CATALYTIC LEACHING OF SILVER WITH FERRICYANIDE-CYANIDE SOLUTION

by

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Abstract

Significantly lower silver extraction than gold has been commonly observed in gold-silver cyanidation plants, especially in heap leaching operations. The different mineralogy of gold and silver in the ores is suspected to be the main reason, e.g., the occurrence of low solubility acanthite may result in low overall silver extraction. Leaching of silver sulfide with ferricyanide and its potential application on gold-silver ores has been investigated with the purpose of increasing the silver extraction. It was found that under the experimental leaching conditions (0.5 g/l NaCN, 0.5 g/l Fe as K$_3$Fe(CN)$_6$, pH =11.5, N$_2$, room temperature), the main reaction during leaching of silver sulfide with ferricyanide-cyanide solution is,

$$\text{Ag}_2\text{S} + 5 \text{CN}^- + 2\text{Fe(CN)}_6^{3-} = 2\text{Fe(CN)}_6^{4+} + \text{CNS}^- + 2\text{Ag(CN)}_2^-$$

indicating that at least 6 kg K$_3$Fe(CN)$_6$ would be needed to extracted 1 kg silver from the pure silver sulfide.

The dissolution of silver sulfide and gold in ferricyanide-cyanide solution was examined by performing a series of rotating disc tests. The results indicated that the dissolution rate of Ag$_2$S in the ferricyanide-cyanide system (0.5 g/l Fe as ferricyanide) is 21$\mu$mol m$^{-2}$ s$^{-1}$ (0.78 $\mu$m/hr), much higher than the value of 13 $\mu$mol m$^{-2}$ s$^{-1}$ (0.38 $\mu$m/hr) in aerated cyanide solution. The dissolution rate of gold disc in the same leaching system gives a value of 19 $\mu$mol m$^{-2}$ s$^{-1}$ (0.74 $\mu$m/hr) which is greater than that in aerated cyanide solution (about 5 $\mu$mol m$^{-2}$ s$^{-1}$, 0.19 $\mu$m/hr). The effect of pH, temperature, ferricyanide and cyanide concentration, and rotating speed on the dissolution rate of silver sulfide and gold in catalytic leaching
system were examined. The results indicate a typical diffusion-controlled process for both Ag$_2$S and Au dissolutions in ferricyanide-cyanide solutions with activation energies of 6.7 kJ/mol and 7.8 kJ/mol respectively.

The leaching kinetics of mixed sulfide minerals in ferricyanide-cyanide solutions showed that non-silver sulfide minerals decrease silver extraction from synthetic silver sulfide to different extents. A significant decrease on silver extraction is observed in the presence of chalcopyrite and pyrrhotite. It is speculated that most of the available ferricyanide has been consumed by the non-silver sulfide minerals.

Catalytic leaching with ferricyanide to improve silver extraction from Veladero and Pierina gold-silver ore has been investigated through tank leaching and column leaching tests. The results of comparison tests show that improvements of Au and Ag extraction are not significant in catalytic leaching over baseline leaching. By analyzing the slurry potential variation, cyanide and alkaline consumptions and sulfide content in the leaching residues, it is believed that non-silver sulfide minerals, such as chalcopyrite, pyrrhotite, or pyrite, may compete for the available ferricyanide with acanthite in the ore and limit the efficiency of ferricyanide.
# Table of Contents

Abstract......................................................................................................................... ii
Table of contents............................................................................................................. iv
List of Tables................................................................................................................... vi
Lists of Figures................................................................................................................ vii
Nomenclature................................................................................................................ xii
Acknowledgement......................................................................................................... xiv

Chapter 1 Introduction.................................................................................................... 1
1.1 Importance and Use of Silver.................................................................................. 1
1.2 Silver Price and Production..................................................................................... 2
1.3 Chemistry of Silver................................................................................................. 2
1.4 Silver Extraction Process.......................................................................................... 3
1.5 Issues of Concern..................................................................................................... 7

Chapter 2 Literature Review......................................................................................... 9
2.1 Silver Mineralogy..................................................................................................... 9
2.2 Silver Cyanidation Chemistry................................................................................ 10
  2.2.1 Thermodynamic................................................................................................ 10
  2.2.1.1 Silver-cyanide-water system........................................................................ 11
  2.2.1.2 Silver-sulfide-water system.......................................................................... 14
  2.2.1.3 Silver-metal-sulfide-cyanide system............................................................. 17
  2.2.1.4 Common metal-cyanide system.................................................................... 18
  2.2.2 Mechanism and kinetics.................................................................................... 22
    2.2.2.1 Methods of kinetics research................................................................. 22
    2.2.2.2 Oxygen reduction.................................................................................... 24
    2.2.2.3 Dissolution of native silver................................................................. 26
    2.2.2.4 Dissolution of silver sulfides............................................................... 32
  2.2.3 Optimization of cyanidation............................................................................. 34
2.3 Alternative Lixivants............................................................................................... 36
  2.3.1 Chloride.......................................................................................................... 37
  2.3.2 Thiourea.......................................................................................................... 38
  2.3.3 Thiosulfate....................................................................................................... 39
  2.3.4 Comparisons and others.................................................................................. 39

Chapter 3 The Leaching of Silver Sulfide and Gold....................................................... 42
3.1 Introduction............................................................................................................. 42
3.2 Experiment and Analysis....................................................................................... 44
  3.2.1 Samples and reagents..................................................................................... 44
  3.2.2 Stoichiometry tests......................................................................................... 49
  3.2.3 Rotating disc tests........................................................................................ 51
  3.2.4 Mineral interaction tests................................................................................. 53
Lists of Tables

Table 1-1 Silver output by source metals (after WSS, 2005) ......................................................... 3
Table 2-1 Standard reduction potential of some metal cyanide species at 25 °C ......................... 21
Table 3-1 Leaching conditions of stoichiometry tests ................................................................. 49
Table 3-2 Analysis results of the final leaching solutions from the stoichiometry tests ......... 55
Table 3-3 Comparative results of stoichiometry tests and theoretical calculations
(according to Reaction 3-8) .............................................................................................................. 56
Table 3-4 Relationship between silver extraction and dissolved species
(25 °C, N₂, 0.5 g/l NaCN, 0.5 g/l Fe as ferricyanide, 48hrs) ..................................................... 79
Table 4-1 Tank leaching results of Veladero and Pierina gold-silver ore .................................. 88
Table 4-2 Column leaching results of Veladero and Pierina gold-silver ore ......................... 101
Lists of Figures

Figure 1-1 Typical flowsheet for cyanidation plant incorporating cyanide leaching and carbon in pulp adsorption as the recovery process .............................................................. 6

Figure 2-1 Eh-pH diagram for Ag-H₂O system at 25°C .......................................................... 12

Figure 2-2 Eh-pH diagram for Ag-CN-H₂O system at 25°C .................................................... 13

Figure 2-3 Eh-pH diagram for Ag-S-CN-H₂O system at 25°C ................................................ 15

Figure 2-4 Solubility of metal hydroxides and sulfides as a function of pH (after Palmer, S. A. K., et al. 1988) ............................................................................................................. 16

Figure 2-5 Eh-pH diagram of Fe-CN-H₂O system at 25°C ....................................................... 20

Figure 2-6 General sequence of oxygen reduction (after Hiskey and Sanchez 1990) .............. 24

Figure 2-7 Mechanistic models for oxygen adsorption at a metal surface (after Fischer & Heibaum, 1980) ........................................................................................................... 26

Figure 3-1 XRD photograph of the synthetic silver sulfide particles ........................................ 45

Figure 3-2 SEM/EDX photograph of the synthetic silver sulfide particles ............................... 46

Figure 3-3 SEM photograph of the Ag₂S disc ............................................................................ 48

Figure 3-4 Photograph of the experimental establishment for stoichiometry tests ................. 50

Figure 3-5 Photograph of the experimental establishment for rotating disc tests .................. 51

Figure 3-6 Reproducibility of leaching kinetics of Ag₂S in ferricyanide-cyanide solution (0.5 g/l NaCN, pH=11.5, 25°C, N₂ atmosphere, 600 RPM) ......................................................... 59

Figure 3-7 Dissolution of silver sulfide disc at different conditions (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)₆³⁻, pH =11.5, 25°C, 600RPM) ................................................................................. 60

Figure 3-8 Effect of rotating speed on the dissolution rate of silver sulfide disc (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)₆³⁻, pH=11.5, 25°C, N₂ atmosphere) ......................................................... 61
Figure 3-9 Effect of temperature on the dissolution rate of Ag\textsubscript{2}S  
(0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, pH=11.5, N\textsubscript{2} atmosphere, 600RPM) ........................................62

Figure 3-10 Effect of ferricyanide concentration on dissolution of Ag\textsubscript{2}S disc  
(0.5 g/l NaCN, pH =11.5, 25 °C, N\textsubscript{2} atmosphere, 600 RPM) ........................................63

Figure 3-11 Plot of Ag\textsubscript{2}S dissolution rate vs ferricyanide concentration  
(0.5 g/l NaCN, pH=11.5, 25°C, N\textsubscript{2} atmosphere, 600 RPM) ........................................63

Figure 3-12 Effect of NaCN concentration on dissolution of Ag\textsubscript{2}S disc  
( 0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, pH=11.5, 25 °C, N\textsubscript{2} atmosphere, 600 RPM) ........................................65

Figure 3-13 Plot of Ag\textsubscript{2}S dissolution rate vs NaCN concentration  
(0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, pH=11.5, 25 °C, N\textsubscript{2} atmosphere, 600 RPM) ........................................66

Figure 3-14 Effect of pH on dissolution of Ag\textsubscript{2}S disc  
(0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, 25 °C, N\textsubscript{2} atmosphere, 600 RPM) ........................................68

Figure 3-15 Mechanism of dissolution of Ag\textsubscript{2}S in ferricyanide-cyanide system ...............69

Figure 3-16 Dissolution of gold disc at different conditions  
(0.5 g/l NaCN, pH=11.5, 25 °C, 600 RPM) .................................................................71

Figure 3-17 Effect of pH on dissolution of gold disc  
(0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, 25°C, N\textsubscript{2} atmosphere, 600 RPM) ........................................72

Figure 3-18 Effect of cyanide concentration on gold dissolution  
(0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, pH =11.5, 25 °C, N\textsubscript{2} atmosphere, 600 RPM) ........................................72

Figure 3-19 Effect of ferricyanide concentration on gold dissolution  
(0.5 g/l NaCN, pH =11.5, 25°C, N\textsubscript{2} atmosphere, 600 RPM) ........................................74

Figure 3-20 Effect of rotating speed on gold dissolution  
(0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, 0.5 g/l NaCN, pH=11.5, N\textsubscript{2} atmosphere, 25 °C) ........................................74

Figure 3-21 Effect of temperature on gold dissolution  
(0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, 0.5 g/l NaCN, pH =11.5, N\textsubscript{2} atmosphere, 600 RPM) ........................................75

Figure 3-22 Plot of Ag extraction from mixed sulfide minerals vs leaching time  
(0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-}, pH =11.5, N\textsubscript{2} atmosphere, room temperature) ........77
Figure 3-23 Plot of solution potential vs leaching time during leaching of mixed sulfide mineral (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5, N$_2$ atmosphere, room temperature)................................. 78

Figure 3-24 Plot of dissolved non-silver sulfide mineral vs leaching time
0.1g/l Ag$_2$S, 0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5,
N$_2$ atmosphere, room temperature)............................................. 79

Figure 4-1 Photograph of experimental establishment of column leaching......................................................... 87

Figure 4-2 Plot of slurry potential vs leaching time in the tank leaching tests
(0.5 g/l NaCN, pH =11.5, 0.1 g/l Fe as Fe(CN)$_6^{3-}$, Air, Room Temperature)................................................................. 90

Figure 4-3 Comparative silver leaching kinetics of sample SDH23-95 in tank leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 90

Figure 4-4 Comparative silver leaching kinetics of sample SDH03-324 in tank leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 91

Figure 4-5 Comparative silver leaching kinetics of sample DDH111-157 in tank leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 91

Figure 4-6 Comparative silver leaching kinetics of Sample SDH04-270 in tank leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 92

Figure 4-7 Effect of ferricyanide concentration on Au and Ag extraction in tank leaching
(Ore sample: SDH23-95, 0.5 g/l NaCN, pH =11.5, natural air, room temperature, 48 hr).......................... 93

Figure 4-8 Comparative leaching kinetics of sample DDH111-157 in column leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 95

Figure 4-9 Comparative leaching kinetics of sample DDH04-270 in column leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 96

Figure 4-10 Comparative leaching kinetics of sample DDH44-429 in column leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)......................................................... 96
Figure 4-11 Comparative leaching kinetics of sample SDH03-324 in column leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$,
Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) ................................................................. 97

Figure 4-12 Comparative leaching kinetics of sample SDH03-124 in column leaching
(0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$,
Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) ................................................................. 97

Figure 4-13 Plot of solution potential vs leaching time of sample DDH111-157
in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) .................. 98

Figure 4-14 Plot of solution potential vs leaching time of sample DDH04-270
in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) .................. 99

Figure 4-15 Plot of solution potential vs leaching time of sample DDH44-429
in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) .................. 99

Figure 4-16 Plot of solution potential vs leaching time of sample SDH03-324
in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) .................. 100

Figure 4-17 Plot of solution potential vs leaching time of sample SDH03-124
in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$) .................. 100

Figure 4-18 Plot of cumulative NaCN and NaOH addition during column
leaching of DDH111-157 (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN) ... 102

Figure 4-19 Plot of cumulative NaCN and NaOH addition during column
leaching of DDH04-270 (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN) ... 103

Figure 4-20 Plot of cumulative NaCN and NaOH addition during column
leaching of DDH44-429 (0.5 g/l NaCN, pH=11.5, Room temperature, Air,
Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN) ... 104
Figure 4-21 Plot of cumulative NaCN and NaOH addition during column leaching of SDH03-324 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN)……105

Figure 4-22 Plot of cumulative NaCN and NaOH addition during column leaching of SDH03-124 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN)……106
Nomenclature

\( \nu \) \hspace{1em} \text{kinematic viscosity, cm}^{-1} \text{s}^{-1} \\
\( \omega \) \hspace{1em} \text{rotating velocity, rad/s} \\
\( \delta \) \hspace{1em} \text{thickness of diffusion layer, \( \mu \text{m} \)} \\
\( \Delta G^\circ \) \hspace{1em} \text{standard Gibss free energy, KJ mol}^{-1} \\
\([ \cdot \cdot \] \hspace{1em} \text{molarity concentration, mol L}^{-1} \text{(denotes the total concentration of dissolved species in this paper)} \\
\( A \) \hspace{1em} \text{area, m}^2 \text{ or cm}^2 \\
\( C_0 \) \hspace{1em} \text{bulk concentration, mol m}^{-3} \\
\( d \) \hspace{1em} \text{diameter, cm} \\
\( D \) \hspace{1em} \text{diffusion coefficient, cm}^2 \text{ s}^{-1} \text{ or m}^2 \text{ s}^{-1} \\
\( e \) \hspace{1em} \text{electron} \\
\( E^\circ \) \hspace{1em} \text{standard potential, v} \\
\( \text{Eh} \) \hspace{1em} \text{potential, v} \\
\( \text{Ext.} \) \hspace{1em} \text{extraction, \%} \\
\( h, \) \hspace{1em} \text{height, cm} \\
\( \text{hr} \) \hspace{1em} \text{hour} \\
\( J \) \hspace{1em} \text{flux, mol m}^{-2} \text{ s}^{-1} \\
\( K \) \hspace{1em} \text{equilibrium constant} \\
\( K_{sp} \) \hspace{1em} \text{solubility constant} \\
\( M \) \hspace{1em} \text{molarity, mol dm}^{-3} \\
\( \text{Me} \) \hspace{1em} \text{metal}
min  minute
Moz  million ounce
n  number of electrons transferred
N_Re  Reynold numbers
pH  negative logarithm to base of the activity of hydrogen ion
PLS  pregnant leaching solution
ppm  part per million
r  rate, mol m\(^{-2}\) s\(^{-1}\)
R  universal gas constant, 8.314 J K\(^{-1}\) mol\(^{-1}\)
Res.  Residue
RPM  rotations per minutes
SHE  standard hydrogen electrode
T  Temperature, °C or K
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Chapter 1 Introduction

1.1 Importance and Uses of Silver

Silver metal has been known since ancient times. Historically it was more widely used in coinage than gold. About 3600 B.C. the value of silver was set by the Egyptians as one fifth of that of gold (Wyslouzil & Salter, 1990). Being in greater supply and of less value, thus being practical for everyday payments, silver was used by most nations as exchange standard with silver coin forming the main circulating currency until the late 19th century. But after a number of gold rushes, silver increasingly gave way to gold and was gradually phased out of regular coinage (WSS, 2005).

As the least expensive of the precious metals, silver has working qualities similar to gold and can achieve the most brilliant polish of any metal. So even nowadays, silver still has significant use in jewelry and silverware. Due to its unique properties, such as the whitest color and highest electrical and thermal conductivity of all the metals, it is widely used in catalysts, electrical and electronics components, and photography. Light-sensitive silver-halide crystals prepared by mixing silver salt solution, usually silver nitrate, with soluble alkali metal halide such as sodium iodide, are widely used in the photographic process. As silver does not spark when subject to electrical charges, it is used as a solder in electronics and as electrical contacts. The most significant use of silver in electronics is in the preparation of thick-film, silver-palladium pastes for use as silkscreen circuit paths in multilayer ceramic capacitors, in the manufacture of membrane switches, silver film in

1.2 Silver Price and Production

In 2005, the silver price traded at an average $7.2 (U.S.) per ounce and continues to move higher at the beginning of 2006 trading at around $12 (U.S.) per ounce. The global mine production of silver also showed strong growth and the significant rise took global output to a record high of 633.2 Moz (19,731t) in 2004. The world’s four largest silver producers, namely, Mexico, Peru, Australia, and China accounted for the main increase and Chile further boosted the figure. World silver output by source metals is listed in Table 1-1 (after WSS, 2005). It shows that more than half of the silver production is coming as a by-product in lead, zinc and copper industry and more than 10% of the total silver is produced in gold processing industry.

1.3 Chemistry of Silver

The atomic mass of silver averages to 107.868 calculated based on that of the 25 known isotopes. The atomic number of silver is 47. Silver is the first element with a Krypton core and a full 4d electron shell. In addition, it has a single 5s electron which leads to the common univalent silver ion. Silver can be incorporated into complex compound, giving silver valences of 2+ and 3+, such as with fluoride and pyridine. Silver forms complexes more readily with sulfur, nitrogen or halogen atoms than with oxygen (Greenwood, 1997, and Wyslouzil & Salter, 1990).
<table>
<thead>
<tr>
<th>Source</th>
<th>2003, Moz</th>
<th>% of total</th>
<th>2004, Moz</th>
<th>% of total</th>
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<tr>
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<td>173.2</td>
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<td>75.6</td>
<td>12</td>
<td>74.4</td>
<td>11</td>
</tr>
<tr>
<td>Others</td>
<td>3.3</td>
<td>1</td>
<td>3.5</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>609.8</strong></td>
<td><strong>100</strong></td>
<td><strong>633.2</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Silver is not attacked by dilute hydrochloric or sulfuric acid and nor by strong alkali. It is dissolved completely and yields univalent $\text{Ag}^+$ ion in nitric acid and concentrated sulfuric acid. In slightly oxidizing conditions, silver may react with cyanide in alkaline media to form soluble anionic complex, $\text{Ag}^{\text{CN}}_2^-$, and react with thiosulfate ions to form $\text{Ag(S}_2\text{O}_3)_2^{3-}$. Silver may also react with thiourea in dilute acid in the presence of ferric ion to form cationic $\text{Ag[CS(NH}_2)_2]^+$(Hiskey & Atluri, 1988). Silver reacts readily with mercury to form amalgam $\text{Ag}_x\text{Hg}_y$. The silver ion can be readily reduced by formic acid, by ferrous or by less noble metals, such as zinc or aluminum.

### 1.4 Silver Extraction Process

Unlike gold, which almost always occurs naturally in metallic form (Marsden & House, 1995), silver is found in many minerals in variable concentrations. In fact, more than two-thirds of the world silver resources are associated with copper, lead, and zinc deposits, often
at great depth. The remaining reserves are in vein deposits in which gold is the most valuable metallic component. Flotation with or without leaching is applied directly to the silver minerals where the silver content in the ore is large enough to justify its recovery as a primary product. When silver is recovered as a by-product of copper, lead, zinc and gold mining, concentrating by flotation of those metals and subsequent smelting may be involved (Wyslouzil & Salter, 1990).

In most cases, silver is recovered along with the process of gold extraction which is predominately designed based on the gold mineralogy with the aim to obtain reasonable gold recovery rather than that of silver which in many cases is neglected. In the 19th century various high-grade gold and silver ores and concentrates were treated directly by pyrometallurgical methods, including direct fusion in a bath of lead and direct smelting with lead-rich fluxes. Amalgamation was the major recovery process for gold and silver before the invention of cyanidation process. Mercury was then removed from silver (gold)-mercury amalgamates by vaporizing and the resulting sponge precious alloy smelted with fluxes to produce metal bullion (Marsden & House, 1995).

The gravity process is the choice when ores with coarse metallic silver content are treated. This process is typically used as the first step to recover coarse gold or silver rather than as a single recovery method. Flotation is a good alternative as most of the silver minerals float well with sulfide collectors. But some difficulties were encountered in treating the finely
disseminated sulfide ores, as fine grinding is required to achieve some degree of liberation and strong depressing conditions are used to achieve selectivity (Hiskey & Atluri, 1988).

An earlier method of gold hydrometallurgy - chlorination was discovered and became a commercially available product in 1774. By the end of the 1860s, various chlorination processes were used in the USA, South America and Australia. But they soon gave the way to cyanidation after cyanidation process was introduced at the end of 19th century (Marsden & House, 1995).

The cyanidation process has been the most important process in the extraction of gold and silver from their ores for the past 100 years. Patented by MacArthur in 1888, the process involves gold and silver dissolutions in aerated cyanide solution to form metal-cyanide complexes. The well-known Elsner (1946) equation describes the stoichiometry of the reactions as following (Marsden & House, 1995),

\[
\begin{align*}
4\text{Ag} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} & = 4\text{Ag(CN)}_2^- + 4\text{OH}^- \quad \text{Reaction 1-1} \\
4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} & = 4\text{Au(CN)}_2^- + 4\text{OH}^- \quad \text{Reaction 1-2}
\end{align*}
\]

In the classical recovery process the pregnant liquid solution (PLS) which contains \(\text{Au(CN)}_2^-\) and \(\text{Ag(CN)}_2^-\) is recovered by solid-liquid separation and the precious metal may then be cemented by zinc powder (Merrill-Crowe process).

\[
2 \text{Ag(CN)}_2^- + \text{Zn} = \text{Zn(CN)}_4^{2-} + 2\text{Ag} \quad \text{Reaction 1-3}
\]
The problem that arises with the Merrill-Crowe process is the solid-liquid separation stage prior to cementation. This costly process usually results in approximately 1% metal loss in wash solutions.

At a latter time the Carbon-in-Pulp (CIP) and Carbon-in-Leach (CIL) processes were developed and become widely adopted by industry. Though the mechanism of adsorption remains unclear, the CIP process in practice is relatively simple and has three main steps, namely adsorption, elution and electrowinning. A typical flowsheet for a cyanidation plant is shown in Figure 1-1.

Figure 1-1 Typical flowsheet for cyanidation plant incorporating cyanide leaching and carbon in pulp adsorption as the recovery process
Though cyanide leaching is a simple process with high selectivity and effectiveness, the obvious drawback lies in the use of extremely toxic cyanide in the leaching solution and the possibility of discharge effluents which have the potential of causing serious environmental problems. A number of alternative lixiviants including thiourea, thiosulfate and ammonia have been studied with the aim to develop less or nontoxic lixiviants and in some cases, to treat complex refractory gold-silver ores. But unfortunately these lixiviants are still limited to the laboratory stage and are far away from widespread practice, due to either the low effectiveness or the high operation costs.

1.5 Issues of Concern

Due to the wide application of cyanide leaching, the gold cyanidation process has been studied on numerous occasions at both industrial and laboratory scale. The thermodynamics and mechanism of kinetics have been studied by many researchers since the cyanidation process emerged. There are still some disputes on the leaching mechanism for gold and unfortunately relatively less attention has been paid to silver.

Conventional extraction results revealed that the relative dissolution rate of silver is noticeably lower than that of gold under the typical cyanidation conditions. Sometime silver extraction is only about half of that of gold in heap leaching operations (Hiskey, 1983). Compared with that measured in electrochemical systems, the relevant results are controversial. Some claimed that the silver dissolution rate is much faster than gold and some believed it is slower (Jeffrey, 1997, Luna-Sanchez & Lapidus, 2000, and Wadsworth, 2000).
The different mineralogy and mode of occurrence between silver and gold in natural ore were suspected as the possible reasons to explain the respective findings. Due to the complicated silver mineralogy, typically the occurrence of silver sulfides, argentojarosites, and manganese minerals, the leaching rate and overall extraction of silver will strongly depend on the ore mineralogy.

In this thesis, a novel leaching system, ferricyanide-cyanide system has been investigated to extract silver from silver sulphide with the purpose of increasing silver extraction from gold-silver bearing ore. Silver mineralogy and cyanide leaching process are reviewed in detail in Chapter 2. The study on the dissolution of pure silver sulfide and gold in the presence of ferricyanide is described in Chapter 3. The study on comparative leaching of Veladero and Pierina gold-silver ores (from Barrick Gold Corporation) is presented in Chapter 4. Finally, some conclusions and recommendations are summarized in Chapter 5.
Chapter 2 Literature Review

2.1 Silver Mineralogy

Silver may combine with sulfur, tellurium and selenium in covalent bonds and with chlorine, bromine and iodine in ionic bonds. Silver also combines with arsenic, antimony, lead, bismuth, tin, mercury and indium, etc in many instances as a minor element in sulfides, sulphosalts, and native element minerals. Cations which silver replaces to a lesser extent than copper and gold are iron, manganese, zinc, and probably nickel and cobalt. There are over 200 minerals bearing silver in major, minor and variable amounts as has been well classified by Gasparrini (1984). Of these minerals only 10 to 12 are economically important. The most common silver-bearing minerals include native silver (Ag), electrum (Ag-Au), acanthite (Ag₂S), and pyrargyrite (Ag₃SbS₃). Tetrahedrite ((Cu, Ag, Fe)₁₂Sb₄S₁₃) and other minerals such as barite (BaSO₄), chlorite ((Fe, Mg, Al)₆(Si, Cl)₄O₁₀(OH)₈), and covellite (CuS) may contain silver in variable amounts. Silver appears to be most commonly associated with lead and copper minerals, such as galena (PbS) and chalcopyrite (CuFeS₂), secondary copper minerals, native gold and electrum, and tends to occur in veins with carbonate minerals with barite as gangue. Silver-bearing minerals also occur in pyritic ores, but in many such occurrences their concentration is too minor to be economic (Zeng, et al., 2000 and Gasparrini & Lowell, 1983).

The type of associations of the silver and the host minerals varies. Galena-tetrahedrite associations are characterized by intergrowths and totally enclosed particles. Associations
with other host minerals are mostly dependent on the general textual features of the ore. Silver deposits and mineral assemblages are well summarized by Boyle (1968). According to Boyle, the greatest silver concentrations are in hypogene veins, lodes, and stock works. Appreciable secondary silver enrichment may occur in near-surface parts of some of these veins because of supergene oxidation process. Silver also commonly occurs in gold placers, veins and lodes. The grain size of silver-bearing minerals is usually less than 100 microns and silver occurs totally enclosed in their host minerals, in fractures, or along grain boundaries. A larger grain size may occur up to 1mm with higher silver grades, e.g., 1-2 percent (Foley, et al, 1993).

As the mineralogical factors including the silver-bearing minerals and their grain size, host minerals and their association affect silver extraction process, some problems (e.g., low silver recovery) were often caused during the leaching of the silver-bearing minerals.

2.2 Silver Cyanidation Chemistry

2.2.1 Thermodynamics

The thermodynamics of gold, silver, and their host minerals dissolution in cyanide solution have been studied by many researchers. Most of research focused on investigating the equilibrium relationships in Me-CN-H₂O system. Different Pourbaix diagrams were established based on different cyanide and metals concentrations, pH, and electrochemical potential. From the early research on the lower potential region (Eh<400mV, SHE) of Ag-CN-H₂O system (Deitz & Halpern, 1953), to the recent research with the aid of computer
program, varied logarithmic activity–activity diagrams, such as log[Me]-pH and log[CN]-pH diagrams were developed to show the predominance of different species and solid/solution equilibrium in the metals-cyanide system to explain the behavior of metals in cyanide solution (Osseo-Asare, et al. 1984).

2.2.1.1 Silver-cyanide-water system

Xue & Osseo-Asare (1985) constructed an Eh-pH diagram for pure silver at 25 °C under the condition of the dissolved silver species having a concentration of $10^{-4}$ M. Like gold, metallic silver has great chemical stability at all pHs in the absence of oxidizing agents and complexing ligands. Native silver is thus one of the most common silver mineral in nature just as is native gold. Silver is univalent in most of its important compound and in aqueous solution the (+1) oxidation state of silver is stable (Hiskey & Atluri, 1988). Figure 2-1 shows the Eh-pH diagram for Ag-H$_2$O system in which the dissolved silver species is set at $10^{-3}$ M.

Figure 2-2 shows the Eh-pH diagram of silver in the presence of cyanides. Xue and Osseo-Asare (1985) calculated some heterogeneous equilibria in Au-CN-H$_2$O and Ag-CN-H$_2$O system. The authors concluded that gold and silver behave similarly in cyanide solution and their cyanide complexes are very stable in the presence of oxygen. Au(CN)$_2$ and Ag(CN)$_2$ are the main complexes ions and in case of depleted cyanide, solid AgCN and AuCN may be formed. The higher complexes, Ag(CN)$_3$ and Ag(CN)$_4$ are stable at high cyanide concentration. The activity-activity diagram indicates that gold is more stable than silver in acidic cyanide free solution and more active than silver in cyanide solution.
Figure 2-1 Eh-pH diagram for Ag-H₂O system at 25 °C ([Ag] = 10⁻³ M)
Figure 2-2 Eh-pH diagram for Ag-CN-H\textsubscript{2}O system at 25 °C
(a) $[\text{Ag}] = 10^{-2} \text{ M}$, $[\text{CN}] = 1 \text{ M}$
(b) $[\text{Ag}] = 1 \text{ M}$, $[\text{CN}] = 10^{-3} \text{ M}$
2.2.1.2 Silver-sulfur-cyanide system

Considering the variety of silver minerals, it is obviously not enough to predict silver dissolution behaviors just based on the thermodynamic calculations of silver-cyanide-water system. For the more common silver minerals, such as silver sulphides (Ag₂S), the dissolution reaction is described by the following reactions,

\[ \text{Ag}_2\text{S}(s) + 2n \text{CN}^- = 2\text{Ag(CN)}_{(n-1)^-} + \text{S}^{2-} \]

where \( n \) is 1, 2, 3, or 4. Reaction 2-1

According to Davis (1962), and Luthy & Bruce (1979), the reactions among cyanide and sulfur species under oxidizing atmosphere could be described as following;

Oxidation of sulfide ion:

\[ \text{S}^{2-} \rightarrow \text{S}_2^{2-} \rightarrow \text{S} \rightarrow \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} \]

Oxidation of cyanide,

\[ \text{CN}^- \rightarrow (\text{CN})_2 \rightarrow \text{CNO}^- \]

And the oxidation of cyanide to thiocyanate (SCN⁻) is considered as,

\[ \text{CN}^- + 1/8 \text{S}_8 = \text{SCN}^- \] Reaction 2-2

\[ \text{CN}^- + \text{S}_2\text{O}_3^{2-} = \text{SCN}^- + \text{SO}_3^{2-} \] Reaction 2-3

\[ \text{CN}^- + \text{S}_x^{2-} = \text{SCN}^- + \text{S}_{x-1}^{2-} \] Reaction 2-4

where \( x \) is 1 to 6.
The Eh-pH diagram of Ag-S-CN-H2O system is shown in Figure 2-3. Zhang, et al (1997) presented a revised diagram of predominance/distribution of silver species in the Ag-S-CN-O2-H2O system. They pointed out that their results are based on the assumption that sulphide ions should be completely oxidized into more stable species with higher oxidation state, e.g., SO$_4^{2-}$. The experiment results, however, do not always confirm the above prediction, e.g. when a silver sulfide-bearing gold ore is treated in cyanide process, silver dissolution is often lower than 30%, compared to the gold dissolution which is generally more than 90%. It is believed that Ag$_2$S would be a predominant solid silver compound instead of Ag(s), AgCN(s) or Ag$_2$O, even in the presence of a much higher concentration of CN$^-$. This is due to the low
solubility of sulfide minerals in aqueous solution. The solubility of metal hydroxides and sulfides versus pH is shown in Figure 2-4. Obviously the solubility of sulfide minerals decreases with the increase of pH (Palmer, S. A. K., et al. 1988).

Considering the following equilibria,

\[ \text{Ag}_2\text{S} = 2\text{Ag}^+ + \text{S}^{2-} \quad \log K_{sp} = -50.1 \]  

\[ \text{Ag}^+ + 2\text{CN}^- = \text{Ag(CN)}_2^- \quad \log K = 20.2 \]

Figure 2-4 Solubility of metal hydroxides and sulfides as a function of pH (after Palmer, S. A. K., et al. 1988)
\[ \text{Ag}_2\text{S} + 4\text{CN}^- = \text{Ag(CN)}_2^- + \text{S}^{2-} \quad \log K = -10.1 \]

It is evident that the equilibrium constant of dissolution of silver sulfide is rather small. Silver dissolution in cyanide solution would be limited by the solubility of silver sulfides and the extent of sulfide oxidation. This would suppress the extraction of silver through the cyanide leaching process.

### 2.2.1.3 Silver bearing metal sulfides-cyanide system

As gold and silver ore usually co-exist with many other minerals, especially the multi-metals/sulfides, e.g., sphalerite(ZnS), chalcopyrite(CuFeS₂), and pyrite(FeS₂), the more complicated Ag-Me-S-CN-H₂O(Me is Cu or Fe) system was constructed by Zhang, et al., 1997. The role of metal-cyanide species, including silver cyanide species, was usually concerned with the purpose of increasing gold extraction rather than silver extraction (Liu & Yen, 1995). Little information on the impact of sulfides mineral on silver recovery was published as silver is generally a by-product of gold cyanidation. From the point of view of thermodynamic, it is not necessary to consider the Eh-pH diagram of the relevant base metal sulfides-cyanide system in gold cyanidation process since the dissolution of these minerals is not required (Zhang, et al., 1997). For example, the predominance region of gold cyanide species in Eh-pH diagram is not affected by the presence of copper or iron. The situation changes greatly while considering silver cyanidation process. The rate of silver cyanidation may be limited by the dissolution of copper and iron sulfide minerals (Zhang, et al., 1997). This is due to preferred dissolution of the copper and iron sulfide. But it should be pointed out that in practice, the effect of sulfide minerals on gold extraction sometimes are critical,
e.g., copper sulfides are always detrimental to gold leaching, either as cyanicides or as dissolved oxygen consumption species (Wang & Forssberg, 1990).

2.2.1.4 Common metal-cyanide system

The role of the co-existing metals which form metal-cyanide complexes makes the cyanidation process more complicated. The behavior of the associated sulfide minerals and their cyanide complexes also influence the silver dissolution, especially the silver sulfide dissolution in cyanide solutions (Vinals, et al. 1995). Some associated metals (and/or sulphides) differ greatly in the formations and reactions with cyanide species. For example, Rees and Deventer (1999) studied the role of metal cyanide species in leaching gold from a copper-rich gold concentrate and found that copper cyanide, zinc cyanide, nickel cyanide and ferrous cyanide can be used to leach gold from copper concentrate. Therefore, it is necessary to understand in some extent the behaviors of these metals/sulfides in cyanide solution in order to optimize the silver cyanidation process.

Metals cyanide complexes can be simply classified with respect to their reactivity with acid as “weak-acid-dissociable (WAD) or “non weak-acid-dissociable” (non-WAD). According to the thermodynamic data, a more accurate classification is as follows (Flynn, 1995).

WAD: Zn, Cd, Ni, Mn, Cr

Partially-WAD: Hg, Cu(I), Ag, Au (I)

Non-WAD: Au(III),Co, Fe
The combination of cyanide and zinc or cadmium is so weak that sometime these cyanide complexes are classified as free cyanide as these complexes easily release CN⁻ in depleted cyanide solution (Luthy & Bruce, 1979). Reaction involving the cyanide complexes of copper and gold is usually conducted in +1 state. The anionic cyanide complexes of copper are rapidly decomposed by acid to form the insoluble binary cyanide, CuCN(s), and so is that of silver. The most stable metal cyanide complexes are cobalt (II) and iron cyanide complexes.

In terms of equilibrium constants for their formation, many metal cyanide complexes are stronger than metal complexes with most other ligands (Luthy & Bruce, 1979). Theoretically soluble sulfides can precipitate silver sulfide (Ag₂S) from solution of its anionic cyanide complexes. For copper and nickel, their sulfides can be obtained from cyanide solution by using H₂S. However, Co(II/III) or Fe(II/III) cyanide complexes are so stable that alkaline sulfides do not precipitate their sulfides. Of particular interest during cyanidation of common gold and silver ore are iron and its sulfides which occur as pyrite (FeS₂), pyrrhotite (Fe₇S₈), and chalcopyrite (CuFeS₂) etc. The Eh-pH diagram of iron-cyanide-water system is shown in Figure 2-5. Over the near-neutral to alkaline pH range the stable compound hexacyanoferrate(II) (Fe(CN)₆⁴⁻) and hexacyanoferrate(III)(Fe(CN)₆³⁻) are formed. Under typical cyanidation process conditions, the reaction of Fe (II) salts with CN⁻ to form [Fe(CN)₆]⁴⁺ is rapid. The formation of hexacyanoferrate(II) is typically faster than the formation of hexacyanoferrate(III) and hexacyanoferrate(II) is more prevalent than hexacyanoferrate(III) (Osseo-Asare, et al 1984)
and Zhang, et al. 1997). A proposed pyrite dissolution reaction in cyanide solutions is as following:

\[
\text{FeS}_2 + 6\text{CN}^- = \text{Fe(CN)}_6^{4-} + \text{S}_2^{2-} \quad \text{Reaction 2-8}
\]

Figure 2-5 Eh-pH diagram of Fe-CN-H$_2$O system at 25 °C ([Fe] = 10$^{-2}$ M)
Under the oxidizing conditions, the sulfides can further be oxidized to form sulfur, thiosulfate or sulfate. Aghamirian (1997) proposed that hexacyanoferrate(III)($\text{Fe(CN)}_6^{3-}$) can be used to oxidize gold in cyanide solution;

$$\text{Au} + \text{Fe(CN)}_6^{3-} + 2\text{CN}^- = \text{Au(CN)}_2^- + \text{Fe(CN)}_6^{4-}$$

Reaction 2-9

And under more strong oxidizing conditions, such as in the presence of HClO, H$_2$O$_2$, and O$_2$, Fe($\text{CN}$)$_6^{4-}$ can be further oxidized to form Fe($\text{CN}$)$_6^{3-}$ (Palmer, S. A. K., 1988). The standard reduction potentials of some metal cyanide species at 25°C are listed in Table 2-1. It shows that zinc could in theory cement metallic Au, Ag, Cu, Cd, Ni, and Co from cyanide solution, but may not react with [Fe($\text{CN}$)$_6$]$^{4-}$. If there is any [Fe($\text{CN}$)$_6$]$^{3-}$ in the solution, it may be reduced to [Fe($\text{CN}$)$_6$]$^{4-}$ by zinc (or by any reduction agent with a potential less than 0.36 V)

Table 2-1 Standard reduction potential of some metal cyanide species at 25 °C (calculated based on the thermodynamic data in CRC Handbook 1975)

<table>
<thead>
<tr>
<th>Half reactions</th>
<th>$E^{0}/v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe(CN)}_6^{3-} + e = \text{Fe(CN)}_6^{4-}$</td>
<td>+0.36</td>
</tr>
<tr>
<td>$\text{Ag(CN)}_2^- + e = \text{Ag(s)} + 2\text{CN}^-$</td>
<td>-0.41</td>
</tr>
<tr>
<td>$\text{Au(CN)}_2^- + e = \text{Au(s)} + 2\text{CN}^-$</td>
<td>-0.49</td>
</tr>
<tr>
<td>$\text{Cd(CN)}_4^{2-} + 2e = \text{Cd(s)} + 4\text{CN}^-$</td>
<td>-0.93</td>
</tr>
<tr>
<td>$\text{Cu(CN)}_3^{2-} + e = \text{Cu(s)} + 3\text{CN}^-$</td>
<td>-1.09</td>
</tr>
<tr>
<td>$\text{Cu(CN)}_4^{2-} + 2e = \text{Cu(s)} + 4\text{CN}^-$</td>
<td>-1.18</td>
</tr>
<tr>
<td>$\text{Ni(CN)}_4^{2-} + 2e = \text{Ni(s)} + 4\text{CN}^-$</td>
<td>-1.12</td>
</tr>
<tr>
<td>$\text{Zn(CN)}_4^{2-} + 2e = \text{Zn(s)} + 4\text{CN}^-$</td>
<td>-1.34</td>
</tr>
<tr>
<td>$\text{Fe(CN)}_6^{4-} + 2e = \text{Fe(s)} + 6\text{CN}^-$</td>
<td>-1.52</td>
</tr>
</tbody>
</table>
2.2.2 Mechanism and Kinetics

2.2.2.1 Methods of kinetics research

The cyanidation kinetics of gold and silver has been studied by many researchers since cyanidation began to be commercialized at the end of 19th century. Some basic techniques to investigate leaching rate were developed and are summarized as follows.

(a) Agitation solution

As a most classical leaching method, the agitated cyanide solution (usually oxygenated) has been applied to measure gold or silver dissolution rate. Usually the test species are metallic gold or silver, or the relevant minerals particles. The leaching test can be conducted in rolling bottles or stirring tanks with impellors and with gas sparging.

Though this method is the cheapest and easiest way to study the leaching kinetics, it is limited to the particular experimental design and can only give reasonable reproducible results in the same equipment system. It is hard to determine the rate controlling steps in the leaching process (diffusion control or reaction control).

(b) Rotating disc

In this method, the targeted metal (or mineral) is manufactured to form a cylinder with a flat disc surface which is rotated about its central axis. Usually epoxy resin is coated on the cylinder to form an inert surface with only one flat disc surface exposed to the leaching solution. The advantage of the rotating disc system is that the flux of reactant to the disc
The surface can be calculated based on the theoretical mathematical expression—Levich equation, which shows that the flux is function of $\omega^{1/2}$ (Levich, 1962):

$$J = 0.62 D_0^{2/3} \nu^{-1/6} \omega^{1/2} C_0$$

Where, $J$ – the flux of reactant O, mol m$^{-2}$ s$^{-1}$

$D_0$—the diffusion coefficient of reactant O, m$^2$ s$^{-1}$

$\nu$ – the kinematic viscosity of the solution, mol m$^{-3}$

$C_0$ – the bulk solution concentration of reactant O, mol m$^{-3}$

The most important feature of the rotating disc system is the "uniformly accessible surface" which means the rate of mass transport to the surface of disc is uniform. The critical condition required by the rotating disc system in kinetic studies is to maintain a laminar flow in which the Reynold's number ($N_{Re} = r^2 \omega / \nu$) is greater than that for natural convection but less than that for turbulence (the critical value is $10^5$).

(c) Rotating cylinder

Similar to the rotating disc, the rotating cylinder is also rotated about its central axis, but with the curved cylinder surface exposed to the leaching solution rather than a disc surface. The advantage over the rotating disc lies in the fact that the surface area of the cylinder enjoys the same linear velocity during the leaching process. But the critical disadvantage compared to the rotating disc is that there is no mathematical solution to the mass transfer flux to the cylinder surface. However, under certain conditions, provided the flow is turbulent, the flux
can be represented by the following equation (Eisenberg, et al, 1954) which is similar to
Levich equation:

\[ J = 0.079 u^{0.7} D_0^{0.644} \nu^{0.344} d^{-0.3} C_0 \]

Where, \( u \) – peripheral velocity of the cylinder, m \( s^{-1} \)
\( d \) – diameter of the cylinder, m

the other parameters are the same as those defined in the Levich equation.

2.2.2.2 Oxygen reduction

Due to the electrochemical nature of gold and silver cyanidation process, it is important to
examine the mechanism and kinetics of the cathodic reduction of oxygen on gold and silver
surface, which may consequently limit the cyanidation rate. Hiskey and Sanchez (1990)
believed that the general sequence of steps for oxygen reduction as shown in Figure 2-6,
where (b) (i) and asterisk represent bulk, interface, and adsorbed \( \text{O}_2 \) concentration,
respectively.

\[
\begin{align*}
\text{O}_2(b) & \quad \rightarrow \quad \text{O}_2(i) \\
\text{O}_2(i) & \quad \leftrightarrow \quad \text{O}_2^* \\
\text{O}_2^* & \quad \leftrightarrow \quad \text{HO}_2^- \\
& \quad \downarrow \ 4e \hspace{1cm} \downarrow \ 2e \\
& \quad \rightarrow \quad \text{OH}^{-} \\
\end{align*}
\]

Figure 2-6 General sequence of oxygen reduction (after Hiskey and Sanchez 1990)
Mechanistic models for oxygen adsorption at a metal surface and subsequent oxygen reduction pathways are shown in Figure 2-7 (Fischer & Heibaum, 1980). In the Griffith model both oxygen atoms in the oxygen molecule bond to a central metal atom, while in the bridge model each of the oxygen atoms bond to different metal atom just like bridged complexes. In the Pauling model only one oxygen atom bond to one metal atom in an 'end-on' manner.

As oxygen discharge at gold and silver surface during cyanidation falls in the range of two to four electrons per mol $O_2$, two pathway of oxygen reduction were proposed (Hiskey and Sanchez 1990). One is the direct 4e path;

$$O_2 + 2H_2O + 4e = 4OH^-$$ \hspace{2cm} \text{Reaction 2-10}

And the other is 2e sequential path involving the formation of hydrogen peroxide ions as an intermediate product which is further reduced to yield $OH^-$;

$$O_2 + H_2O + 2e = HO_2^- + OH^-$$ \hspace{2cm} \text{Reaction 2-11}

$$HO_2^- + H_2O + 2e = 3 OH^-$$ \hspace{2cm} \text{Reaction 2-12}
2.2.2.3 Dissolution of native silver

The kinetics and mechanism of gold and silver cyanidation has been the subject of numerous investigations and much more attention has focused on the factors influencing the leaching kinetics of gold than that of silver. As early as 1934, Barsky, et al examined the kinetics of the dissolution of pure gold and pure silver in cyanide solution. They reported the maximum rates of gold and silver dissolution in a 0.01 M NaCN solution at 25 °C were 4.58 ×10⁻⁹ mol cm⁻² s⁻¹ and 3.42 ×10⁻⁹ mol cm⁻² s⁻¹ respectively. But the rate of silver dissolution in dilute NaCN solution (0.002M) was approximately 3.5 times greater than that of gold dissolution. Deitz and Halpern (1953) examined the kinetics of silver dissolution under various oxygen pressures. They found that at 5.5 ×10⁻² M NaCN and 24°C, the rate of silver dissolution
followed a first-order dependence on oxygen partial pressure. At low cyanide concentrations, the rate was independent of the oxygen partial pressure. While $P_{O_2}$ is at 1 atm, 24 °C, and NaCN concentration at $3.5 \times 10^{-2}$ M, the rate of silver dissolution was determined to be $9.66 \times 10^{-9}$ mol cm$^{-2}$ s$^{-1}$. Some research results tend to support that the dissolution rate is controlled by surface reactions (Jeffrey, 1997 and Wadsworth, 2000). For the purpose of comparison, sometimes silver dissolution kinetics was examined to illustrate the dissolution mechanism or to compare with the leaching behaviors of gold.

Though the earlier studies of the rate of precious metal dissolution in cyanide solution by Christy (1900) and Thompson (1991) both suggested the electrochemical nature of the reaction, the two landmark works on pure gold(silver) cyanidation kinetics should be attributed to Kudryk and Kellogg (1954) and Habashi (1967) both of who supported diffusion control theory. And it was Kudryk and Kellogg (1954) who for the first time implemented a rotating gold electrode system to study the rate-controlling factors by conducting current-potential curves for the anodic and catholic reactions. The typical anodic and cathodic reactions of gold cyanidation were suggested as following:

**Anodic:** $Au + 2CN^- = Au(CN)_2^- + e$  \hspace{1cm} Reaction 2-13

**Cathodic:** $O_2 + 2H_2O + 4e = 4OH^-$  \hspace{1cm} Reaction 2-14
They concluded that gold dissolution rate is controlled either by oxygen diffusion or by cyanide diffusion to the gold surface and that the dissolution rate then could be increased by the usual factors which can increase diffusion rates: increased agitation, diffusion-limited reactant concentration, and temperature. Hydroxyl ion rather than peroxide was believed to be the product of oxygen reduction in gold cyanidation process. A fundamental electrochemical model of gold cyanidation kinetics was also established to predict gold dissolution rate and controlling step by means of current-potential curves.

Habashi (1967) also studied the electrochemical nature of gold and silver cyanidation, and suggested that oxygen was reduced to form peroxide at the cathodic zone. Dissolution rate of gold (silver) could be expressed as,

\[ r = 2AD_{CN}D_{O_2} [CN][O_2]/\delta \{D_{CN}[CN^-] + 4D_{O_2}[O_2]\} \]

Where, \( r \) – rate, mol m\(^{-2}\) s\(^{-1}\)

\( D_{O_2} \) - diffusion coefficient of oxygen, mol s\(^{-1}\)

\( D_{CN} \) - diffusion coefficient of CN\(^-\), mol s\(^{-1}\)

\([CN^-]\) - concentration of CN\(^-\), mol m\(^{-3}\)

\([O_2]\) – concentration of oxygen in solution, mol m\(^{-3}\)

\( \delta \) – thickness of the boundary layer, m

According to this expression, it is obvious that the dissolution rate of Au and Ag depends only on the cyanide concentration at low cyanide concentration and depends only on oxygen
concentration while at low oxygen concentration. It was the ratio of concentration of free cyanide and oxygen concentration that dominates the cyanidation kinetics and theoretically the maximum dissolution rate occur at [CN']/[O2] equal to 6.

A further study on the mechanism and kinetics of silver cyanidation was conducted by Hiskey and Sanchez (1990) who analyzed the factors influencing the dissolution kinetics of pure silver in cyanide solution in terms of electrochemical mechanism. Like gold, the anodic oxidation of silver at various cyanide concentrations follows the mixed kinetic model involving coupled mass transfer and charge transfer which could be simply expressed as,

\[
\frac{1}{i_a} = \frac{1}{K_d[CN]} + \frac{1}{K_a[CN] \exp(-\frac{E_a}{2RT})}
\]

where, \(i_a\)—anodic current density, A
\(K_a\)—the charge transfer rate constant, mol m\(^2\) s\(^{-1}\)
\(K_d\)—the diffusion rate constant of cyanide, mol m\(^2\) s\(^{-1}\)
\(E_a\)—anodic overpotential, v
\([CN]\)—cyanide concentration, mol m\(^3\)
\(R\)—the universal gas constant, J K\(^{-1}\) mol\(^{-1}\)
\(T\)—Temperature, K

A diffusion coefficient of \(1.77 \times 10^{-5}\) cm\(^2\) s\(^{-1}\) for cyanide was determined from the results of their investigations. They suggested that the fundamental difference between the dissolution rates of gold and silver in cyanide solution was attributed to the different oxygen reduction pathways. It was found that the discharge of oxygen at a silver surface is markedly different from that on a gold surface. Silver proceeds by a four-electron direct path instead of the two-electron path for gold. And oxygen adsorption follows a Freundlich isotherm on silver.
surface and a Langmuir isotherm on gold surface. Based on these findings, under typical cyanidation conditions silver dissolves at a rate slower than gold, though the anodic oxidation of gold and silver exhibits essentially the same behavior.

Li and Wadsworth (1993) conducted an electrochemical study on silver dissolution in cyanide solutions. Rate processes of the anodic dissolution of silver were examined by using a rotating disk electrode. They suggested that the silver dissolution may be separated into two elementary steps: an electrochemical reaction followed by a chemical reaction which could be expressed as following;

\[
\begin{align*}
\text{Ag} + \text{CN}^- &= \text{AgCN} + e^- \quad \text{Reaction 2-15} \\
\text{AgCN} + \text{CN}^- &= \text{Ag(CN)}_2^- \quad \text{Reaction 2-16}
\end{align*}
\]

A combined Butler-Volmer and Levich equation was used to calculate the dissolution rate. The diffusion coefficients of cyanide ions in 0.5 M KNO₃ solutions (pH = 11, [Ag] = 5×10⁻⁵ M and [CN] = 5×10⁻⁴ - 1×10⁻² M) was found to be 1.6×10⁻⁵ cm² s⁻¹ and the activation energy was 13.7 kJ/mol. The apparent exchange current density in the solutions has an activation energy of 21.1 kJ/mol and the transfer coefficient is close to 0.5 but changes with temperature falling in the range 0.46- 0.53.
Obviously these findings are different from the anodic dissolution mechanism of gold proposed by Kirk, et al (1979) who suggested that gold oxidation occurs in three steps at the region of overpotential -400mV:

Step 1: \( \text{Au} + \text{CN}^- = \text{AuCN}_{\text{ads}}^- \)  
Reaction 2-17

Step 2: \( \text{AuCN}_{\text{ads}}^- = \text{AuCN}_{\text{ads}} + e \)  
Reaction 2-18

Step 3: \( \text{AuCN}_{\text{ads}} + \text{CN}^- = \text{Au(CN)}_2^- \)  
Reaction 2-19

And it was believed that the rate of gold oxidation is controlled by the second step (Pan & Wan 1979 and MacArthur, 1972) which were further studied and confirmed by Savaguchi et al., (1995).

Dorin and Woods (1990) determined the leaching rates of gold, silver, palladium and platinum in cyanide solution according to the corrosion potential and voltammograms of the anodic oxidation reaction, and proved that the order of reactivity was \( \text{Au} > \text{Ag} > \text{Pd} > \text{Pt} \). The leaching rate was a maximum at about pH = 10 for each metal. Choi, et al (1991) studied the dissolution behavior of Ag/Au alloy in cyanide solutions and suggested that the silver and gold dissolution rate is partially controlled by surface chemical reaction but largely by solution mass transfer. The activation energies were in the range from 20.1 to 28.6 kJ/mol and from 22.2 to 29.4 kJ/mol for silver and gold components respectively. Sun, et al (1996) examined the anodic and cathodic behaviors of pure silver and gold-silver alloys in aerated cyanide solutions using the potentiodynamic method and found that the anodic dissolutions of pure silver and Au/Ag alloys initially increase with an increase of the overpotential and then exhibit a limiting current. Cathodic reductions of oxygen on pure silver and Au/Ag alloys
took place in two stages and the difference between the two stages increases with the increase of the gold concentration in the alloys. They concluded that the dissolution rate of pure silver (and Ag/Au alloys) was generally limited by the transport of either oxygen or cyanide and in some cases, it was mixed controlled.

### 2.2.2.4 Dissolution of silver sulfides

The cyanidation kinetics of argentojarosite was examined by Cruells, et al (2000) and a shrinking core model in different alkaline media was developed. They found that the cyanidation of argentian potassium jarosite in alkaline media was characterized by an induction period followed by a conversion period as was observed in other synthetic jarosites. A chemical reaction control process were suggested with the activation energy 43 kJ/mol in NaOH-CN- system and 80 KJ/mol in Ca(OH)$_2$-CN system, respectively.

Roca, et al (2003) studied the kinetics of alkaline decomposition of argentojarosite with two-step process in series, induction period and conversion period. They claimed that decomposition curves show an induction period which is dependent on particle size and decreases exponentially with the increase of temperature. The conversion period is characterized by the creation of a reaction of hydroxides around an unreacted jarosite core. The kinetic data indicate a chemical control process.

Luna-Sanchez and Lapidus (2000) studied the kinetics of the dissolution of silver sulfides in cyanide solution by using the synthetic silver sulphide. They assumed that the formation of
SCN⁻ in cyanide solution is attributed to the reaction of CN⁻ with solid sulfur, dissolved Sₓ²⁻ or S₂O₃²⁻ formed by oxidation of sulfide minerals, e.g. by dissolved oxygen (Greenwood, 1997). However, the extent of the sulfide oxidation is limited by kinetics rather than by thermodynamics. It results in only one of several sulfur species that can exist in cyanidation process, e.g., only thiosulfate ion (S₂O₃²⁻). The stoichiometric relation was suggested to be expressed as following (Luna-Sanchez and Lapidus, 2000);

\[ \text{Ag}_2\text{S(s)} + 4\text{CN}^- + 1/2\text{H}_2\text{O} + \text{O}_2 = 2\text{Ag(CN)}_2^- + \text{S}_2\text{O}_3^{2-} + \text{OH}^- \] Reaction 2-20

They claimed that the only sulphide species detected in the cyanide solution was the S₂O₃²⁻ when pure oxygen and a 0.01M NaCN solution were applied. The mechanism of the reaction was found following the direct formation of hydroxyl ions without proceeding through hydrogen peroxide. Comparison tests were conducted in which silver sulfide bearing concentrates were leached. At the condition of constant temperature and ambient pressure (20 °C and 1 atm), the silver extraction rate increases when the cyanide concentrations varied from 0.001 M to 0.3 M. This is different than in the case of pure silver where a maximum stable extraction value is reached at a relatively low cyanide concentration. A mathematical model was developed based on the calculations on the redox reaction and complex equilibria in solution phase. They believed that the leaching of silver sulfide was kinetically controlled by a second order reaction relative to a local oxygen and sulfide ion concentrations.

An integrated approach using SEM and electrochemical analysis was applied by Luna-Sanchez, et al (2002, 2003) to evaluate the leaching behaviors of silver in cyanide solution.
from a silver sulfide (acanthite) bearing concentrate. Silver mineralogy of the concentrate and the leached residue was analyzed by SEM and it was found that 97% acanthite (Ag$_2$S) is leachable with cyanide. Cyclic voltammetric method was employed to determine the mechanism of the dissolution of carbon paste electrode made of the electro-active species—silver sulfide concentrates. The differences between the oxidation behavior of the high pure acanthite concentrate and the analytical silver sulfide in cyanide solution were analyzed according to the Evans diagram and the leaching results of the stirred tank leaching process. They observed that the oxidation of acanthite is mixed reaction-diffusion controlled while that of analytical silver sulfide solely diffusion controlled.

### 2.2.3 Optimization of cyanidation

Numerous researches were conducted with the aim to raise the gold and silver cyanidation rate and to optimize cyanidation process. According to the mechanism and kinetics of gold and silver cyanidation, most relevant studies focused on the effect of cyanide and oxygen ratio, additives (e.g. soluble lead salts) and the associated minerals.

Heath and Rumball (1998) used a gold and silver alloy (96% Au and 4% Ag) disc electrode which was put in the leaching pulp to determine the optimum oxygen and cyanide ratio. The authors suggested that cyanide and dissolved oxygen ratio should be kept at 10.5 ppm : 1 ppm. Ellis and Senanayake (2003) studied the effect of dissolved oxygen and cyanide dosage
on gold extraction from a pyrrhotite rich ore and confirmed that pre-oxidation and appropriate \([\text{CN}]/[\text{O}_2]\) ratio during cyanidation is critical to achieving good leaching kinetics.

The electrochemical interactions between gold and its associated mineral during cyanidation were examined by Lorenzen and Deventer (1992). They concluded that minerals such as chalcopyrite, pyrite, and pyrrhotite cause a significant decrease in the rate of gold dissolution; Lead ions increase the rate of dissolution of gold at low concentration but retard the leaching rate at higher concentration. Deschenes et al (1998) investigated the effect of the composition of sulfide minerals on cyanidation and confirmed that the cyanidation process of sulfide-bearing ore is related to the mineralogical compositions. Pre-leaching process is effective for diminishing high cyanide consumption caused by pyrrhotite but has no beneficial effect on chalcopyrite bearing ores.

Tshilombo and Sandenbergh (2001) suggested that the addition of small amount of lead nitrate to aqueous cyanide solution significantly increase the anodic activity of gold at a potential just positive over the reversible potential. Sulfides in solution decrease the anodic activity of the gold in the active region but increase it at the potential where gold would normally be passive. Jeffrey, et al (2000) believed that it was the presence of hydrosulfide in cyanide leaching solution that results in the formation of passive layer of sulfur on the gold surface which significantly reduces gold cyanidation rate. The main role of lead is to catalyze the oxidation of hydrosulfide ions. Jeffrey and Richie (2000) claimed that silver can
significantly increase gold leaching rate and they believed that silver enhances the half reactions of gold oxidation and oxygen reduction.

Some interesting evidence comes from the research results of Liu & Yen (1995). After investigating the effects of sulfide minerals and dissolved oxygen on gold and silver dissolution in cyanide solution by using the silver rotating disc, they claimed that the leaching behaviors of gold and silver depend strongly on both the solubility of the sulfides and oxygen concentration. In the oxygen-enriched cyanide solution, the presence of some sulfide minerals, such as pentlandite, chalcopyrite, pyrrhotite, sphalerite, arsenopyrite, and pyrite increase the gold dissolution rate, while others, such as galena, stibnite and chalcocite cause the reverse effect. Silver dissolution rate was significantly improved by leaching with oxygen-enriched cyanide solution, but the rate of silver dissolution with the association of sulfides minerals was still lower than that without the associated sulphide minerals.

2.3 Alternative Lixiviants

For the purpose of increasing gold and silver dissolution rate and recovery, and/or seeking the non-toxic leachants, the alternative lixiviants including leaching systems of ammonia-thiosulfate, ferric-sulfate, thiourea-ferric-sulfate, chloride, nitric acid solutions and other complexes media were studied by numerous workers.
2.3.1 Chloride

Scheiner, et al (1976) reported a sulfurous acid-sodium chloride system to recover silver which is mineralogically associated with iron and manganese. The principal reactions involved in the process are listed below:

\[
\begin{align*}
\text{MnO}_2(s) + \text{SO}_2(g) &= \text{MnSO}_4(l) \quad \text{Reaction 2-21} \\
\text{SO}_2(g) + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2(g) &= \text{H}_2\text{SO}_4 \\
\text{MnO}(s) + \text{H}_2\text{SO}_4 &= \text{MnSO}_4 + \text{H}_2\text{O} \\
\text{Fe}_2\text{O}_3(s) + 6\text{H}^+ &= 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \\
\text{Ag}_2\text{S}(s) + 4\text{Cl}^- &= 2\text{AgCl} + \text{SO}_4^{2-} + 2\text{Cl}^- \\
\text{AgCl} + 3\text{Cl}^- &= \text{AgCl}^4^- 
\end{align*}
\]

Their results indicated that a majority of the associated manganese and iron must be dissolved or removed from the ore to achieve 80%-85% silver extraction. To further liberate the remaining 15%-20% silver from the argentojarosite minerals, higher concentrations of strong acid was required.

Dutrizac (1994) investigated the leaching of synthetic Ag\textsubscript{2}S in FeCl\textsubscript{3}-HCl and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-H\textsubscript{2}SO\textsubscript{4} media using the rotating disc techniques. It was found that silver sulphide dissolves relatively rapidly in FeCl\textsubscript{3}-HCl system, and the dissolution reaction obeys the parabolic rate law under all conditions studied. The leaching reaction generates mostly elemental sulfur and the porous sulphur layer is probably the cause of parabolic kinetics. The leaching rate in FeCl\textsubscript{3}-HCl media increases moderately with the increase of temperature over the range 40-95
°C and the apparent activation energy is 40.7 kJ/mol. It was believed that the rate control step is the outward diffusion of the AgCl reaction products (as various Ag-Cl complexes) through the solution trapped in the porous of the constantly thickening elemental sulphur product layer.

2.3.2 Thiourea

Pesic and Seal (1990) used the rotating disc method to study silver dissolution in thiourea solution in the presence of ferric sulfate. They claimed that the reaction of metallic silver with thiourea is dependent on the concentration ratio of ferric sulfate to thiourea. In excess ferric sulfate, a solid silver-thiourea complex is formed which passivates the silver surface and stops the dissolution of silver. With an excess of thiourea, the solid silver-thiourea complex re-dissolves and silver is leached into solution.

Balaz, et al (2000) studied the intensification of thiourea leaching of silver from silver bearing complex sulphide concentrates (Casapllca, Peru) by using mechanochemical alkaline leaching as a pretreatment step. With the pretreatment step, 90% of the silver was leached within 10 min compared to 5% Ag dissolution for the “as-received” concentrates. It indicated that mechanochemical alkaline pretreatment of complex sulphide has a positive influence on silver leaching from tetrahedrite.
2.3.3 Thiosulfate

Murthy and Prasad (1996) investigated the leaching process of gold and silver from the Miller process by using thiourea and thiosulfate. They found that thiourea leaching of the calcined dross resulted in about 84% extraction of gold, but the leaching of silver was very poor. A two-stage leaching of the salt-roasted dross with thiosulfate followed by thiourea leaching showed better gold and silver extractions (98.5% and 96.8% respectively).

Briones and Lapidius (1998) studied the leaching of silver sulfide with the thiosulfate-ammonia-cupric ion system. They found that the leaching reaction of silver sulphide is by substitution of copper in the solid (see the Reactions below). It differentiates silver sulfide leaching from metallic gold and silver extraction where an oxidant (presumably the cupric ion) is necessary. And in any case, the ratio of ammonia to thiosulfate is an important factor in the extraction velocity.

\[
2\text{Cu}^+ + \text{Ag}_2\text{S} = 2\text{Ag}^+ + \text{Cu}_2\text{S} \quad \text{(chalcocite)} \quad \text{Reaction 2-27}
\]

\[
\text{Cu}^{2+} + \text{Ag}_2\text{S} = 2\text{Ag}^+ + \text{CuS} \quad \text{(Covellite)} \quad \text{Reaction 2-28}
\]

2.3.4 Comparisons and others

Almeida and Amarante (1995) assessed three alternative processes to extract a silver-bearing sulphide by-product: Cyanidation, thiourea, and chloride leaching. The sulphides were verified that silver occurs both as mathildite, (AgBiS₂) and in solid solution in galena. The cyanidation route exhibited high cyanide consumptions and led to the formation of an
insoluble compound of silver. Thiourea leaching can be achieved without the introduction of ferric ions but is not economical. Chloride leaching of the product in its original particle size showed a better silver extraction even without ferric ions. Operating under $[\text{Cl}^-] > 3 \text{ M}$ at 80-90 °C for at least 3hr, it was possible to dissolve 60-80% of the total silver and high recovery of lead and bismuth was also achieved at the same time.

Maudos, et al (1996) investigated the kinetics of silver chloride dissolution in the complex media. The samples of jeweler workshop sweeps and wastes previously chlorinated and then leached in four leaching system: $\text{CS(NH}_2\text{)}_2/\text{H}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4/\text{NaOH}$, $\text{NaCN/NaOH}$, and $\text{NH}_4\text{OH}$. A general kinetics model describing leaching system based on Langmuir's hypothesis was proposed.

Holloway, et al (2004) investigated the leaching of silver sulphide precipitates with nitric acid at different temperature, pressures, acid concentrations and solid concentrations. A maximum Ag extraction of 96.1% was achieved by leaching at 150°C, 1100Kpa, and 9.6% solids with twice the stoichiometric amount of nitric acid.

Leaching system of sulfuric acid-hydrogen peroxide to recover silver from manganese-silver associated ores was studied by Jiang, et al (2003) and Jiang, et al (2003*). The thermodynamics of the Ag-Mn-H_2O system was examined and a kinetic reaction model was developed which confirmed the diffusion control process.
All these researches are focused on special types of silver-bearing ore and it seems more work need to be done to apply the suggested processes in practice. To consider the ease of the reasonability of economic and the availability of techniques, the cyanidation process is still more competitive and practical even though the concerns about the environment remained. In fact the successful running of the process for more than a century proved that the negative influence of the application of cyanide could be minimized to an acceptable low point by well-established management and operating systems, and by the continuous technical innovations on the process.
Chapter 3 The Leaching of Silver Sulfide and Gold

3.1 Introduction

Silver sulfide has a low solubility in dilute cyanide solution and this may limit the rate of silver extraction from acanthite. The catalytic leaching of silver sulfide with dissolved ferricyanide in cyanide solutions was introduced with the aim to increase the dissolution rate of silver sulfide and hence to raise the overall silver extraction from gold-silver ores. The following basic information on the general chemistry of the catalytic process is presented to further assess its potential application on gold-silver ore cyanidation process.

The dissolution of silver sulfide in water is governed by the following reaction,

$$\text{Ag}_2\text{S} = 2\text{Ag}^+ + \text{S}^{2-} \quad \log K_{sp} = -50.1 \quad \text{Reaction 3-1}$$

and in cyanide solution, silver cyanide complex is formed,

$$\text{Ag}^+ + n \text{CN}^- = \text{Ag(CN)}_{n(n-1)}^3, \quad \text{while } n = 1, 2, 3, 4 \quad \text{Reaction 3-2}$$

In the case of high cyanide concentration, Ag(CN)$_3^{2-}$ and Ag(CN)$_4^{3-}$ would form and in low cyanide concentration insoluble AgCN will precipitate (Xue & Osseo-Asare, 1985). For convenience, in the following discussions and calculations, only Ag(CN)$_2^-$ is used to represent the dissolved silver species unless specified. Combine the two reactions above, then

$$\text{Ag}_2\text{S} + 4 \text{CN}^- = 2\text{Ag(CN)}_2^- + \text{S}^{2-} \quad \Delta G^o = 52.5 \text{ kJ/mol} \quad \text{Reaction 3-3}$$

From Reaction 3-3, it can be calculated out that in 0.01 M NaCN solution (equivalent to ~ 0.5 g/l NaCN) and in absence of oxygen, the solubility of silver sulfide is only about 0.25 mg/l Ag which indicates a very small solubility of silver sulfide.
Considering the situation in the presence of oxygen, sulfide ion may be oxidized to $S_{x}^{2-}$, $S$, $\text{CNS}^{-}$, $S_{2}O_{3}^{2-}$, $\text{SO}_{3}^{2-}$ and $\text{SO}_{4}^{2-}$ (Davis, 1962 and Luthy & Bruce, 1979). Two important half reactions should be pointed out here;

\[
\text{SCN}^{-} + 2e^{-} = S^{2-} + \text{CN}^{-} \quad E^{\circ} = -0.86 \text{ v (SHE)} \quad \text{Reaction 3-4}
\]

\[
S_{2}O_{3}^{2-} + 3\text{H}_{2}\text{O} + 8e^{-} = 2S^{2-} + 6\text{OH}^{-} \quad E^{\circ} = -0.62 \text{ v (SHE)} \quad \text{Reaction 3-5}
\]

If the oxidation of sulfide ion only reaches the step of thiocyanate, then the following reaction is expected,

\[
2\text{Ag}_{2}S + 10 \text{CN}^{-} + 2\text{H}_{2}\text{O} + \text{O}_{2} = 4\text{Ag(CN)}_{2}^{-} + 2\text{SCN}^{-} + 4\text{OH}^{-} \quad \Delta G^{\circ} = -388.42 \text{ kJ/mol} \quad \text{Reaction 3-6}
\]

It shows that thermodynamically the dissolution of silver sulfide would proceed to the right in the presence of oxygen.

If only ferricyanide species is involved as oxidant in cyanide solution,

\[
\text{Fe(CN)}_{6}^{3-} + e = \text{Fe(CN)}_{6}^{4-} \quad E^{\circ} = 0.36 \text{ v (SHE)} \quad \text{Reaction 3-7}
\]

The following reactions can be obtained by combining Reaction 3-3, 3-4, and 3-7 or Reaction 3-3, 3-4, and 3-7,

\[
\text{Ag}_{2}S + 5 \text{CN}^{-} + 2\text{Fe(CN)}_{6}^{3-} = 2\text{Fe(CN)}_{6}^{4-} + \text{CNS}^{-} + 2\text{Ag(CN)}_{2}^{-} \quad \Delta G^{\circ} = -271.2 \text{ kJ/mol} \quad \text{Reaction 3-8}
\]

\[
2\text{Ag}_{2}S + 8\text{CN}^{-} + 8\text{Fe(CN)}_{6}^{3-} + 6\text{OH}^{-} = 8\text{Fe(CN)}_{6}^{4-} + S_{2}O_{3}^{2-} + 4\text{Ag(CN)}_{2}^{-} + 3\text{H}_{2}\text{O} \quad \Delta G^{\circ} = -111.9 \text{ kJ/mol}
\]
For gold, the following reaction was proposed (Aghamirian, 1997),

\[
\text{Au} + 2 \text{CN}^- + \text{Fe(CN)}_6^{3-} = \text{Fe(CN)}_6^{4-} + \text{Au(CN)}_2^-
\]

In this work, the purpose of the stoichiometry tests was to identify the main products of catalytic leaching of silver sulfide with ferricyanide and to suggest the most possible reactions involved. The leaching kinetics of silver sulfide and gold in ferricyanide-cyanide solution was further investigated by rotating disc tests. The effects of non-silver sulfide minerals on silver extraction from silver sulfide in ferricyanide-cyanide system were examined through agitated tank cyanide leaching of the mixed sulfide mineral samples.

3.2 Experimental and Analysis

3.2.1 Samples and reagents

(a) Synthetic silver sulfide

A synthetic silver sulfide (sources unspecified, particle size P80 = 16 μm) was applied in all the cyanidation tests in this research. The chemical analysis of this silver sulfide showed 84.90 % Ag and 12.93 % total Sulfur with 12.8 % S\(^2\)\(^-\). The composition is quite similar to that of pure Ag\(_2\)S: 87.06 % Ag and 12.93 % S. X-ray diffraction (XRD) analysis of the silver sulfide particles indicated only Ag\(_2\)S of the acanthite structure (Figure 3-1). Study by the scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) shows
only Ag\textsubscript{2}S crystals (Figure 3-2). The reference composition of silver and sulfur given by EDX is 83.49 % Ag and 16.51 % S which is qualitatively similar to the chemical analysis results.

Figure 3-1 XRD photograph of the synthetic silver sulfide particles.
Figure 3-2 SEM/EDX photograph of the synthetic silver sulfide particles
(b) Ag$_2$S and Au rotating disc

The fine silver sulfide particles were pressed under a moderate pressure (1.5 atm) with Caver Presser (New Jersey, U.S.A.) to form a 1 cm thick disc with a diameter of 2.4 cm. No sintering process was applied to avoid the decomposition of the mineral. The disc had a density 6.52 g/cm$^3$ which was about 89% of the theoretical value of acanthite density (7.326 g/cm$^3$). The discs were coated with epoxy resin and one flat surface was left exposed and polished. The discs then were analyzed with SEM/EDX. The inspection indicated that there was no change in composition due to pressing or polishing of the disc. But sporadically some of the silver sulfide particles on the surface of the discs were coated by epoxy resin which had penetrated the disc during the coating process (Figure 3-3).

A pure gold disc was cast in an epoxy cylinder with an exposed surface area of 4.52 cm$^2$. This disc was used in all the catalytic leaching tests to determine the leaching kinetics of gold in ferricyanide-cyanide system.
(c) Sulfide minerals

Five natural sulfide minerals (sources unspecified), namely chalcopyrite (CuFeS₂), pyrite (FeS₂), pyrrhotite (Fe₇S₈), galena (PbS), and sphalerite (ZnS), were used to determine the effects on silver extraction from silver sulfide in catalytic leaching process. The analysis of these minerals by XRD and by SEM/EDX showed the major minerals were present with some minor impurities (see Appendix C).

(d) Reagents

All the solutions used in the tests were made from de-ionized water. The potassium hexacyanoferrate(III) (K₃Fe(CN)₆), sodium cyanide, sodium hydroxide, lime (CaO) and
nitrogen used in this study were all certified analytical grade chemicals. For K\textsubscript{3}Fe(CN)\textsubscript{6}, further chemical analysis indicated less than 0.5 % K\textsubscript{4}Fe(CN)\textsubscript{6} (analyzed by titration).

3.2.2 Stoichiometry tests

The stoichiometry tests were conducted in covered 2 L PYREX glass beakers. The cover had several different size openings, which allowed insertion of the agitator, nitrogen and reagents injection and sampling tubes. Mixing was provided by an agitator with 2 cm stainless steel impellers powered by a variable-speed electric motor. A photograph of experimental equipment connection is shown in Figure 3-4.

The agitation speed was kept constant at 450 RPM. For each test, 0.1 g synthetic silver sulfide and 1 Liter potassium hexacyanoferrate(III)-sodium cyanide (or solely sodium cyanide) solutions were used. Three groups of tests, ST1, ST2, and ST3 were conducted with two tests conducted at the same conditions in each group to verify reproducibility. The leaching conditions for each group of tests are listed in Table 3-1.

Table 3-1 Leaching conditions of stoichiometry tests

<table>
<thead>
<tr>
<th></th>
<th>ST1</th>
<th>ST2</th>
<th>ST3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag\textsubscript{2}S, g</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>11-11.5</td>
<td>11-11.5</td>
<td>11-11.5</td>
</tr>
<tr>
<td>Initial NaCN, g/l</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Initial Fe as Fe(CN)\textsubscript{6}\textsuperscript{3⁻}, g/l</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Leaching time, hr</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Air</td>
<td>Air</td>
<td>N\textsubscript{2}</td>
</tr>
</tbody>
</table>
When necessary, nitrogen was injected into the solution for 30 minutes to flush the dissolved oxygen before the silver sulfide samples were added. After that the N$_2$ injector tube was kept at 3-5 mm above the surface of the turbulent solutions and N$_2$ injection rate was kept at a constant rate to maintain an inert atmosphere above the leach slurry. The solution pH was measured constantly using a standard pH probe with a TPS 900 series meter calibrated with standard pH buffer solutions. The solution pH was maintained between 11-11.5, which was adjusted by addition of 2 M NaOH solution. At the end of each test, the leaching slurry was filtered with No. 42 filtration paper and the volume of the filtrate was measured. The solution samples then were analyzed to obtain the relevant species contents and the solid residue after filtration was weighted after drying for 24 hours.

Figure 3-4 Photograph of the experimental establishment for stoichiometry tests
3.2.3 Rotating disc tests

The silver sulfide disc and the gold disc described in section 3.2.1 were used for the rotating disc tests. The ferricyanide-cyanide solutions were prepared in the same manner as in the stoichiometry tests. The dissolution rate measurements of the rotating disc were carried out in a 2L cylindrical cell with several holes in the cover for optionally inserting disc holder, pH meter, nitrogen tube, condenser tube, and sampling tube. A photo of the connection of experimental equipment and facilities for the rotating disc tests is shown in Figure 3-5.

Figure 3-5 Photograph of the experimental establishment for rotating disc tests
The cylindrical reactor was put in a water bath in which the temperature of the leaching solution could be automatically controlled. A condenser was connected to the reactor to minimize the effect of evaporation of water and cyanide from leaching solutions. The disc was glued on a cylindrical rod connected to the electric rotating controller.

Before each test, the Ag$_2$S and Au discs were polished with P4000 carbide paper and then washed with deionized water. Leaching was conducted in the 800mL thermostatically controlled solutions. The relative large volume was designed to minimize oxidant concentration changes during leaching. When necessary a nitrogen atmosphere was established following the same procedure described in section 3.2.2. The desired solution pH was adjusted with drops of 2 M NaOH solutions. Different leaching conditions were studied by adjusting rotating speed, temperature, pH and solution compositions, etc. Leaching solutions were sampled (3 mL) at periodic intervals (10, 20, 30 and 40 minutes) and stored for subsequent analysis of silver or gold contents.

The effects of rotating speed, temperature, ferricyanide and NaCN concentration, and solution pH on dissolution rates of silver sulfide and gold discs were studied respectively in a designed range with the other factors maintained at baseline values. The leaching conditions are summarized as following;

Rotating speed: 300, 450, 600, 750, 900, and 1050 RPM; Baseline, 600 RPM;

Temperature: 25 °C, 35 °C, 45 °C, and 55 °C; Baseline, 25 °C

Ferric concentration (in ferricyanide): 0.05, 0.25, 0.5, and 1 g/l; Baseline, 0.5 g/l;
NaCN concentration: 0.05, 0.1, 0.25, 0.5, and 1 g/l; Baseline, 0.5 g/l

Solution pH: 10, 10.5, 11, 11.5, and 12; Baseline, 11.5.

3.2.4 Mineral interaction tests

The equipment for these tests was the same as that for stoichiometry tests. The mineral samples were obtained by mixing synthetic silver sulfide with various sulfides minerals at different fractions. A total of 7 mixed sulfide mineral samples were examined, including 0.1 g Ag$_2$S combined with 0.1 g CuFeS$_2$, 0.1 g FeS$_2$, 0.1 g Fe$_7$S$_8$, 0.1 g PbS, 0.1 g ZnS, 1 g CuFeS$_2$, and 1 g Fe$_7$S$_8$ respectively.

The leaching conditions of the tests are summarized as following:

- Volume of solution, 1 L
- Solution pH, 11.5
- Temperature, Room temperature
- Atmosphere, N$_2$
- Leaching time, 48 hr
- Initial K$_3$Fe(CN)$_6$, 0.5 g/l Ferric in potassium ferrycanide
- NaCN, 0.5 g/l

During leaching, 3 mL solution samples were removed at periodic time (1, 2, 4, 8, 12, 24, 36, 48 hr) and stored for subsequent analysis. An equivalent volume of fresh solution (0.5 g/l NaCN, no ferricyanide) was added to maintain a constant solution volume.
3.2.5 Analysis

Silver and gold content in solutions were analyzed using Atomic Absorption Spectrometer (AAS) by Chem Met Co., a certified assayer located in Vancouver, BC. Silver, gold and sulfide content in solids were also analyzed by Chem Met. Some of the solution samples were analyzed using Varian 240 AAS.

Metal ions in solutions, including copper, iron, lead, and zinc, were measured using inductively coupled plasma (ICP) by International Plasma Limited (IPL), a certified assayer located in Vancouver, BC.

Free cyanide, ferricyanide, and thiocyanate contents in solutions were analyzed by titration methods summarized in Appendix B.

3.3 Results and Discussion

3.3.1 General chemistry

The analysis results of the final leaching solution obtained in the stoichiometry tests are listed in Table 3-2. It is observed that the ultimate free cyanide concentrations in all solutions are between 0.44 -0.5 g/l. After leaching more than 60hrs, the silver sulfides in tests ST1 and ST3 are nearly completely dissolved with only trace amount of solids left resulting in very clear solutions. However, little change was observed with the slurry in test ST2 and the weight of the solids obtained after filtering is still near the initial value of 0.1 g.
Table 3-2 Analysis results of the final leaching solutions from stoichiometry tests

<table>
<thead>
<tr>
<th></th>
<th>ST1</th>
<th>ST2</th>
<th>ST3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCN, g/l</td>
<td>0.44</td>
<td>0.49</td>
<td>0.48</td>
</tr>
<tr>
<td>Ag, mg/l</td>
<td>83</td>
<td>3.5</td>
<td>83</td>
</tr>
<tr>
<td>Solid (dry), g</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>Fe as Fe(CN)₆³⁻, mg/l</td>
<td>44.3</td>
<td>--</td>
<td>42.8</td>
</tr>
<tr>
<td>CNS⁻, mg/l</td>
<td>12</td>
<td>&lt;2</td>
<td>18.8</td>
</tr>
<tr>
<td>S₂O₃²⁻, mg/l</td>
<td>59.2</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

ST1: 0.5g/l Fe as Ferricyanide + natural air
ST2: no Ferricyanide + natural air
ST3: 0.5g/l Fe as Ferricyanide + N₂

According to the data from ST3 where only the oxidant hexacyanoferrate(3+) was applied, the content of the possible products then was obtained to compare with the theoretical results calculated based on Reaction 3-8. The results are shown in Table 3-3.

While examining the experimental results, it is found that they are in good agreement with that proposed by the Reaction 3-8 suggesting the reduction of ferricyanide to ferrous cyanide and the formation of thiocyanate. This seems to be the main reaction involved under the experimental leaching conditions. The deviation on ferricyanide content between the experimental and theoretical results may be attributed to the titration accuracy. But on the other hand there is still the possibility of the formation of thiosulfate, either from the oxidation of sulfide (Reaction 3-10) or from the further oxidation of thiocyanate by hexacyanoferrate (3+),


\[ \text{Ag}_2\text{S} + 3\text{CN}^- + 6\text{Fe(CN)}_6^{3-} + 6\text{OH}^- + \text{CNS}^- = 6\text{Fe(CN)}_6^{4-} + \text{S}_2\text{O}_3^{2-} + 2\text{Ag(CN)}_2^- + 3\text{H}_2\text{O} \]

Reaction 3-10

Table 3-3 Comparative results of stoichiometry tests and theoretical calculations (according to Reaction 3-8)

<table>
<thead>
<tr>
<th>Species</th>
<th>IN, mol</th>
<th>Exp. OUT, mol</th>
<th>Theo. OUT, mol</th>
<th>Rel. Err</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag\textsubscript{2}S</td>
<td>4.04*10^-4</td>
<td>0</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Ag in Ag\textsubscript{2}S</td>
<td>7.74*10^-4</td>
<td>0</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>S in Ag\textsubscript{2}S</td>
<td>3.99*10^-4</td>
<td>0</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Fe(CN)\textsubscript{6}^{3-}</td>
<td>1.58*10^-4</td>
<td>7.67*10^-5</td>
<td>7.90*10^-5</td>
<td>3%</td>
</tr>
<tr>
<td>Fe(CN)\textsubscript{6}^{4-}</td>
<td>9.27*10^-7</td>
<td>8.29*10^-5</td>
<td>8.06*10^-5</td>
<td>3%</td>
</tr>
<tr>
<td>Ag in Ag(CN)\textsubscript{n}^{(n-1)-}</td>
<td>0</td>
<td>8.07*10^-4</td>
<td>8.07*10^-4</td>
<td>--</td>
</tr>
<tr>
<td>S in CNS\textsuperscript{-}</td>
<td>0</td>
<td>3.63*10^-4</td>
<td>3.99*10^-4</td>
<td>9%</td>
</tr>
<tr>
<td>S in S\textsubscript{2}O\textsubscript{3}^{2-}</td>
<td>0</td>
<td>&lt;9*10^-5</td>
<td>0</td>
<td>--</td>
</tr>
</tbody>
</table>

In fact, from the view of thermodynamics, polysulfide (S\textsubscript{x}^{2-}) and S\textsubscript{2}O\textsubscript{3}^{2-} may exist in trace amount in the solutions as hexacyanoferrate(III) may oxidize most of S\textsubscript{x}^{2-} to CNS\textsuperscript{-}. In experiment ST3, no S\textsubscript{2}O\textsubscript{3}^{2-} was detected in the final solutions. S\textsubscript{2}O\textsubscript{3}^{2-} may exist in such a low concentration that it could not be detected effectively by the analysis method adopted. Therefore, Reaction 3-8 is proposed as the most probable stoichiometric reaction in the catalytic cyanidation process by ferricyanide species. According to this reaction, at least 6 kilogram potassium ferricyanide would be needed to extract 1 kg silver from the pure silver sulfide.
The situation tends to be more complicated when oxygen from air is involved during catalytic leaching. The results of tests ST2 shows that the solubility of silver sulfide in aerated cyanide solutions is much higher than that in water, but is still very small (note there may still be some oxidation of \(\text{Ag}_2\text{S}\) even with presence of nitrogen sparging). The silver extraction was less than 5% after leaching 60 hrs in 0.5g/l NaCN solutions. This indicates that it may be difficult to extract silver from silver sulfide by conventional cyanidation process due to the low solubility of silver sulfide and the slow kinetics of oxygen reduction in the system.

By observing the analysis results from Tests ST1 which was conducted with the addition of 100% excess of ferricyanide (based on the stoichiometry of Reaction 3-8 at air atmosphere), it is found that, though the final ferricyanide content is 41.3 mg/l which is nearly the same as that in ST3 solutions, the content of CNS\(^-\) in ST1 is only half of that in ST3 solutions and thiosulfate ion is detected in ST1 solutions, giving a value of 59.2 mg/l. The total amount of sulfur species in CNS\(^-\) and \(\text{S}_2\text{O}_3^{2-}\) is near to the mass of sulfides in the reactant silver sulfides. The sulfur content in thiosulfate accounts for about 25% of the total dissolved sulfur species. Obviously some of CNS\(^-\) has been oxidized to \(\text{S}_2\text{O}_3^{2-}\). As it may be difficult for ferricyanide species to further oxidize CNS\(^-\), the most likely reaction could be the oxidation of CNS\(^-\) by oxygen to form thiosulfate,

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} = 4\text{OH}^- + 2e & \quad E^o = 0.4 \text{ v(SHE)} \quad \text{Reaction 3-11} \\
\text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} + 2\text{CN}^- + 4e = 2\text{SCN}^- + 6\text{OH}^- & \quad E^o = -0.25 \text{ v(SHE)} \quad \text{Reaction 3-12} \\
\text{O}_2 + 2\text{CNS}^- + 2\text{OH}^- = \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} + 2\text{CN}^- & \quad \Delta G^o = -282 \text{ KJ/mol} \quad \text{Reaction 3-13}
\end{align*}
\]
Some research claimed that the oxidation of SCN⁻ by oxygen is extremely slow at ambient temperature. The cyanidation of sulfur species is also affected by the kinetic factors. No detail information on catalysis of this reaction and no kinetic data were available. Some Cu(2+) species might catalyze the reaction of SCN⁻ with oxygen (Flynn, 1995), although copper was not present in the current experiment.

Obviously it is not enough to justify the catalytic cyanide leaching of acanthite just based on data obtained above. Some factors would be further discussed in section 3.3.2 which would focus on study of the dissolution of silver sulfide using rotating disc method.

3.3.2 Dissolution of Ag₂S disc

As described in section 2, the rotating disc technique is a powerful tool for the study of chemical reaction mechanism. Characterized by a well-defined surface area and thickness of the liquid diffusion film layer, the mathematical model for mass transfer of the system was derived by Levich in the case when a heterogenous reaction is much faster than the mass transfer rate.

(a) Reproducibility

The dissolution of Ag₂S disc in ferricyanide–cyanide system was investigated using the rotating disc method. The reproducibility of the leaching system was first examined and the results are shown in Figure 3-6. An earlier pre-test has shown that the dissolved silver concentration in the leaching cell is proportional to the leaching time up to 1 hour (initial
ferric in ferricyanide and NaCN are both at 0.5 g/l, and solution pH =11.5, 25 °C), indicating the reaction is under steady-state conditions. So leaching time of 40 minutes was adopted in all the following tests. From Figure 3-6, the reproducibility of the leaching system is acceptable with an average value of Ag$_2$S dissolution rate at 21 μmol m$^{-2}$ s$^{-1}$ (equivalent to 0.78 μm/hr).

![Figure 3-6 Reproducibility of leaching kinetics of Ag$_2$S in ferricyanide-cyanide solution (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5, 25°C, N$_2$ atmosphere, 600 RPM)](image)

Figure 3-6 Reproducibility of leaching kinetics of Ag$_2$S in ferricyanide-cyanide solution (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5, 25°C, N$_2$ atmosphere, 600 RPM)

(b) Leaching results in the absence and presence of oxidants

The dissolution of Ag$_2$S at different leaching conditions has been examined and the results are shown in Figure 3-7. It is observed that the dissolution rate of silver sulfide is quite low in 0.5 g/l NaCN solutions without the presence of any oxidants. The dissolution rate of Ag$_2$S disc in 0.5 g/l Fe as Fe(CN)$_6^{3-}$ and 0.5 g/l NaCN solution is much higher than that in aerated cyanide solution (0.5 g/l NaCN, natural air). According to Figure 3-7, the dissolution rate of Ag$_2$S in ferricyanide-cyanide system gives the value of 21 μmol m$^{-2}$ s$^{-1}$ (0.78 μm/hr) compared to the value of 13 μmol m$^{-2}$ s$^{-1}$ (0.48 μm/hr) in aerated cyanide solution. The later
one is in great agreement with that claimed by Luna-Sanchez (2003) who investigated the dissolution of silver sulfides in aerated cyanide solution using RDE and suggested the dissolution rate of $\text{Ag}_2\text{S}$ at $8.8 \mu\text{mol m}^{-2}\text{s}^{-1}$ ($8.8 \times 10^{-10} \text{mol cm}^{-2}\text{Ag}_2\text{S s}^{-1}$). When both air and ferricyanide exist, there is only a minor increase on dissolution rate ($22 \mu\text{mol m}^{-2}\text{s}^{-1}$) over that with just ferricyanide. Though theoretically the oxidation ability of oxygen is higher than that of ferricyanide, oxygen is limited by the low solubility of oxygen in cyanide solutions and by low reactivity. For a typical cyanide solution, i.e., 0.5 g/l NaCN, and pH =11.5, the pulp potential was measured giving a value of 260-270 mV (vs Ag/AgCl) in the condition of saturated air and 380-400 mV (vs Ag/AgCl) while the ferricyanide concentration is 0.5 g/l Fe as ferricyanide at N$_2$ atmosphere. These results indicate that the ferricyanide-cyanide solution is potentially a more effective cyanidation system for leaching silver sulfide.

![Figure 3-7 Dissolution of silver sulfide disc at different conditions](image)

Figure 3-7 Dissolution of silver sulfide disc at different conditions (0.5 g/l NaCN, pH = 11.5, 25 °C, 600 RPM)
(c) Rotating speed

The effect of rotating speed on the dissolution rate of Ag$_2$S in the catalytic leaching system is shown in Figure 3-8. It was observed that the dissolution rate of Ag$_2$S increases with the increase of rotating speed. According to the Levich equation, the dissolution rate as a function of the square root of rotating speed should be linear. The plot of the dissolution rate of Ag$_2$S versus square root of rotating speed shows a near linear relationship. The diffusion-controlled mechanism was confirmed based on these results.

Figure 3-8 Effect of rotating speed on the dissolution rate of silver sulfide disc (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH =11.5, 25 °C, N$_2$ atmosphere)
(d) Temperature

The effect of temperature on the dissolution rate of Ag$_2$S was investigated in the range of 25°C to 55°C. The results are shown in Figure 3-9. The activation energy was calculated from the slope of the Arrhenius plot to a value of 6.7 kJ/mol. A typical mass transfer controlled process is further confirmed.

![Arrhenius plot](image)

**Figure 3-9** Effect of temperature on the dissolution rate of Ag$_2$S
(0.5 g/l NaCN, 0.5g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5, N$_2$ atmosphere, 600RPM)

(e) Effect of ferricyanide concentration

The effect of ferricyanide concentration on the dissolution rate of Ag$_2$S was examined in the range of 0.05 g/l to 1g/l Fe as ferricyanide and the result is shown in Figure 3-10. The plot of Ag$_2$S dissolution rate versus ferricyanide concentration is shown in Figure 3-11. It is observed that the dissolution rate of Ag$_2$S increases proportionally with the increase of ferricyanide concentration within the range concerned.
Figure 3-10 Effect of ferricyanide concentration on dissolution of Ag$_2$S disc
(0.5 g/l NaCN, pH = 11.5, 25 °C, N$_2$ atmosphere, 600 RPM)

Figure 3-11 Plot of Ag$_2$S dissolution rate vs ferricyanide concentration
(0.5 g/l NaCN, pH = 11.5, 25 °C, N$_2$ atmosphere, 600 RPM)
(f) Effect of cyanide concentration

The effect of NaCN concentration on the dissolution rate of Ag$_2$S has been examined in the range of 0.01 g/l to 1 g/l NaCN (shown in Figure 3-12). The plot of dissolution rate of Ag$_2$S versus NaCN concentration is shown in Figure 3-13. It was found that the dissolution rate increases sharply with an increase of NaCN concentration in the range of 0.01 g/l to 0.25 g/l and then tends to increase smoothly. This is different from the effect on dissolution rate of gold or silver in aerated cyanide solution in which the dissolution rate increases proportionally with cyanide concentration at low cyanide content and then reaches a limit value when NaCN concentration exceeds a critical value.

Considering the dissolution of silver sulfide in cyanide solution,

$$\text{Ag}_2\text{S} + 4 \text{CN}^- = 2\text{Ag(CN)}_2^- + \text{S}^2-$$  \hspace{1cm} \text{Reaction 3-3}

Apparently a high cyanide concentration would result in a high solubility of silver sulfide even without any oxidant. It is quite different from the dissolution of pure silver in cyanide solution where an oxidant is critical. In the presence of ferricyanide, the dissolution of silver sulfide in cyanide solution is catalyzed as sulfide is oxidized to form thiocyanate. So cyanide is also a key factor in complexing sulfur species,

$$\text{CN}^- + 1/8 \text{S}_8 = \text{SCN}^-$$ \hspace{1cm} \text{Reaction 2-2}

$$\text{CN}^- + \text{S}_2\text{O}_3^{2-} = \text{SCN}^- + \text{SO}_3^{2-}$$ \hspace{1cm} \text{Reaction 2-3}

$$\text{CN}^- + \text{S}_x^{2-} = \text{SCN}^- + \text{S}_{x-1}^{2-}$$ \hspace{1cm} \text{Reaction 2-4}

In ferricyanide-cyanide leaching system, there would be little chance for the formation of Ag$_3$Fe(CN)$_6$ and Ag$_4$Fe(CN)$_6$ in high cyanide concentration. But the precipitation reaction
between metal ions and ferricyanide could happen at low cyanide concentration or at high metal concentration (Flynn 1995);

\[
\text{Ag}_3\text{Fe(CN)}_6 = 3\text{Ag}^+ + \text{Fe(CN)}_6^{3-} \quad \text{Log } K_{sp} = -28 \quad \text{Reaction 3-14}
\]

\[
\text{Ag}_4\text{Fe(CN)}_6 = 4\text{Ag}^+ + \text{Fe(CN)}_6^{4-} \quad \text{Log } K_{sp} = -38 \quad \text{Reaction 3-15}
\]

The insoluble \(\text{Ag}_3\text{Fe(CN)}_6\) and \(\text{Ag}_4\text{Fe(CN)}_6\) could form a thin film at the surface of disc which would passivate the dissolution of silver sulfide and decrease the mass transfer rate of the oxidant, \(\text{Fe(CN)}_6^{3-}\). Therefore, the interactive reactions among cyanide, metal ions and sulfur species make the cyanide a critical factor beyond the simple complex function.

Figure 3-12 Effect of NaCN concentration on dissolution of Ag\(_2\)S disc (0.5 g/l Fe as Fe(CN)_6^{3-}, pH = 11.5, 25 °C, N\(_2\) atmosphere, 600 RPM)
Figure 3-13 Plot of $\text{Ag}_2\text{S}$ dissolution rate vs NaCN concentration
(0.5 g/l Fe as Fe(CN)$_6$$_3$, pH =11.5, 25 °C, N$_2$ atmosphere, 600 RPM)

(g) Effect of pH

The effect of pH on dissolution rate of $\text{Ag}_2\text{S}$ was examined in the range of 10 to 12 at which conventional cyanidation process is usually performed. The results are shown in Figure 3-14. It can be observed that in this pH range the silver sulfide dissolution rate does not change, having a mean value of 21 $\mu$mol m$^{-2}$ s$^{-1}$ (0.78 $\mu$m/hr).
(h) Mechanism of Ag$_2$S Dissolution in Ferricyanide-cyanide system

According to the results obtained above, the mechanism of silver sulfide dissolution in ferricyanide-cyanide system is suggested as following (shown in Figure 3-15); Two mechanism models were speculated, namely chemical reaction and electrochemical reaction models. In the chemical reaction model, the dissolution steps would include,

1) dissolution of Ag$_2$S: $\text{Ag}_2\text{S} = \text{Ag}^+ + \text{S}^{2-}$  
2) oxidation of S$^{2-}$: $2\text{Fe(CN)}_6^{3-} + \text{S}^{2-} = 2\text{Fe(CN)}_6^{4-} + \text{S}$  
3) complexing by cyanide: $\text{Ag}^+ + 2\text{CN}^- = \text{Ag(CN)}_2^-$  
   $\text{S} + \text{CN}^- = \text{SCN}^-$

The oxidation and complexing of sulfide species could happen at the same time,

$$2\text{Fe(CN)}_6^{3-} + \text{S}^{2-} + \text{CN}^- = 2\text{Fe(CN)}_6^{4-} + \text{SCN}^-$$

The characteristic of this mechanism is that all the oxidation and complexation reactions involved are homogeneous (reacting in solutions) which electrons transfer from S$^{2-}$ to Fe(CN)$_6^{3-}$.

In the electrochemical reaction model, the dissolution of Ag$_2$S in ferricyanide-cyanide solution include two half reactions, the anodic dissolution of Ag$_2$S where thiocyanate is formed and the cathodic reduction of Fe(CN)$_6^{3-}$ to Fe(CN)$_6^{4-}$.

Anodic reaction: $\text{Ag}_2\text{S} + 3 \text{CN}^- -2e = \text{Ag(CN)}_2^- + \text{SCN}^- \quad \text{E}^\circ = -1.13 \text{ v(SHE)}$  
Cathodic reaction: $\text{Fe(CN)}_6^{3-} + e = \text{Fe(CN)}_6^{4-} \quad \text{E}^\circ = +0.36 \text{ v(SHE)}$
Though it has not yet been proved, it is strongly believed the dissolution of Ag$_2$S in ferricyanide-cyanide solution would follow the electrochemical mechanism.

Figure 3-14 Effect of pH on dissolution of Ag$_2$S disc
(0.5 g/l NaCN, 0.5g/l Fe as Fe(CN)$_6^{3-}$, 25°C, N$_2$ atmosphere, 600 RPM)
Surface reaction: $\text{Ag}_2\text{S} + 5 \text{CN}^- + 2\text{Fe(CN)}_6^{3-} = 2\text{Fe(CN)}_6^{4-} + \text{CNS}^- + 2\text{Ag(CN)}_2^-$

Total reaction: $\text{Ag}_2\text{S} + 5 \text{CN}^- + 2\text{Fe(CN)}_6^{3-} = 2\text{Fe(CN)}_6^{4-} + \text{CNS}^- + 2\text{Ag(CN)}_2^-$

Figure 3-15 Mechanism of dissolution of $\text{Ag}_2\text{S}$ in ferricyanide-cyanide system

((a)- chemical reaction model; (b) electrochemical reaction model.)
### 3.3.3 Dissolution of gold disc

Dissolution of gold in the same leaching system as that for silver sulfide has been examined. The plots of gold dissolution in the leaching solutions are always near linear under the typical leaching conditions applied in the research, thus confirming that the gold dissolution takes place under steady-state conditions in the leaching period. According to the results of comparison tests (shown in Figure 3-16), the dissolution rate of gold in aerated cyanide solution gives a value of about $5 \mu\text{mol m}^{-2}\text{s}^{-1}$ (0.19 $\mu\text{m/hr}$) which is consistent with the results claimed by Jeffrey (1997) and Wadsworth (2000), but is much lower than that claimed by Guzman et al (1999). It is believed some critical factors including impurities in gold disc and leaching solutions, surface treatment, and leaching and measurement system, etc. may lead to the different results. Guzman et al (1999) suggested it was necessary to heat the gold plate in a Bunsen flame before the experiment in order to remove hydrocarbons absorbed on the gold surface. Limited by the coating material, this process was not applied on the rotating Au disc tests in this research. The dissolution rate of gold in ferricyanide-cyanide solutions (0.5 g/l Fe as Fe(CN)$_6^{3-}$ and 0.5 g/l NaCN) gives a value of $19 \mu\text{mol m}^{-2}\text{s}^{-1}$ (0.74 $\mu\text{m/hr}$) which is much greater than that in aerated cyanide solutions. This indicates that ferricyanide is an effective oxidant to dissolve gold and may serve to accelerate the leaching rate of gold in a cyanide solution.

The influence of pH on the kinetics of gold dissolution in ferricyanide-cyanide solutions has been determined in the range of 10 to 12. The corresponding results were shown in Figure 3-17. Little effect on gold dissolution rate was observed in the pH range studied. Guzman et al (1999) claimed that the dissolution rate of gold tends to decrease at high pH value (pH > 12).
This is not the case at pH up to 12 in the catalytic leaching of Au in ferricyanide-cyanide system.

The effect of cyanide concentration on gold dissolution was examined in the range of 0.01 g/l to 1 g/l. As shown in Figure 3-18, the dissolution rate of gold increases with the increase of cyanide concentration from 0.01 g/l to 0.25 g/l after which it reaches a limit value of 20 μmol m$^{-2}$ s$^{-1}$. It is speculated that this is due to the change in the mechanism as cyanide is involved in both the adsorption step to form AuCN$_{ads}$ and the complexation step to form the dissolved Au(CN)$_2^-$.

![Figure 3-16 Dissolution of gold at different conditions](image-url)
Figure 3-17 Effect of pH on dissolution of gold disc
(0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, 25°C, N$_2$ atmosphere, 600 RPM)

Figure 3-18 Effect of cyanide concentration on dissolution of gold disc
(0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH = 11.5, 25°C, N$_2$ atmosphere, 600 RPM)
The effect of ferricyanide concentration on the gold dissolution rate has been investigated in the range of 0.05 g/l Ferric in Fe(CN)$_6^{3-}$ to 1 g/l Ferric in Fe(CN)$_6^{3-}$. As shown in Figure 3-19, ferricyanide concentration strongly influences the dissolution rate of gold and the gold dissolution rate increases proportionally with the increase of the ferricyanide concentration in the range concerned.

The influence of rotating speed on the kinetic of gold dissolution was examined. A direct proportionality between gold dissolution rate and the square root of rotating speed is observed (shown in Figure 3-20). These results indicate that under the experimental conditions applied in the research, gold leaching in ferricyanide-cyanide solutions is a diffusion-controlled process.

The examination on the effect of temperature on gold dissolution further proved the suggestion above. The Arrhenius plot is shown in Figure 3-21. Based on the data shown in Figure 3-21, the apparent activation energy is calculated which gives a value of 7.8 kJ/mol suggesting a typical diffusion-controlled process.
Figure 3-19 Effect of ferricyanide concentration on gold dissolution
(0.5 g/l NaCN, pH =11.5, 25°C, N₂ atmosphere, 600 RPM)

Figure 3-20 Effect of rotating speed on gold dissolution
(0.5 g/l Fe as Fe(CN)₆³⁻, 0.5 g/l NaCN, pH =11.5, N₂ atmosphere, 25 °C)
Figure 3-21 Effect of temperature on gold dissolution
(0.5 g/l Fe as Fe(CN)$_6^{3-}$, 0.5 g/l NaCN, pH = 11.5, N$_2$ atmosphere, 600 RPM)

3.3.4 Leaching of mixed sulfide minerals

The effect of some typical sulfide minerals on the leaching kinetics of silver sulfide in ferricyanide-cyanide solutions has been investigated by comparing silver extraction from combined sulfide minerals samples. The leaching results are shown in Figure 3-22. The slurry potential variation with leaching time is shown in Figure 3-23. It is observed that in the ferricyanide-cyanide leaching system, the presence of the non-silver sulfide minerals decreases the leaching rate of silver sulfide to different extents. There is a slight decrease in silver extraction with the presence of a small amount of galena and sphalerite after leaching 48 hours. A moderate decrease in silver leaching rate is observed with the presence of pyrite,
while the presence of chalcopyrite and pyrrhotite created a significant decrease in the dissolution rate of silver sulfide. Obviously the leaching rate of silver sulfide is depressed more when more chalcopyrite or pyrrhotite mineral were added due to the lack of ferricyanide. It is also observed that more cyanide and alkali are needed during leaching with the presence of these sulfide minerals. The solution potential decreases more quickly during leaching with the presence of base metal sulfide minerals indicating more rapid ferricyanide consumption, which may result from the oxidation of these sulfide minerals, i.e.,

\[
\begin{align*}
\text{FeS}_2 + 2\text{Fe(CN)}_6^{3-} + 8 \text{CN}^- &= 2 \text{Fe(CN)}_6^{4+} + 2\text{SCN}^- \\
\text{CuFeS}_2 + 4\text{Fe(CN)}_6^{3-} + 10 \text{CN}^- &= \text{Cu(CN)}_2^- + 4 \text{Fe(CN)}_6^{4+} + 2\text{SCN}^- \\
\text{Fe}_7\text{S}_8 + 14\text{Fe(CN)}_6^{3-} + 50 \text{CN}^- &= 21 \text{Fe(CN)}_6^{4+} + 8\text{SCN}^-
\end{align*}
\]

Reaction 3-20  
Reaction 3-21  
Reaction 3-22

When both silver sulfide and these typical non-silver sulfide minerals exist in the ferricyanide-cyanide solution, the latter ones may have consumed some or most of the available ferricyanide resulting in a lower silver extraction.

The leaching rate of the non-silver sulfide minerals in ferricyanide-cyanide system with presence of 0.1g Ag$_2$S was calculated based on the dissolved metal concentration in the leaching solutions. As shown in Figure 3-24, chalcopyrite and pyrrhotite exhibit a relatively high solubility in ferricyanide-cyanide solutions. The reducibility of the sulfide minerals may dominate their leaching behaviors and the other factors such as particle size may also play important roles.
Figure 3-22 Plot of Ag extraction from mixed sulfide mineral samples vs leaching time (0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5, N$_2$ atmosphere, room temperature)

It was speculated that the presence of other sulfides minerals would further decrease the solubility of silver sulfide as these sulfide minerals would liberate some sulfide ions into the solutions. As shown in Figure 2-3, the solubility of PbS and ZnS is much higher than that of Ag$_2$S (Palmer, S. A. K., et al. 1988). Ferricyanide may oxidize the liberated sulfide ions to element sulfur which is further reacted to form thiocyanate with free cyanide,

\[ 2\text{Fe(CN)}_6^{3-} + S^{2-} + \text{CN}^- = \text{SCN}^- + 2\text{Fe(CN)}_6^{4-} \]  

Reaction 3-23

According to the leaching results, the relationship between dissolved sulfur species and silver extraction from silver sulfide are shown in Table 3-4. Apparently silver extraction decreases
with an increase of dissolved sulfur species under the leaching conditions. It indicates that the presence of sulfide minerals would greatly influence silver extraction in the catalytic leaching of silver sulfide with ferricyanide.

Figure 3-23 Plot of solution potential vs leaching time during leaching of mixed sulfide mineral (0.5g/l NaCN, 0.5g/l Fe as Fe(CN)₆³⁻, pH=11.5, N₂ atmosphere, room temperature)
Figure 3-24 Plot of dissolved non-silver sulfide mineral vs leaching time
(0.1 g/l Ag$_2$S, 0.5 g/l NaCN, 0.5 g/l Fe as Fe(CN)$_6^{3-}$, pH=11.5, N$_2$ atmosphere, room temperature)

Table 3-4 Relationship between silver extraction and dissolved species (25 °C, N$_2$, 0.5 g/l NaCN, 0.5 g/l Fe as ferricyanide, 48hrs)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S^a$/mg</th>
<th>$S^b$/mg</th>
<th>Total $S^c$/mg</th>
<th>Ag Ext. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1gAg$_2$S</td>
<td>--</td>
<td>12.56</td>
<td>12.56</td>
<td>94.21</td>
</tr>
<tr>
<td>0.1gAg$_2$S + 0.1g ZnS</td>
<td>0.14</td>
<td>12.29</td>
<td>12.30</td>
<td>94.47</td>
</tr>
<tr>
<td>0.1gAg$_2$S + 0.1g PbS$_3$</td>
<td>1.5</td>
<td>12.22</td>
<td>13.73</td>
<td>93.95</td>
</tr>
<tr>
<td>0.1gAg$_2$S +0.1gFeS$_2$</td>
<td>8.6</td>
<td>11.49</td>
<td>20.11</td>
<td>88.38</td>
</tr>
<tr>
<td>0.1gAg$_2$S+0.1gCuFeS$_2$</td>
<td>19.68</td>
<td>8.82</td>
<td>28.50</td>
<td>67.83</td>
</tr>
<tr>
<td>0.1gAg$_2$S+0.1gFe$_7$S$_8$</td>
<td>57.13</td>
<td>7.03</td>
<td>64.16</td>
<td>54.08</td>
</tr>
</tbody>
</table>

$^a$, dissolved sulfur species from silver sulfide
$^b$, dissolved sulfur species from other sulfide mineral
$^c$, total dissolved sulfur species
3.4 Summary

The general chemistry of catalytic leaching of silver sulfide with hexacyanoferrate(3+) was studied by conducting a series of stoichiometry tests. The analysis of the leaching results indicates that under the typical leaching conditions (0.5 g/l NaCN, 0.5 g/l Fe as K₂Fe(CN)₆, pH =11, N₂, room temperature), the main reaction between synthetic silver sulfide with ferricyanide-cyanide species is,

\[
\text{Ag}_2\text{S} + 5 \text{CN}^- + 2\text{Fe(CN)}_6^{3-} = 2\text{Fe(CN)}_6^{4-} + \text{CNS}^- + 2\text{Ag(CN)}_2^- \quad \text{Reaction 3-8}
\]

With the involvement of oxygen from air, further oxidation of thiocyanate to thiosulfate was observed. According to this reaction, at least 6 kg K₂Fe(CN)₆ would be needed to extract 1 kg silver from the pure silver sulfide.

The leaching kinetics of Ag₂S and Au in ferricyanide-cyanide solution has been investigated by using rotating disc method. The effect of different conditions of pH, temperature, ferricyanide and cyanide concentration, and rotating speed on the dissolution rates of silver sulfide and gold in catalytic leaching system with ferricyanide were examined. The results indicate typical diffusion-controlled processes for both Ag₂S and Au dissolutions in ferricyanide-cyanide solution under the experiment conditions, giving the activation energies the value of 6.7 kJ/mol and 7.8 kJ/mol respectively.

The effect of some typical sulfide minerals on the leaching kinetics of silver sulfide in ferricyanide-cyanide solutions has been investigated by comparing leaching kinetics of mixed
sulfide minerals samples. Non silver-sulfide minerals influence silver extraction from silver sulfide to different extents and the most significant decreases are observed in the presence of chalcopyrite and pyrrhotite. It was speculated that the liberation of the dissolved sulfur species resulting from the oxidation of the non-silver sulfide minerals by ferricyanide limits the dissolution of silver sulfide and consumes some or most of the available ferricyanide.
Chapter 4 Study of Leaching of Gold-Silver Ores

4.1 Introduction

In this chapter leaching of two gold-silver ore samples, namely Veladero and Pierina ore samples provided by Barrick Gold Corporation, has been investigated by performing comparison tests – baseline leaching and catalytic leaching with ferricyanide with the purpose to improve overall gold and silver extraction. The Veladero deposit (Argentina) is just to be exploited while the Pierina deposit (Peru) has been processed for some time. Both deposits are treated by conventional cyanide heap leaching process. The grade of gold and silver in Veladero ore samples range from 1-1.3 g/t Au and 16-100 g/t Ag respectively. The average extractions of Au and Ag from the ore are reported by Barrick Gold Corporation to be 80-90% and 30-50% respectively. Obviously silver extraction is much lower than that of gold and much of the silver is expected to remain in tailings. Column leaching studies of the Veladero ore as part of the Barrick Gold feasibility study program also indicated poor silver extraction.

The mineralogical analysis indicates the possible occurrence of acanthite which was considered as the possible reason for the relatively low silver extraction (Chen, et al). As shown in the leaching results from the leaching experiments on synthetic silver sulfide, dissolution rates of gold and silver sulfide increase with the presence of ferricyanide in cyanide solution. The potential application of this leaching system to improve the overall
gold and silver extractions from Veladero ore was examined by tank leaching and column leaching tests. Comparison tests on Pierina gold-silver ore were also examined with the same method to determine the effectiveness of ferricyanide on improvement of gold and silver extractions.

4.2 Experimental and Analysis

4.2.1 Samples

Six gold-silver ore samples (each with two different particle size, $P_{80} = 38 \mu m$ and $P_{80} = 10$ mesh) were sourced from Veladero (Barrick Gold), an open pit mine with heap leaching process applied. The range of gold value is reported between 1 g/t to 1.27 g/t compared that of silver, 16–100 g/t. According to the mineralogical analysis, most of gold exist in native gold as free grains with a trace amount associated with goethite and quartz. It was reported that the major silver carrier is acanthite. Argentojarosite and silver chloride are also found in some ore samples. Gold extraction by conventional cyanidation process gives a value of up to 90% while silver extraction less than 50% and usually less than 30%.

The other ore sample was sourced from Pierina (Barrick Gold). The average grade of gold and silver is 1g/t and 10g/t respectively. A total of 10 samples (6 Veladero ore samples, 4 Pierina ore samples with the particle size $P_{80} = 38 \mu m$) were studied in the tank leaching. Five of the Veladero ore samples with the particle size of as-received $P_{80} = 10$ mesh were studied in column leaching.
4.2.2 Tank leaching tests

The leaching cells for the tank leaching tests were made of PYREX glass and had a 600 mL capacity. Mixing was provided by an axial agitator powered by a variable-speed electric motor. The agitation speed was kept at 450 RPM in all leaching tests. The leaching solutions were prepared with the same method as described in section 3.2.2. Certified reagent grade lime was used for adjusting the slurry pH. Before the addition of sodium cyanide to the slurry, 30 minutes pre-conditioning with lime was performed to neutralize the acidic mineral in the slurry. Slurry pH was maintained around 11.5 during the tests. At the end of pre-conditioning, there was no filtration and the pulp was directly used to perform baseline or catalytic cyanide leaching. Free cyanide was measured and adjusted at 1h, 4h, 8h, 24h and 48h to maintain an average concentration of free cyanide at 0.5 g/l. The leaching conditions are summarized as following;

- Pulp density: 33.3 % (100 g solid and 200 mL liquid)
- Room temperature, 20 -22 °C
- Atmosphere: natural air
- Slurry pH: 11-11.5
- Free NaCN: 0.5 g/l
- K\textsubscript{3}Fe(CN)\textsubscript{6}: For catalytic leaching, 0.1g/l Fe as Fe(CN)\textsubscript{6}\textsuperscript{3-} unless specified;
  For baseline leaching, no ferricyanide

A 10 mL pulp sample was taken after leaching for 4h, 24h, and 48h. After filtration, 2mL solution was taken with a pipette for the subsequent analysis of free cyanide and silver content. The solid and the same volume of fresh solution (0.5g/l NaCN, 2mL) were returned to the reactor. At the end of the test, the slurry was filtered and the filter cake was washed.
first with dilute NaOH solution (pH=11) and then with deionized water. Both the PLS and wash solution were analyzed for gold and silver content. The cake was dried in an oven for 24 hours and then weighed and analyzed. A mass balance for gold and silver was performed for each experiment based on the analysis results of the solution and solid samples.

4.2.3 Column leaching tests

Column leaching tests were conducted in 10 columns (d =2.0” and h=2.95”) for 5 Veladero ore samples. Baseline (no ferricyanide) and catalytic leaching (with ferricyanides) were performed at the same time. The counter-flow circulation of the leaching solution was applied where the leaching solution was forced to flow in from the inlet at the bottom of the column and then flow out from the outlet at the top of columns. A photo of experimental connection is shown in Figure 4-1. The leaching conditions of the column tests are summarized as below:

- Solids, 200g
- Circulated leaching solution, 2 L
- Flow rate: 10 L/min/m² (one full circulation/3 days)
- NaCN, 0.5 g/l and pH = 11.5
- Ferricyanide: baseline, no ferricyanide; catalytic leaching, 0.5 g/l Fe as Fe(CN)₆³⁻
- Atmosphere: natural air
- Temperature: room temperature (20-22 °C)

The operation procedures of column leaching are as following:

- Put 200 g solids sample in the column, seal and connect the pumps and tubes.
• First use about 1.8L pH=11.5 alkali solution to pre-treat the solids (counter-flow, 100 L/min/m²) for 6 hours. Solution pH was measured every 30min and adjusted with 2M NaOH solution to keep at 11.5;

• When the pH was stable, add NaCN and maintain at 0.5 g/l NaCN; In case of catalytic leaching, add ferricyanide (0.5 g/l ferric in ferricyanide); adjust the solution volume up to 2L and the flow rate at 10 L/min/m² and the leaching process is started;

At the beginning of the tests, pH was examined every 4 hrs and kept at 11.5 and free NaCN concentration was determined every day and kept at 0.5 g/l. After 3 days, pH was measured twice a day and free cyanide once every 3 days. The leaching solution potential was measured every day. The solution samples were taken at 1, 3, 7 days and then each week to analyze the silver content; Leaching tests lasted for 56 days. After leaching, the solids residue was washed first with weak alkaline solution and then with deionized water. The leachate and wash solution were collected and sampled to analyze Au and Ag content. The solids were dried and then ground to -74 μm to analyze Au and Ag content. Mass balance of gold and silver were made based on the analysis results.

4.2.4 Analysis

The same analysis methods as listed in section 3.2.4 were applied to the samples produced in tanks and column leaching tests.
4.3 Tank Leaching Results

The results of tank leaching tests on Veladero and Pierina ore samples are summarized in Table 4-1. Though the dissolution rate of pure silver sulfide and gold increase in ferricyanide-cyanide solutions as discussed in Chapter 3, it is observed that, for all the ore samples, there is little increase in the overall silver extraction in catalytic leaching with ferricyanide over that in baseline cyanide leaching. The same can be said for results with gold extraction. Little difference occur between silver grade in baseline leaching residue and that in catalytic leaching residue, indicating little effect of ferricyanide on the dissolution of the silver minerals in the ore samples. From Table 4-1, it is also found that silver extractions vary in a
Table 4-1 Tank leaching results of Veladero and Pierina gold-silver ore*

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fe$^{3+}$/g/l Head Ag/g/t</th>
<th>Res.Ag/g/t</th>
<th>Ag% Head Au/g/t</th>
<th>Res. Au/g/t</th>
<th>Au%</th>
<th>NaCN/kg/t</th>
<th>Lime/kg/t</th>
<th>S$^2$ in Res.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDH23-95</td>
<td>0</td>
<td>37.39</td>
<td>23.6</td>
<td>37.33</td>
<td>0.53</td>
<td>0.06</td>
<td>88.75</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>36.61</td>
<td>22.2</td>
<td>39.79</td>
<td>0.53</td>
<td>0.06</td>
<td>88.75</td>
<td>1.72</td>
</tr>
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<td>SDH03-324</td>
<td>0</td>
<td>60.41</td>
<td>11.60</td>
<td>80.95</td>
<td>0.26</td>
<td>0.03</td>
<td>88.36</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>63.91</td>
<td>10.60</td>
<td>83.55</td>
<td>0.29</td>
<td>0.03</td>
<td>89.90</td>
<td>1.85</td>
</tr>
<tr>
<td>DDH111-157</td>
<td>0</td>
<td>25.29</td>
<td>17.8</td>
<td>30.19</td>
<td>2.23</td>
<td>0.17</td>
<td>92.43</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>24.23</td>
<td>17</td>
<td>30.47</td>
<td>1.56</td>
<td>0.17</td>
<td>89.17</td>
<td>1.75</td>
</tr>
<tr>
<td>DDH04-270</td>
<td>0</td>
<td>48.17</td>
<td>23.5</td>
<td>51.61</td>
<td>0.73</td>
<td>0.17</td>
<td>76.76</td>
<td>1.52</td>
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<td>45.08</td>
<td>1.8</td>
<td>52.02</td>
<td>0.49</td>
<td>0.14</td>
<td>71.59</td>
<td>1.64</td>
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<tr>
<td>DDH03-124</td>
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<td>28.9</td>
<td>69.30</td>
<td>48.44</td>
<td>0.24</td>
<td>99.51</td>
<td>1.37</td>
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<td></td>
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<td>19.7</td>
<td>75.91</td>
<td>34.32</td>
<td>0.17</td>
<td>99.57</td>
<td>1.63</td>
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<tr>
<td>DDH44-429</td>
<td>0</td>
<td>75.68</td>
<td>60.5</td>
<td>20.70</td>
<td>82.61</td>
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<td>1.87</td>
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<tr>
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<td>82.61</td>
<td>66.1</td>
<td>20.63</td>
<td>0.47</td>
<td>0.03</td>
<td>93.64</td>
<td>1.87</td>
</tr>
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<td>PIE-1</td>
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<td>7.77</td>
<td>2.4</td>
<td>69.37</td>
<td>2.20</td>
<td>0.1</td>
<td>95.50</td>
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</tr>
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<td>69.83</td>
<td>1.82</td>
<td>0.1</td>
<td>94.55</td>
<td>1.7</td>
</tr>
<tr>
<td>PIE-2</td>
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<td>23.10</td>
<td>4.2</td>
<td>61.08</td>
<td>5.91</td>
<td>0.51</td>
<td>91.44</td>
<td>1.42</td>
</tr>
<tr>
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<td>23.10</td>
<td>--</td>
<td>59.96</td>
<td>4.53</td>
<td>0.07</td>
<td>98.47</td>
<td>1.61</td>
</tr>
<tr>
<td>PIE-3</td>
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<td>2.80</td>
<td>--</td>
<td>63.93</td>
<td>0.43</td>
<td>0.14</td>
<td>66.56</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
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<td>2.80</td>
<td>--</td>
<td>62.79</td>
<td>0.45</td>
<td>0.07</td>
<td>85.45</td>
<td>1.59</td>
</tr>
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<td>PIE-4</td>
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<td>2.76</td>
<td>1.4</td>
<td>49.66</td>
<td>0.54</td>
<td>0.03</td>
<td>94.53</td>
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</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.98</td>
<td>1.3</td>
<td>56.70</td>
<td>0.30</td>
<td>0.03</td>
<td>90.09</td>
<td>1.87</td>
</tr>
</tbody>
</table>

*Ferric in ferricyanide, g/l
Res..Ag(Au) - Ag(Au) grade in the leaching residue
Head Ag(Au)- Ag(Au) in head based on calculation
Ag(Au)/% - Ag(Au) extraction, %
NaCN(Lime)/kg/t- cyanide or lime consumption, kg/t ore
wide range according to different samples (from 20% to 90%) with most of which are below 70% compared to around 90% gold extraction, even though silver grade is apparently much higher than gold. Higher NaCN consumptions are also observed in all catalytic leaching tests than in baseline leaching tests and in most cases lime consumptions are higher.

The variations of slurry potential during leaching were measured and plotted in Figure 4-2. It shows that in catalytic leaching the slurry potential drops quickly at the beginning of the tests and then decreases smoothly during catalytic leaching, indicating ferricyanide may have been consumed quickly at the beginning of leaching. The slurry potentials in baseline leaching for sample SDH23-95 exhibit relatively stable after leaching about 4 hrs, which reach a constant value around 50 – 100 mV vs Ag/AgCl (shown in Figure 4-2 SDH-23-95-B). Similar results were observed in baseline leaching of the other samples. It should be pointed out that the quite low slurry potentials shown in Figure 4-2 may have been in error due to a faulty electrode. A new electrode then was used in the latter tests.

The plots of silver extraction versus leaching time for four Veladero ore samples have been examined and plotted in Figure 4-3 to Figure 4-6. Apparently for these four ore samples, the leaching rate of silver in catalytic leaching is nearly the same as that in baseline leaching. For sample SDH23-95 and sample SDH03-324, silver leaching rate is very fast at beginning and then increases little with leaching time. For the other two ore samples, silver extraction is still increasing with leaching time even after leaching for 48 hr.
Figure 4-2 Plot of slurry potential vs leaching time in the tank leaching tests (0.5 g/l NaCN, pH =11.5, 0.1 g/l Fe as Fe(CN)$_6^{3-}$, Air, Room Temperature)

Figure 4-3 Comparative silver leaching kinetics of sample SDH23-95 in tank leaching (0.5 g/l NaCN, pH =11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)
Figure 4-4 Comparative silver leaching kinetics of sample SDH03-324 in tank leaching (0.5 g/l NaCN, pH =11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)

Figure 4-5 Comparative silver leaching kinetics of sample DDH111-157 in tank leaching (0.5 g/l NaCN, pH =11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.1 g/l Fe as Fe(CN)$_6^{3-}$)
The effect of ferricyanide concentration on silver and gold extraction has been investigated over sample SDH23-95 and the result is shown in Figure 4-7. It shows that silver and gold extractions increase little even when the initial ferricyanide addition increases up to 1 g/l Fe as Fe(CN)$_6^{3-}$. For this sample, the final silver extraction is only about 40 % which is only half of the gold extraction.
Though the results from catalytic leaching of synthetic silver sulfide prove the effectiveness of ferricyanide on increasing the dissolution rate of silver sulfide, the application of the process on improvement tests for Veladero and Pierina ore samples is limited and exhibits little effect on the overall silver and gold extractions. The formation of metal ferricyanide precipitates, such as silver, copper, zinc or iron ferricyanide, was considered, i.e.,

\[2[Fe(CN)_{6}]^{3-} + 2K^{+} + 3Zn^{2+} = K_2Zn_3[Fe(CN)_{6}]_2 \]  

But as free cyanide concentration in the slurry was maintained high enough (which is around 0.5 g/l) during cyanidation, there is little chance for these precipitates to form. So it was speculated that the mineralogy of the ore samples (such as silver occurrence and mineral content) be a key factor. Though acanthite is detected in some Veladero ore samples, its content is not well determined. If acanthite content in the samples were in trace amount, the
catalytic function of ferricyanide would be limited. More important is the presence of the reductive minerals and their content in the ore, especially the sulfide minerals, such as chalcopyrite(CuFeS₂), pyrrhotite(Fe₇S₈) and pyrite(FeS₂), etc. As determined in section 3.4, the sulfide minerals would decrease the solubility of silver sulfide in cyanide solution, and may compete for the available ferricyanide with silver sulfide during leaching and therefore lead to the low silver extraction from the ore samples. The sulfide content in the leaching residues from the comparison tests was analyzed and the results are shown in Table 4-1. It is found that for all samples, sulfide content in catalytic leaching residues is usually lower than that in baseline leaching residues, indicating that ferricyanide has reacted with the non-silver sulfide minerals rather than with acanthite during catalytic leaching.

4.4 Column Leaching Results

Silver leaching kinetics in the column leaching tests for five Veladero ore samples are shown in Figure 4-8 to Figure 4-12. It is observed that the leaching rate of silver of catalytic leaching with ferricyanide is again nearly the same as that of baseline cyanide leaching. These results are consistent with those from tank leaching tests. It is also found that for all the samples, silver extractions quickly reach a limit value in several days and then change little. For different samples, silver extraction varied from the lowest 7% (SDH03-124) to the highest 64% (DDH111-157). Some improvement is observed at the beginning of catalytic leaching of sample DDH04-270 over the baseline leaching. As the silver extractions for the two tests reach the same value after 21 days, the extracted silver apparently is leachable by conventional cyanide leaching process. With the presence of ferricyanide, the leaching of
native silver can be promoted if there is no reductive minerals present which could compete for ferricyanide in the leaching solution;

\[ \text{Ag} + \text{Fe(CN)}_6^{3-} + 2\text{CN}^- = \text{Ag(CN)}_2^- + \text{Fe(CN)}_6^{4+} \]

**Reaction 4-2**

---

**Figure 4-8** Comparative leaching kinetics of sample DDH111-157 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)_6^{3-}, Catalytic: 0.5 g/l Fe as Fe(CN)_6^{3-})
Figure 4-9 Comparative leaching kinetics of sample DDH04-270 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)

Figure 4-10 Comparative leaching kinetics of sample DDH44-429 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)
Figure 4-11 Comparative leaching kinetics of sample SDH03-324 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5g/l Fe as Fe(CN)$_6^{3-}$)

Figure 4-12 Comparative leaching kinetics of sample SDH03-124 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5g/l Fe as Fe(CN)$_6^{3-}$)
The variations of solution potential with leaching time are shown in Figure 4-13 to Figure 4-17. For catalytic leaching, solution potential drops quickly at the beginning of leaching and then tends to be smooth after that. It is observed that solution potential decreases from 380 mV vs Ag/AgCl to around 150 - 200 mV Ag/AgCl depending on different samples. For baseline leaching, solution potential fluctuates in a narrow range at the first several days and then changes little. Obviously the ferricyanide has been consumed according to these results, but has exhibited little effect on improvement of silver extraction from the ore samples.

Figure 4-13 Plot of solution potential vs leaching time of sample DDH111-157 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(\(\text{CN}\))\(_6\))\(^{3-}\), Catalytic: 0.5 g/l Fe as Fe(\(\text{CN}\))\(_6\))\(^{3-}\)
Figure 4-14 Plot of solution potential vs leaching time of sample DDH04-270 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)

Figure 4-15 Plot of solution potential vs leaching time of sample DDH44-429 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)
Figure 4-16 Plot of solution potential vs leaching time of sample SDH03-324 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)

Figure 4-17 Plot of solution potential vs leaching time of sample SDH03-124 in column leaching (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$)
Higher consumptions of NaCN and alkali (NaOH) were observed with catalytic leaching and the results are shown in Figure 4-18 to Figure 4-22. The comparisons of leaching results of this research with a separate report from Barrick are summarized in Table 4-2. The results indicated that silver extraction is very consistent and the minor difference in gold extraction may be caused by sampling and analysis error or by variation in head grade.

Table 4-2 Column leaching results of Veladero and Pierina gold-silver ore*

<table>
<thead>
<tr>
<th>Samples</th>
<th>SD</th>
<th>Head Ag/g/t</th>
<th>Res.Ag/g/t</th>
<th>Ag/%</th>
<th>Head Au/g/t</th>
<th>Res. Au/g/t</th>
<th>Au/%</th>
</tr>
</thead>
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<tr>
<td>111-157</td>
<td>B</td>
<td>28.79</td>
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<td>7.16</td>
<td>1.78</td>
<td>0.3</td>
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<td></td>
<td>F</td>
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<td>26.8</td>
<td>7.11</td>
<td>1.92</td>
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<td>83.28</td>
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<td></td>
<td>Ba</td>
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<td></td>
<td>13.25</td>
<td>2.22</td>
<td></td>
<td>76.96</td>
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<tr>
<td>04-270</td>
<td>B</td>
<td>49.19</td>
<td>26.8</td>
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<td>0.18</td>
<td>63.51</td>
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<tr>
<td></td>
<td>F</td>
<td>49.16</td>
<td>26.6</td>
<td>43.63</td>
<td>0.67</td>
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<tr>
<td></td>
<td>Ba</td>
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<td>44-429</td>
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<td>74.64</td>
<td>65</td>
<td>12.03</td>
<td>0.79</td>
<td>0.09</td>
<td>89.06</td>
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<td></td>
<td>F</td>
<td>75.32</td>
<td>65.7</td>
<td>11.91</td>
<td>0.59</td>
<td>0.09</td>
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<td></td>
<td>Ba</td>
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<td>17.51</td>
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<tr>
<td>03-324</td>
<td>B</td>
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<td>22.8</td>
<td>54.70</td>
<td>0.33</td>
<td>0.03</td>
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<td></td>
<td>Ba</td>
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<td>Ba</td>
<td>96.71</td>
<td></td>
<td>63.99</td>
<td>39.64</td>
<td></td>
<td>97.55</td>
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</table>

* SD; source of data,
  B-baseline column leaching
  F-catalytic leaching, 0.5 g/l Fe as Fe(CN)₆³⁻
  Ba-report from Barrick Gold Corporation
  Res.-Ag(Au) - Ag(Au) grade in the leaching residue
  Head Ag(Au)- Ag(Au) in head based on calculation
  Ag(Au)/%-Ag(Au) extraction, %
Figure 4-18 Cumulative NaCN and NaOH addition during column leaching of DDH111-157 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$;  a-- NaOH; b-- NaCN)
Figure 4-19 Cumulative NaCN and NaOH addition during column leaching of DDH04-270 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN)
Figure 4-20 Cumulative NaCN and NaOH addition during column leaching of DDH44-429 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)₆³⁻, Catalytic: 0.5 g/l Fe as Fe(CN)₆³⁻; a-- NaOH; b-- NaCN)
Figure 4-21 Cumulative NaCN and NaOH addition during column leaching of SDH03-324 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN)
Figure 4-22 Cumulative NaCN and NaOH addition during column leaching of SDH03-124 (0.5 g/l NaCN, pH=11.5, Room temperature, Air, Baseline: no Fe(CN)$_6^{3-}$, Catalytic: 0.5 g/l Fe as Fe(CN)$_6^{3-}$; a-- NaOH; b-- NaCN)
4.5 Summary

Two gold-silver ore samples, Veladero ore and Pierina ore have been investigated by performing comparison cyanidation tests – baseline leaching and catalytic leaching with ferricyanide in tank and column leaching. The results of the tank leaching tests show that improvement of Au and Ag extractions are not significant in catalytic leaching over baseline leaching. It is found that the slurry potential drops quickly during catalytic leaching and higher lime and cyanide consumptions are observed. The same results are observed in column leaching tests. Lower sulfides content in catalytic leaching residue were observed. It is speculated that ore mineralogy may account for these results, especially the presence of other sulfide minerals, such as chalcopyrite, pyrrhotite, or pyrite, which may compete for ferricyanide with acanthite resulting in the ineffectiveness of catalytic leaching with ferricyanide.
Chapter 5 Conclusions and Recommendations

The catalytic leaching of silver sulfide with ferricyanide and its potential application on cyanidation of gold-silver ore has been investigated. The results of general chemistry tests indicate that under the typical cyanide leaching conditions (0.5 g/l NaCN, 0.5 g/l Fe as ferricyanide, pH =11.5, N₂, room temperature), the main reaction involved in catalytic leaching of synthetic silver sulfide with ferricyanide species is,

\[ \text{Ag}_2\text{S} + 5 \text{CN}^- + 2\text{Fe(II)CN}_6^{3-} = 2\text{Fe(II)CN}_6^{4-} + \text{CNS}^- + 2\text{Ag(CN)}_2^- \]  

Reaction 3-8

According to this stoichiometric reaction, at least 6 kg K₃Fe(CN)₆ would be needed to extracted 1 kg silver from the pure silver sulfide.

By performing a series of rotating disc tests, the catalytic leaching kinetics of silver sulfide and gold in ferricyanide-cyanide solutions has been investigated. The catalytic cyanidation process proved effective in increasing silver and gold dissolution rate from pure silver sulfide and pure gold. The dissolution rate of Ag₂S in the ferricyanide-cyanide system (0.5 g/l Fe as Fe(CN)₆³⁻ and 0.5 g/l NaCN, pH=11.5, N₂ atmosphere, 25°C) gives a value of 21 µmol m⁻² s⁻¹, (0.78 µm/hr) much higher than the value of 13 µmol m⁻² s⁻¹ (0.38 µm/hr) in aerated cyanide solution. The dissolution rate of gold in ferricyanide-cyanide solutions at the same leaching
system gives a value of 19 μmol m\(^{-2}\) s\(^{-1}\) (0.74 μm/hr) which is greater than that in aerated cyanide solutions with no added ferricyanide (about 5 μmol m\(^{-2}\)s\(^{-1}\), 0.19 μm/hr).

The effect of pH, temperature, ferricyanide and cyanide concentration, and rotating speed on the dissolution rate of silver sulfide and gold discs in catalytic leaching system were examined. The analysis results indicate diffusion-controlled process for both Ag\(_2\)S and Au dissolution in ferricyanide-cyanide solution under the experimental conditions, giving activation energies of 6.7 kJ/mol and 7.8 kJ/mol respectively.

The leaching kinetics of silver sulfide in ferricyanide-cyanide solutions with the presence of other sulfide minerals has been investigated. By comparing leaching kinetics of mixed sulfide minerals samples, it shows that different sulfide minerals decrease silver extraction from silver sulfide to different extent with an obvious decrease of silver extraction at the presence of chalcopyrite and pyrrhotite. It is speculated the liberation of dissolved sulfur species resulting from the oxidation of sulfide minerals by ferricyanide limits the dissolution of silver sulfide and has consumed some or most of available ferricyanide, leading to the decrease of silver extraction.

The potential application of the catalytic leaching with ferricyanide to improve silver extraction from Veladero and Pierina gold-silver ore has been studied by tank leaching and column leaching tests. The results of comparative tank cyanidation tests show that the improvement of Au and Ag extraction are not significant in catalytic leaching over baseline
leaching. The same results were observed in comparative column leaching tests for five Veladero ore samples. By analyzing the slurry potential variation, cyanide and alkaline consumption and sulfides contents in the leaching residues, it is speculated that the silver mineralogy, especially the presence of other sulfide minerals, such as chalcopyrite, pyrrhotite, or pyrite, may compete for ferricyanide with acanthite in the ore resulting in the ineffectiveness of the catalytic function of ferricyanide.

Recommendations
As shown in the research, the dissolution rates of silver sulfide and gold increase with the presence of ferricyanide in cyanide solution but little effects occur on Veladero and Pierina ore samples. Some further recommendations are proposed based on these results.

The mechanism of catalytic leaching of silver sulfide in ferricyanide–cyanide solution has been interpreted though an electrochemical reaction model. Study on the dissolution of Ag₂S in a well designed electrochemical system would further determine the silver sulfide leaching behavior. It is also suggested to conduct further study on determination of the products on the surface of rotating disk to examine the possible formation of Ag₃Fe(CN)₆/Ag₄Fe(CN)₆.

The behaviors of different associated minerals in gold–silver ore have not been well examined. There is a possibility that not only the sulfide minerals but also some other minerals limit the catalytic function of ferricyanide.
As there is some disagreement on the silver mineralogy in Veladero and Pierina ore, especially the content of acanthite is not known, it would be more meaningful to investigate the application of the catalytic leaching with ferricyanide on an ore or concentrate abundant of acanthite to examine the practical effect of ferricyanide on overall gold and silver extraction.
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World Silver Survey 2005, GFMS limited/The silver Institute, 2005 (http://www.silverinstitute.org)


Appendix A Sample Calculations

Head

Head of Ag (Au) = mass of Ag(Au) in the ore sample / mass of the ore sample * 10^6 g/t

In which,

Mass of Ag (Au) in the ore sample = mass of Ag (Au) in solid residue + mass of Ag (Au) in PLS + mass of Ag (Au) in wash solution + mass of Ag(Au) loss during sampling

Mass of Ag(Au) in residue = Ag(Au) content in residue * mass of residue

Mass of Ag(Au) PLS = Ag(Au) content in PLS * volume of PLS

Mass of Ag(Au) wash solution=Ag(Au) content in wash solution*volume of wash solution

For example, for sample SDH23-95, baseline tank leaching,

Ag content in PLS, 5.9mg/l Volume of PLS, 235ml
Ag content in wash solution, 0.1mg/l Volume of wash solution, 345ml
Ag content in residue, 23.6 mg/t mass of residue, 99.3 g
Mass of the ore sample, 100 g

Then,

Mass of Ag in the ore sample =5.9 mg/l *0.235 l /10^3 mg/g + 0.1 mg/l * 0.345 l/10^3mg/g
+ 23.6 mg/t *99.3g/10^9 mg/t

=0.00374 g
Head Ag in the sample = $0.00374g/(100g/10^6g/t)$

= 37.39 g/t

**Extraction**

Extraction = mass of metal in the solution/mass of metal in the ore sample *100%

In which,

Mass of metal in solution = mass of metal in PLS + mass of metal in wash solution + mass of metal loss during sampling

Mass of metal in the ore sample = Head of metal * mass of the ore sample

For example, for sample SDH23-95, baseline tank leaching after 48hrs, according to the data above,

Extraction (Ag, 48hrs), % = \((5.9 \text{ mg/l} * 0.235 \text{ l}/10^3 \text{ mg/g} + 0.1 \text{ mg/l} * 0.345 \text{ l}/10^3 \text{ mg/g} + 23.6 \text{ mg/t} * 99.3 \text{ g}/10^9 \text{ mg/t})/0.00374g\)

= 37.33%

While calculating extraction during leaching, the constant volume of leaching solutions is assumed (200ml in tank leaching and 2L in column leaching).

For example, for sample SDH23-95, baseline tank leaching after 24hrs,

Ag content in leaching solution, 6.28 mg/l  Volume of leachate, 200 ml

Ag content in 4hrs sample solution, 6.2mg/l  volume of 4hrs solution sample, 2ml

124
Extraction (Ag, 4hrs), % = \( \frac{(6.28 \times 10^{-3} \text{mg/g} \times 0.2) + (6.2 \times 10^{-3} \text{mg/l} \times 0.002)}{0.00374 \text{g}} \)
\[ = 33.59\% \]

**Cyanide Consumption**

Cyanide consumption = mass of cyanide consumed/ mass of the ore sample \( \times 10^3 \text{kg/t} \)

Mass of cyanide consumed = total mass of cyanide added – mass of free cyanide left in leachate – mass of cyanide loss during sampling

For example, for sample SDH23-95, baseline tank leaching,

Total cyanide added = 1.66g  
Mass of free cyanide left in leachate = 0.08g  
Mass of cyanide loss during sampling = 0.003 g  
Mass of the ore sample = 100 g  
Cyanide consumption = \( \frac{1.66 \times 10^3}{100 \times 10^6} \text{g/kg/(100g/10^6g/t)} = 1.58 \text{ kg/t} \)

**Lime Consumption**

Lime consumption = mass of lime consumed/ mass of the ore sample \( \times 10^3 \text{kg/t} \)

= total lime added / mass of the ore sample \( \times 10^3 \text{kg/t} \)

For example, for sample SDH23-95, baseline tank leaching,

Total lime added = 0.7g  
Mass of the ore sample = 100g  
Lime consumption = \( \frac{0.7 \times 10^3}{100 \times 10^6} \text{g/kg/(100g/10^6g/t)} = 7 \text{ kg/t} \)
Appendix B Analysis Methods

B-1 Free Cyanide

Principle
Free cyanide is defined as the uncomplexed cyanide ion, CN\(^-\), and molecular hydrogen cyanide, HCN. The concentration of free cyanide is the sum of the CN\(^-\) and HCN concentration. The most common method for determining free cyanide, titration with silver nitrate (AgNO\(_3\)) was adopted in this research. The end point is determined by use of rhodamine as the indicator. A blank correction is required before performing the titration.

Pour 50 ml of 0.25 M NaOH into a 250 ml Erlenmeyer conical flask and add enough water to make the volume up to 150 ml. Add 10-15 drops rhodamine solution and titrate with standard AgNO\(_3\) solution and the blank value can be obtained. The silver nitrate solution can be standardized by any convenient method, such as with standardized NaCl solution with chromate as the indicator. The titration reactions and calculation are:

\[ \text{Ag}^+ + 2\text{CN}^- = \text{Ag(CN)}_2^- \]

\[ [\text{CN}^-] = \frac{([\text{AgNO}_3] \times (V_t-V_b) \times 2 \times DF)}{V_s} \]

where,

\[ [\text{CN}^-] = \text{Cyanide content, mol/l (multiply by 26.018 for CN in g/l)} \]

\[ [\text{AgNO}_3] = \text{silver in titrant concentration, mol/l} \]

\[ V_t = \text{titration volume, ml} \]
\( V_b = \) blank correction volume, ml

\( V_s = \) sample volume, ml

DF = dilution factor.

**Apparatus and Reagents**

- Radiometer ABU 80 Autoburette, equipped with a 10-ml buret
  - 250 ml Erlenmeyer conical flask
  - magnetic stirring plate and Teflon coated magnetic stir bar

- deionized water

- 0.25 M NaOH (10 g/l)

- 1 M NaOH (40 g/l)

- 0.018 M AgNO\(_3\) solution (3.06 g/l), prepare weekly and store in a glass vessel in the dark

- \( p \)-dimethylaminobenzal rhodamine indicator (200 ml/l in acetone)

- Standard NaCl solution, 0.04 M

- Chromate indicator (50 g/l)

**Procedure**

- Add 30-40 ml 0.25 M NaOH into a 250ml Erlenmeyer flask;

- Take 1 ml solution sample (as in most cases in the experiments, this volume of solutions contain at least 0.5 mg of cyanide) and put it into the flask;
• Add 6 – 10 drops of rhodamine indicator and put the flask on the magnetic stirring plate;
• Titrate with 0.018 M AgNO₃ solution using the autotitrator (Radiometer ABU 80).

Comments
The accuracy of the titration method was affected by the presence of heavy metals. Copper and iron cyanide complexes may interfere with the end point. An alternative method is by an amperometric technique that employs measuring the current of cyanide soluble electrode and comparing it against a reference electrode. The rate of dissolution and hence the current varies linearly with the concentration of free cyanide. This method is especially suitable for automated process control.

B-2 Thiocyanate

Principle
Thiocyanate, SCN⁻, reacts with Ag⁺ to form AgSCN solid, a white precipitate. Standard Ag⁺ is added to the acidic sample of SCN⁻ containing Fe(3+). Ferric forms an intense red complex with SCN⁻. As Ag⁺ consumes SCN⁻ the color fades and eventually disappears. The silver nitrate solution is standardized with the same method mentioned above. The reactions and calculations are as following

\[
\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN}
\]

\[
\text{Fe}^{3+} + x\text{SCN}^- \leftrightarrow [\text{Fe(SCN}_x]^{3-x} \text{ (red-brown)}
\]
Ag\(^+\) + \(1/x\) [Fe(SCN\(_x\))]\(^{3-x}\) = AgSCN + Fe\(^{3+}\)

\([SCN^-] = \frac{[AgNO_3] \times V_t \times DF}{V_s}\)

where,

\([SCN^-]\) = thiocyanate concentration, mol/l

\([AgNO_3]\) = silver in titrant concentration, mol/l

\(V_t\) = titration volume, ml

\(V_s\) = sample volume, ml

\(DF\) = dilution factor.

The titration must be done in an acidic solution to avoid hydrolysis of Fe(3+) which also gives an orange-brown color. While titrating, the color fades gradually and the end point is when the red-brown color just disappears.

**Apparatus and Reagents**

- Radiometer ABU 80 Autoburette, equipped with a 10 ml burret
- 100 ml and 250 ml Erlenmeyer conical flask
- Magnetic stirring plate and Teflon coated magnetic stir bar
- Deionized water
- 0.02 M standard NaSCN solution
- 36 % wt Fe(NO\(_3\))\(_3\) solution as indicator
- 0.02 M AgNO\(_3\) solution, prepare weekly and store in a glass vessel in the dark
- Standard NaCl solution, 0.04 M
- Chromate indicator (50 g/l)
- 6 M HNO₃ solution

Procedure

- Take out designated volume solutions into a 100 ml beaker (usually 50-100 ml leaching solution in this research as thiocyanate concentration is relatively low);
- Add 30-50 ml deionized water and add enough 6 M HNO₃ to make the solution up to 0.8 M HNO₃ (about 6 ml 6 M HNO₃);
- Heat the solution and N₂ gas was sparged into the solution for about 30-40 minutes to volatilize HCN; If there is any precipitate, it should be filtered and the filtrate for next-step titration;
- Add 1ml Fe(NO₃)₃ indicator and titrate with the stand AgNO₃ solution;
- Read the end point is when red brown color just disappears.

Comments

The titration is interfered by the presence of free cyanide. It is necessary to volatilize HCN from the sample solution as much as possible. pH adjustment is also a critical factor. The titration is a tedious process and it takes a long time to reach the end point.
Iron cyanide species

Principle

Total iron content in solution is analyzed by AAS. Ferrous cyanide concentration can be calculated out if ferric cyanide concentration is known. Ferric cyanide was determined by titration with iodides in this research. The reversible reaction is,

\[ 2[\text{Fe(CN)}_6^{3-}] + 2 \Gamma \leftrightarrow 2 \text{Fe(CN)}_6^{4+} + I_2 \]

In strongly acid solution the reaction proceeds from left to right, but is reversed in almost neutral solution. Oxidation also proceeds quantitatively in a slightly acid medium in the presence of a zinc salt. The low solubility potassium zinc ferrous cyanide is formed, and the hexacyanoferrate(2+) ions are removed by precipitation:

\[ 2[\text{Fe(CN)}_6^{4+}] + 2K^+ + 3Zn^{2+} = K_2Zn_3[\text{Fe(CN)}_6]_2 \]

The product \( I_2 \) then can be titrated with standard thiosulfate solution.

\[ 2 S_2O_3^{2-} + I_2 = S_4O_6^{2-} + \Gamma \]

which leads to

\[ [\text{Fe(CN)}_6^{3-}] = \left( [S_2O_3^{2-}] x V_i x DF \right) / V_s \]

where,

\[ [\text{Fe(CN)}_6^{3-}] = \text{ferricyanide concentration, mol/l} \]
[S_2O_3^{2-}] = thiosulfate concentration, mol/l

V_t = titration volume, ml

V_s = sample volume, ml

DF = dilution factor.

**Apparatus and Reagents**

-Radiometer ABU 80 Autoburette, equipped with a 10-ml buret

-250ml Erlenmeyer conical flask

-magnetic stirring plate and Teflon coated magnetic stir bar

-deionized water

-0.01M standard NaS_2O_3 solution

-0.1M Zn(NO_3)_2 solution

-2-3 % KI solution

-0.3 M HNO_3 solution

-starch

**Procedure**

- Take out designated volume solutions (10 ml – 25 ml depending on the ferric cyanide concentration in the samples) and add about 35 ml deionized water;

- Add 2-5 ml 0.3 M HNO_3 solution to adjust solution pH = 2.5-3;

- Add 1ml 0.1M Zn(NO_3)_2 solution and 0.1-0.2 g starch;
- Titrate the liberated iodine immediately with standard 0.01M NaSzO3 solution
- Read the end point when the blue color has just disappeared.

**Comments**

It was found that the titration limit of this method is about $10^{-4}$ M ferricyanide in cyanide solution which is equivalent to 10 ppm Fe$^{3+}$. The titration process is interfered by impurity metals such as copper. An alternative method is by AAS. As mentioned before, the total iron in solution sample can be determined by AAS. Then add zinc nitrate solution to the solution sample and filter with No. 44 filter paper. The ferrous cyanide species is removed and the filtrate is analyzed by AAS to determine the iron content. The distribution of iron cyanide species can be calculated. The amount of zinc nitrate addition is critical and it is found that some ferricyanide can be precipitated if too much zinc ions is added.
Appendix C SEM/EDX/XDR photos of mineral samples

Figure C-1 SEM/EDX photograph of silver sulfide disk
Figure C-2 SEM/EDX photograph of chalcopyrite powders
Figure C-3  SEM/EDX photograph of pyrrhotite powders
Figure C-4 SEM/EDX photograph of galena powders
Figure C-5 SEM/EDX photograph of sphalerite powders
Figure C-6 SEM/EDX photograph of pyrite powders
Figure C-7 XRD photograph of synthetic silver sulfide
(Consistent with PDF# 014-0072, synthetic acanthite)

Figure C-8 XRD photograph of chalcopyrite
(Consistent with PDF# 037-0471, chalcopyrite)
Figure C-9 XRD photograph of pyrite
(Consistent with PDF# 042-1340, pyrite)

Figure C-10 XRD photograph of pyrrhotite
(Consistent with PDF# 075-0600, Fe0.95S1.05, pyrrhotite)
Figure C-11 XRD photograph of sphalerite
(Consistent with PDF# 005-00056672, synthetic sphalerite)

Figure C-12 XRD photograph of galena
(Consistent with PDF# 078-1055, synthetic galena)
Appendix D Thermodynamic Data

All Eh-pH diagrams in the paper were generated based on the thermodynamic data listed in CRC Handbook of chemistry and physics (www.Hbcpnetbase.com). The main thermodynamic data for the calculations are listed below.

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