon columns could be used to absorb the iodide species before the zinc recovery. Another approach could be the use of silver sulphate to precipitate iodide from the zinc solution. The details of these need further investigations and such studies are outside the scope of the present work.

High total sulphide oxidation occurs with high sulphur yield during the pressure oxidation of complex sulphides. The extent of iron precipitation and the neutralisation of the slurry are very high leaving a pregnant solution, which require minimal removal of iron before the zinc recovery and a residue, which require minimal neutralisation before cyanidation for silver extraction.
5.1 Conclusions from the Study

The following are the principal conclusions reached from this study of the chemical behaviour of silver in the pressure oxidation of complex sulphides ores and concentrates.

1. Silver sulphide, which is the principal mineral of silver, reacts in the autoclave under the conditions similar to that of the treatment of complex sulphide. Ionic silver is released into the solution. The predominant product of reaction is elemental sulphur. The process can be described by an ionic transfer mechanism, which is based on the ionic conductivity of silver sulfide and the high mobility of the silver ions in the crystal lattice. Once the silver is released, the sulphide ion (S^2-) at the surface of the mineral is oxidised to elemental sulphur by ferric ions. The oxidation of the sulphide ions (S^2-) is the rate-determining step and in the absence of ferric, the overall oxidation reaction is slow. The rate of reaction increases with increasing temperature and with the presence of ferric ions. However, the rate of reaction decreases with increasing silver sulfate concentration. The kinetics is controlled by chemical reaction with activation energy of 72.6 kJ/mol.

2. The reaction kinetics of aqueous silver (released by sulphide) and iron in the presence of lead sulphate suspension were studied at a temperature range of 110-150°C and under conditions that were relevant to industrial zinc concentrate pressure oxidation. The neutralisation of the solution prior to precipitation was avoided. At low concentration of silver ions, the major collector of silver is plumbojarosite specie and it is the precipitation of this jarosite specie, which drives the silver deportment into the jarosite phase. The kinetics of iron and silver precipitation increased with increasing temperature and concentration of initial ferric and lead sulphate suspension, but the kinetics decreased with increasing concentration of acid. The initial acid level has a pronounced effect on the rate of formation of jarosite by reducing the rate of hydrolysis and probably by reducing the formation of the most favourable hydroxo complex of ferric. Both result in the reduction of the rate of crystallisation. The effect of temperature and seeding suggest that the
reaction rate is controlled by a chemical reaction step occurring at the surface of the jarosite crystals.

3. The chemical compositions of the resulting precipitates revealed that silver-hydronium-lead jarosite is formed in the temperature range of 110°-150°C. The hydronium ion content increases with increasing temperature because hydronium jarosite stability is favoured at elevated temperature. Also, the silver content decreases with temperatures in the same trend which was observed by Arauco and Doyle (1986) during the pressure oxidation of silver-bearing zinc sulfide.

4. Under the optimal conditions for iron precipitation such as high temperatures and lead suspension, silver precipitation is fast and finishes first, however, the precipitation of iron continues after the complete precipitation of silver. This leads to the zoning of silver-rich jarosite in the core of the jarosite structures. During cyanidation of these products, only the silver ion in the outer crystal planes of the jarosite structures is accessible to and can react with free cyanide ions in the pulp leading to low extraction of silver. Prior grinding of the jarosite specie, followed by cyanidation does not improve the silver extraction and this suggests that the silver-rich jarosite may be concentrated at a sub-micron level, which may be difficult to access by mechanical grinding or the silver-rich jarosite cannot pass the ferric hydroxide as silver cyanide.

5. Sulphur is a predominant product of complex sulphide oxidation in the temperature range of 110°-150°C. Under deoxygenated conditions, silver may be precipitated by elemental sulphur as silver sulphide. The reaction involves the reduction of aqueous silver to metallic silver and the subsequent reaction of metallic silver with sulphur. The reduction of aqueous silver is very rapid under the high reducing conditions (high ferrous/ferric ratio) and the rate of silver precipitation increases with increasing initial sulphur concentration. The effect of the initial level of sulphur on the rate of reaction suggests that the reaction of metallic silver with sulphur may be the rate-determining step.

6. Under the pressure oxidation condition, the presence of oxygen and oxidising conditions minimises the re-precipitation of silver as silver sulphide. Silver precipitation became less favourable at high temperature and under the oxidising conditions, leaving high final concentration of silver in the solution at the end of the reaction. It is unlikely that the silver
sulphide precipitation plays a significant role in the low extraction of silver from autoclave residue because the silver sulphide is soluble in cyanide solution.

7. The deportment of silver as silver iodide is an effective way of controlling the chemical behaviour of silver during the pressure oxidation. However, the silver extraction from the resulting residue was below 100% when jarosite precipitation was carried out with silver iodide. This suggests that some silver iodide dissolves with time and precipitates as a jarosite specie during the iron precipitation. The extent of silver iodide dissolution and the subsequent incorporation into the jarosite phase increased with increasing temperature. The migration of some silver ions to the jarosite phase is promoted by the decrease in stability of silver iodide at high temperature and the increase in the stability of jarosite specie at high temperature.

8. Although the silver iodide formation is a precipitation reaction that is expected to be fast, but in the presence of both hydrolysed ferric, sulphate and iodide, some aqueous silver may react preferentially with hydrolysed ferric and sulphate to form jarosite. The resulting jarosite specie may prevent the rapid and total deportment of silver as silver iodide especially when the silver is incorporated into the core of the jarosite specie. If the end member silver jarosite is formed along with the silver iodide, some of the silver jarosite may re-crystallise to form hydronium jarosite, thus freeing the silver to form silver iodide.

9. High zinc extraction into a solution suitable for recovery by electrowinning can be achieved by pressure oxidation of zinc-lead-iron complex sulphides and stoichiometric iodide addition to prevent both loss of silver into the jarosite phase and iodine deportment to the autoclave freeboard. High extraction of silver (~98%) from the oxidised residue can be achieved without compromising zinc extraction and sulphide oxidation in the temperature range of 110°-150°C. At high temperatures (140-150°C), silver extraction decreases (70-85%) because of the enhanced stability and kinetics of lead-hydronium jarosite. This can be overcome by increasing the acidity of the autoclave slurry. The use of high acidity without iodide addition does not prevent silver loss during pressure oxidation.

5.2 Conceptual flowsheet for the treatment of Complex Sulphide Concentrate for Silver

A simple conceptual flowsheet for the treatment of complex sulphides consists of the flotation
of bulk concentrate followed by pressure oxidation to liberate the silver for subsequent leaching. Stoichiometric iodide is added to precipitate silver as iodargyrite (AgI). The iodide is not lost and should be recovered because the economics of the process depends on the iodide recovery.

Figure 5-1. Conceptual flowsheet for the treatment of complex sulphide concentrate for silver.

The conceptual flowsheet shows "Ag and Au Recovery" after the cyanide leach of the autoclave solids and this may be done by the Merill-Crowe system, which releases zinc cyanide and iodide into the solution. The iodide is recycled by returning the spent solution to the autoclave and the cyanide may be oxidized (Van Weert, 2001). However, the kinetics of cyanide oxidation under the autoclave conditions is not known from the literature. Therefore, the addition of cyanide stripping step may be considered and the recycling of the HCN to the process will reduce the operational costs.
5.3 Relationships between the Objectives and the Outcomes of Study

The primary objective of this study which was to investigate the chemical behaviour of silver during the acid pressure oxidation in the range of 110-150°C has been addressed. The kinetics of silver sulphide oxidation mineral was provided and it was observed that silver was released into solution. The reaction chemistry and the kinetics of the various deportment of the aqueous silver were investigated. The fundamental understanding on the reactions of silver during the acid pressure oxidation has been provided and the effects of oxidation conditions on the deportment of silver have been presented. Also, the study showed that it was possible to sequence silver into a residue, which is suitable for silver extraction by adding small amounts of soluble iodide combined with careful control of temperature, oxidation kinetics and solution composition. The secondary objective which was to deport the silver into the recoverable form without compromising the high zinc extraction was also achieved.

5.4 Benefits to the Metallurgical Practice

The acid pressure oxidation followed by cyanidation of the residue can be adapted to a variety of concentrates and ores (such as copper ores and concentrates). This research has improved the fundamental understanding of the behaviour of silver during the acid pressure oxidation. The knowledge provided on the chemistry and the kinetics of silver reactions can be combined with the knowledge on the oxidation of sulphides to process complex sulphide materials. A hydrometallurgical process, which is capable of selectively extracting the base metals (zinc and copper) without the loss of precious metals, is attractive and the recovery of silver and gold along with the base metals will increase the revenues to the base metal operations.
CHAPTER 6
RECOMMENDATION FOR FURTHER WORK

The present studies have shed new light on the chemical behaviour of silver in the pressure oxidation of complex sulphide ores and concentrates. It is recommended that the following points be considered for future work.

1. Jarosite Specie Precipitation

The pressure oxidation studies have established that silver sulphide is oxidised to aqueous silver, which precipitates subsequently as sulphide or jarosite species (depending on the conditions). Silver incorporated into the core of hydronium-lead jarosite cannot be recovered by cyanidation because only the silver ion in the outer crystal planes of the jarosite structures is accessible to and can react with free cyanide ions. Further precipitation and characterization studies are required to define the silver distribution across the jarosite planes and determine the conditions, which will deport silver to the outer plane, where it may be recovered by subsequent cyanidation.

2. Roles of the Individual minerals

Due to time constraints, it was impossible to mount a serious study into the roles of the individual minerals. The silver bearing minerals may oxidise prior to galena or sphalerite or vice versa. If the galena reacts before the silver sulphide to form insoluble lead sulphate, this may trap the silver or the silver mineral and consequently, affects the silver extraction. The galvanic interactions occurring when the sulphides are in contact with one another can be investigated by electrochemical techniques. The mineral with lower rest potential becomes anodic and dissolves preferentially to the other. Therefore, a good knowledge of the rest potentials of sulfides (Table A1-3, Appendix A1.4) and galvanic interactions between mixed sulphides as a function of pH and oxidation potential could be considered further to explain the roles play by individual minerals.
3. Kinetics of Cyanidation

The dissolution of silver iodide in cyanide liquors is fast due to fine AgI crystal size and fast reaction kinetics with cyanide. The fast dissolution of silver iodide may offer advantages such as reduction of residence time and cyanide consumption by side reaction. The potential benefits of these process factors should be investigated further.

Elemental sulphur was the predominant product of the pressure oxidation in the temperature range of 110°-150°C. The gold may be trapped in the elemental sulphur and if this is the case, cyanide leach for silver could be a flash leach, while gold will take some time. These variations may be economically significant and require further investigation.

4. Effect of Iodide on Purification/Electrowinning

The effects of iodide on the zinc electrolyte purification and electrowinning have not been reported in the literature and this could not be addressed in these studies. Also, a low concentration of iodide may be required before electrowinning and a possible approach is to carry out a precipitation by adding copper sulphate (CuSO₄) and a source of metallic copper. The cupric is reduced to cuprous and the iodide is precipitated. This approach will require the recovery/recycling of the copper. The details of this need further investigation.

\[
CuSO_4 + ZnI_2 + Cu \rightarrow 2CuI + ZnSO_4 \quad \Delta G^° = -100.99 \text{ kJ} \tag{6-1}
\]

5. Iodine species during the Pressure Oxidation

The distribution of iodine species in the solution and between solution and the autoclave freeboard cannot be calculated since equilibrium may not be achieved during the pressure oxidation. Attempts were made to determine the aqueous iodine and iodide (total iodide in solution) by chemical analysis. These required sending the samples out to the local Vancouver analytical laboratories. The results were not reproducible and the compositions changes with time. The determination of the iodine species will require immediate determination of the composition of the samples.
6. Reaction of Silver Minerals during the Pressure Oxidation

This study has provided knowledge on the oxidation kinetics of silver sulphide mineral because of its role as the principal source of silver. Also, this study has provided information on the behaviour of the iodargyrite (AgI) during the acid pressure oxidation. The behaviour of chlorargyrite (AgCl) during the acid pressure oxidation has been investigated previously by Dutrizac and Jambor (1987). Therefore, there is need to investigate the behaviours of other important silver minerals such as polybasite ((Ag, Cu)$_{16}$Sb$_2$S$_{11}$), proustite (Ag$_3$AsS$_3$) and tetrahedrite ((Cu, Fe)$_{12}$Sb$_4$S$_{13}$) during the pressure oxidation.
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APPENDIX A
LITERATURE REVIEW

A1.1 Silver-Sulfur-Water System

Table A1-1. Equation for the Theoretical Reaction of Ag-S-H2O (Warren et al., 1984)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Potential</th>
<th>Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Ag + H2S = Ag2S + 2 H+ + 2e-</td>
<td>E=-0.067 - 0.059 pH -0.0295 log[H2S]</td>
<td>22</td>
</tr>
<tr>
<td>2 Ag + HS- = Ag2S + H+ + 2e-</td>
<td>E=-0.274 - 0.0295 pH -0.0295 log[HS-]</td>
<td>23</td>
</tr>
<tr>
<td>Ag2S + 4H2O = 2Ag + SO42- + 8H+ + 6 e-</td>
<td>E= 0.427 - 0.079 pH +0.010 log[SO42-]</td>
<td>25</td>
</tr>
<tr>
<td>Ag2S + 4H2O = 2Ag + HSO4- +7H+ +6 e-</td>
<td>E= 0.408 - 0.069 pH +0.010 log[HSO4-]</td>
<td>26</td>
</tr>
<tr>
<td>2 Ag + HSO4- = Ag2SO4 + H+ + 2 e-</td>
<td>E= 0.711 - 0.0295 pH -0.0295 log[HSO4-]</td>
<td>27</td>
</tr>
<tr>
<td>2 Ag2S + H2O = Ag2SO4 + H+</td>
<td>pH=-3.00 - log{[ Ag+][HSO4-]}</td>
<td>28</td>
</tr>
<tr>
<td>Ag2SO4 + H2O = Ag2O + SO42- + 2 H+</td>
<td>pH=-8.78 - 0.5 log[SO42-]</td>
<td>31</td>
</tr>
<tr>
<td>Ag + SO42- = Ag2SO4 + 2 e-</td>
<td>E= 0.654 - 0.0295 log[SO42-]</td>
<td>32</td>
</tr>
<tr>
<td>Ag = Ag+ + 2 e-</td>
<td>E= 0.799 + 0.059 log[Ag+]</td>
<td>37</td>
</tr>
<tr>
<td>Ag2S +4H2O=2Ag+ + HSO4- +7H+ + 8e-</td>
<td>E=0.506-0.052pH+0.007log{[ Ag+][HSO4-]}</td>
<td>38</td>
</tr>
<tr>
<td>Ag2S = 2 Ag+ + S° + 2 e-</td>
<td>E= 1.008 + 0.059 log[Ag+]</td>
<td>39</td>
</tr>
</tbody>
</table>

A1.2 Estimation of Thermodynamics Data at High Temperature

In order to determine the $\Delta G^o_T$, the following are considered;

\[
\Delta G^o_{298} = \Delta H^o_{298} - 298.\Delta S^o_{298}
\]

\[
\Delta G^o_T = \Delta H^o_T - T.\Delta S^o_T
\]

and subtracting equation A1-1 from equation A1-2, gives the following;

\[
\Delta G^o_T = \Delta G^o_{298} + (\Delta H^o_T - \Delta H^o_{298}) - T.\Delta S^o_T + 298.\Delta S^o_{298}
\]

Knowing that,

\[
\Delta H^o_T - \Delta H^o_{298} = \int_{298}^{T} \Delta C^o_p dT
\]

\[
= \Delta C^o_p_{298}(T - 298)
\]

In order to predict the heat capacity ($\Delta C^o_p_{298}$), the following are considered;

Since $C_p = \left(\frac{dH}{dT}\right)_p = T\left(\frac{dS}{dT}\right)_p$
At constant pressure;

\[ \Delta S = S^\circ_T - S^\circ_{298} = \int_{298}^{T} \frac{\Delta C_p}{T} dT \]  

\[ = \int_{298}^{T} \Delta C_p d\ln T \]  

\[ \equiv \Delta C_p^\circ_{298} \ln \left( \frac{T}{298} \right) \]  

Then, \[ \Delta S^\circ_T \equiv \Delta S^\circ_T + \Delta C_p^\circ_{298} \ln \left( \frac{T}{298} \right) \]  

By substituting equation (A1-5) and (A1-10) into equation (A1-3), then we obtain the following equation;

\[ \Delta G^\circ_T = \Delta G^\circ_{298} + \Delta C_p^\circ_{298} \left[ T - 298 - T \ln \left( \frac{T}{298} \right) \right] - (T - 298) \Delta S^\circ_{298} \]  

Where \( \theta = \left( T - 298 - T \ln \left( \frac{T}{298} \right) \right) \)

Then, \[ \Delta G^\circ_T = \Delta G^\circ_{298} + \Delta C_p^\circ_{298} \theta - (T - 298) \Delta S^\circ_{298} \]  

For the non-ionic species, \( C_p \int_{298}^{T} \frac{C_p(T) dT}{dT} = 298 \frac{\int_{298}^{T} C_p(T) dT}{\int_{298}^{T} dT} \)  

Therefore, \( C_p \int_{298}^{T} \frac{(a + bT + cT^2 + dT^2) dT}{T - 298} \)  

\[ \frac{a(T - 298) + \frac{b}{2} (T^2 - 298^2) - c \left( \frac{1}{T} - \frac{1}{298} \right) + d \left( T^3 - 298^3 \right)}{T - 298} \]  

\[ = a + \frac{b(T + 298)}{2} + \frac{c}{298} + \frac{d(T^2 + 298T + 298^3)}{3} \]  

Where a, b, c and d are the heat capacity functions, which can be obtained from the Outokumpu HSC Chemistry (version 3.0). For the ionic species, the method of Criss and Cobble (1964a and 1964b) can be used to determine the heat capacity by the following equations;
\[ C_p^{o} T = \alpha T + \beta T \bar{S}^{o} \]  
(A-18)

\[ \bar{S}^{o} = S^{o} + z \bar{S}_{abs}(H^+) \]  
(A-19)

Where \( \alpha \) and \( \beta \) are the Criss-Cobble heat capacity constants, which are available for 60, 100, 150, 200, 250 and 300°C. The values of free energies \((G^{o})\) and entropies \((S^{o})\) are available in the literature (Bard et al., 1985) for equation A-13. The above technique was used to estimate the free energies of the jarosite specie at high temperatures (100° and 150°C). The heat capacity functions were obtained by adding up the heat capacity functions of the constituents as shown below for potassium jarosite.

<table>
<thead>
<tr>
<th>Species</th>
<th>( S^{o}_{298} )</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2}K_2SO_4(s) )</td>
<td>88.00</td>
<td>60.20</td>
<td>49.80</td>
<td>-8.91</td>
<td>0.00</td>
</tr>
<tr>
<td>( 2Fe(OH)_3(s) )</td>
<td>213.40</td>
<td>171.07</td>
<td>246.54</td>
<td>-30.25</td>
<td>-84.55</td>
</tr>
<tr>
<td>( \frac{1}{2}Fe_2(SO_4)_3(s) )</td>
<td>153.75</td>
<td>135.34</td>
<td>112.67</td>
<td>-29.92</td>
<td>-39.49</td>
</tr>
<tr>
<td>( KFe_3(SO_4)_2(OH)_6 )</td>
<td>455.15</td>
<td>366.61</td>
<td>409.01</td>
<td>-69.08</td>
<td>-124.04</td>
</tr>
</tbody>
</table>

**A1.3 Speciation Calculation**

The concentration of the ferric hydroxyl ions and other species could not be determined directly; therefore the concentration of each was obtained via a speciation calculation routine. The method is based on the fact that at equilibrium the total Gibbs free energy of the system has its minimum value (Smith and Van Ness, 1975). Therefore, when an expression for the total Gibbs free energy is written the composition that minimises total Gibbs free energy must be found. The minimum value for the combined material balances and the total Gibbs free energy function then occurs when its partial derivative with respect to the number of each atom type present equals zero. For any single species \( k \) at equilibrium, the Gibbs free energy is given by the expression:

\[ \Delta G_k = \Delta G_k^o + RT \ln K_k = 0 \]  
(A-20)

When there is equilibrium between \( j \) species, the expression becomes:
\[ \Delta G_k = \sum_j v_{jk} \left( \Delta G_j^0 + RT \ln a_j \right) \]  
(A-21)

Where \( a_j \) is the activity of species \( j \) and \( v_{jk} \) is the stoichiometric factor of species \( j \) in reaction \( k \).

By defining Lagrange’s unspecified multipliers such that for any species \( j \) composed of elements \( i \):

\[ \Delta G_j^0 + RT \ln a_j + \sum_i a_y \lambda_i = 0 \]  
(A-22)

Where \( a_y \) is the number of elements \( i \) involved in species \( j \), then for all values of \( \lambda_i \):

\[ \sum_k v_{jk} \sum_i a_y \lambda_i = 0 \]  
(A-23)

To find a solution, the Gibbs free energy functions must be solved simultaneously for all species \( j \):

\[ \Delta G_j^0 + RT \ln a_j + \sum_i a_y \lambda_i = 0 \]  
(A-24)

and the set of mole balances for all elements \( i \):

\[ \sum_j a_y m_j = m_i \]  
(A-25)

For dissolved species: \( \ln a_j = \ln m_j + \ln \gamma_j \)  
(A-26)

For precipitates: \( \ln a_j = 0 \)  
(A-27)

This is the basis of the calculation routine (Dixon, 2001). The routine used Davis theory to estimate activity coefficients. The free energy values at 25°C for the iron-water system can be obtained from various literature (Bard et al., 1985; Rossini et al., 1952) and they are presented in Table A1-3.
Table A1-3. Thermodynamic data for some species in ferric-sulphate-water systems

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$, (kJ/mol)</th>
<th>$S^\circ$, (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>-157.29</td>
<td>-10.88</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>-744.63</td>
<td>20.08</td>
</tr>
<tr>
<td>$HSO_4^-$</td>
<td>-756.01</td>
<td>131.80</td>
</tr>
<tr>
<td>$Fe^{3+}$</td>
<td>-4.60</td>
<td>-315.90</td>
</tr>
<tr>
<td>$Fe(OH)^{2+}$</td>
<td>-229.41</td>
<td>-142.00</td>
</tr>
<tr>
<td>$Fe(OH)_2^{+}$</td>
<td>-446.40</td>
<td>-29.29</td>
</tr>
<tr>
<td>$Fe(OH)_3$</td>
<td>-660.00</td>
<td>75.40</td>
</tr>
<tr>
<td>$Fe(OH)_4$</td>
<td>-830.00</td>
<td>25.50</td>
</tr>
<tr>
<td>$Fe_2(OH)_2^{4+}$</td>
<td>-466.97</td>
<td>-355.64</td>
</tr>
<tr>
<td>$FeSO_4^{+}$</td>
<td>-772.80</td>
<td>-129.70</td>
</tr>
<tr>
<td>$Fe(SO_4)_2^{2-}$</td>
<td>-1524.65</td>
<td>-43.07</td>
</tr>
<tr>
<td>$Fe_2(SO_4)_3$</td>
<td>-2243.00</td>
<td>-571.53</td>
</tr>
<tr>
<td>$FeHSO_4^{2+}$</td>
<td>-776.03</td>
<td>-18.68</td>
</tr>
<tr>
<td>$H_2O(l)$</td>
<td>-237.18</td>
<td>69.96</td>
</tr>
<tr>
<td>$Fe(OH)_2$</td>
<td>-486.90</td>
<td>87.99</td>
</tr>
<tr>
<td>$FeSO_4$</td>
<td>-824.89</td>
<td>120.96</td>
</tr>
<tr>
<td>$FeSO_4.H_2O$</td>
<td>-1079.28</td>
<td>157.74</td>
</tr>
<tr>
<td>$FeSO_4.4H_2O$</td>
<td>-1793.57</td>
<td>282.42</td>
</tr>
<tr>
<td>$FeSO_4.7H_2O$</td>
<td>-2509.74</td>
<td>409.20</td>
</tr>
<tr>
<td>$Fe(OH)_3$</td>
<td>-696.49</td>
<td>106.70</td>
</tr>
<tr>
<td>$Fe_2O.OH$</td>
<td>-487.37</td>
<td>60.38</td>
</tr>
<tr>
<td>$Fe_2O_3.H_2O$</td>
<td>-975.87</td>
<td>118.83</td>
</tr>
<tr>
<td>$Fe_2O_3$</td>
<td>-742.29</td>
<td>87.40</td>
</tr>
<tr>
<td>$Fe_2(SO_4)_3$</td>
<td>-2262.75</td>
<td>307.52</td>
</tr>
</tbody>
</table>

A1.4 Oxidation of Complex Sulphide: The role of Individual minerals

Table A1-4. Rest Potentials of sulfide minerals (Majima, 1968)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Rest Potential, (V vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>0.66</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.56</td>
</tr>
<tr>
<td>Galena</td>
<td>0.40</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.46</td>
</tr>
<tr>
<td>Argentite</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Appendix A References


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APPENDIX B
EXPERIMENTAL PROCEDURE

B.1 Characterization of solids

X-ray diffraction patterns of the feeds were helpful in determining the initial phases, which were present before pressure oxidation. The transformation of these phases due to oxidation reaction was also monitored by a similar method. The instrument used for this purpose was a Siemens D5000 powder diffractometer in the Department of Earth and Ocean Science at UBC. It uses monochromatized CuKα radiation and was operated at 30 mA and 40 kV. The spectra were collected from 3 to 70° (2θ) in 0.01° steps at a count-rate of 0.4 s per step. Small samples from the feeds and oxidized residues were ground further in a mortar to obtain fine powder. The fine powder was mixed with ethanol to form a paste, which was spread on a glass slide to form thin layers and allowed to dry before inserting into the instrument for analysis. After obtaining the spectra, background subtraction and data smoothing were carried out with a PC X-ray pattern processing software program. The peaks were matched with computer data files to identify the various phases, which were present in the feeds and the residues. The limitation of the X-ray diffraction technique is that the peaks of phase, which constitutes less than 5% of the bulk sample, may not appear in the scan.

Also, the scanning electron microscope (SEM) was used to examine the dissolution features and morphology (forms and structure) of the particles and comparisons were made at different stages of reaction. A Kevex 8000 energy dispersive X-ray spectrometer (EDX) in the Department of Metals and Materials Engineering at UBC was employed. For the analysis, powder particles were mounted on a stand with double stick and coated carbon. EDX-spectra were collected with the following conditions: accelerating voltage 20 KV, live time 200 seconds (30% dead time). The SEM-EDX provided qualitative analysis vis-à-vis the elemental composition analysis of each grain by using spot analysis.

B.2 Method of gold and silver analysis by fire assay/AAS

The following procedures were used by International Plasma Laboratory (IPL): 10 to 30 grams of sample was weighed into a fusion pot which contained a combination of fluxes such as lead
oxide, sodium carbonate, borax, silica flour, baking flour or potassium nitrate. After the sample and fluxes had been mixed thoroughly, some silver inquart and a thin layer of borax were added on top. The sample was then charged into a fire assay furnace at 2000°F for one hour, at this stage, lead oxide would be reduced to elemental lead and slowly sunk down to the bottom of the fusion pot and collected the gold and silver along the way. After one hour of fusion, the sample was then out and pour into a conical cast iron mould, the elemental lead which contained precious metals would stay at the bottom of the mould and any unwanted materials called slag would float on top. The slag was removed by hammering and a “lead button” was formed.

The lead button was then put back in the furnace onto a preheated cupel for a second stage separation, at 1650°F, the lead button was liquefied and absorbed by the cupel, but gold and silver which have higher melting points would stay on top of the cupel. After 45 minutes of cupellation, the cupel was then taken out and cooled, the dore bead which contained precious metals was then weighed and transferred into a test tube and dissolved in hot Aqua Regia solution heated by a hot water bath.

The gold in solution is determined with an Atomic absorption spectrometer. The gold value, in parts per billion or grams per tonne is calculated by comparison with a set of known gold standards. The silver result is determined by subtracting the gold value from the dore bead, and then reported in parts per million.
Figure C1. The EDS spectra of internal area of silver-lead-hydronium jarosite.

Figure C2. The EDS spectra of peripheral area of silver-lead-hydronium jarosite.