MODELING THE CYANIDE HEAP LEACHING
OF CUPRIFEROUS GOLD ORES

by

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ABSTRACT

A mathematical model of cyanidation heap leaching of cupriferous gold ores which includes the speciation of all cyanide, cyanate, thiocyanate, hydroxide and sulfate complexes, and their corresponding copper and gold precipitates, was developed to facilitate the treatment of these complex ores. The concepts of back mixing and solution retention are represented by two fundamentally different fluid elements: i) the bulk solution flowing through the heap, and ii) a stagnant solution reservoir adjoining and enclosed by the ore particles.

Four 1.5 m tall column tests simulating actual heap leaching behavior under different nominal influent cyanide concentrations were operated for a period of up to seven months, along with semi-batch coarse ore and batch fine ore leaching tests. The resulting experimental data were used for the calibration and validation of the model.

It was found that, in the presence of significant copper sulfate mineralization, the pH of the solution would naturally buffer to approximately 4.6. Further pH decrease to 3.5 is provoked by the oxidation of cyanide to cyanate by cupric ions. At such low pH levels, it is thought that cuprous and aurous cyanide salts tend to precipitate out of solution both within and around porous ore particles. As a result, neither dissolved gold nor dissolved copper from secondary copper sulfides appear in the column effluent for a significant period of time, depending on the influent cyanide concentration and the height of the column. Once dissolved again, gold appears in the column effluent, whereas its leaching kinetics are a strong function of leaching kinetics of secondary copper sulfide minerals such as covellite and chalcocite.

Furthermore, the combined effect of covellite leaching and copper sulfate discharge is synergistic in that both promote the precipitation of copper hydroxide. This leads to the dispersal of a $\text{Cu}(\text{OH})_{2(s)}$ reserve throughout the column which has the effect of increasing the long term cyanide consumption. This, in turn, affects the leaching of secondary copper sulfides, and hence, of gold.

SOMMAIRE

Un modèle mathématique de la lixiviation en pile a été développé. Il inclut la spéciation de tous les composés cyanurés, les cyanates, les thiocyanates et les sulfates ainsi que les précipités correspondants de cuivre et d'or. Le concept de rétention de solution est représenté par deux portions de liquides fondamentalement différents: i) une solution liquide qui coule au travers de la colonne et ii) un réservoir liquide stagnant contigu aux particules de minerais.

Quatre colonnes simulaient le comportement réel de la pile à différentes concentrations de cyanure. Elles ont été en opération pendant plus de sept mois conjointement à des tests cinétiques. Les résultats expérimentaux obtenus ont été utilisés pour la calibration et la validation du modèle.

Il a été trouvé qu'en présence d'une minéralisation importante de sulfure de cuivre, le pH de la solution se fixe naturellement à 4.6. Avec le temps, l'oxydation du cyanure à cyanate est forcée par la présence de cuivre(II) qui fait descendre le pH à 3.5. À un tel pH, le cuivre et l'or précipitent sous forme de cristaux de cyanure à l'intérieur des pores du minerais. Conséquemment, il n'y a pas d'or, ni cuivre issu de la lixiviation des sulfures de cuivre qui apparaissent dans l'effluent pour une certaine période de temps, selon la concentration initiale de cyanure et la grosseur de la pile. Une fois dissout, l'or apparaît dans l'effluent de la colonne où son taux de lixiviation est contrôlé presque totalement par le taux de lixiviation des sulfures de cuivre secondaires comme la covellite et la calcocite.

De plus, l'effet combiné de la lixiviation de la covellite et la décharge de sulfate de cuivre est stratégique puisque les deux promouvoient la précipitation d'hydroxides de cuivre. Ceci entraîne la dispersion d'une réserve de $\text{Cu}(\text{OH})_{2(s)}$ à travers la colonne ayant pour effet d'augmenter la consommation de cyanure à long terme, affectant ainsi la lixiviation des sulfures de cuivre.

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LIST OF NOTIFICATIONS

- K, k All letters K or k refer to constants defined by their respective subscripts except for k_f .
- (..) Roman number in parenthesis beside an element refers to the oxidation state of the element, e.g. Cu(I) is monovalent copper and Cu(II) is divalent copper.
- (aq), (s), (g) Aqueous and solid states are specified when it is unclear, e.g. $\text{CuCN}_{(\text{aq})}$ and $\text{HCN}_{(\text{aq})}$ but $\text{Cu}(\text{CN})_2^-$.
- [..] Brackets denote concentration of a substance (mol/L), e.g. $[\text{CN}^-]$ is the concentration of free cyanide in solution.
- [..]_F Subscript F beside concentration brackets denotes the sum of the free species of the component in bracket, e.g. $[\text{CN}]_F$ is equivalent to $[\text{CN}^- + \text{HCN}_{(\text{aq})}]$.
- X Double underline aqueous elements or ligands are defined as “conservable” i.e. the total concentration does not change but its components may be distributed differently among complexes and free ions. For instance, $[\underline{\text{CN}}]$ includes the total stoichiometric concentration of CN^- , $\text{HCN}_{(\text{aq})}$, $\text{CuCN}_{(\text{aq})}$, $\text{AuCN}_{(\text{aq})}$, 2 moles of $\text{Cu}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$, 3 moles of $\text{Cu}(\text{CN})_3^{2-}$, and 4 moles of $\text{Cu}(\text{CN})_4^{3-}$. The precipitates $\text{CuCN}_{(\text{s})}$ and $\text{AuCN}_{(\text{s})}$ are not included in the mass balance because they do not take part in the rate limited reactions.
- [..]_{Total} Subscript Total denotes all the species of the corresponding component including the aqueous and solid species. It is X combined with the precipitates.

LIST OF VARIABLES

Roman letters

A	Surface area of gold (cm^2) (equation (5-20))
A, B	Constants of the Debye-Hückel equation (equation (7-1))
a	Specific mass transfer interfacial area between the bulk and the reservoir per unit heap volume (cm^{-1})
a_i	Ion size parameter for species i in the Debye-Hückel equation ($\text{\AA}$) (equation (7-1))
C	Concentration (mol/cm^3)
C_{A_0}	Initial concentration of reagent A (mol/cm^3)
C_b	Concentration in the bulk solution (mol/cm^3)
C_r	Concentration in the reservoir solution (mol/cm^3)
C_{S_0}	Initial concentration of reactant S (mol/cm^3)
c_i	Concentration of ionic species i (mol/cm^3) (equation (7-2))
CV	Statistical coefficient of variation
D	Particle diameter (mm)
D	Diffusion coefficients defined by subscript (section 5.2.3)
$\bar{D}$	Average particle diameter (mm)
D^*	Normalizing particle size (mm)
D_{eff}	Effective diffusivity (cm^2/min)
F_{t,r_0}	Mass fraction of mineral extracted (or conversion, X) from a rock radius, r_0 , in time t
G_i	Initial grade of mineral i (g mineral/g ore)

k_l	Liquid film-side oxygen mass transfer coefficient (cm/min)
M	Molecular weight of solids (g/mol)
m	Gates-Gaudin-Schuhmann (GGS) distribution parameter (section 3.1.3)
N_i	Number of moles of element i (equation 5-20)
n	Particle number index (equation (2-21))
n	Empirical reaction order (equation (5-21))
Q	Liquid solution flow (cm ³ /min)
r_b^L	Reaction rate in liquid bulk solution (moles/cm ³ ·min)
r_o	Initial rock radius (cm)
r_r^L	Rate of homogeneous reaction in the reservoir solution (mol/cm ³ ·min)
S	Bulk solution flow cross-sectional area (cm ²)
t	Time (min)
t_a	Advection timescale (equation (5-5)) (min)
t_d	Diffusion timescale (equation (2-24)) (min)
t_m	Mass transfer timescale (equation (5-5)) (min)
t_r	Reaction timescale (equation (3-4)) (min)
u_s	Superficial liquid velocity (cm ³ /cm ² ·min)
X_i	Conversion of mineral i
x_i	Natural logarithm of concentration i
z	Depth (cm)
z_i	Charge on ion i (equation (7-2))
Z	Total column height (cm)

Variables (Greek letters)

α	Dimensionless concentration of the reagent A
σ	Dimensionless concentration of the solid reactant S
ζ	Dimensionless depth
β	Dimensionless measure of the reagent strength relative to the grade of solid reactant S
ξ	Dimensionless particle radius
δ	Nernst boundary layer thickness (cm) (equation (5-20))
ε_b	Ratio of bulk solution volume to the total column volume
ε_h	Bed void fraction (not including particle pores)
ε_o	Initial ore porosity
ε_r	Ratio of the reservoir solution volume to the total column volume
γ_i	Activity coefficient of species i
ρ_{ore}	Ore density (g/cm^3)
ϕ	Ratio of bulk volume to reservoir volume
ϕ_A	Apparent reaction order in the concentration of reagent A
ϕ_B	Apparent reaction order in the free cyanide concentration with respect to gold leaching
ϕ_C	Apparent reaction order in the free cyanide concentration with respect to copper leaching
ϕ_S	Apparent reaction order in the concentration of reactant S
v	Ratio of ore porosity to the bulk solution volume (Section 2.4.3)
v_{ij}	Stoichiometric factor for component I in homogeneous reaction j (Section 5)
μ	Mean ionic strength of the solution (equation (7-2))

LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic absorption spectrometry
AVR	Acidification-volatilization-reneutralization
EDTA	Ethylenediaminetetraacetate
GGs	Gates-Gaudin-Schuhmann
ICP	Induction couple plasma
PCR	Post column reaction
PMET	Pittsburgh Mineral & Environmental Technologies Laboratories
PSD	Particle size distribution
UBC	University of British Columbia
UV	Ultra-violet
WAS	Weak-acid soluble
XRD	X-ray diffraction

1. Introduction

The heap leaching of cupriferous gold ores has received considerable attention in recent years as a result of the lower gold grades found in the earth's crust, decreasing gold prices and discoveries of major gold deposits containing significant amounts of copper. Cupriferous minerals come only after pyrite and arsenopyrite as the primary host metal sulfide minerals associated with gold. However, it is often found that when a gold ore contains more than 0.5% of cyanide soluble base metals (i.e. copper and iron), extraction by direct cyanidation is often challenging and rarely economic (Ibrado and Fuerstenau, 1989). Their presence affects gold extraction primarily by consuming large amounts of cyanide and oxygen, and high copper concentrations in solution significantly reduce carbon loading capacity for the precious metals. Moreover, the intrinsic characteristics of heap leaching, such as slow kinetics and concentration gradients, render this type of ore even more complex to treat. It is thus of primary importance to be able to maximize gold extraction through optimization, and this can only be done by computer modeling or by expensive laboratory experimentation. In this project, the development of a mathematical model is proposed as a tool for understanding the cyanidation heap leaching behavior of these mineralogically complex ores, and for facilitating their economic treatment.

1.1 Organization of the thesis

Chapter 2 illustrates several examples of the challenges faced by mines around the world that use the heap leaching process to treat their cupriferous gold ores. A brief description, including the advantages and drawbacks, of the current alternatives such as ammonia-cyanide leaching,

masking of copper minerals, etc. is also provided. Finally, some of the existing modeling methods are discussed with respect to their ability to predict current heap leaching problems.

In chapter 3, the batch and semi-batch leach tests are discussed, while column tests are discussed in chapter 4. Data from the semi-batch coarse ore and batch fine ore leaching tests are used to estimate the form of the rate equations which are specific to the ore sample. Column leaching tests represent the core of the experimental effort by simulating actual heap leaching behavior under different nominal influent cyanide concentrations. Chapter 5 introduces the general heap leaching model which is comprised of two parts: a kinetic subroutine and a speciation subroutine. This model is then validated in chapter 6 by comparing the experimental data from the column leaching tests to the computed results of model simulations. Finally, chapter 7 outlines recommendations for future work in the field of heap leaching of cupriferous gold ores.

Appendix A supplies supplementary chemical assays, appendix B provides the complementary experimental data for the figures in the body of the thesis, and appendix C contains the FORTRAN source code for the general heap leaching model.

2. Review of literature

This review of literature demonstrates the challenges faced by the cupriferous gold ore mining industry. The heap leaching process flow sheet is first described and the design development parameters are enumerated. The chemistry of the principal cyanide consumers, copper and iron, is illustrated with respect to the mineralogy of each. Several examples of actual processes which deal with those cyanide consumers are also described. Finally, existing mathematical models developed for the simulation of the heap leaching process are presented.

2.1 Flow sheet and design development

The heap leaching process is defined as the percolation leaching of relatively coarse ore piled on an impervious surface (Potter, 1981). One advantage of the heap leaching process is its flexibility. Plants may be very simple, comprising leaching of uncrushed ore on a locally-obtained clay-lined pad and shipment of gold and silver recovered in the form of loaded carbon or zinc precipitates; such a plant would have a relatively low capital investment. More elaborate plants for larger ore bodies may be planned to include crushing, cyclic pad use, and solvent extraction or ion exchange recovery. The following section outlines the flow sheet of the heap leaching operation.

2.1.1 Flow sheet of heap leaching process

This is the typical design development of a heap (**Figure 2-1**):

1. Ore preparation: Most ores not containing excessive clay will support adequate percolation when crushed as fine as 10 mm. Ores presenting percolation problems may be agglomerated by alkaline water that may or may not contain cyanide.
2. Ore sampling: Many heap leaching feeds are not homogeneous. Automatic sampling will provide a large bulk sample of ore.
3. Heap construction: Heaps up to 4-5 m deep may be built without driving a truck over the heap. Heaps may also be built by conveyor belt delivery and tripper distribution from a bridge unit. It is recommended that no truck ride on top of the heap due to higher compacting leading to lower aeration.
4. Pad design: Hot rolled asphalt is probably the best material for cyclic use. A 50 mm layer of asphalt, followed by a rubberized seal coat, and 100-150 mm of hot rolled asphalt are also satisfactory. Slopes are generally at least 3° in two directions to provide for solution recovery in a parallel ditch.
5. Solution application: Centrifugal pumps deliver solutions to pads via plastic pipes. Solution application is usually sufficient at 1.4 to 3.4 mL/m²·s. Steady flow appears satisfactory in most cases. Pregnant solutions may show increased value after a “rest” period which allows better oxygen penetration into the heap. Various mechanical sprayers have satisfactorily applied leach solutions.
6. Solution recovery: Pregnant solutions draining from heaps flow by gravity in plastic or asphalt ditches and through plastic pipes to storage. The storage tank or pond should be large

7. Processing recovery solutions: The solution is passed through recovery cells which contain, in most cases, activated carbon. Solvent extraction and ion exchange are technologies of growing importance in this field. Finally, the concentrated “clear” solution is electrowon and metallic gold is retrieved at the cathode.

Figure 2-1: Schematic diagram of a heap leaching operation

2.1.2 Testing for scale-up

Because each ore body is different, each heap must be based on individual tests. Tests may be made in bottle rolls, small columns, large columns and actual heaps of various sizes. Using these methods as guides to scale-up and design is recommended. Some essential design factors obtainable from column testing include the following.

1. Amount of solution needed to saturate the ore
2. Amount of solution that drains from saturated ore
3. Amount of moisture retained by drained ore
4. Crushing size versus leaching time

5. Optimum cyanide strength and consumption
6. Choice of alkali strength, alkali consumption and pH
7. Solution application rate
8. Height of the leaching ore column
9. Draining and washing time
10. Oxygen content of effluent

Upon testing, other parameters will need to be taken into account such as the formation of precipitates from cyanide consumers, dissolution of unwanted species into pregnant solution, recycling of solution, use of pre-coating organics to reduce the action of cyanide consumers, etc. Present gold and silver prices compared to capital and operating costs favor the continued growth of the heap leaching method. Therefore, design of an optimal heap is important and understanding its complexity is essential. The following section is dedicated to the study of the influence of cyanicides on cyanidation heap leaching.

2.2 Influence of cyanide consumers on the heap leaching process

The presence of copper sulfides such as chalcocite and covellite complicates the process of cyanidation because of their tendency to consume cyanide and to form copper cyano-complexes in solution along with the gold (Marsden, 1992; Gasparrini, 1983). This process not only leads to excessive cyanide consumption, but also results in high copper content in the pregnant solutions. For this reason, these minerals are named cyanicides or cyanide consumers. Copper, iron, zinc and sometimes mercury are the most important cyanicides. However, the study of the

cyanidation of those metals in the literature is rare and relatively recent. Because of their importance with respect to this project, copper and iron are discussed extensively.

2.2.1 Chemistry of copper in cyanide solutions

The main minerals from which copper is extracted are listed in **Table 2-1**. These minerals occur in only small grades in present-day ores and it is now rare to find a large deposit averaging more than 2% Cu. Copper ores containing a minimum of 1% Cu are being mined underground while ores at 0.5% Cu are being mined by open-pit methods (Biswas, 1994).

The majority of copper minerals are highly leachable in cyanide solution except for chalcopyrite (Hedley, 1955). Copper dissolves readily in cyanide solution to give $\text{Cu}(\text{CN})_3^{2-}$ as the main complex ion, as can be seen on the E_h -pH diagram in **Figure 2-2**. For this diagram, the copper concentration is set at $[\text{Cu}] = 0.0001 \text{ mol/L}$ and $[\text{CN}] = 0.001 \text{ mol/L}$.

Cu(II) oxidizes CN^- and is reduced to Cu(I) (Flynn, 1995). The reaction,

with uncomplexed Cu(I) as a product, has a log K value of 39.4. In reality, the product Cu(I) is always precipitated or complexed by cyanide and the value of log K is larger. For instance, copper(II) cyanide complexes are unstable with respect to reduction of Cu(II). For the reaction,

log K is equal to 93.4 at 25°C. The log K value for this reaction is so large that there is no known complexing agent for Cu(II) that will prevent the reduction of Cu(II) by CN^- (Smith, 1989). Consequently, Cu(II) in any form, such as CuO, ammonia complexes, or EDTA complex, oxidizes CN^- . In alkaline solution, copper(II) is expected to oxidize the CN^- in all weak acid soluble (WAS) metal cyanide species.

Table 2-1: Principal minerals from which copper is extracted (Biswas, 1994)

Mineral	Theoretical composition	Theoretical (% Cu)	Conversion in 1 g/L of $\text{NaCN}^\dagger$	Specific gravity (g/cm^3)
METAL COPPER	Cu	100	90.0	8.8
SULPHIDES				
Chalcopyrite	CuFeS_2	34.6	5.6	4.2
Chalcocite	Cu_2S	79.9	90.2	5.7
Bornite	Cu_5FeS_4	63.3	70.0	4.2
Covellite	CuS	66.4	N.A.	4.6
CARBONATE, OXIDES, SILICATES and SULFATES				
Malachite	$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	57.5	90.2	4.0
Azurite	$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	55.3	94.5	3.8
Cuprite	Cu_2O	88.8	85.5	6.0
Tenorite	CuO	79.9	N.A.	6.0
Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$	36.2	11.8	2.1
Antlerite	$\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2$	53.8	N.A.	3.9
Brochantite	$\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2$	56.2	N.A.	3.9

[†] Percent total Cu dissolved at 23°C in continuously agitated tank for 24 hours, ratio of solution to ore 10:1 (Hedley, 1955)

Figure 2-2: Eh-pH diagram for the Cu-CN-H₂O system at 25°C

Copper sulfides (for example, chalcocite, Cu₂S) react with cyanide to form copper cyano-complexes and soluble bisulfide (HS⁻) (equation (2-5)). Bisulfide ion undergoes further oxidation, ultimately forming sulfate (equations (2-3) and (2-4)). Furthermore, bisulfide ion reacts with cyanide in the presence of oxygen and forms thiocyanate (equation (2-6)). In addition to all these chemical transformations, sulfide ion may form a protective coating on the surface of gold particles and thus retard the cyanidation process (Haque, 1992).

Reaction of chalcocite with cyanide:

Kakovskii and Potashnikov (1962) studied the dissolution of chalcocite in cyanide solution in the presence of oxygen. Both sulfur and covellite films were reported to form on the rotating disk. Thiocyanate was also observed in solution. On the other hand, in the absence of oxygen, sulfide entered solution as sulfide ion. Covellite, chalcocite and argentite all exhibit first order kinetics with regard to cyanide ion. The kinetics are reaction controlled for covellite and argentite but diffusion controlled for chalcocite.

Unlike chalcocite, cyanidation of cupric sulfide or covellite (CuS) requires the reduction of cupric to cuprous, which forms cyanate at the expense of cyanide (equation (2-8)) (Haque, 1992).

Reaction of covellite with cyanide:

Dissolution of chalcopyrite in cyanide solution is very slow and high consumption of cyanide is expected. In fact, for every two moles of copper, 17 moles of cyanide are irretrievably lost to the formation of 2 hexacyanoferrate(II) complexes, one cyanate ion and four thiocyanate ions (Haque, 1992).

Reaction of chalcopyrite with cyanide:

OVERALL: $2 \text{ CuFeS}_2 + 23 \text{ CN}^- + 2 \text{ O}_2 + 6 \text{ H}^+ \rightarrow$

Interestingly, if copper is considered an important cyanicide in the case of gold heap leaching, Shantz (1977) studied the possibility of using cyanide as the lixiviant for a process to treat flotation tails containing chalcopyrite and mixed chalcocite and pyrite minerals as an alternative to smelting. He notes several advantages to leaching chalcocite in cyanide solution. The reaction is rapid, pyrite is not attacked, and sulfur dioxide is not produced. Also, the copper extractions are relatively high. However, recovery of copper from cyanide solution is difficult. The high free energies of the complexes lead to low current efficiencies during electrowinning, and direct acidification reprecipitates cuprous sulfide.

All of the cuprous cyanide complexes are decomposed by dilute acids, precipitating CuCN and evolving HCN gas:

2.2.2 Chemistry of iron in cyanide solutions

Iron is present in practically all gold ores, and thus represents a strong potential source of cyanide consumption during leaching (Gasparrini, 1983). Pyrite, which is the most common iron sulfide mineral associated with gold, fortunately seldom interferes with the cyanidation process (Habashi, 1966 and 1980). However, unlike gold and copper, iron has two stable cyanide

complexes under typical leaching conditions (**Figure 2-3**). They are hexacyanoferrate(II) complex, $\text{Fe}(\text{CN})_6^{4-}$ and hexacyanoferrate(III) complex, $\text{Fe}(\text{CN})_6^{3-}$.

Figure 2-3: Eh-pH diagram for the Fe-CN-H₂O system at 25°C (Osseo-Asare et al, 1984)

Marcasite and pyrrhotite react readily with cyanide to form iron cyano-complexes and soluble sulfide (equations (2-11) to (2-15)). Soluble sulfide undergoes oxidation and forms various products. Reactive iron sulfides, like the reactive copper sulfides, consume both cyanide and oxygen (Haque, 1992).

Reaction of pyrrhotite with cyanide:

The hexacyanoferrate(II) complex, Fe(CN)_6^{4-} is extremely stable, the degree of dissociation being practically zero (Hedley, 1955). Ferrocyanide salts of the alkali metals, the alkaline earth metals, and the ammonium ion are soluble in water. Sodium ferrocyanide is practically unaffected by cold dilute hydrochloric or sulfuric acid. Concentrated sulfuric acid decomposes sodium ferrocyanide as follows:

Sodium ferrocyanide is relatively stable when the solutions are exposed to air (Hedley, 1955). For this reason, they do not consume the oxygen in cyanide solutions and it is unlikely, therefore, that they retard the dissolution of gold or silver.

The heavy metal ferrocyanides are insoluble in water (Hedley, 1955). They are sparingly soluble in dilute acids but dissolve readily in caustic soda, ammonia or alkaline cyanide solution. As in the case of the soluble ferrocyanides, heavy metal ferrocyanides may contain more than one metal ion in the salt. Typical copper metal ferrocyanides are the cupro potassium ferrocyanide $\text{Cu}_2\text{K}_2\text{Fe(CN)}_6$ and $\text{Cu}_3\text{KFe(CN)}_6$. These salts are white or colorless and oxidize rapidly to the reddish-brown cuprous salts (Hedley, 1955; Sharpe, 1976). These compounds nearly always form as colloids of gelatinous precipitates that are not stoichiometric. They contain variable quantities of the alkali ion from the hexacyanometallate salt and a variable number of waters of hydration. Because of these compositional variations, there are few quantitative studies of their solubility equilibria, and the available data are of uncertain reliability (Beck, 1987).

2.3 Actual methods for treating cupriferous gold ores

Typically, cupriferous ores that contain low gold grade have received little interest during the past century for obvious economical reasons. At that time, the only method to leach such ores was to employ high cyanide concentration and to tolerate high cyanide consumption. In spite of the work that has been done in the area of upgrading these ores (see **Table 2-2**), particularly in attempts to reduce the reactivity of certain copper minerals in cyanide solution, little success has been achieved. This problem is complex and recently, some mines have pursued their financial objectives of maximizing gold extraction while minimizing the consumption of cyanide. Some examples of their work are illustrated here.

Table 2-2: Copper/Gold ore treatment options (Zheng et al, 1995)

Treatment	Applicability	Status	Reference
Float Cu concentrate for smelting	High Cu sulfide ores, preferably low arsenic	Conventional process	Dunne, 1991
Cyanidation with free CN^- recovery by AVR	Preferably low Cu(II)	Run at plant scale	Mudder et al, 1989
Selective leaching with ammonia-cyanide mixtures	Low to medium copper levels	Sensitive to mineralogy, runs at plant scale	Vukcevik, 1996
Pretreat to remove Cu (Acid/ NH_3 preleach)	Cu not amenable to flotation	Cyanide consumption high, tried at 1 plant	Deng et al, 1995
Mask copper minerals		Lab scale only	Bennett et al, 1988
Direct cyanide leach	Less than 1% Cu_xS_y ore, <0.5% Cu_xO_y ore	Conventional process for low copper ores	La Brooy, 1992

2.3.1 Float copper concentrate for smelting

With reasonably high grades of sulfide copper ores, the most economic solution to recovering gold is to float and smelt a copper concentrate, and extract the gold from the anode slimes of the copper electrorefining circuit (Muir et al, 1991). Unfortunately, it may take months before the gold value is realized and significant amounts of gold may be left in low grade copper tailings and stockpiled for future possible processing.

With oxidized ores, it is more difficult to float and obtain an acceptable copper concentrate, and accordingly, various sulfidization pretreatment methods have been tried to improve flotation recoveries, particularly of mixed oxide/sulfide ores. Sulfidization of surface oxidized copper is usually carried out by pre-treating the ore with a solution of sodium sulfide, but reproducibly high recoveries of copper by flotation with xanthate collectors is difficult to achieve in practice.

Overall there appears to be scope for improved flotation and copper recoveries but inevitably a significant fraction of the gold will remain in the flotation tailings, according to the mineralogy of the ore, making this approach less attractive than treating the whole ore.

2.3.2 Direct cyanidation with free CN^- recovery

The method of direct cyanidation with free CN^- recovery is actually run at plant scale. It consists of leaching directly the whole cupriferous gold ore with cyanide, recovering the copper and gold, and recycling the associated cyanide back to the leach circuit. This method regards copper as a valuable co-product instead of a detrimental cyanide consumer. Therefore, the first benefit from

this method is economic since it is possible to recover both copper and cyanide which otherwise would be lost. The second benefit is environmental since cyanide is re-used. As a direct result, the closure of the mine can then be carried through more readily.

There are different ways to recover free CN^- from the leach circuit. Use of AVR (acidification-volatilization-reneutralization) (Riveros et al, 1996; McNamara, 1989), electrolysis (Lower, 1969) and adsorption onto activated carbon (Sceresini, 1991) have been studied extensively. These processes suffer from incomplete recovery of cyanide, incomplete recovery of copper, low-value copper products (e. g. CuCN , Cu_2S , and CuSCN) and most importantly, they are complicated and require expensive flow sheets. Therefore, solvent extraction is suggested by Dreisinger et al (1995) in order to concentrate copper in solution as cyanide complexes and produce a pregnant solution suitable for electrolysis.

2.3.3 Selective leaching with ammonia-cyanide mixtures

As an alternative process of selectively leaching gold from copper-gold ores, the ammonia-cyanide system may offer lower cyanide consumption (according to the copper mineralogy). Again, kinetics and mechanisms of gold leaching are influenced by specific geo-physical and geo-chemical characteristics of minerals which accompany the gold. The adsorption characteristics of the gangue minerals in the gold ore also affect the kinetics of gold leaching.

Vukcevic (1996) has published a broad work on ammoniacal cyanide leaching. His results are interesting as they show the interrelations between copper and gold dissolution. Along with cyanide reactions, the effect of ammonia involves other important chemical reactions as follows:

While copper(I) cyanide may exist in solution, gold cyanidation occurs due to the presence of ammonia. Moreover, ammonia prevents precipitation of copper(II) by complexation of the $\text{Cu}(\text{NH}_3)_4^{2+}$ species. Therefore, ammonia has two positive roles in the cyanide system by both preventing copper(II) reduction and helping gold leaching. Ammonia-cyanide leaching shows good possibilities for ore containing relatively high amounts of the copper sulfides Cu_2S and CuS . However, the main drawback of this process is its strong dependence on having a very precise optimum mixture of ammonia and cyanide. Consequently, this method is totally unacceptable for heap leaching where reagent gradients are large along the depth of the heap.

2.3.4 Pre-treat to remove Cu (acid or ammonia pre-leach)

Since copper minerals are cyanide consumers, Deng and Muir (1995) propose to leach copper prior to the recovery of gold by cyanidation. An oxygenated chloride leaching process was tested on a Telfer off-grade copper-gold bulk concentrate. The dominant copper minerals in the concentrate are chalcocite and digenite, which are rather easy to leach under relatively moderate conditions. This process was chosen due to its high selectivity over pyrite and its ability to leach

a wide range of copper minerals at moderate temperature without requiring expensive autoclaving or roasting.

The process operates in dilute sulfuric acid with low chloride concentrations: 0.3 mol/L H_2SO_4 , 0.5 mol/L NaCl, 150 mL/min O_2 , L/S ratio (v/w) of 25:1 and a temperature of 85°C. Under those conditions, 95% Cu is readily extracted in 2 hours. Chalcocite dissolution takes place in two stages. It is oxidized stepwise at first to covellite via a series of copper deficient intermediates:

where x tends to 1 which corresponds to the formation of covellite. The produced covellite is further oxidized to cupric ions and the net reaction is:

The oxidation of covellite actually occurs in parallel to that of the remaining chalcocite but at a much slower rate. Thus, the first stage, which gives up to 40% copper extraction, can be considered to describe approximately the rate of chalcocite dissolution. All other parameters (copper concentration, sulfuric acid concentration, oxygen flow rate, L/S ratio) show little or no influence on the leaching rate. This process leaches a copper-gold bulk flotation concentrate which contains chalcocite as the dominant copper mineral. Nearly 98% of copper present in the concentrate is leached within 4 to 5 hours.

The choice of an acid or alkaline pre-leach process will usually be determined by the ore mineralogy. However, since cyanidation must be performed in alkaline solution, ammonia pre-

leach in alkaline solution has a clear advantage over acid pre-leach. Most oxidized copper minerals, except chrysocolla, dissolve readily in ammonia solutions but the overall copper recovery is generally only 60-70%.

Overall, it would appear that the opportunities for economically pre-treating low grade copper ores, particularly sulfides, are limited by the reagent cost and if necessary, by the acid neutralization step. Besides, if the ore was mined for its gold value, bacterial oxidation over several years as a pre-treatment is untenable in any case.

2.3.5 Mask copper minerals

Bennett et al (1988) have acquired an American patent for a process to treat Cu containing precious metal ores prior to cyanidation and recovery of precious metals. The process involves addition to the ores, before or after milling, of a water soluble or water dispersible surface active agent in the form of a fatty alkyl amine; preferably an ethoxylated fatty alkyl amine. The agent reduces the high cyanide consumption which is caused by copper dissolution, by passivating the mineral surface.

The quantity of surface active agent required depends on the amount of cyanide consuming copper minerals in the ore. Also, the optimum quantity to reduce copper dissolution during cyanidation at a reasonable cost can be determined experimentally. It is estimated that 0.01 to 1 kg of surface active agent per ton of ore can be enough. The surface active agent should be water-soluble or dispersible so as not to complicate the cyanidation process. The surface active

agents slightly increased gold extraction and reduced copper extraction. However, the reduction of sodium cyanide consumption was greater than that attributable to the reduction in copper extraction. This appeared to be partly due to reduced thiocyanate formation, possibly resulting from coverage of the copper sulfide surfaces.

It appears that copper passivation is enhanced by adding surfactants with lower degrees of amine ethoxylation and longer alkyl chain lengths. However, amines having longer chain lengths tend to be more viscous and less water-soluble and hence, less easy to pump and handle.

2.4 Description of existing heap modeling methods

In this section, four existing heap modeling methods which illustrate well the different advances in modeling heap leaching are presented. First, Bartlett (1992) developed numerous deterministic models for the most common heap problems: cyanide leaching of gold ores and acid leaching of copper oxide ore. The conditions for these two problems are different and for this reason are treated separately. Afterwards, model by Dixon and Hendrix (1993) combines elegantly many dimensionless parameters, and therefore, is more general than the previous ones. The first heap model concerned with the multiple leaching reactions and their relative rates was developed by Box and Prosser (1986). These models are briefly described in the following sections with respect to their ability to predict current heap leaching problems.

2.4.1 Gold cyanidation model

The dissolution kinetics of gold grains is fast because of their submicron size and cyanide consumption from the reaction with gold is negligible since there are stoichiometrically small amounts of gold present in the ore. Consequently, the gold extraction rate during heap leaching of these ores is controlled by diffusion only and can be expressed for the diffusion from a porous sphere:

$$F_{t,r_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp\left(\frac{-D_{eff} \cdot n^2 \cdot \pi^2 \cdot t}{r_o^2}\right) \quad (2-21)$$

where F_{t,r_o} is the mass fraction of gold extracted from a rock radius, r_o , in time, t , and D_{eff} is the effective diffusivity. This model is valid if the lixiviant concentration, C_A , is essentially uniform throughout the particle which is not the case when large amounts of cyanide consumers are present inside the heap.

2.4.2 Model for acid leaching of copper oxide ore

The amount of copper extracted from a typical oxide copper ore consumes a significant amount of acid not to mention the acid consuming gangue minerals in the ore. Even though the copper mineral dissolution kinetics are fast, gradients of reagent concentration are encountered inside an ore particle. Dissolution gradually progresses inward with an expanding shell or rim (**Figure 2-4**). This model was first developed by Braun et al (1974) and Sohn and Wadsworth (1979) and later supplemented by Bartlett (1991). The copper extraction rate is described using a quasi-

steady-state continuity equation for reagent species in spherical coordinates where C_{A_0} and C_{A_c} are the reagent concentration at the surface and at the core of the particle respectively.

$$1 - \frac{2}{3} \cdot F_{t,r_o} - (1 - F_{t,r_o})^{2/3} = K_D \cdot (C_{A_0} - C_{A_c}) \cdot \left(\frac{D_{eff}}{r_o^2} \right) \cdot t \quad (2-22)$$

Unlike oxidized gold ore leaching, the copper lixiviant (which is sulfuric acid) will be depleted as it trickles through the heap with faster rates of copper extraction occurring towards the top of the heap. This fact must be considered in the macro-model of copper oxide heap leaching.

Figure 2-4: Partial copper extraction from a porous ore particle of radius r_o showing a leached rim surrounding an unleached core (Bartlett, 1997)

For both oxidized gold ores and oxidized copper ores, the extraction, F_{t,r_o} depends on D_{eff}/r_o^2 .

Consequently, in both cases, crushing the ore reduces the rock size, r_o , shortens diffusion distances, and speeds up the metal extraction process. Particle size distribution equations, such as

the Gates-Gaudin-Schuhmann (GGS) relation, are combined with the leaching equations to calculate extraction versus leaching time.

2.4.3 Combined reaction and diffusion model

The model developed by Dixon and Hendrix (1993A and 1993B) simulates both reaction and diffusion controlled mechanisms simultaneously depending on a choice of dimensionless parameters such as reaction, diffusion and advection times, Peclet, Damköhler I and Damköhler II. It is not the purpose of this literature review to elaborate on these parameters but a brief outlook on how the model is built is presented. The general model is divided into two parts, the micro- or particle-scale model, and the macro- or heap-scale model. The kinetic rates occurring in the particle scale may be controlled by either reaction or diffusion. The continuity equation for the rate-controlling reagent A becomes:

$$\frac{1}{t_d} \cdot \left[\frac{\partial^2 \alpha}{\partial \xi^2} + \frac{2}{\xi} \cdot \frac{\partial \alpha}{\partial \xi} \right] - \frac{\beta \cdot \sigma \cdot \alpha}{t_r} = \frac{\partial \alpha}{\partial t} \quad (2-23)$$

where α and σ are the dimensionless concentrations of the reagent A and the solid reactant S respectively, and ξ is the dimensionless particle radius. The first term of equation (2-23) represents diffusion and the second term the reaction rate. Some dimensionless leaching parameters are also present in this equation. They are: β , the dimensionless measure of reagent strength relative to the grade of solid reactant S , the diffusion timescale, t_d , and the reaction timescale, t_r . Those parameters are calculated from characteristics of the ore such as the porosity ϵ_o , the applied concentration of reagent A and the grade of solid reactant S , etc. and can be

measured by independent, well-defined experiments. The diffusion time and the reaction time may be expressed as follows:

$$t_d = \frac{\varepsilon_o r_o^2}{D_{eff}} \quad t_r = \left(k \cdot C_{S_o}^{\phi_S - 1} \cdot C_{A_o}^{\phi_A} \right)^{-1} \quad (2-24)$$

In the macro-model, the overall kinetics may be controlled by either advection (i.e. flow of lixiviant solution downward through the heap) or by kinetics at the particle scale. The mass balance equation for reagent A is written:

$$-\frac{1}{t_a} \cdot \frac{\partial \alpha}{\partial \zeta} - \frac{3 \cdot v}{t_d} \cdot \frac{\partial \alpha}{\partial \xi} \bigg|_{\xi=1} = \frac{\partial \alpha}{\partial t} \quad (2-25)$$

where ζ is the dimensionless heap depth. The dimensionless leaching parameters v and t_a complement the previous parameters and correspond to the volume ratio of solution held up within the particle pores to the bulk lixiviant and the advection time respectively.

$$t_a = \frac{\varepsilon_b \cdot Z}{u_s} \quad v = \frac{\varepsilon_o \cdot (1 - \varepsilon_h)}{\varepsilon_b} \quad (2-26)$$

where Z is the heap depth, u_s is the flow rate, ε_h is the void fraction of the bed (not including the particle pores), and ε_b is the relative volume of the bed occupied by bulk lixiviant.

Figure 2-5: Comparison of solutions to the heap leaching model for the one-reactant ($n=1$) and two-reactant ($n=2$) systems. Solid lines are heap concentration profiles of reagent A and dotted lines are the fractional conversion profiles of solid reactant S_1 (Dixon, 1993B)

The present model is capable of calculating the effect of two competing reactants S_1 and S_2 for the same reagent A as shown in **Figure 2-5**. In the first diagram, reactant S_1 dissolves effectively throughout the heap, and the reagent gradients are insignificant. In the presence of the solid reactant S_2 , however, the reaction shifts towards the top of the heap, and the reagent gradients are steep. In addition, the reagent gradients within the heap approach a steady-state. Hence, the conversion kinetics of reactant S_1 are approximately described by the model for reagent A using the reaction term of S_2 alone, at steady-state. However, similarly to the models presented previously, it does not account for solution chemistry inside the heap and speciation of the different metal-ligand complexes. Therefore, more complex systems such as cupriferous gold ores where the different reactants are interrelated and wherein precipitates may form would not be simulated accurately by this model.

2.4.4 Multi-species and multi-reagent model

Box and Prosser (1986) developed a model where competing, complementary and sequential reactions involving several minerals and several reagents are simulated. They derive a hypothetical reaction matrix in which some minerals are classified as reacting slowly, some others reacting rapidly, and so on. The whole procedure is based on the assumption that the rate of reaction of each mineral is controlled by diffusion of the corresponding reagent to the reactive mineral.

They explore the example of heap leaching by sulfuric acid of a cupriferous ore containing malachite, chrysocolla, chalcopyrite, calcite and magnesite. The matrix can become quite complex, with 4 reagents and 7 minerals. Dissolved copper and ferrous sulfates are included as reagents since they may react with calcite and magnesite. The products of those reactions, the hydrated oxides, are included as minerals since they could react with acid as well. By comparing their calculations with experimental results, they concluded that the simulation may be satisfactory if the stoichiometric factors are constant in time and space within the heap. The principal stages of the programming procedure are:

1. Identification of the possible rates of reaction of each mineral with a corresponding reagent;
2. Combination of reactions that always occur independently with appropriate stoichiometric factors;
3. Calculation of the incremental extent of reaction for each coherent group of reactions and the consequential changes in the solution composition;
4. Steps 1 and 2 are repeated for each increment of space and time into which the heap is divided.

Unfortunately, there seems to be no follow-up of these ideas. From an extensive literature review, there is no further practical testing of this model. Also, they assume that the rates of all reactions are controlled only by molecular diffusion into the particles. This assumption is false in the presence of equilibrated or slow reactions. Finally, no speciation of the solution composition and thus, no formation of precipitates is incorporated into the model at step 3.

In conclusion, from the previous literature review, it appears that the development of a more general heap leaching model including some of the mathematical aspects of the Dixon and Hendrix model, with a speciation model to describe solution chemistry, is required to simulate heap leaching of cupriferous gold ores.

3. Preliminary experimentation

This section contains a physical and mineralogical description of the Telfer Composite 'E' ore, general experimental procedures and preliminary experimentation. Batch fine ore leaching tests and semi-batch coarse ore leaching tests constitute the essential step for the validation and calibration of the heap leaching model and thus, their results will be emphasized.

3.1 Description of Telfer Composite 'E' ore

A single large batch of ore sample was prepared for use in all leaching experiments. Approximately 700 kg of the Telfer Composite 'E' ore sample lot was screened to remove all material not passing one inch. This coarse material was then reduced to a size of minus one inch in a gyratory crusher, and recombined with the passing material. Finally, the whole sample was coned, quartered, split and placed in plastic bags for storage (see **Figure 3-1**). The same procedure was used every time a smaller homogeneous sample was needed. The ore density, ρ_{ore} , was measured at 2.59 g/cm^3 and the initial ore porosity, ϵ_o , at 0.18.

Figure 3-1: Schematic diagram of sampling procedure

3.1.1 Elemental and mineralogical characteristics

Partial elemental analysis for Au, Ag, Fe, Al and As by induction coupled plasma (ICP) of the Telfer Composite 'E' ore is given in **Table 3-1**. More comprehensive data may be found in appendix A. XRD analysis performed in the geology department at UBC identified the major minerals within the ore (**Figure 3-2**). The presence of these minerals is also confirmed by optical microscopic analysis made by Wolfgang Baum at the Pittsburgh Mineral & Environmental Technology laboratories (PMET) (refer to **Table 3-2**). He reported that the bulk of the sample consists of siliceous/quartz rich, highly altered, sericitic rock material which contains elevated amounts of pyrite and iron oxides/hydroxides with minor amounts of jarosite.

Table 3-1: Partial elemental analysis of Telfer Composite 'E' ore sample

Au (ppm)	Ag (ppm)	S ²⁻ (%)	S _T (%)	Cu (ppm)	Fe (%)	Al (%)	As (ppm)
0.58	0.80	2.48	2.58	2580	6.29	0.15	850

He comments further that the major copper-bearing minerals are secondary copper sulfides; mostly covellite with lesser amounts of chalcocite. Both of these minerals occur as ultrafine (<20 µm) inclusions within iron oxides/hydroxides and they are also replacing pyrite (rimming and fracture-related replacements). Also, there are minor amounts of relatively coarse-grained covellite (± 260 µm in diameter). About 20%v/v of the pyrite particles exhibit signs of bacterial oxidation, i.e. oxidation channels which are filled with a mixture of copper-bearing iron oxides, covellite and chalcocite.

Figure 3-2: XRD analysis on Telfer Composite 'E' ore

Table 3-2: Qualitative microscopic modal analysis of Minus 10 Mesh head sample performed at PMET laboratories, PA

Mineral	Grade (%v/v) (Qualitative)	Expected NaCN solubility (Qualitative)
Gangue (with inclusions of iron oxides, pyrite and traces of copper sulfides)	80.00	X
Iron oxides/hydroxides	8.60	X
Pyrite	6.52	X
Manganese oxides	2.33	X
Covellite/Chalcocite	2.00	Moderate
Copper-stained clay	0.50	Fast to a certain extent
Native copper (partially oxidized into iron oxides and chalcocite)	0.03	Fast
Malachite	0.02	Fast
Chalcopyrite	<0.01	Very slow
Total	100.00	

The sample also contains trace amounts of native copper most of which is partially oxidized into copper-bearing iron oxides and chalcocite. The particle size range of the native copper is from less than 10 μm to 200 μm . Finally, there are ultrafine (< 20 μm) inclusions of chalcopyrite within the pyrite and traces of malachite. Some copper-stained clay is the result of ultrafine dispersion of malachite within the clay. Gold particles were not detected.

Supplementary acid digestion tests show that approximately 31%w/w of copper is non-sulfidic, as determined by 5% H_2SO_3 acid leaching for 2 hours while total copper measured by $\text{HNO}_3/\text{HClO}_4$ digestion amounts to 0.258%w/w of the ore.

3.1.2 Natural acidity

Telfer composite 'E' ore was found to buffer effluent column leaching solutions very rapidly to a pH of approximately 4.0. In order to measure the extent of this drop in pH, a base titration with sodium hydroxide was performed. The results are presented in **Figure 3-3**.

Figure 3-3: Titration of Telfer composite 'E' ore with 0.5 mol/L NaOH

From the comparison of the titration curves with a solution of 0.5 mol/L sodium hydroxide and with de-ionized water, there is an instantaneous decrease in pH down to 4.0 and a buffering

effect which lasts up to 3.3 mL of titration solution. This corresponds to 1.65 millimoles of NaOH for 50 g of fine ore. It is difficult to assess the cause of this drop in pH but the dissolution of copper sulfate is suspected.

Similar titration tests with a solution of 0.5 mol/L acetic acid showed that the buffering effect of the ore is much weaker in acid solution.

3.1.3 Particle size distribution

The particle size distribution (PSD) of the Telfer Composite 'E' ore is presented in **Table 3-3** where $\bar{D}$ is the arithmetic average diameter between the passing and resting screens. The weight measured represents the rock material on the resting screen. According to the Gates-Gaudin-Schuhmann (GGS) distribution, the parameter m can be calculated easily from the coefficient of variation ($CV^2 = 0.82861$) of the particle size distribution:

$$CV^2 = \frac{1}{m(m+2)} \quad (3-1)$$

The value of the GGS parameter m is equal to 0.486 at an effective maximum particle size of 26.9 mm. The dimensionless particle size may be expressed as $\xi = D/D^*$ where D^* is the normalizing size different for each PSD function (Randolph et al, 1988). **Figure 3-4** compares the GGS cumulative distribution function, $F_{GGS}(\xi) = \xi^m$, with the experimental data cumulative distribution, $F(classifier)$. Both agree well with particles larger than 1 mm but experimentally

tend to be underestimated at smaller particles sizes. Hence, the GGS approximation is a poor fit at fine particle sizes.

Figure 3-4: Particle size distribution of Telfer Composite 'E' ore

3.2 General experimental procedure

All leaching samples were kept in a refrigerator to retard oxidation of cyanide and disintegration of the different cyanide complexes. Copper and iron concentrations were measured by atomic absorption spectrometry (AAS) to a precision of 0.1 ppm. The accuracy is probably 2% depending on how many times dilution was made. When necessary, samples were diluted with a solution of pH 11.7 (by addition of drops of 1 mol/L NaOH) and 500 ppm NaCN. Standard solutions were prepared accordingly with particular attention to the enhancing effect of sodium concentration on the AAS flame. Gold measurements were performed by Ron Williams at Chem Met Consultants Inc., Vancouver, BC. The pH measurements were made with a conventional pH

probe. The free cyanide concentration of the stock solution was measured by silver nitrate titration with a 5% KI indicator (see also note on titration for free $[\text{CN}^-]$ in section 4.5).

Table 3-3: Summary results of PSD calculation with GGS method

$\bar{D}$ (mm)	w/w of total ore (%)	$F(\text{classifier})$	ξ	$F_{\text{GGS}}(\xi)$	Normalized $F_{\text{GGS}}(\xi)$
20.2	21.123	0.211	1.118	1.056	0.183
11.505	14.542	0.357	0.637	0.803	0.322
8.095	12.545	0.482	0.448	0.677	0.440
5.72	7.997	0.562	0.317	0.572	0.539
4.06	5.371	0.616	0.225	0.484	0.623
2.53	9.065	0.706	0.140	0.385	0.690
1.445	3.367	0.740	0.080	0.293	0.740
1.02	2.438	0.764	0.056	0.248	0.783
0.722	2.582	0.790	0.040	0.209	0.820
0.5055	2.415	0.814	0.028	0.176	0.850
0.357	2.463	0.839	0.020	0.149	0.876
0.2535	2.073	0.860	0.014	0.126	0.898
0.195	1.324	0.873	0.011	0.111	0.917
0.165	0.857	0.882	0.009	0.102	0.935
0.128	1.296	0.895	0.007	0.090	0.950
0.0905	1.025	0.905	0.005	0.076	0.964
0.064	4.343	0.948	0.004	0.065	0.975
0.049	3.914	0.987	0.003	0.057	0.985
0.0415	0.478	0.992	0.002	0.052	0.994
0.019	0.782	1.000	0.001	0.036	1.000
TOTAL	100.000			5.769	

3.3 Batch fine ore leaching tests

The objective of the batch fine ore leaching tests is to measure the reaction timescale of the different minerals in the heap; i.e., the intrinsic time for a reagent to dissolve completely a solid reactant. By definition, other mechanisms such as diffusion and advection are assumed to be nonexistent or negligible. To simulate those conditions, the ore was finely ground (80% passing 80 μm) and the batch reactor intensely agitated to minimize any diffusion layer encircling the particles.

3.3.1 Development of the reaction time parameter

Since reactant grains within an ore particle tend to exhibit a range of grain sizes, none of which is precisely known, it is often more convenient simply to represent the rate of dissolution with a pseudo-homogeneous variable-order rate law of the form:

$$\frac{dC_S}{dt} = -k \cdot C_S^{\phi_S} \cdot C_A^{\phi_A} \quad (3-2)$$

where C_S = grade of solid reactant S at particle radius r (mol/cm^3);

C_A = reagent concentration at particle r (mol/cm^3);

k = rate constant expressed per unit particle mass;

ϕ_S = apparent reaction order in the concentration of reactant S ;

ϕ_A = reaction order in the concentration of reagent A ;

Equation (3-2) may be written in dimensionless form:

$$\frac{d\sigma}{dt} = - \frac{\sigma^{\phi_S} \cdot \alpha^{\phi_A}}{t_r} \quad (3-3)$$

where σ = dimensionless grade of solid reactant S over the initial grade (C_S/C_{Sio});

α = dimensionless reagent concentration over the initial concentration (C_A/C_{Ao});

And t_r is the reaction time parameter which is given by the following equation:

$$t_r = \left[k \cdot C_{S_o}^{\phi_S-1} \cdot C_{A_o}^{\phi_A} \right]^{-1} \quad (3-4)$$

Considering equation (3-3), if a batch leaching test is performed at constant cyanide concentration, the value of reaction time becomes solely dependent on the rate of leaching of the mineral S (i.e. the value of α^{ϕ_A} becomes 1.0). Hence, a straightforward method which allows the calculation of reaction time is to measure the slope of the $X-t$ curve at $t(X=0; \sigma=1)$ and interpolate to $t(X=1; \sigma=0)$ which will correspond geometrically to the calculated value of the reaction time, t_r (see **Figure 3-5**).

3.3.2 Experimental procedures of batch fine ore leaching tests

The method adopted was to place small amounts of ground ore sample (12.000 ± 0.001 g) into a relatively large quantity of cyanide solution (2.00 ± 0.01 L), such that the initial cyanide represented a stoichiometric excess of a least ten-fold relative to the formation of the tricyanocuprate(I) complex, $\text{Cu}(\text{CN})_3^{2-}$. A 2000-mL glass beaker was arranged with four plastic baffles and left open to the air. Mixing was provided by a Caframo stirrer with a three-blade

impeller agitating at roughly 1350 ± 10 rpm. This speed was adjusted to keep all particles in suspension without introducing excess gas which would cause problems in sampling. The initial pH was adjusted to 10.60 ± 0.05 .

Figure 3-5: Calculation of reaction time parameter

About ten milliliters of sample was pipetted at intervals during the test for copper analysis. Normally, samples were taken frequently during the first hour of the experiment because the slope at $t(X=0; \sigma=1)$ is essential to the success of the model. Later, the frequency of sampling was decreased. Most leach times were extended to twenty four hours and were independent of the initial cyanide concentration. Because the maximum copper concentration in most samples was 15.5 ppm, no dilution was required. Hence, analysis by AAS of all samples was performed

at once on the following day to prevent copper precipitation and to simulate constant experimental conditions.

3.3.3 Presentation of results

The results of the batch fine ore leaching tests at four different constant cyanide concentrations, typically 100, 400, 1000 and 2000 ppm NaCN, are presented in **Figure 3-6**. From these tests, it would appear that the rapidly dissolving copper comprises approximately 30% of the total calculated copper head grade based on the column results (see **Table 4-4**). This is consistent with the 5% H_2SO_3 acid leaching which determined that 31% of the copper was non-sulfidic (see section 3.1.1). Finally, the leaching rate deviates from linearity at around 72% of the total copper for all constant [NaCN] tests. Labile copper sulfides leached with moderate speed up to 100% copper dissolution.

Figure 3-6 allows the estimation of the reaction time for labile copper sulfides. The region from 31% (i.e. $\sigma = 0$) to 100% (i.e. $\sigma = 1$) of the total copper is presented in **Figure 3-7**. A best fit polynomial on each profile using the method illustrated in **Figure 3-5** gives the slopes at $t(\sigma=0)$ and the respective reaction times for the labile copper minerals listed in **Table 3-4**. A least squares regression analysis of the reaction times versus the cyanide concentration at 25°C gave a slope 0.9979 (i.e. the value of the exponential ϕ_A in equation (3-3)) at a 99.71 percent confidence on the R^2 fitting (**Figure 3-8**). This is a first order reaction for the cyanidation of labile copper sulfides.

Figure 3-6: Batch fine ore leaching tests at constant cyanide concentration

Figure 3-7: Representation of batch fine ore leaching behavior of secondary copper sulfides in constant cyanide concentration

Table 3-4: Reaction time values for a secondary copper mineral at different constant cyanide concentration measured from batch fine ore leaching tests

[NaCN] (ppm)	[NaCN] (mol/L)	Reaction time (min)
100	0.00204	310
400	0.00816	87
1000	0.02041	34
2000	0.04082	15

Figure 3-8: Least square regression analysis of the reaction times versus the cyanide concentration at 25°C

3.4 Semi-batch coarse ore leaching tests

These tests were conducted in short columns each containing a coarse ore sample as described in section 3.1, and were run at approximately five times the flow rate of the regular column tests (approximately 5 mL/min). In this way, it was possible to determine the leaching rates of copper

and gold from the ore directly, in the absence of the effects which result from the depletion of cyanide occurring in the taller column tests. The tests were run for three days and samples were taken directly from the short column (not from the effluent bucket). The following individual characteristics are tabulated in **Table 3-5**. The diameter of the columns was 7 cm, which was slightly less than the diameter of the tall columns described in section 4.

Table 3-5: Main characteristics of semi-batch coarse ore leaching tests

	Short column #7	Short column #8	Short column #9
[NaCN] _o (ppm)	500	1000	2000
Weight ore loaded (g)	1156.3	1216.1	1103.7
Column height (cm)	18.0	19.5	17.5

3.4.1 Presentation of results

Figure 3-9 presents the copper recovery for the three semi-batch tests #7, #8 and #9 (also named short columns) run at cyanide concentrations of 500, 1000 and 2000 ppm respectively while **Figure 3-10** shows the corresponding pH data for the first 15 hours. Several features on these plots merit comment:

- the extraction curve is very parabolic for all semi-batch experiments. This suggests pure chemical reaction control, which is expected for a short column and high reagent concentrations. Unfortunately, the test was stopped after 3 days because at the higher flow rate, the cyanide waste became too large to handle. Nevertheless, the rate of copper leaching was slow after 3 days and no copper was extracted past 70%;
- both copper recovery and pH have a strong dependence on the influent cyanide concentration;

c) Two pH buffer points are located, at around pH 5.0 and pH 8.0 on all but short column #9.

The influent cyanide concentration strongly influences the rate of increase in pH and may explain why short column #8 follows a pattern closer to short column #7 than to short column #9.

These semi-batch tests are an approximate representation of the upper portion of the tall columns. It can be seen that for influent cyanide concentration up to 1000 ppm NaCN, the pH and most likely, cyanide concentration may drop very rapidly within a depth of only 15 cm. For this reason, the semi-batch experiments did not serve their purpose of measuring the leaching rates of copper and the conversion rate of cyanide to cyanate explicitly. Nevertheless, the general heap leaching model can be calibrated based on the simulation of these semi-batch experiments.

Figure 3-9: Semi-batch coarse ore leaching tests, copper extraction

Figure 3-10: Semi-batch coarse ore leaching tests, pH data (first 15 hours of operation)

4. Column leaching tests

The column leaching tests form the basis of the model validation because they simulate actual heap leaching behavior under different nominal influent cyanide concentrations. The physical characteristics and experimental parameters of each column are discussed. The leaching behavior of copper and gold is presented by four diagrams: effluent concentration, recovery (or conversion) curves, effluent concentration on a metal/cyanide ratio basis and leached residual ore grades. The second and fourth ones are based on calculated head assays. Iron is represented by effluent concentration only. Results of cyanide, thiocyanate and pH results of the pregnant solution at regular intervals are also included.

4.1 Physical characteristics and experimental parameters

The columns were made of rigid transparent acrylic with a inner diameter of 8.9 cm (**Figure 4-1**). Each column was loaded with 15.0 ± 0.05 kg Telfer Composite 'E' ore, screened and crushed as described in section 3.1. To ensure a homogeneous particle distribution inside the column, the loading of a column was performed within a few seconds with the help of a large steel funnel. The experimental parameters of each column are presented in **Table 4-1**. The irrigation rates were different because of the difficulty of calibrating all peristaltic pumps to pump at the same rate. Fresh cyanide solution from an airtight carboy (i.e. no recycling) was passed constantly through the columns. The cyanide concentration of the stock solutions was measured regularly by silver nitrate titration and was found to decrease slowly by approximately 2.5% over a period of one month under lab visible radiation (Silver, 1969).

Table 4-1: Main characteristics of the column leaching tests

Column number	6	7	8	9
Nominal $[\text{NaCN}]_0$ (ppm)	200	500	1000	2000
Irrigation rate (mL/min)	0.8662	0.8574	0.8698	0.9283
Superficial velocity (mL/m ² ·s)	2.269	2.246	2.279	2.432
Ore height (cm)	143	143	145	148

Figure 4-1: Picture of experimental set-up for column tests

4.2 Presentation of the copper leaching behavior

The following identification of three different types of copper mineral is suggested based on the copper recovery behavior shown in **Figure 4-2**, and from the stereomicroscopic examination of the leached residual ore by the PMET Labs (see section 4.2.1):

1. the rapid dissolution of a weak-acid soluble copper (later denoted WAS-Cu) during the first day of leaching in every column;
2. the cyanide complexation of a labile copper sulfide, typically chalcocite and covellite recognized by the strong dependence of the leaching rates on the influent cyanide concentration;
3. the very slow cyanide leaching of refractory copper mineral which consists primarily of chalcocite and covellite encapsulated in ferruginous bio-oxidation products or in impervious siliceous gangue. This is recognized by the gradual change in the leaching rate at approximately 65% extraction. The dependence on influent cyanide concentration is not as distinct as for the labile copper sulfides.

The transition from the WAS-Cu to the labile copper sulfide is remarkable for its unusual pattern. An enlarged plot of this section of **Figure 4-2** is presented in **Figure 4-3** with the time axis put on a logarithmic scale to better illustrate the contrast between each curve. The different aspects of this plot are summarized in **Table 4-2**. It is shown that the columns with the higher nominal cyanide concentration actually discharge proportionally less WAS-Cu than the ones with lower nominal cyanide concentration. Column #7 seems to be an exception because it recovers a lower overall copper percentage (i.e. 12.8%) during the first day. However, after 3

Figure 4-2: Copper recovery behavior for columns #6, #7, #8 and #9

Figure 4-3: Enlarged plot of Copper recovery behavior for columns #6, #7, #8 and #9

days, the previous observation becomes entirely valid. Other observations are related to the transition point where the leaching of labile copper sulfides commences. This point is located at a time which is inversely proportional to the influent cyanide concentration. Again, column #7 falls short by two days but still follows the pattern relatively well. Finally, the amount of copper released up to this transition point is also inversely proportional to the influent cyanide concentration for all columns.

Table 4-2: General observations on the enlarged plot of the copper recovery curves

Column number	6	7	8	9
Nominal $[\text{NaCN}]_0$ (ppm)	200	500	1000	2000
% Cu at Day 1 (± 0.5)	14.5	12.8	13.7	13.1
% Cu at beginning of labile copper sulfide leaching (± 0.1)	20.0	17.7	16.6	14.5
Time at which labile copper sulfide leaching begins (days)	25	10	6	3

The fine features of the copper effluent concentration response are more easily seen in **Figure 4-**

4. In these graphs, we notice more interesting aspects of the copper leaching behavior:

1. The effluent copper concentration in the first drippings as listed in **Table 4-3** exceeds by a large margin the stoichiometry of the typical cuprous cyanide complex $\text{Cu}(\text{CN})_3^{2-}$. Hence, the dissolution of WAS-Cu is unconstrained by the influent cyanide concentration;
2. Immediately after, the high copper concentration falls abruptly to practically zero, prior to the establishment of the “normal” leaching behavior of the labile copper sulfides. This lag time is inversely proportional to the nominal influent cyanide concentration;

Figure 4-4: Effluent copper concentration behavior for columns #6, #7, #8 and #9

3. During the leaching of the labile copper sulfide minerals, two distinct peaks in the effluent copper concentration (seen clearly in all but column #9) become more separated and distinctive with decreasing cyanide concentration;
4. The effluent copper concentration declines once it has passed the second peak. The intensity of the decline is related to the cyanide concentration in the columns with higher nominal cyanide concentration presenting a sharper drop;
5. The copper concentration tapers off at approximately 30 ppm, independent of the nominal cyanide concentration.
6. The stoichiometric cyanide requirement per unit copper recovery decreases with decreasing nominal influent cyanide concentration (recognized by comparing the relative heights of the curve peaks in **Figure 4-5**) except for column #6 which is clearly lower than column #7.

Table 4-3: General observations on copper concentration curves

Column number	6	7	8	9
Nominal [NaCN] ₀ (ppm)	200	500	1000	2000
First drippings [Cu] (ppm)	13711	10014	14771	12966
Lag time (days)	16	7	5	3
Stage 2: First peak (ppm)	115	284	558	-
Stage 2: Second peak (ppm)	127	359	668	950

Figure 4-5: Copper concentration on copper/cyanide ratio basis for columns #6, #7, #8 and #9

The following procedure is used to measure the copper and gold grades in the leached residual ore. The wet ore is emptied from the column onto brown paper, on which it is allowed to dry overnight. The dried ore is then separated in five equal parts of approximately 3 kg each. The samples taken from the top of the column correspond to section 1, and from the bottom, to section 5. The analysis results by strong $\text{HNO}_3/\text{HClO}_4$ acid digestion are presented in **Figure 4-6**. Except for section 2, in most cases, the copper leaching behavior is relatively uniform for all columns. The average calculated head copper grade for Telfer 'E' composite ore is 2562 ppm (see **Table 4-4**). This value is close to the initial copper grade measured at 2580 ppm.

Table 4-4: Calculating the copper head grade

Column number	6	7	8	9
Nominal $[\text{NaCN}]_0$ (ppm)	200	500	1000	2000
Net copper leached (g)	26.6	30.7	33.0	31.0
Net copper in residual ore (g)	11.2	7.7	7.9	6.2
Total net head copper (g)	37.8	38.4	40.9	37.2
Weight of ore in column (g)	14928	14926	15236	15092
Head copper grade (ppm)	2536	2569	2683	2460

Figure 4-6: Copper grades in leached residual ore for columns #6, #7, #8 and #9

4.2.1 Leached residual ore mineralogical analysis

Section 3 of column #8 was sent to Wolfgang Baum of the PMET Labs for stereomicroscopic examination. Unleached copper occurs primarily as ultrafine chalcocite and covellite, both of which are present in ultrafine layers of 1 to 15 μm thickness on the surface of pyrite particles (**Figure 4-7** and **Figure 4-8**). The layers consist of a mixture of ferruginous gangue slimes, some of which may be bio-oxidation precipitates. Further, residual unleached covellite occurs in noticeable amounts mixed with ferruginous bio-oxidation precipitates in bacterial oxidation channels within pyrite particles (**Figure 4-9** and **Figure 4-10**). The analysis of the bio-oxidation precipitates revealed that these consist primarily of jarosite.

Finally, there were trace amounts of disseminated covellite and chalcocite locked in impervious siliceous gangue and/or covellite or chalcocite particles. Those particles were in turn associated with pyrite which was encapsulated in dense gangue. Minor amounts of copper were contributed by micro-inclusions of chalcopyrite within pyrite. These chalcopyrite inclusions were less than 5 to 30 μm in diameter. An approximated distribution of copper is presented in **Table 4-5**.

Table 4-5: Approximated distribution of copper in leached residual ore performed at PMET laboratories

Minerals	Grade (%v/v)
Secondary copper sulfides (covellite & chalcocite)	75
Acid-soluble copper (copper sulfates admixed with ferruginous precipitates)	15
Chalcopyrite	10
Total	100

Figure 4-7: Photomicrograph showing a large pyrite particle which contains ultrafine chalcocite particles in a partially oxidized rim

Figure 4-8: SEM digital X-ray image of the particle shown in Figure 4-7

Figure 4-9: Photomicrograph showing a pyrite particle with bacterial oxidation channels. The channels are filled with ferruginous bio-oxidation precipitate (jarositic material) which has entrained residual covellite and traces of chalcocite

Figure 4-10: SEM digital X-ray image of the particle shown in Figure 4-9. The jarosite fillings in the bacterial oxidation channels are outlined by the yellow dot mapping of potassium

4.3 Presentation of the gold leaching behavior

The gold recovery behavior is presented in **Figure 4-11** and the corresponding effluent gold concentrations are shown in **Figure 4-12**. As with labile copper sulfides, gold leaching behavior is heavily dependent on the influent cyanide concentration. Columns with a high $[\text{NaCN}]_0$ (i.e. columns #8 and #9) produce a distinctive peak and a downward tail until all the amenable gold in the column is leached. Conversely, columns with a low influent cyanide concentration (i.e. columns #6 and #7) do not show a peak but instead reveal a more regular plateau. These leaching behaviors will be discussed in more detail in section 6. As for copper and iron, a definite breakthrough time must elapse before gold is detected in the effluent. Again, these times are roughly in inverse proportion to the nominal influent cyanide concentration. However, they are not nearly as long as those of iron (refer to the following section).

The heights of the effluent gold concentration peaks from all four columns are well normalized with respect to nominal influent cyanide concentration as shown in **Figure 4-13**. This confirms the uniform stoichiometry of the gold(I)-cyanide complex and, more importantly, by inference, the variable stoichiometry of the copper-cyanide system. In addition, the timing of those peaks is inversely proportional to the nominal influent cyanide concentration, whether measured from time zero or from the times of gold breakthrough.

Figure 4-11: Gold recovery behavior for columns #6, #7, #8 and #9

Figure 4-12: Effluent gold concentration behavior for columns #6, #7, #8 and #9

Figure 4-13: Gold concentration on gold/cyanide ratio basis for columns #6, #7, #8 and #9

The leached residual grade is presented in **Figure 4-14**. For most columns, the leaching rate of gold is relatively constant. The Telfer 'E' composite ore contains approximately 20% gold which is refractory to cyanide as confirmed by assaying the leached residual ore shown in **Table 4-6**. The average gold head grade is 0.717 ppm. It will be noted that linear segments of curves on **Figure 4-12** and **4-9** are due to analytical precision (i.e., the smallest significant figure was ± 0.01 ppm Au).

Table 4-6: Calculating the gold head grade

Column number	6	7	8	9
Nominal [NaCN] ₀ (ppm)	200	500	1000	2000
Net gold leached (mg)	26.6	30.7	33.0	31.0
Net gold in residual ore (mg)	2.47	2.29	1.98	2.58
Total net gold (mg)	8.2	8.4	8.1	9.1
Weight of ore in column (mg)	14928	14926	15236	15092
Calculated Head gold grade (ppm)	0.712	0.716	0.663	0.777

Figure 4-14: Gold grades in leached residual ore for columns #6, #7, #8 and #9

4.4 Iron leaching behavior

Figure 4-15 shows the iron concentration in the effluent. The following points are observed and summarized in **Table 4-7**:

1. Iron is found in moderate concentrations during the first day of operation, probably due to small amounts of a weak-acid soluble iron (WAS-Fe) associated with WAS-Cu;
2. The slow cyanide complexation of refractory iron is best identified by the onset of iron in solution. This is particularly evident in columns #8 and #9 with sharp increases in iron concentration which correspond very closely to the breakthrough times for free cyanide (refer to following section).
3. Eventually, the iron concentration in the effluent levels off to approximately 1 ppm of iron for columns #6, #7 and #8 while column #9 maintains a slightly higher iron concentration at 3.1 ppm. Due to the fact that so little cyanide is complexed by iron, the effect of initial cyanide concentration is probably negligible.

Table 4-7: General observations on iron concentration curves

Column number	6	7	8	9
Nominal [NaCN] ₀ (ppm)	200	500	1000	2000
Lag time (days)	109	55	31	16
Stage 3: Peak (ppm)	2.8	2.7	5.7	32.4
Average [Fe] after tail (ppm)	0.9	0.8	0.9	3.1

Figure 4-15: Effluent iron concentration behavior for columns #6, #7, #8 and #9

4.5 Effluent cyanide concentration behavior

It is acknowledged that the titration for “free cyanide” with silver nitrate and a 5% KI indicator is more of a qualitative method than an accurate quantitative method. The endpoint is indicated by the formation of a yellowish opalescence due to AgI. Some effluent solutions contain enough copper to yield erroneous results due to the instability of $\text{Cu}(\text{CN})_4^{3-}$. Aside from this point, the species commonly found in cyanide leach solutions such as SCN^- , $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, OCN^- , and possibly sulfide and $\text{S}_2\text{O}_3^{2-}$ would interfere since those species form stable compounds with silver. By experience, it was found that in titrating NaCN solutions with 0.05 mol/L AgNO_3 , the first four species mentioned above do not present significant interference. Ferricyanide is yellow in solution and if present makes the endpoint a little harder to observe, but with practice, this causes no problem. Fortunately, while thiosulfate interferes, it is not likely to be found in cupriferous gold ore leach effluents. With this in mind, care must be taken in interpreting the following results.

It is proper to place the effluent copper and iron concentration and the effluent cyanide depletion (calculated as the actual influent cyanide concentration minus the effluent “free cyanide” on a percentage scale) on the same diagram since the breakthrough in cyanide concentration is intimately associated with those two metals. All the comparisons are presented in **Figure 4-16**. The effluent iron concentration is multiplied by 25 for ease of visibility. It was observed that the day of the breakthrough in terms of “free cyanide” corresponds exactly to the resurgence of iron in the effluent. Whereas column #6 sees its effluent copper concentration prolonged further than the other columns, the downfall in cyanide depletion resembles closely the decline in effluent

copper concentration. However, by looking closely, the influence of the effluent iron concentration on the cyanide depletion curve is also perceptible, particularly in column #6.

a) Column #6: 200 ppm NaCN, 0.86 mL/min

b) Column #7: 500 ppm NaCN, 0.86 mL/min

c) Column #8: 1000 ppm NaCN, 0.87 mL/min

d) Column #9: 2000 ppm NaCN, 0.93 mL/min

Figure 4-16: Comparison of the effluent cyanide depleted versus copper and iron concentration in effluent solution

4.6 Effluent thiocyanate concentration behavior

The thiocyanate concentration in the effluent solution is measured by silver nitrate titration to a cream-colored end-point. However, because free cyanide would obviously compete for the silver, the sample is first acidified with 0.5 mol/L H_2SO_4 and sparged with nitrogen gas for 30 minutes to drive off all free cyanide as HCN gas. The sample is then re-acidified with 6 mol/L HNO_3 and 2 mL of ferric nitrate. The latter, which serves as the indicator solution, is added just before the titration starts. This procedure is particularly tedious and was thus applied to only a selection of the samples from columns #7, 8 and 9 (i.e. column #6 was not analyzed) as shown in **Figure 4-17**.

The absence of thiocyanate during the copper lag at the beginning of the leach was unexpected. This implies that cyanide (i.e. free, $\text{HCN}_{(\text{aq})}$ or complexed) does not last for very long in concentrated cupric sulfate solution since it must be present to participate in the formation of thiocyanate (equation (2-6)). Consequently, it is reasonable to suspect the wholesale oxidation of cyanide to cyanogen or cyanate by cupric ions, and this is the subject of discussion in section 5.2.1. Eventually, thiocyanate appears in the effluent solution as soon as the leaching of labile copper minerals begins. While the copper concentration forms double peaks and a tail, however, the concentration of thiocyanate is relatively uniform throughout the leaching process. In fact, according to equations (2-7) and (2-8), the nature of the copper minerals has a strong influence on the relative stoichiometry of copper and thiocyanate in solution. Moreover, the oxidation of bisulfide to thiosulfate, ultimately forming sulfate according to equations (2-3) and (2-4) also

competes with the formation of thiocyanate. Hence, the sulfide chemistry is complex in cyanide solutions.

a) Comparison of effluent [Cu] and [SCN] for column #7

b) Comparison of effluent [Cu] and [SCN] for column #8

c) Comparison of effluent [Cu] and [SCN] for column #9

Figure 4-17: Comparison of effluent copper and thiocyanate in effluent solutions

4.7 Presentation of pH data

The last results to be presented are the pH data, displayed in **Figure 4-18**. They contain an exceptional amount of information and comprise a very valuable tool for modeling the leaching behavior of the columns.

The first striking feature is the pH values of the first solution samples as shown in **Table 4-8**. Since the pH of the influent cyanide solution is maintained at approximately 10.6, its value decreased sharply during the first pass when the percolating solution was wetting the column. As noted earlier in section 4.2, the dissolution of WAS-Cu is certainly responsible for this drop in

pH, which is independent of the nominal cyanide concentration. Moreover, separate titration tests indicate that the Telfer Composite 'E' ore buffers to pH 4.0 much more strongly in alkaline solutions than in weak acid solution (see also section 3.1.2).

Table 4-8: General observations on pH data

Column number	6	7	8	9
Nominal $[\text{NaCN}]_0$ (ppm)	200	500	1000	2000
pH of first solution sample	3.60	3.73	3.52	3.49
pH of buffering point (± 0.2)	7.6	7.7	7.8	7.9
Final pH (± 0.2)	9.8	10.1	10.2	10.3

The influence of the nominal cyanide concentration on the pH is immediately apparent. Its value increases at a rate dependent on $[\text{NaCN}]_0$ for all columns and hits a buffer point located at approximately pH 7.6. Column #9 reaches this buffer point in less than 10 days while the pH curve of column #6 is not very stable and even presents an intermediate buffer point at around pH 6.0. Furthermore, once the breakthrough in cyanide occurs, the pH begins to increase again up to a final buffer point which is slightly lower than the stock solution pH and also dependent upon $[\text{NaCN}]_0$.

4.8 Summary of results

It can be seen that the column results present many distinctive and interesting features such as a pH drop during the first pass associated with a large and rapid discharge of WAS-Cu. Later, the presence of two definitive peaks for all columns except column #9 reveals the need for the modeling of leaching behavior based on both reaction kinetics and speciation. For this reason,

the following section is dedicated to the development of a heap leaching model specific for cupriferous gold ores.

Figure 4-18: pH data for column #6, #7, #8 and #9

5. Development of heap leaching model

After several modeling attempts, it was found that backmixing and solution retention inside the column are concepts essential to the proper simulation of heap leaching behavior. Hence, the development of a model in which a column packed with both a portion of solution flowing through the column (bulk) and a stagnant portion of solution adjoining and enclosed by the ore particles (reservoir) is proposed. Since those two fluid elements are fundamentally different, separate mass balance equations are derived for each in sections 5.1.3 and 5.1.4.

In light of the complexity of the chemical reactions occurring during heap leaching, it is unavoidable that the model be constructed in two parts. The first one is kinetic, in which only the rates of irreversible chemical reactions are computed. Reaction rates are measured from previous batch and semi-batch experiments or inferred from the literature.

The second step is the development of a speciation subroutine which computes the concentration of species defined for a given metal-ligand system. The data entries are the metal concentrations, the ligand concentrations and the acid-base balance. Equilibrium constants are determined from equilibrium reactions and the mass balance equations for each component are the sum of all the related species based on their respective stoichiometry. The precipitates (i.e. the supersaturated species) as well as the aqueous species are included in the mass balance equations. The Newton-Raphson method is used for solving these non-linear equations. The cuprous cyanide system is given in section 5.4 as an example of the development and demonstration of the general speciation model.

5.1 Conceptualization of fluid elements

There are three forces acting on the solution in an ore heap undergoing percolation leaching: gravity, surface tension, and atmospheric pressure (Bartlett, 1997). As solution flows through an ore heap, those forces contribute to fluid resistance translated as shear stresses acting tangentially to the surface of the solid and shear viscous stresses due to the internal friction of the fluid itself. When application of the leaching solution ceases, the excess water will drain away until gravity and surface tension forces are in balance, at which time solution flow will cease at the bottom of the column. The specific retention of the ore heap is the ratio of volume of solution retained after drainage to the total heap volume. This water can only be removed by evaporation.

Based on the above conjuncture, the heap leaching model is represented by two different fluid regimes called the “bulk” and the “reservoir” (see **Figure 5-1**). The bulk corresponds to the fluid flowing inside the packed bed, and hence, is the medium by which dissolved species can migrate from the top of the column to the bottom at a superficial velocity u_s . The bulk species are in contact (dashed line) with the reservoir by mass transfer. The hypothetical reservoir is a well-mixed receptacle in which stagnant liquid is in direct contact with ore particles. In reality, it represents the liquid trapped in the ore interstices and in the particles pores i.e. retained after drainage. It will be noted that precipitates may form in both fluid elements, and hence, the speciation subroutine is applied separately to each.

By experience, it was also found that the first pass of solution through the column was fundamentally different from each successive pass. This is because the ore particles are initially

dry and the column must first be wetted. In other words, both the reservoir and the bulk are being filled like a sponge. Consequently, the advection time of the first pass, $t_a^{(1)}$, does not correspond to the advection time of the successive passes, $t_a^{(2...N)}$, and in fact, is on the order of ten times longer. A special computation procedure is proposed for the first pass in section 5.1.6.

Figure 5-1: Schematic representation of a fluid element indicating the directions of inputs and outputs. Dashed arrows represent speciation and solid arrows are kinetic.

5.1.1 General assumptions of the heap leaching model

The model is based on the following general assumptions:

- 1) The solid structure is macroscopically uniform and all ore characteristics such as density and porosity are unchanged by leaching;
- 2) Diffusion into ore particles may be modeled as part of the mass transfer into the reservoir, and by rate kinetic calibration from experimental results;

- 3) The system is isothermal at 25°C and at an ambient pressure of 1 atm;
- 4) Any precipitates, once formed, remain fixed at the position where they formed;
- 5) Ideal solutions are assumed.
- 6) The bulk solution is a uniform flowing liquid through the heap. It is not to be confound with channeling effects.

5.1.2 Concept of conservability

Fundamental to the simplification of the leaching model, the concept of conservability defines elements and ligands as “conservable”. In other words, their concentrations are dependent only on the kinetic rates of reaction and the laws of transport. These conservable species may be distributed differently among complexes and free ions. For instance, the concentration of the conservable cyanide ligand, denoted by a double underline, $\underline{\underline{\text{CN}]}}$, is the sum of the concentrations of dissolved CN^- , $\text{HCN}_{(\text{aq})}$, $\text{CuCN}_{(\text{aq})}$, $\text{AuCN}_{(\text{aq})}$, 2 moles of $\text{Cu}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$, 3 moles of $\text{Cu}(\text{CN})_3^{2-}$, and 4 moles of $\text{Cu}(\text{CN})_4^{3-}$. The precipitates $\text{CuCN}_{(\text{s})}$ and $\text{AuCN}_{(\text{s})}$ are not included in this quantity because they take part in neither transport phenomena nor in any irreversible reactions (they are dealt with in the speciation subroutine). Details of the specie $\underline{\underline{\text{OH}}}$ are provided in section 5.6.1.

5.1.3 Derivation of the mass balance equation for the bulk solution

The aqueous species $\underline{\underline{\text{Cu(II)}}}$, $\underline{\underline{\text{Cu(I)}}}$, $\underline{\underline{\text{Au(I)}}}$, $\underline{\underline{\text{CN}}}$, $\underline{\underline{\text{OCN}}}$, $\underline{\underline{\text{SCN}}}$, $\underline{\underline{\text{OH}}}$ and $\underline{\underline{\text{SO}_4}}$ from the previous fluid element are inputs in the bulk liquid solution which flows at a superficial velocity u_s between z and $z+\Delta z$. Mass transfer of the eight species between the bulk and the reservoir occurs

simultaneously with the kinetic reactions in the bulk liquid solution, r_b , (i.e. oxidation of cyanide by aqueous copper(II)). The solution is then subsequently passed on to the next fluid element. All terms are expressed in moles per time. The ratios of bulk and reservoir solution volume to the total column volume is expressed as ϵ_b and ϵ_r respectively. Similarly, concentrations in the bulk and in the reservoir are C_b and C_r .

$$\text{RATE IN: } Q \cdot C_b \Big|_z \quad \text{RATE OUT: } Q \cdot C_b \Big|_{z+\Delta z} \quad (5-1)$$

$$\text{NET RATE OF RESERVOIR-BULK MASS TRANSFER: } k_l a \cdot (C_r - C_b) \cdot S \Delta z$$

$$\text{NET RATE OF FORMATION BY CHEMICAL REACTIONS: } r_b \epsilon_b \cdot S \Delta z$$

$$\text{RATE OF ACCUMULATION: } S \Delta z \epsilon_b \cdot \frac{\partial C_b}{\partial t}$$

The following mass balance can be formulated for each of the eight conservable species in the bulk solution

$$S \Delta z \cdot \epsilon_b \cdot \frac{\partial C_b}{\partial t} = Q \cdot (C_b \Big|_z - C_b \Big|_{z+\Delta z}) - k_l a \cdot (C_b - C_r) \cdot S \Delta z + r_b \epsilon_b \cdot S \Delta z \quad (5-2)$$

Both sides of the equation are divided by the volume of the bulk $S \Delta z$ and the superficial fluid velocity u_s is equivalent to the solution percolation flow rate per unit area, Q/S , or "specific discharge". Since any derivative may be interpreted as the instantaneous rate of change of one variable per unit change in the other (Thomas, 1960), applying the rule of the limit as Δz approaches zero of equation (5-2) gives equation (5-3).

$$\varepsilon_b \cdot \frac{\partial C_b}{\partial t} = -u_s \cdot \frac{\partial C_b}{\partial z} - k_l a \cdot (C_b - C_r) + r_b \varepsilon_b \quad (5-3)$$

Multiplying both sides by Z/u_s leads to the following definitions of advection time t_a , dimensionless depth ζ , and mass transfer time t_m .

$$\frac{\varepsilon_b Z}{u_s} \cdot \frac{\partial C_b}{\partial t} + Z \cdot \frac{\partial C_b}{\partial z} = -\frac{k_l a Z}{u_s} \cdot (C_b - C_r) + \frac{\varepsilon_b Z}{u_s} r_b \quad (5-4)$$

$$t_a = \frac{\varepsilon_b \cdot Z}{u_s} \quad \zeta = \frac{z}{Z} \quad t_m = \frac{\varepsilon_b}{k_l \cdot a} \quad (5-5)$$

Equation (5-4) becomes,

$$\frac{\partial C_b}{\partial (t/t_a)} + \frac{\partial C_b}{\partial \zeta} = -\frac{t_a}{t_m} \cdot (C_b - C_r) + t_a r_b \quad (5-6)$$

Equation (5-6) may be expressed into an ordinary differential equation by applying the definition of the substantial rate derivative:

$$\frac{D}{D\zeta} = \frac{\partial}{\partial (t/t_a)} + \frac{\partial}{\partial \zeta} \quad (5-7)$$

This transformation facilitates the mathematical treatment of the heap leaching model from the Laplacian viewpoint, i.e., via the tracking of fluid elements from the top of the heap to the bottom. Finally, the mass balance for the bulk solution becomes,

$$\boxed{\frac{DC_b}{D\zeta} = -\frac{t_a}{t_m} \cdot (C_b - C_r) + t_a r_b} \quad (5-8)$$

The first term on the right-hand-side of the above equation expresses the unidirectional flow of dissolved species from the bulk to the reservoir. The second term is the net rate of production of dissolved species in the bulk solution.

5.1.4 Derivation of the mass balance equation for the reservoir solution

As in the case of the bulk solution, the reservoir mass balance equations are expressed in terms of moles per time. Since the reservoir is a stagnant but hypothetically well mixed volume by definition, only the rates of reservoir-bulk mass transfer and of irreversible reactions need to be incorporated into the reservoir mass balance equations.

$$\text{NET RATE OF RESERVOIR-BULK TRANSFER: } -k_l a \cdot (C_r - C_b) \cdot S \Delta z \quad (5-9)$$

$$\text{NET RATE OF FORMATION BY CHEMICAL REACTIONS: } r_r \cdot \epsilon_r \cdot S \Delta z$$

$$\text{RATE OF ACCUMULATION: } S \Delta z \cdot \epsilon_r \cdot \frac{\partial C_r}{\partial t}$$

The following mass balance can be formulated for each of the eight conservable species in the reservoir solution. Both sides of the equation are divided by $S \Delta z$ and ϵ_r .

$$\epsilon_r \frac{\partial C_r}{\partial t} = -k_l a (C_r - C_b) + \epsilon_r r_r \quad (5-10)$$

Using the definition of the mass transfer time t_m , and the volume ratio factor $\phi = \epsilon_r/\epsilon_b$, equation (5-10) becomes,

$$\boxed{\frac{\partial C_r}{\partial t} = -\frac{1}{t_m \cdot \phi} (C_r - C_b) + r_r} \quad (5-11)$$

The first term on the right-hand-side in the above equation expresses the mass transfer of dissolved species from the reservoir to the bulk. The second term is the net rate of production of dissolved species in the reservoir solution due to both homogeneous and heterogeneous (leaching) reactions.

Because the algorithm for the first pass is more complex than the successive and ordinary passes, the latter will be presented first.

5.1.5 Algorithm for ordinary passes

The sequential computation technique for the ordinary passes is shown in **Figure 5-2**. At first, the bulk mass balance equation is computed based on the bulk concentration of the previous increment, $C_b|_z$, and the concentration in the reservoir calculated from the previous pass, $C_r^{(n-1)}$. At that point, speciation is applied to the new bulk concentration $C_b|_{z+\Delta z}$. Finally, the bulk concentration for this fluid element, $C_b^{(n)}$, is the average value of $C_b|_z$ and $C_b|_{z+\Delta z}$.

As well, the concentration in the reservoir is computed from the averaged bulk concentration $C_b^{(n)}$, and the old value of reservoir species concentration, $C_r^{(n-1)}$. The new calculated species $C_r^{(n)}$

are equilibrated by the speciation subroutine. The value of the time increment Δt is dependent on the reaction rates. It is very short at the beginning of the column leaching test and may be extended along with leaching time as the net rates of change decrease with decreasing ore values.

Figure 5-2: Schematic of the computation technique for the ordinary passes (bold variables represent the computation results, shaded areas are speciated)

5.1.6 Algorithm for the first pass

The algorithm for the first pass is illustrated in **Figure 5-3**. The horizontal axis represents the passing time and the vertical axis, the height of the heap. The bottom half of the rectangle delineates the dry ore while the upper half is wet. The median line is thus the “filling” wave going down the column in advection time $t_a(1+\phi)$ where ϕ can be on the order of 10 depending on the ore characteristics. It is now sound reasoning to think that if all the column was wet, flowing fluid elements would reach the bottom in an ordinary advection time t_a as shown for the ordinary passes. This is also represented by the nearly vertical and parallel lines crossing the rectangle. However, during the first pass, those fluid elements are unable to reach the bottom in a time t_a because they must intersect the “filling” wave. At that point, they become part of the filling wave and contribute to the wetting of the ore. The algorithm for the first pass is then slightly modified in order to account for the presence of the “filling” wave. Finally, it should be

noted that, in reality, the filling wave is not instantaneous as supposed in this section. For instance, some time is necessary for the water to be absorbed by the rock particle.

Figure 5-3: Symbolic representation of the first and successive and ordinary passes

5.2 Development of the kinetic subroutine

The rate at which a chemical reaction proceeds is determined by kinetics, through rate constants, concentration parameters and their respective orders. However, the nature of those rate equations is more difficult to discern. Key questions include which kinetic reactions are occurring at what rate, with or without a catalyst, and under which circumstances. These questions must be answered either through experimentation or from the literature.

We have seen in section 5.1.5 that the kinetic and speciation subroutines must be executed sequentially during modeling since speciation is considered instantaneous as opposed to kinetic reactions which are inherently time dependent. However, in reality everything happens simultaneously. In this case, the concept of conservability greatly facilitates the execution of those subroutines by reacting all the conservable elements or ligands as single species. Hence, only one equation complying to the proper stoichiometry need be expressed for the oxidation of cyanide to cyanate instead of a possibility of 320 ($8 \underline{\text{Cu(II)}} \times 2 \underline{\text{CN}} \times 2 \underline{\text{OH}} \times 5 \underline{\text{Cu(I)}} \times 2 \underline{\text{OCN}}$)! In the case of cupriferous gold ore leaching, the following three kinetically controlled reactions are proposed:

As mentioned before, the concept of conservability helps to write the balance equations to reflect two rates: the rate of component formation, r_i , and the rate of reaction, r_j . Both rates have units of $\text{mol/cm}^3 \cdot \text{min}$. In this way, the stoichiometric factors may be removed from the mass balance equations.

$$\begin{bmatrix} -2 & 0 & 0 \\ 2 & 0 & 2 \\ 0 & 1 & 0 \\ -1 & 0 & -2 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \\ -2 & 1 & 4 \\ 0 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} r_A \\ r_B \\ r_C \end{bmatrix} = \begin{bmatrix} r_{\text{Cu(II)}} \\ r_{\text{Cu(I)}} \\ r_{\text{Au(I)}} \\ r_{\text{CN}} \\ r_{\text{OCN}} \\ r_{\text{SCN}} \\ r_{\text{OH}} \\ r_{\text{SO}_4} \end{bmatrix} \quad (5-15)$$

Reaction A is fast in solution and is considered irreversible. The rates of reactions B and C are kinetically slow.

$$r_B = \frac{\rho_{\text{bulk}} G_{\text{Au}}}{M_{\text{Au}} \epsilon_r} \cdot \frac{dX_B}{dt} \quad (5-16)$$

$$r_C = \frac{\rho_{\text{bulk}} G_{\text{CuS}}}{M_{\text{Cu}} \epsilon_r} \cdot \frac{dX_C}{dt} \quad (5-17)$$

The functions $f(1-X_B)$ and $f(1-X_C)$ depend on the intrinsic characteristics of the ore such as its refractoriness, its particle size distribution and its mineral distribution within the gangue rock and may be expressed analogously to equation (3-2).

$$\frac{dX_B}{dt} = k_B \cdot [\text{CN}]_F^{\phi_B} \cdot f(1-X_B) \quad \frac{dX_C}{dt} = k_C \cdot [\text{CN}]_F^{\phi_C} \cdot f(1-X_C) \quad (5-18)$$

They represent the conversion behavior of each mineral with time. $[\text{CN}]_F$ is the concentration of free cyanide, which is the sum of the cyanide ion and aqueous hydrogen cyanide concentrations, and k_B and k_C are rate constants.

5.2.1 Oxidation rate of cyanide to cyanate

Oxidation of cyanide to cyanate occurs in basic solution with many oxidants, in particular those oxidants of interest concerning cyanide destruction. Some of these are hydrogen peroxide (H_2O_2), ozone (O_3), oxygen (O_2) and hypochlorite (ClO^-) (Flynn and Haslem, 1995). The first study concerned with the kinetics of oxidation of cyanide to cyanogen by copper(II) in dilute acid solution was published by Duke and Courtney (1952). They estimated the reaction to obey the following stoichiometry

with the corresponding rate expression

$$-\frac{d[\text{Cu}^{2+}]}{dt} = k_A \cdot [\text{Cu}^{2+}] \cdot [\text{CN}^-]^4 \quad (5-20)$$

from which they concluded that the slow step involves the species $\text{Cu}(\text{CN})_4^{2-}$. Baxendale and Westcott (1959) reported that in actuality, the reaction is much slower in acid solution and very sensitive to acid and cyanide concentrations. In acid solution, the cyanide is present almost entirely as $\text{HCN}_{(\text{aq})}$, and it seems probable that the pH affects the rate *via* the acid dissociation of cyanide because the cyanide reacts only in its ionic form. In this case, the overall rate of reaction is

$$\boxed{r_A = k_A \cdot [\text{Cu}^{2+}]^2 \cdot [\text{CN}^-]^6} \quad (5-21)$$

The very high order in CN^- probably arises because the reacting species in the rate determining step are present in equilibrium with Cu^{2+} and CN^- . Thus, assuming the slow step is

and $\text{Cu}(\text{CN})_3^-$ is formed via the rapidly established equilibrium,

the above reaction will follow provided a small fraction of Cu^{2+} is present. Addition of water to cyanogen in acid solution gives NCCON, which in turn undergoes addition of a second molecule of water to yield oxamide, NOCCON. In dilute acid solutions with a $\text{pH} > 0$, NCCON is isolable (Wang et al, 1987). Kinetic data for the addition of H_2O to cyanogen in acid solution were unable to be located. However, both studies mentioned above reported that cyanogen is found to hydrolyze slowly compared with the rate of the oxidation reaction. On the other hand, the hydrolysis reaction of cyanogen in basic solution (Sharpe, 1976) may be written as

wherein cyanogen disproportionates rapidly to CN^- and OCN^- , in part *via* the addition of H_2O to cyanoformamide, NCCON (Flynn and Haslem, 1995). In that case, the half life of cyanogen varies from 2 s at 0°C to about 0.07 s at 40°C , at $\text{pH} 11.0$.

As reported by Parkash and Zyka (1972), the overall chemistry of oxidation of cyanide to cyanogen and then to cyanate can become complex due to speciation of both copper(II)-cyanide and copper(I)-cyanide systems. Also, the oxidation kinetics are difficult to measure because of the competing hydrolysis of cupric ions in alkaline solution.

In conclusion, this reaction is indirectly incorporated into the general model by applying reaction A and by running the speciation subroutine. It is assumed an irreversible reaction which can be very fast in comparison with the leaching of minerals.

5.2.2 Leaching rate of labile copper sulfides

We have seen in section 3.3 that the rate of leaching of the secondary copper sulfides in the Telfer E ore may be defined as first order with respect to the free cyanide concentration in alkaline solution. In other words, the exponent ϕ_C in equation (5-18) equals 1.0. Semi-batch experiments are helpful in validating the heap leaching model, particularly in terms of determining the shape of the conversion curve for the secondary copper sulfides.

5.2.3 Leaching rate of gold

No validating experiments were performed with atomic absorption analysis for gold. Hence, it is difficult to estimate the function $f(1-X_B)$ and the exponent ϕ_B in equation (5-18). Many researchers have attempted to model the kinetics of gold dissolution and a number of rate equations have been published. They have examined the different relationships between cyanide concentration, dissolved oxygen concentration, etc. Two types of rate equations however, have been developed: i) mechanistic ones, which are more comprehensive or fundamental, and ii) empirical ones, which are more numerical. Habashi (1966) published the first comprehensive study on pure gold cyanidation and explained the variations in the rate of gold dissolution with cyanide and oxygen concentrations. He concluded that the rate of pure gold dissolution depends

on the rate of diffusion through the film of cyanide ions or dissolved oxygen towards the surface of gold. The rate of gold dissolution was given as:

$$-\frac{dN_{Au}}{A dt} = \frac{2 \cdot D_{CN^-} \cdot D_{O_2} [CN^-] \cdot [O_2]}{\delta \cdot \{D_{CN^-} [CN^-] + 4 \cdot D_{O_2} [O_2]\}} \quad (5-25)$$

where δ : The Nernst boundary layer thickness, cm

D : Diffusion coefficients, cm^2/s

A : Surface area of gold, cm^2

This equation was capable of explaining most of the experimental behavior observed in the gold leaching process. For instance, when the concentration of cyanide is low, the rate of gold dissolution depends primarily on cyanide concentration. Conversely for high cyanide concentration, the rate of dissolution depends mainly on the oxygen concentration (Habashi, 1970). In practice, in most gold mills a high level of cyanide is maintained rather than a high dissolved oxygen (D.O.) level in solution. As a result, they operate at cyanide levels such that the gold dissolution is controlled by oxygen diffusion.

Habashi's equation describes convincingly the mechanisms of gold dissolution in cyanide solutions. The serious limitations of its use are the difficulty in measuring the exact surface area of gold in the ore and the Nernst boundary layer thickness. Therefore, empirical equations of the following form have been developed by various authors (Nicol, 1984; Chéfaï, 1991; Ling, 1996):

$$-\frac{d[Au]}{dt} = k([Au] - [Au]_{\infty})^n \quad (5-26)$$

where the term $[Au]_{\infty}$ refers to the gold concentration in the ore at infinite time. The constants k and n are given different values and/or equations according to each authors. Typical equations for the constant k may include linear functions of concentrations of both free cyanide $[CN^-]$ and dissolved oxygen $[O_2]$.

It is recognized that because of the complex nature of gold ores, it is extremely difficult to establish a good constant k and thus, a unified rate equation that can be used to model different types of gold ores. In the case of empirical equations, it is necessary to "test" each category of ores and fit the data subsequently. The concentrations of both cyanide and dissolved oxygen are not the only factors that may have strong influences. The pH of the solution, particle size, leaching times and the presence of other species such as lead ions and calcium ions, also may contribute to the characteristics of the rate equations. Therefore, this method suffers from either the specificity of the ore tested or of confinement within a small range of operating conditions because it does not account explicitly for concentration effects.

This said, referring to what has been discussed in section 2.4.3 concerning two competing reactants S_1 and S_2 for the same reagent A (Dixon, 1993B), it is tempting to assume the rate of gold leaching to be equal to labile copper sulfide leaching. This assumption would justify leaving the oxygen concentration out of the rate equations since the rate controlling step is no more the availability of oxygen but the proportionally high copper concentration.

5.3 Mathematical development of the Newton-Raphson method

Prior to the development of the speciation subroutine in section 5.4, the Newton-Raphson method (also known as Newton's method), which is probably the best known method for numerically solving systems of nonlinear equations (Haung, 1989; Melançon, 1985; Zhang, 1997), is introduced. The immense advantage of this method is that the convergence is very rapid. Unfortunately, the method is very sensitive to the choice of the initial set of values. Seed values from previous calculations are not infallible because the previous increment may have contained different precipitation conditions. Consequently, if the Newton-Raphson method is included in a larger program, the method does not always converge even when the initial estimates are near the final solution. For this reason, seed values of the calculations are based on intuition. With experience, choosing the value of $\exp(-0.5)$ as an initial guess for all variables was found to be the most reliable method. Computation time is prolonged but convergence is almost assured.

In the simple case of a system of 2 simultaneous non-linear equations of the form:

$$f_1(x_1, x_2) = 0 \quad (5-27)$$

$$f_2(x_1, x_2) = 0 \quad (5-28)$$

If x_1 and x_2 are approximate solutions to the set of equations and if $x_1 = x_1 + \Delta x_1$ and $x_2 = x_2 + \Delta x_2$ are exact solutions then;

$$f_1(x_1 + \Delta x_1, x_2 + \Delta x_2) = 0 \quad (5-29)$$

$$f_2(x_1 + \Delta x_1, x_2 + \Delta x_2) = 0 \quad (5-30)$$

Also, both f_1 and f_2 can be expanded as a Taylor's series about x_1 and x_2 . Therefore,

$$f_1(x_1 + \Delta x_1, x_2 + \Delta x_2) = f_1(x_1, x_2) + \Delta x_1 \cdot \frac{\partial f_1(x_1, x_2)}{\partial x_1} + \Delta x_2 \cdot \frac{\partial f_1(x_1, x_2)}{\partial x_2} \quad (5-31)$$

$$f_2(x_1 + \Delta x_1, x_2 + \Delta x_2) = f_2(x_1, x_2) + \Delta x_1 \cdot \frac{\partial f_2(x_1, x_2)}{\partial x_1} + \Delta x_2 \cdot \frac{\partial f_2(x_1, x_2)}{\partial x_2} \quad (5-32)$$

Thus, Δx_1 and Δx_2 must satisfy equations (5-31) and (5-32) which may be written in a matrix form as equation (5-33). The two-dimensional matrix is called the Jacobian matrix and combined with the right-hand-side vector can be solved by any matrix solver.

$$\begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} \end{bmatrix} \cdot \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \end{bmatrix} = \begin{bmatrix} -f_1 \\ -f_2 \end{bmatrix} \quad (5-33)$$

The Newton-Raphson method algorithm can be described as follows:

- i) Assume a set of initial values for each of x_1 and x_2 ;
- ii) Evaluate the augmented coefficient matrix at the points (x_1, x_2) ;

$$a_{ij} = \frac{\partial f_i}{\partial x_j} \quad \text{with } i = 1, 2 \text{ and } j = 1, 2 \quad (5-34)$$

$$\text{and } a_{i,3} = -f_i \quad \text{with } i = 1, 2 \quad (5-35)$$

- iii) Use the decomposition or elimination method to solve the set of linear equations for Δx_1 and Δx_2 ;

- iv) Calculate $x_i = x_i + \Delta x_i$ with $i = 1, 2$;

v) Repeat steps ii), iii) and iv) until $\max|\Delta x_i| < \varepsilon$ or $[\max|\Delta x_i|/\max|x_i|] < \varepsilon$, with $i = 1, 2$ or a fixed number of iterations.

As noted earlier, a good set of initial solution values is essential in most cases and convergence characteristics of the Newton-Raphson method can also be improved by applying under-relaxation i.e. in step iv), calculate $x_i = x_i + \alpha \cdot \Delta x_i$, $i = 1, 2$ where α is the under-relaxation parameter ($0 < \alpha < 1$).

5.4 Practical example of the speciation subroutine: cuprous-cyanide system

The cuprous-cyanide system is given as a practical example of the speciation subroutine. It is composed of the cuprous-cyanide species including cuprous ion, cyanide ion and aqueous hydrogen cyanide (hydrogen cyanide is assumed non-volatile); and finally, the proton H^+ as listed in **Table 5-1**. Since in our example, the carbon and nitrogen are not dissociable, cyanide is considered a single ligand component. The solution is assumed dilute enough to allow the assumption of ideality (i.e., unit activity coefficients for all species).

Table 5-1: List of species involved in the copper-cyanide system

Copper-cyanide	Cyanide	Acid
Cu^+ , $CuCN$, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$	CN^- , HCN	H^+

The system contains three components: H^+ , Cu^+ and CN^- . For demonstration purposes, the proton concentration (i.e. pH) is fixed. Accordingly, for the corresponding 7 species for which the concentration is unknown, seven equations are required. Two mass balance equations can be derived from the initial cuprous and cyanide concentrations (equations (5-41) and (5-42)). In addition, five chemical equilibria are also represented in the Jacobian matrix (equations (5-36) to (5-40)). It is more convenient to use the natural logarithm because the order of magnitude of the concentrations may be large. In this example, the specie $CuCN$ remains aqueous.

$$\ln(K_{CuCN1}) = \ln[CuCN_{(aq)}] - \ln[Cu^+] - \ln[CN^-] \quad (5-36)$$

$$\ln(K_{CuCN2}) = \ln[Cu(CN)_2^-] - \ln[CuCN_{(aq)}] - \ln[CN^-] \quad (5-37)$$

$$\ln(K_{CuCN3}) = \ln[Cu(CN)_3^{2-}] - \ln[Cu(CN)_2^-] - \ln[CN^-] \quad (5-38)$$

$$\ln(K_{CuCN4}) = \ln[Cu(CN)_4^{3-}] - \ln[Cu(CN)_3^{2-}] - \ln[CN^-] \quad (5-39)$$

$$\ln(K_{HCN}) = \ln[HCN] - \ln[H^+] - \ln[CN^-] \quad (5-40)$$

$$\begin{aligned} \exp(\ln[Cu_{Total}]) &= \exp(\ln[Cu^+]) + \exp(\ln[CuCN_{(aq)}]) + \exp(\ln[Cu(CN)_2^-]) \\ &\quad + \exp(\ln[Cu(CN)_3^{2-}]) + \exp(\ln[Cu(CN)_4^{3-}]) \end{aligned} \quad (5-41)$$

$$\begin{aligned} \exp(\ln[CN_{Total}]) &= \exp(\ln[CN^-]) + \exp(\ln[HCN]) + \exp(\ln[CuCN_{(aq)}]) + \\ &\quad + \exp(\ln(2[Cu(CN)_2^-])) + \exp(\ln(3[Cu(CN)_3^{2-}])) + \exp(\ln(4[Cu(CN)_4^{3-}])) \end{aligned} \quad (5-42)$$

To construct the Jacobian matrix of the form presented in equation (5-33), the following parameters are defined:

$$x_1 = \ln[CuCN_{(aq)}] \quad (5-43)$$

$$x_2 = \ln[Cu(CN)_2^-] \quad (5-44)$$

$$x_3 = \ln[Cu(CN)_3^{2-}] \quad (5-45)$$

$$x_4 = \ln[\text{Cu}(\text{CN})_4^{3-}] \quad (5-46)$$

$$x_5 = \ln[\text{Cu}^+] \quad (5-47)$$

$$x_6 = \ln[\text{CN}^-] \quad (5-48)$$

$$x_7 = \ln[\text{HCN}] \quad (5-49)$$

Therefore, equations (5-36) to (5-42) may be rewritten in the same form as equations (5-27) and (5-28).

$$f_1 = x_1 - x_5 - x_6 - \ln(K_{\text{CuCN1}}) \quad (5-50)$$

$$f_2 = x_2 - x_1 - x_6 - \ln(K_{\text{CuCN2}}) \quad (5-51)$$

$$f_3 = x_3 - x_2 - x_6 - \ln(K_{\text{CuCN3}}) \quad (5-52)$$

$$f_4 = x_4 - x_3 - x_6 - \ln(K_{\text{CuCN4}}) \quad (5-53)$$

$$f_5 = x_7 - \ln[\text{H}^+] - x_6 - \ln(K_{\text{HCN}}) \quad (5-54)$$

$$f_6 = \exp(x_5) + \exp(x_1) + \exp(x_2) + \exp(x_3) + \exp(x_4) - [\text{Cu}_{\text{Total}}] \quad (5-55)$$

$$f_7 = \exp(x_6) + \exp(x_7) + \exp(x_1) + 2 \exp(x_2) + 3 \exp(x_3) + 4 \exp(x_4) - [\text{CN}_{\text{Total}}] \quad (5-56)$$

The coefficients of the Jacobian matrix, the solution vector and the right-hand-side vector can be expressed as follows:

$$\begin{bmatrix} 1 & 0 & 0 & 0 & -1 & -1 & 0 \\ -1 & 1 & 0 & 0 & 0 & -1 & 0 \\ 0 & -1 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 \\ e^{x_1} & e^{x_2} & e^{x_3} & e^{x_4} & e^{x_5} & 0 & 0 \\ e^{x_1} & 2e^{x_2} & 3e^{x_3} & 4e^{x_4} & 0 & e^{x_6} & e^{x_7} \end{bmatrix} \cdot \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta x_4 \\ \Delta x_5 \\ \Delta x_6 \\ \Delta x_7 \end{bmatrix} = \begin{bmatrix} -f_1 \\ -f_2 \\ -f_3 \\ -f_4 \\ -f_5 \\ -f_6 \\ -f_7 \end{bmatrix} \quad (5-57)$$

5.5 Specific case of precipitation: cuprous-cyanide system

The speciation subroutine for the cuprous-cyanide system when $\text{CuCN}_{(s)}$ precipitates is slightly different from the previous case when all species are aqueous. The normal procedure is to calculate the distribution of the aqueous species first. These primary results are then used to verify whether or not super-saturation occurs by calculating the corresponding precipitation criterion. The neutral species $\text{CuCN}_{(aq)}$ forms but is not well characterized in the literature owing to the sparing solubility of $\text{CuCN}_{(s)}$ and the instability of the cuprous ion at low cyanide concentrations. Nevertheless, since we are interested mainly in the possible precipitation of $\text{CuCN}_{(s)}$ in the heap, we need to assess the extent of its presence under varying conditions.

If saturation does occur, the weight of $\text{CuCN}_{(s)}$ must be included in both the mass balance equations of copper and cyanide. The concentration of $\text{Cu(CN)}_{(aq)}$ becomes constant at 1×10^{-9} mol/L at equilibrium. All solid precipitates are assumed concentrations (activities) of unity. Therefore, the new x_1 becomes $\ln[\text{CuCN}_{(s)}]$ and the previous x_1 becomes $\ln(1 \times 10^{-9})$. The set of equations (5-50) to (5-56) and correspondingly the Jacobian matrix i.e. $a(1,1) = 0$ and $a(2,1) = 0$, also undergo modification:

$$f_1 = \ln(1 \times 10^{-9}) - x_5 - x_6 - \ln(K_{\text{CuCN1}}) \quad (5-58)$$

$$f_2 = x_2 - \ln(1 \times 10^{-9}) - x_6 - \ln(K_{\text{CuCN2}}) \quad (5-59)$$

$$f_3 = x_3 - x_2 - x_6 - \ln(K_{\text{CuCN3}}) \quad (5-60)$$

$$f_4 = x_4 - x_3 - x_6 - \ln(K_{\text{CuCN4}}) \quad (5-61)$$

$$f_5 = x_7 - \ln[\text{H}^+] - x_6 - \ln(K_{\text{HCN}}) \quad (5-62)$$

$$f_6 = \exp(x_5) + \exp(x_1) + 1 \times 10^{-9} + \exp(x_2) + \exp(x_3) + \exp(x_4) - [\text{Cu}_{\text{Total}}] \quad (5-63)$$

$$f_7 = \exp(x_6) + \exp(x_7) + \exp(x_1) + 1 \times 10^{-9} + 2 \exp(x_2) \\ 3 \exp(x_3) + 4 \exp(x_4) - [\text{CN}_{\text{Total}}] \quad (5-64)$$

With this method, the system is able to “switch” from one case to another very easily depending on whether the criterion for precipitation of $\text{CuCN}_{(s)}$ is satisfied. The case of multiple precipitation will be discussed in section 5.6.4. **Figure 5-4** show the results of the speciation subroutine for the cuprous-cyanide system.

a) Speciation of copper in cyanide solution at a ratio $[\text{CN}]_{\text{total}}/[\text{Cu}]_{\text{total}} = 2.00$

b) Speciation of copper in cyanide solution at a ratio $[CN]_{total}/[Cu]_{total} = 8.00$

Figure 5-4: Results of the speciation subroutine for the cuprous-cyanide system with pH fixed and at different copper to cyanide ratios

5.6 General speciation subroutine

The general speciation subroutine for the leaching of cupriferous gold ore without ferrous and ferric species is summarized in **Table 5-2**. Functions 1-7 for the copper(I)-cyanide system were described in the practical example above. Functions 8-10 correspond to gold(I)-cyanide system. The pH is set as a dependent variable in functions 11-12. The copper(II)-hydroxide system is defined by the functions 13-20 and cyanate ion is introduced into the subroutine by the functions 21-22. Finally, functions 23-24 represent the thiocyanate ion and functions 25-27, the copper(II)-sulfate system.

5.6.1 Acid-Base balance

The assumption that there is an infinite source of water leads to the H^+ and OH^- balance. The acid-base mass balance is defined as the subtraction of the mass balance of the proton from the mass balance of hydroxide where L is a ligand (either CN^- , SCN^- , OCN^- or SO_4^{2-}).

$$[OH^-] + \sum y \cdot [Cu_x(OH)_y] + [H_2O] = 0 \quad (5-65)$$

$$- [H^+] - \sum [HL] - [H_2O] = 0 \quad (5-66)$$

$$\text{OVERALL:} \quad [OH^-] - [H^+] + \sum y \cdot [Cu_x(OH)_y] - \sum [HL] = 0 \quad (5-67)$$

5.6.2 Review of equilibrium constants

The acidic dissociation constant of hydrogen cyanide in water is fairly well recognized in the published literature (Beck, 1987). The recommended value at 25°C is 9.21 ± 0.02 . Most of the studies have been directed toward the cyano-complexes of cuprous ion since it is a more stable system than the redox cupric-cyanide system. The stability constants of the tricyano and tetracyano complexes are given by Izatt et al (1967) and confirmed by Solis et al (1996). The dissociation constant of $CuCN_{(s)}$ was derived by Flynn and Haslem (1995) from an estimate of $\log K = -9$ for $CuCN_{(s)} = CuCN_{(aq)}$. Flynn and Haslem give values for the thermodynamic system of aurous-cyanide at 25°C. Beck considered that there was no reliable stability constant referring to $Au(CN)_2^-$ even though it is one of the most stable cyano-complexes. Similarly with $CuCN_{(s)}$, the dissociation constant of $AuCN_{(s)}$ was derived by Flynn and Haslem from an estimate of $\log K = 5$ for $AuCN_{(s)} + CN^- = Au(CN)_2^-_{(aq)}$. It is almost certain that no higher gold complexes are formed in normal heap leaching operation. For those reasons, the cupric-cyanide and auric-cyanide systems are not included in the general speciation subroutine.

Table 5-2: Chemical reactions and equilibrium constants (25°C, 1 atm)

Equilibrium and mass balance equations	log K or β	function #
$\text{Cu}^+ + \text{CN}^- = \text{CuCN}_{(\text{aq})}$	10.4	1*
$\text{CuCN}_{(\text{aq})} + \text{CN}^- = \text{Cu}(\text{CN})_2^-$	11.2	2
$\text{Cu}(\text{CN})_2^- + \text{CN}^- = \text{Cu}(\text{CN})_3^{2-}$	5.3	3
$\text{Cu}(\text{CN})_3^{2-} + \text{CN}^- = \text{Cu}(\text{CN})_4^{3-}$	1.5	4
$\text{H}^+ + \text{CN}^- = \text{HCN}_{(\text{aq})}$	9.21	5
Cu(I) total		6
CN total		7
<hr/>		
$\text{Au}^+ + 2\text{CN}^- = \text{Au}(\text{CN})_2^-$	19.0	8
$\text{Au}^+ + \text{CN}^- = \text{AuCN}_{(\text{aq})}$	18.0	9*
Au(I) total		10
<hr/>		
Acid-base balance		11
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	-14	12
<hr/>		
$\text{Cu}^{2+} + \text{H}_2\text{O} = \text{CuOH}^+ + \text{H}^+$	-7.97	13
$\text{Cu}^{2+} + 2\text{H}_2\text{O} = \text{Cu}(\text{OH})_{2(\text{aq})} + 2\text{H}^+$	-16.24	14*
$\text{Cu}^{2+} + 3\text{H}_2\text{O} = \text{Cu}(\text{OH})_3^- + 3\text{H}^+$	-26.62	15
$\text{Cu}^{2+} + 4\text{H}_2\text{O} = \text{Cu}(\text{OH})_4^{2-} + 4\text{H}^+$	-39.7	16
$2\text{Cu}^{2+} + \text{H}_2\text{O} = \text{Cu}_2\text{OH}^{3+} + \text{H}^+$	-6.71	17
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} = \text{Cu}_2(\text{OH})_2^{2+} + 2\text{H}^+$	-10.55	18
$3\text{Cu}^{2+} + 4\text{H}_2\text{O} = \text{Cu}_3(\text{OH})_4^{2+} + 4\text{H}^+$	-20.95	19
Cu(II) total		20
<hr/>		
OCN ⁻ total		21
$\text{OCN}^- + \text{H}^+ = \text{HOCN}$	3.47	22
SCN ⁻ total		23
$\text{SCN}^- + \text{H}^+ = \text{HSCN}$	1.6	24
$\text{SO}_4^{2-} + \text{H}^+ = \text{HSO}_4^-$	1.99	25
$\text{SO}_4^{2-} + \text{Cu}^{2+} = \text{CuSO}_4$	2.30	26*
SO ₄ total		27

The hydrolysis of Cu^{2+} ion is a much more stable process than is the hydrolysis of the Cu^+ ion which tends to oxidize given the same conditions. Plyasunova et al (1997) gave a recent critical evaluation of the thermodynamics of hydrolysis and hydroxo-complexes of Cu^{2+} at 298.15K.

Thiocyanate and cyanate are the products of sulfide minerals leaching and of the oxidation of cyanide. The acid dissolution constant for thiocyanate was published by Ghosh and Nair (1970) and for cyanate, by Clegg and Brimblecombe (1989). Finally, the copper sulfate and sulfuric acid system equilibrium constants are provided by Sillén and Martell (1964).

5.6.3 Discrimination of the oxidation state

The speciation subroutine does not discriminate between the various oxidation states of the two main elements concerned, namely copper and gold. We have seen previously that copper and gold do not pose too many problems because the Cu(II) and Au(III) cyano-complexes are rather unstable, as are the copper(I) hydroxo-complexes. The case of iron is more difficult to discern because both of the species Fe(CN)_6^{3-} and Fe(CN)_6^{4-} can be found in solution (section 2.2.2). Also, there are many studies referring to the formation of ferrous cyano-complex salts with cations leading to a complex situation with many salts co-existing (James and Murray, 1975; Gaspar and Beck, 1983; Busey, 1965). The same conclusion may be drawn with hydroxo-ferrous and hydroxo-ferric species. The iron concentration level in most experiments is negligible in comparison to the copper (see section 4.4) and thus, it was decided to neglect all ferrous and ferric species. However, further investigation and modeling is indispensable in order to judge the influence of iron, particularly the different iron cyano-complex salts, on the leaching of gold.

5.6.4 Computation procedure for multiple precipitation

According to the general speciation subroutine, four precipitates may form: $\text{CuCN}_{(s)}$, $\text{AuCN}_{(s)}$, $\text{Cu}(\text{OH})_{2(s)}$ and $\text{CuSO}_{4(s)}$ corresponding to functions 1, 9, 14 and 26 respectively. The Jacobian matrix has been written in such a way that it is possible to interchange easily between these four functions from aqueous to solid products and vice-versa as described in the case of the cuprous-cyanide example. As mentioned before in section 5.5, if saturation does occur, the program has to find which solid species will precipitate under the new conditions by applying a precipitation criterion. If four solids may precipitate at any given time, then sixteen possibilities exist (two states, four species: $2^4 = 16$).

The computation technique for multiple precipitation is displayed schematically in **Figure 5-5**. The speciation subroutine is first computed with the initial condition that all four species are aqueous for a defined number of iterations (usually 10). At this point, the conditions for precipitation are usually well defined, and in the case at hand, a final iteration is used to confirm the precipitation condition in **Figure 5-5**.

However, a diverging condition will be recognized by setting a maximum number of iterations (usually 200). The subroutine is then allowed to proceed onto another precipitation condition until convergence is achieved.

Figure 5-5: Schematic of the computation procedure for multiple precipitation

6. Modeling results and discussion

With all the experimental results and the development of the heap leaching model in mind, it is now possible to interpret the meaning of the lag times for copper as well as the pH buffering points. In practice, it was found that the short columns (15 cm long, 1150 g ore) were calibrated satisfactorily with 20 depth increments for smooth concentration behavior. However, time and depth increments are particularly sensitive during the extensive dissolution of cupric ions at the beginning of the leaching cycle. For this reason, the use of the heap leaching model combined with the general speciation subroutine described in section 5.6 is limited and cannot be applied easily to the simulation of the tall column tests. Therefore, the validation of the heap leaching model will be confined to short columns for demonstration purposes. The discussion is divided according to events which occur at two different timescales. Firstly, the effects of the rapid discharge of WAS-Cu on the leaching behavior of the columns is discussed thoroughly. Secondly, the leaching of labile copper sulfides and gold is reviewed.

6.1 Calibration of the rate equations

An overview of the rate equations is presented in section 5.2 and the experimental results of the semi-batch coarse tests are placed in **Figures (3-9) and (3-10)**. The calibration gives the following rate constants for the oxidation of cyanide (A) and the leaching of labile copper sulfides (C) respectively (**Figure 6-1**).

$$A. \quad r_A = 0.06 \cdot \left\{ \lambda [\underline{\text{Cu(II)}}] + \theta (1 - \lambda) [\text{CN}]_F \right\} \quad (6-1)$$

$$\text{where } \lambda = \frac{[\text{CN}]_F}{[\underline{\text{Cu(II)}}] + [\text{CN}]_F} \quad \text{and} \quad \theta = \frac{v_{\text{Cu(II)}}}{v_{\text{CN}}} \quad (6-2)$$

$$C. \quad \frac{dX_C}{dt} = 1.0 \cdot [\text{CN}]_F \cdot (1 - X_C)^{6.25} \quad (6-3)$$

Figure 6-1: "Extractable" copper conversion for Short column #7 (500 ppm NaCN)

Equation (5-21), found in the literature, is not practical for the model because of the large exponent associated with the free cyanide concentration. Hence, during the execution of the modeling program, the rate equation becomes too sensitive to small variations. Therefore, the above equation for reaction A expressed as a function of the weakest specie (either cyanide or copper(II)) is preferred. The two reaction rates are essential for the validation of the heap

leaching model since copper is the most prevalent product in the effluent solution. Finally, as noted in section 5.2.4, the gold leaching rate will be approximated by the labile copper sulfide leaching rate.

$$\text{B.} \quad \frac{dX_B}{dt} = 1.0 \cdot [\text{CN}]_F \cdot (1 - X_B)^{6.25} \quad (6-4)$$

6.2 WAS-copper(II) and its repercussions

The influence of WAS-Cu on the overall leaching of cupriferous gold ores was recognized during the experimental work. For instance, it is thought that its effects on the natural acidity of the ore creates a lag in the leaching of gold, labile copper sulfides and iron. This section aims towards a better understanding of the first 80 minutes of the leaching test, including the wetting period. A short column loaded with 1150 g of ore and leached with a stock cyanide solution of 500 ppm is used as the mathematical support for various simulations. Hence, the following results do not necessarily reflect actual experimental behaviors.

6.2.1 General leaching parameters

The values of ϵ_b and ϵ_r are estimated at 0.02 and 0.1 respectively. The mass transfer term, $k_f \cdot a$, is approximated at $5 \times 10^{-2} \text{ min}^{-1}$ which is translated into an efficient transport of species between the bulk and the reservoir. Advection time, mass transfer time and reservoir/bulk volume ratio have values of 2.3 min, 0.4 min, and 5.0, respectively. If the first drop at the bottom of the column is accepted as time zero, the wetting time of the column is considered to be negative. The effluent solution is approximated by the last bulk fluid element. Finally, the leaching rates of

gold and labile copper sulfides are set to zero initially to study the effect of WAS-copper(II) only.

6.2.2 Effect of WAS-copper(II) on pH

The effect of WAS-Cu on pH is first calculated with plain water as stock solution (i.e. pH = 7.0, no cyanide added). It is found that the pH is rapidly buffered to approximately 4.6 (**Figure 6-2**). During wetting, rapidly dissolving copper(II) accumulates towards the bottom of the column where the breakthrough in copper concentration is recognized by a logarithmic decline (**Figure 6-3**).

Surprisingly, by applying a stock cyanide solution of 500 ppm NaCN and pH 10.6, it is found that the copper(II) sulfate discharge is identical to the simulation with water only. Once again, the pH equilibrates very rapidly to a buffer point of approximately 5.8 which is in direct correlation with the presence of the $\text{CuSO}_{4(\text{aq})}$ complex (**Figure 6-4**). However, the presence of cyanide in the column introduces new and interesting features. The slower but steady decrease in pH from 5.8 to 3.5 is caused by the oxidation of cyanide to cyanate which, according to the following reaction, consumes 2 moles of OH for every mole of CN.

Figure 6-2: pH behavior in bulk and in reservoir for Short column (water only, pH=7.0)

Figure 6-3: Copper(II) concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN or water only)

Figure 6-4: pH behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN)

This evidence is also supported by the presence of the reaction products Cu(I) and OCN (**Figures 6-5** and **6-6** respectively). The bulk can be considered the preferential source of cyanide. Consequently, the reservoir and the bulk respond differently. For instance, the pH buffers at 3.5 for up to an hour in the reservoir while in the bulk, only the bottom of the column displays a sharper decrease in pH. Finally, it can be noted that the free cyanide concentration behavior (**Figure 6-7**) inside the column resembles very closely the aforementioned pH behavior (**Figure 6-4**). This corroborates the strong influence of the stock cyanide concentration on the capacity of the column to “recover” from a copper(II) discharge.

6.2.3 Dissolution and precipitation cycles of cyanide salts

One of the ideas proposed to explain the lag times for gold, labile copper sulfides and iron was the existence of dissolution and precipitation cycles of cyanide salts inside the column. Dissolved metal species inhabit the solution as it flows. As cyanide is further consumed from the flowing solution, the copper complexes in that solution undergo dissociation. Copper in solution thereby becomes a source of free cyanide, thus maintaining the level of free cyanide in solution at higher and more prolonged concentrations than would be the case if the dissociation did not occur. However, eventually the cyanide levels become low enough that cuprous cyanide is precipitated from solution. Of course, once the cyanide levels in solution rise to sufficient levels, these cyanide salts re-dissolve as aqueous complexes.

Figure 6-5: Copper(I) concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN)

Figure 6-6: Cyanate concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN)

Figure 6-7: Free cyanide concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN)

It is obvious that only modeling is capable of demonstrating such an hypothesis without shutting down the column test and verifying on site. For this reason, the study of the behavior of the two main copper precipitates $\text{CuCN}_{(s)}$ and $\text{Cu(OH)}_{2(s)}$ is emphasized. The term “concentration” is applied to precipitates as well as to aqueous species for modeling simplicity. It is therefore recommended that the reader interprets the precipitate “concentration” of $\text{CuCN}_{(s)}$ or $\text{Cu(OH)}_{2(s)}$ as if these species were fully dissolved in the corresponding fluid element (either bulk or reservoir).

The precipitate $\text{CuCN}_{(s)}$ is present at low pH and disappears rapidly when the pH is greater than about 5.0 (**Figure 6-8**). Therefore, one may conclude that the conditions are insufficient for any leached copper(I) to re-precipitate once the pH has increased substantially. Having said that, it is acknowledged that the mass transfer time is critical to the formation of precipitates in the reservoir. For demonstration purposes, a similar simulation with a mass transfer time of 4 minutes is presented in **Figures 6-9** and **6-10**. If the reservoir element sees a slow decrease in copper(II) concentration, the discharge in the bulk is also larger. It can therefore be recognized that the copper(II) sulfate discharge behavior is radically different from **Figure 6-3** for which the mass transfer time is rather fast at 0.4 minutes. In other words, as t_m increases, the transfer of species between the two fluid elements is slower and the segregation between the bulk and the reservoir becomes sharper. Evidently, this leads to a longer low pH regime in the reservoir. As a direct consequence of this, copper(I) and $\text{CuCN}_{(s)}$ can last much longer in the reservoir than in the bulk solution (**Figure 6-10**). Hence, the above hypothesis becomes more plausible and partially accounts for the WAS-Cu discharge behavior presented in **Figure 4-3**.

Figure 6-8: CuCN_(s) "concentration" behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN)

Figure 6-9: Copper(II) and sulfate concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN) with mass transfer time of 4 minutes

Figure 6-10: Copper(I) and CuCN_(s) concentration behaviors in reservoir for Short column #7 (500 ppm NaCN) with mass transfer time of 4 minutes

Finally, the precipitate $\text{Cu}(\text{OH})_{2(s)}$ also presents a cyclic precipitation and dissolution behavior. The precipitation intensity is controlled by pH until the copper(II) concentration becomes too low to sustain precipitation (**Figure 6-11**). The cycle is relatively short, lasting at most 90 minutes in the bulk. The following section will reveal the significance of this cycle as the leaching of labile copper sulfides begins.

6.3 Leaching of labile copper sulfides

In order to study the leaching of labile copper sulfides, the calculated time must be carefully extended from 80 minutes to 150 hours. A constant and shorter time step ($\Delta t = 30$ s), is used for fast reactions while slow reactions are allowed a longer time step ($\Delta t = 5$ min). The actual time step is calculated based on the predominant reaction, whether it is fast or slow.

According to mineralogy (section 3.1.1), the secondary copper sulfides consist essentially of covellite. Since the cyanidation of covellite produces Cu(II) (Deng, (1995)), it is coupled with equation (6-5). The overall leaching reaction may be expressed as:

Figure 6-11: Cu(OH)_{2(s)} "concentration" behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN)

which is equivalent to equation (2-8) found in the literature review. The coupling is performed intrinsically in the model. Hence, by examining the leaching behaviors of both copper(I) and copper(II) (**Figures 6-12** and **6-13** respectively), it is possible to follow the actual stepwise leaching of covellite.

The copper(II) concentration follows a chromatographic pattern resulting from the diffusion of dissolved complexes into, and then out of, the ore pores and stagnant interstices early in the leach cycle. On the other hand, initially, the copper(I) concentration peak takes a fairly long time to reach its maximum value.

6.3.1 Aftereffects of copper hydroxide precipitation

In the case at hand, the combined effect of covellite leaching and WAS-Cu discharge is synergistic since they both promote copper hydroxide precipitation. This is revealed in **Figure 6-14** where the $\text{Cu(OH)}_{2(s)}$ "concentration" is 20 times larger than what it would be without covellite leaching (**Figure 6-11**). Thus, the dispersal of a $\text{Cu(OH)}_{2(s)}$ reserve throughout the column has the direct effect of increasing the cyanide consumption *via* reaction A which in turn affects the leaching of labile copper sulfides.

Figure 6-12: Copper(I) concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

Figure 6-13: Copper(II) concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

Figure 6-14: Cu(OH)_{2(s)} “concentration” behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

It is astonishing to see that the discharge in WAS-Cu influences the overall column leaching behavior in a fashion that is almost independent of the solution pH. Indeed, if the pH is low (i.e. below 5.0), dissolution and precipitation of $\text{CuCN}_{(s)}$ occur (section 6.2.3). On the other hand, if the pH is high (i.e. above 5.0), the precipitation of $\text{Cu}(\text{OH})_{2(s)}$ is favored because of higher hydroxyl ions in solution. From a practical point of view, however, it is not clear which precipitation scenario is favorable. If $\text{Cu}(\text{OH})_{2(s)}$ precipitation allows the pH to remain high enough to facilitate cyanide leaching, it has the economical drawback of consuming much more cyanide on the long term. Conversely, at a lower pH, $\text{CuCN}_{(s)}$ precipitates and the bound cyanide is “recovered” later. In this case, cyanide is not irretrievably lost but the overall free cyanide concentration in solution is reduced, affecting the cyanide leaching.

This conclusion fits well with the general observations of copper leaching behavior in section 4.2 where the stoichiometric cyanide requirement per unit copper recovery decreases with augmentation of nominal influent cyanide concentration (**Figure 4-5**). Only column #6, with the lowest influent cyanide concentration, did not follow the expected trend but required more cyanide than column #7. Under these conditions, leaching may possibly be hindered by the lower free cyanide concentration in solution.

6.3.2 Free cyanide and covellite conversion profiles

Free cyanide concentration behavior is displayed in **Figure 6-15**. It can be seen from the figure that beyond the copper(I) peak (**Figure 6-12**), the free cyanide concentration behavior is a close analog of the mirror image of the copper(I) concentration.

Figure 6-15: Free cyanide concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

To compare the solutions of Dixon and Hendrix (1993B) (**Figure 6-16**) to the simplified continuity equations (refer to section 2.4.3, equation (2-25)) for free cyanide concentration in the bulk solution (α_b) and the fractional covellite conversion (X_C) as a function of heap depth with this work, **Figure 6-15** is expressed non-dimensionally and constructed with time increments (**Figure 6-17**).

The dimensionless free cyanide profiles in the bulk solution of short column #7 coincides with the middle right plot where the advection limitation becomes significant and the reagent concentration profiles are monotonic. Covellite conversion occurs at fairly uniform rate throughout the column. These results are expected since short column #7, as its name implies, is short (i.e. 15 cm only) and the flow rate applied is moderately fast for a typical heap leaching operation at 13.1 mL/m²·s.

The corresponding free cyanide profiles in the reservoir must be approached differently because of the preferential cyanide diffusion from the bulk to the reservoir. In fact, the free cyanide profiles in the reservoir are almost identical to the covellite conversion. Hence, this outlines the primary role of the reservoir as a concentration buffer (i.e. a temporary storage facility for aqueous species) whose profiles may be interpreted as a diffusion response to the more advection controlled bulk.

Figure 6-16: Solutions to the heap leaching model for reagent A (α_b) and the fractional conversion of one solid reactant X (Dixon, 1993B)

Figure 6-17: Dimensionless free cyanide profiles in bulk and in reservoir for Short column #7 combined with covellite conversion (500 ppm NaCN), 150 hours execution

Figures 4-6 and **4-14** show the copper and gold grades in the leached residual ores after column leaching respectively. Although, it seems that the leaching is fairly uniform throughout the column height (also validated by modeling), section 2 from the top of the tall column has clearly a higher than average mineral grade. From **Figure 6-14**, there is a chromatographic effect in the reservoir and thus, it is possible that some $\text{Cu}(\text{OH})_{2(s)}$ and/or $\text{Fe}(\text{OH})_{3(s)}$ slimes may be occluding the gold and labile copper sulfides at this specific position of the column early during the leaching cycle.

6.4 Leaching of gold

Since the gold cyanidation rate is almost exclusively controlled by the leaching rate of labile copper sulfides, the central part of this thesis has been concerned with the copper concentration behavior. This is observed experimentally by comparing their analogous recovery profiles in **Figures 4-2** and **4-11**. Moreover, the fact that they both have similar refractoriness at approximately 80%, suggests that gold occurs as ultrafine inclusions associated with labile copper sulfides.

By comparing **Figure 6-18** from **Figure 6-12**, it is found that the gold concentration behavior is different from the copper(I) concentration behavior. In fact, it follows the more typical diffusion chromatographic behavior also seen on copper(II) and $\text{Cu}(\text{OH})_{2(s)}$ profiles (**Figure 6-13** and **6-14** respectively). In a short column leached at cyanide concentration of 550 ppm, no $\text{AuCN}_{(s)}$ was found to precipitate at any depth increment owing to the relative instability of this cyanide salt. Moreover, gold leaching is not highly affected by the precipitation of copper hydroxide as

implied by the regular stoichiometry of the gold(I)-cyanide complex (**Figure 4-13**). Hence, this may explain why the lag times are slightly shorter than for the labile copper sulfides (**Figure 4-4**).

However, further simulation tests found that gold cyanide does precipitate in short column #9 leached at a higher cyanide concentration of 2000 ppm (**Figure 6-19**). The reason comes from the fact that gold is leached at a faster rate, and hence, is allowed to accumulate towards the bottom of the column where it precipitates.

6.5 Scale-up effects

The relative magnitudes of advection, mass transfer and reaction investigated by Dixon and Hendrix (1993B) as a function of heap size, nominal cyanide concentration and ore characteristics are also revealed to be a strong function of speciation.

It is believed that a copper sulfate discharge is mostly responsible for all the abnormal features occurring at the beginning of the leaching cycle. In fact, its marked influence on the precipitation of cyanide and/or copper hydroxide salts for the short column can become considerable once mathematical scale-up to taller column tests and, ultimately, to heaps is permitted. For instance, the lag times for copper, which were practically non-existent in a short column of 15 cm, extended to 7 days for a 150 cm column leached at a nominal cyanide concentration of 500 ppm. Hence, the general features discussed in this section tend to increase dramatically with scale-up.

Figure 6-18: Gold concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

Figure 6-19: AuCN_(s) "concentration" behavior in bulk and in reservoir for Short column #9 (2000 ppm NaCN)

6.6 Non-validated experimental features

Two experimental features observed during column leaching tests were not validated in this modeling effort: i) the pH buffer point at approximately 7.7 in **Figure 4-18** for all columns, and ii) the double copper concentration peaks observed on all but column #9 in **Figure 4-4**.

It was hoped that the model would divulge the causes of the buffering pH during the leaching of labile copper sulfides. However, it can be seen in **Figure 6-20** that the pH increases rapidly to the nominal stock cyanide solution pH (i.e. 10.656) as soon as the WAS-Cu discharge is completed. Explanations for this pH behavior are difficult to discern because of the complexity of the leaching system. However, possible causes may include: 1) Precipitation of iron cyano-complexes, 2) Dissolution of magnesium oxides which react similarly to iron cyano-complexes (Williams, 1948; also refer to mineralogy section 3.1.1, **Table 3-2**).

Finally, it seems that the double peaks in copper concentration are another example of a scale-up effect. The sum of copper(I) and copper(II) concentrations (**Figure 6-12** and **Figure 6-13** respectively) is plotted in **Figure 6-21** to visualize the double peaks. It can be seen that in a short column, the double peaks are virtually non-existent. However, the possibility that double peaks exist in a taller column is plausible since one type of copper species reacts so fast with cyanide as to be virtually in equilibrium with it while another does not. Thus, it is expected to see at least two chromatographic events as multiple “waves” of copper move down the column. The following section looks at some potential future solutions to some of the problems encountered during the experimental and modeling work.

Figure 6-20: pH behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

Figure 6-21: Total copper concentration behavior in bulk and in reservoir for Short column #7 (500 ppm NaCN), 150 hours execution

7. Conclusion and future work

The column leaching test results were very satisfactory in outlining most of the intricate features of cupriferous gold ores cyanidation. From copper concentration to pH behavior, the regularity of the experimental data from one column to another was remarkable. This led to the development of a heap leaching model that answered most of the following questions:

- 1) the presence of weak-acid soluble copper(II) and its tangible effects on the natural acidity of the ore, cyanidation kinetics and cyanide consumption;
- 2) the causes of lag times for gold and labile copper sulfide products (i.e. copper(I) and thiocyanate);
- 3) the behavior of numerous cyanide-derived species such as cyanate, thiocyanate, and free cyanide, whose concentrations are often difficult or impossible to measure because of interference from copper and iron species.

For such a complex project, it is inevitable that future work is anticipated for both the experimental and the modeling parts of this thesis. All recommendations discussed in this section aim towards the development of a more flexible and principally more reliable general heap leaching model.

7.1 Future experimental work

The study of cyanidation kinetics for copper minerals is highly recommended in this field. The work of Rubisov et al (1996) on the fundamental kinetic models for gold ore cyanide leaching is promising and should be considered for application towards relevant kinetic studies.

7.1.1 Use of ion chromatography

The use of ion chromatography may be useful in measuring the behavior of cyanide in gold cyanidation leachates as reported by Fagan et al (1997). In particular, the copper to cyanide mole ratio could be analyzed by the ion chromatography method on a Nova-Pak C-18 column using an ion interaction eluent with both UV and post column reaction (PCR) detection. Thiocyanate and other cyano-complexes such as Au(CN)_2^- , Au(CN)_4^+ and Fe(CN)_6^{4-} are also detected by this method.

7.1.2 Auto-titration batch tests

During the summer of 1997, a significant amount of effort was expended on designing a batch fine ore leaching test for both ground ore samples and pure minerals. An ion-selective AgS/AgI electrode, connected to an autoburette metering concentrated basic sodium cyanide solution in constant potential mode, was used to maintain the free cyanide concentration at constant values during the leaching tests. It was hoped that in this way the intrinsic cyanidation kinetics of ground samples could be determined without having to account manually for the changing free cyanide concentrations in solution during the test. However, the electrode was found to drift and

foul in the more concentrated cyanide solutions above 500 ppm NaCN, and it was decided finally that the method was not reliable enough for rate determinations.

Despite its nonsuccess, the idea is worthwhile enough to continue its examination with the possible advent of more resistant cyanide measuring electrodes or more dilute cyanide solutions. This idea could be implemented for other leaching systems where kinetics need to be measured in a constant reagent concentration. In this case, pH and E_h probes are much more stable and reliable.

7.1.3 Influence of oxygen on cyanidation

Previous column leaching tests by the author could not conclude with certainty the influence of oxygen on the cyanide leaching of cupriferous gold ores. However, it seems that oxygen played a minor role in enhancing the cyanidation of copper minerals. More work in this direction may be advised.

7.2 Future modeling work

The modeling work performed in this project was innovative from many points of view. However, some aspects of the modeling were left for further investigation because of either a difficulty in assessing the problem or a lack of time.

7.2.1 Uniqueness of copper(I)-cyanide species

During the definition of the leaching rate equations for gold and the labile copper sulfides, all the cyano-complexes are assumed to react at the same rate. This simplification is inaccurate since some publications have established that the copper(I)-cyanide complexes leach gold at very different rates.

For instance, Zheng et al (1995) studied gold leaching in oxygenated solutions containing cyanide and copper using a rotating quartz crystal microbalance. **Figure 7-1** shows the dissolution of gold in an air saturated cyanide solution at pH 10.5, with a gold disc rotating at 300 rpm as a function of the total copper concentration for a fixed total cyanide concentration of 0.032 mol/L. As can be seen, the dissolution curve has a sigmoidal shape. At low values of the copper concentration, the amount of free cyanide in solution tends towards the total amount of cyanide and the leaching rate approaches that for 0.032 mol/L free cyanide, namely $3.7 \times 10^{-3} \text{ gm}^{-2}\text{s}^{-1}$. On the other hand, at high copper concentrations, the amount of free cyanide becomes very low and species such as CuCN and $\text{Cu}(\text{CN})_2^-$ dominate the system. Since La Brooy (1992), reported that oxygen, in the presence of $\text{Cu}(\text{CN})_2^-$ leaches gold very slowly or not at all, it is not surprising that the leaching rate at high copper concentration tends to zero.

One possible explanation of the sigmoidal shape of the leaching curve shown in **Figure 7-1** is that it simply reflects the leaching by free cyanide in solution. It is clear from a comparison of the calculated dissolution rate (according to Kudryk, 1954) and measured curves for gold leaching, that free cyanide alone cannot account for the measured leaching rate. The difference

between the two curves must be due to leaching associated with one or more of the copper (I)-cyanides.

Figure 7-1: Effect of total copper concentration on gold leaching rate from solutions: total cyanide concentration of 0.032 M; saturated with air; pH=10.5; ω =300 rpm (a) solid curve: experimental results (b) Dashed curve: calculated dissolution rate (Zheng et al, 1995)

Figure 7-2: Gold leaching rates due to copper cyanide species Curve 1: calculated from the data in Figure 7-1. Curves 2,3 and 4 represent the calculated equilibrium concentration of $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ respectively (Zheng et al, 1995)

As can be seen in **Figure 7-2**, there is a good correlation between the leaching rate and the fraction of copper present as $\text{Cu}(\text{CN})_3^{2-}$. On the other hand, there is no correlation with the presence of $\text{Cu}(\text{CN})_2^-$ or $\text{Cu}(\text{CN})_4^{3-}$. This confirms the stability of the copper species $\text{Cu}(\text{CN})_3^{2-}$ in the Cu-CN- H_2O E_h -pH diagram presented in **Figure 2-1**. The lack of correlation between the leaching rate and $\text{Cu}(\text{CN})_2^-$ is to be expected since, as mentioned before, oxygen in the presence of $\text{Cu}(\text{CN})_2^-$ does not leach gold. However, here the influence of $\text{Cu}(\text{CN})_4^{3-}$ is negligible which is in contradiction with similar tests carried out by La Brooy et al (1991). In those tests, solutions of copper(I)-cyanide are freshly prepared by dissolving CuCN with a stoichiometric amount of NaCN in solution. The rates of leaching gold from a rotating disc, measured in pure NaCN, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ solutions at pH 10.5, are compared in **Figure 7-3**.

Figure 7-3: Comparison of CN^- , $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ as reagents for leaching gold using rotating disc (pH 10.5; 20°C; 300 rpm) (La Brooy, 1992)

Clearly copper(I)-cyanide is an effective reagent for gold in aerated solution, particularly at high concentrations (> 1 g/L total CN^-) and under conditions where the $\text{Cu}(\text{CN})_4^{3-}$ complex predominates.

From the modeling point of view, it is difficult to derive leaching rate equations for each of the above copper(I)-cyanide species, especially if the model is built empirically on the macro-scale only.

7.2.2 Speciation of the iron species

In this project, the iron species were not included in the speciation subroutine for the reason outlined in section 5.6.3. The work of James and Murray (1975), and Gaspar and Beck (1983) help in understanding the behavior of iron in cyanide solutions. The most reliable thermodynamic data for ion pairs involving of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ were published by Beck (1987) (see also section 2.2.2). All the alkali and alkaline earth ions form stable ion-pairs which in most cases are colloids or gelatinous precipitates which would likely move with the solution flow (contrary to assumption 5 in section 5.1)

7.2.3 Faster speciation subroutine with modified Newton-Raphson algorithms

It was found that the Newton-Raphson method may converge rapidly in some cases but on average, still required considerable computing time to solve the Jacobian matrix. Also as noted in section 5.3, choosing the fitting seed values may become very difficult since it is impossible to

evaluate divergence before the matrix solver actually overshoots. Gill and Murray (1978) present a summary of the available algorithms for the solution of nonlinear least-squares problems. Since the derivations of the mass balance equations are very easily attained, it is recommended to modify the Newton-Raphson algorithm by including the second order derivative matrix called the Hessian. This new method seeks to compute the search direction and as a result, improves the chance of convergence, with the choice of seed values becoming less restrictive.

7.2.4 Activity coefficients of cyanide solution

It was assumed for the purpose of simplifying the speciation subroutine that the leaching solutions were dilute enough to assume unit activity coefficients. However, for the first pass when the effluent copper concentration is, on average, 13 g/L (see **Table 4-3**), this assumption is most likely inaccurate. Nevertheless, activity coefficients for the calculation in cyanide systems have not been studied in great detail in comparison with the acidic chloride and sulfate systems. Shantz (1977) has accounted for the ionic strength of the solution analytically. A finite ionic radius form of the Debye-Hückel equation was used to calculate activity coefficients. For species i , the natural logarithm of the activity coefficient, γ_i , is given by equation (7-1).

$$-\ln(\gamma_i) = \frac{Az_i^2\mu^{1/2}}{1 + Ba_i\mu^{1/2}} \quad (7-1)$$

where the mean ionic strength, μ , is given by the following equation in molality.

$$\mu = \frac{1}{2} \sum_i c_i z_i^2 \quad (7-2)$$

Finally, the equilibrium equation for $\text{Cu}(\text{CN})_4^{3-}$ becomes,

$$K_{\text{CuCN}_4} = \frac{[\text{Cu}(\text{CN})_3^{2-}] \cdot [\text{CN}^-]}{[\text{Cu}(\text{CN})_4^{3-}]} \cdot \exp \left\{ A\mu^{1/2} \cdot \left[\frac{9}{1 + B\mu^{1/2}a_{\text{CuCN}_4^{3-}}} - \frac{4}{1 + B\mu^{1/2}a_{\text{Cu}(\text{CN})_3^{2-}}} - \frac{1}{1 + B\mu^{1/2}a_{\text{CN}^-}} \right] \right\} \quad (7-3)$$

In the opinion of the author, the addition of the ionic strength term in equation (7-3) will more or less triple the computation time of the speciation subroutine outlined in section 5.6. The main difficulty comes from the theoretical definition of the ionic radius a since it represents a distance of closest approach. This subject would be worth considerably more attention in the future.

7.2.5 Modeling the diffusion of species: the micro-model

The development of a micro-model similar to the Dixon and Hendrix model is impeded by the need to solve the speciation subroutine at every radius index (see section 2.4.3) and to define diffusion and reaction times for every species. Therefore, the model described in section 5.1 indirectly accounts for the chromatographic effect of the diffusion of dissolved species into and out of the ore particles by assuming mass transfer between the reservoir and the bulk solution. The rate equations of leaching are calibrated by the semi-batch coarse ore experiments, which account globally for both diffusion and reaction kinetics. In doing so, the intrinsic characteristics of the heap are empirically included in a general leaching equation.

Modeling ideas are indispensable in this area and may actually be made possible with the advancement of faster computers.

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Appendix A. Supplementary chemical assays

Supplementary ICP chemical assays of the Telfer 'E' composite ore was performed by Chemex Lab Ltd. in North Vancouver. The sample was received grounded and a nitric-aqua regia digestion was performed on the following 30 elements.

Table A-1: Supplementary ICP chemical assays of the Telfer 'E' composite ore (Certificate A9736663)

Ag (ppm)	Al (%)	As (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Co (ppm)	Cr (ppm)
0.8	0.15	850	30	< 0.5	< 2	0.01	< 0.5	49	121
Cu (ppm)	Fe (%)	Ga (ppm)	Hg (ppm)	K (%)	La (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (ppm)
2590	6.29	< 10	< 1	0.06	< 10	< 0.01	30	2	< 0.01
Ni (ppm)	P (ppm)	Pb (ppm)	Sb (ppm)	Sc (ppm)	Sr (ppm)	Ti (%)	U (ppm)	V (ppm)	Zn (ppm)
19	40	72	10	< 1	5	< 0.01	< 10	8	8

Appendix B. Complementary experimental results

The appendix B contains the complementary experimental data from which figures presented in the thesis are constructed from. The following information is given for each tests:

1. Batch fine ore leaching tests

Effluent copper concentration

2. Semi-batch coarse ore leaching tests

Effluent copper concentration

Effluent pH

3. Column leaching tests

a) (column by column basis)

Stock cyanide concentration

Effluent iron concentration

Effluent copper concentration

Percentage copper recovery

Effluent gold concentration

Percentage gold recovery

Effluent pH

Effluent color and/or precipitates

b)

Percentage of cyanide consumed

Effluent thiocyanate concentration

Table B-1: General results of batch fine ore leaching tests

Time (min)	100 ppm NaCN	400 ppm NaCN	Time (min)	1000 ppm NaCN	2000 ppm NaCN
0	0.0%	0.0%	0	0.0%	0.0%
0.33	25.9%	33.4%	0.33	46.0%	50.4%
5	30.4%	41.6%	5	50.6%	57.4%
10	34.1%	42.3%	10	54.1%	60.4%
20	37.9%	49.3%	15	55.0%	66.9%
30	40.4%	51.7%	20	60.0%	71.4%
45	43.9%	55.8%	25	61.1%	72.6%
60	45.0%	58.1%	30	62.7%	77.0%
90	49.4%	63.1%	45	67.9%	81.2%
120	51.8%	68.9%	60	74.9%	88.2%
150	54.3%	71.7%	90	77.7%	90.1%
180	55.7%	74.0%	120	82.3%	92.4%
240	57.7%	77.5%	150	83.7%	94.2%
300	61.1%	82.0%	180	85.5%	94.8%
360	62.2%	84.4%	240	90.7%	98.1%
420	64.5%	85.6%	300	94.0%	98.4%
480	66.2%	88.5%	360	93.8%	99.5%
540	66.7%	88.8%	450	94.1%	98.6%
600	69.9%	89.2%	510	96.0%	99.5%
1380	79.2%	98.1%	570	94.9%	100.3%
1560	80.2%	98.7%	630	97.3%	100.6%
			750	97.0%	100.6%
			870	96.8%	100.0%
			1500	100.2%	100.8%
			1560	100.6%	100.9%

Table B-2: Copper recovery data for semi-batch coarse ore tests,

Hour	S. C. #7, 500 ppm NaCN	S. C. #8, 1000 ppm NaCN	S. C. #9, 2000 ppm NaCN
0	0.2%	0.5%	0.2%
0.5	2.2%	5.0%	2.3%
1	5.5%	7.4%	4.9%
1.5	7.5%	8.7%	7.8%
2	8.1%	10.0%	10.9%
2.5	8.7%	11.2%	13.6%
3	9.5%	12.3%	16.1%
3.5	10.4%	13.4%	18.3%
4	11.2%	14.3%	20.4%
5	12.8%	16.0%	23.9%
6	14.3%	17.5%	26.9%
7	15.7%	18.9%	29.6%
8	17.1%	20.1%	32.0%
9	18.3%	21.2%	34.1%
10	19.5%	22.4%	36.0%
11.5	21.2%	24.0%	38.4%
13	22.7%	25.5%	40.5%
15	24.6%	27.4%	42.9%
24	31.6%	34.9%	50.3%
26	32.8%	36.4%	51.5%
28	33.9%	37.8%	52.6%
30.5	35.2%	39.4%	53.9%
32.5	36.2%	40.5%	55.0%
49	42.2%	48.1%	61.8%
53	43.3%	49.4%	63.0%
55	43.7%	50.0%	63.6%

Hour	S. C. #7, 500 ppm NaCN	S. C. #8, 1000 ppm NaCN	S. C. #9, 2000 ppm NaCN
74	47.4%	54.6%	67.6%
77	47.8%	55.1%	68.1%
80.5	48.3%	55.7%	68.6%
96.5	50.0%	57.8%	70.4%

Table B-3: Effluent pH data for semi-batch coarse ore tests

Hour	S. C. #7, 500 ppm NaCN	S. C. #8, 1000 ppm NaCN	S. C. #9, 2000 ppm NaCN
0	5.82	4.67	8.26
0.5	4.7	5.01	8.56
1	4.81	8.14	8
1.5	5.45	7.87	8
2	7.71	7.99	8.87
2.5	8.01	8.47	9.09
3	7.87	8.83	9.47
3.5	7.7	8.97	9.5
4	7.89	9.21	9.77
5	7.94	9.31	10.03
6	8.08	9.68	9.97
7	8.27	9.84	10.04
8	8.97	9.72	10.06
9	8.73	9.82	10.05
10	8.56	9.78	10.03
11.5	9.29	9.79	10.06
13	8.71	9.81	10.04
15	9.52	9.83	10.06

Table B-4: General results of column #6 (200 ppm NaCN, Whole Telfer 'E' ore, 0.8662 mL/min)

Date	Day	Vol. (mL)	[CN] ⁻ _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu ⁺	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
8-Aug	0	24	201		13711	0.9%	0.000	0.0%	3.60	b
9-Aug	1	959	201	27.1	5392	14.5%	0.000	0.0%	3.96	p b
10-Aug	2	1051	201	1.9	798	16.7%	0.000	0.0%	4.21	c
11-Aug	3	1220	201	0.0	284	17.7%	0.000	0.0%	4.31	c
12-Aug	4	1260	201	0.0	164	18.2%	0.000	0.0%	4.44	c
13-Aug	5	1280	201	0.0	110	18.6%	0.000	0.0%	4.54	c
14-Aug	6	1240	201	0.0	81	18.8%	0.000	0.0%	4.66	c
15-Aug	7	1310	201	0.0	61	19.1%	0.000	0.0%	4.82	c
19-Aug	10	4075	201	0.0	37	19.5%	0.000	0.0%	5.31	c
21-Aug	14	4640	199	0.0	15	19.6%	0.000	0.0%	6.37	c
24-Aug	16	2580	199	0.0	6	19.7%	0.038	0.9%	5.97	c
27-Aug	19	3880	199	0.0	9	19.8%	0.050	2.7%	5.70	c
30-Aug	22	3437	213	0.0	14	19.9%	0.050	4.4%	5.95	c
2-Sep	25	2489	213	0.0	18	20.0%	0.050	5.5%	6.07	c
5-Sep	28	3701	213	0.0	30	20.3%	0.063	7.7%	5.99	c
8-Sep	31	3550	213	0.0	50	20.8%	0.063	9.8%	6.60	c
11-Sep	34	3835	213	0.0	73	21.5%	0.075	12.5%	6.72	c
14-Sep	37	3657	213	0.0	86	22.4%	0.063	14.7%	6.83	c
17-Sep	40	3270	208	0.0	99	23.2%	0.063	16.6%	6.95	c
20-Sep	43	3790	208	0.0	108	24.3%	0.063	18.9%	7.03	c
23-Sep	46	3526	208	0.0	115	25.4%	0.063	21.0%	7.24	c
26-Sep	49	3712	208	0.0	109	26.4%	0.063	23.2%	7.27	c

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #6 is 2536 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #6 is 0.712 ppm

Date	Day	Vol. (mL)	[CN ⁻] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [†]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
29-Sep	52	3580	208	0.0	106	27.4%	0.050	24.9%	7.33	c
2-Oct	55	3853	208	0.0	116	28.6%	0.063	27.1%	7.37	c
5-Oct	58	3507	208	0.0	119	29.7%	0.050	28.8%	7.39	c
8-Oct	61	3670	208	0.0	119	30.9%	0.050	30.5%	7.38	c
11-Oct	64	3715	208	0.0	116	32.0%	0.050	32.3%	7.38	c
14-Oct	67	3560	208	0.0	119	33.1%	0.050	33.9%	7.38	c
17-Oct	70	3850	195	0.0	119	34.4%	0.050	35.8%	7.48	c
20-Oct	73	3542	195	0.0	123	35.5%	0.038	37.0%	7.55	c
23-Oct	76	4015	195	0.0	124	36.8%	0.038	38.5%	7.51	c
26-Oct	79	3667	195	0.0	124	38.0%	0.038	39.8%	7.56	c
29-Oct	82	3773	195	0.0	127	39.3%	0.038	41.1%	7.64	c
1-Nov	85	3899	195	0.0	125	40.6%	0.025	42.0%	7.63	c
4-Nov	88	3560	195	0.0	125	41.7%	0.025	42.9%	7.62	c
7-Nov	91	3814	195	0.0	122	43.0%	0.025	43.8%	7.65	c
10-Nov	94	3847	195	0.0	121	44.2%	0.038	45.1%	7.64	p y
13-Nov	97	3891	195	0.0	122	45.5%	0.025	46.1%	7.64	y
16-Nov	100	3736	195	0.6	121	46.6%	0.025	46.9%	7.78	o
19-Nov	103	3634	195	0.6	118	47.8%	0.025	47.8%	7.65	o
22-Nov	106	3895	195	0.6	116	49.0%	0.025	48.7%	8.00	o
25-Nov	109	3836	195	1.2	112	50.1%	0.025	49.6%	8.24	o
28-Nov	112	3795	195	1.2	108	51.2%	0.025	50.5%	8.59	o
1-Dec	115	3788	195	1.2	104	52.2%	0.025	51.4%	8.55	o
4-Dec	118	3995	195	1.6	99	53.3%	0.025	52.3%	8.50	o
7-Dec	121	3651	195	1.9	95	54.2%	0.025	53.2%	7.96	o

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #6 is 2536 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #6 is 0.712 ppm

Date	Day	Vol. (mL)	[CN] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rey of Cu [‡]	[Au] (ppm)	%Rey of Au [§]	pH	color [†]
10-Dec	124	3691	195	2.8	87	55.0%	0.025	54.1%	8.88	o
13-Dec	127	3795	195	1.5	83	55.9%	0.025	55.0%	8.33	o
16-Dec	130	3849	195	1.4	80	56.7%	0.025	55.9%	9.28	o
19-Dec	133	3910	195	1.6	77	57.5%	0.025	56.8%	8.44	o
22-Dec	136	3996	195	1.3	72	58.2%	0.025	57.7%	8.39	o
26-Dec	140	4929	195	1.0	71	59.2%	0.025	58.9%	8.98	o
29-Dec	143	3651	195	1.2	69	59.8%	0.025	59.7%	9.49	o
1-Jan	146	4082	198	1.7	67	60.5%	0.025	60.7%	9.60	o
5-Jan	150	4643	198	0.9	62	61.3%	0.025	61.8%	9.65	y
8-Jan	153	3937	198	0.9	61	61.9%	0.025	62.7%	8.92	y
11-Jan	156	3991	198	1.1	59	62.6%	0.025	63.7%	8.91	y
14-Jan	159	3726	198	1.1	56	63.1%	0.025	64.5%	9.64	y
17-Jan	162	4084	198	2.2	52	63.7%	0.025	65.5%	9.69	o
20-Jan	165	3835	198	2.0	50	64.2%	0.025	66.4%	9.82	o
23-Jan	168	3631	198	2.5	47	64.6%	0.025	67.3%	9.92	o
26-Jan	171	3592	198	1.5	43	65.0%	0.025	68.1%	9.91	o
29-Jan	174	4109	198	1.9	41	65.5%	0.025	69.1%	9.93	o
2-Feb	178	4751	198	1.8	39	66.0%	0.013	69.6%	9.93	o
5-Feb	181	4178	198	1.0	38	66.4%	0.013	70.2%	9.88	y
8-Feb	184	3736	198	1.0	35	66.7%	0.013	70.6%	9.83	y
11-Feb	187	3580	198	0.9	35	67.1%	0.013	71.0%	9.81	o
14-Feb	190	4004	198	0.8	34	67.4%	0.013	71.5%	9.79	p y
17-Feb	193	3675	198	0.7	32	67.7%	0.013	72.0%	9.71	p y
20-Feb	196	3771	198	0.8	31	68.0%	0.013	72.4%	9.76	p y

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #6 is 2536 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #6 is 0.712 ppm

Date	Day	Vol. (mL)	[CN] ⁻ ₀ (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [‡]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
23-Feb	199	3904	198	0.6	30	68.4%	0.013	72.9%	9.77	p y
26-Feb	202	3962	198	0.7	29	68.7%	0.013	73.4%	9.77	p y
2-Mar	206	4915	198	1.3	28	69.0%	0.013	74.0%	9.84	p y
5-Mar	209	3853	198	1.1	27	69.3%	0.013	74.5%	9.84	p y
8-Mar	212	3959	198	0.8	26	69.6%	0.013	75.0%	9.87	p y
11-Mar	215	4248	198	0.9	26	69.9%	0.013	75.5%	9.85	p y
14-Mar	218	3429	198	0.8	25	70.1%	0.013	75.9%	9.89	p y
17-Mar	221	3674	198	0.6	25	70.4%	0.013	76.4%	9.86	p y

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #6 is 2536 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #6 is 0.712 ppm

Table B-5: General results of column #7 (1000 ppm NaCN, Whole Telfer 'E' ore, 0.8574 mL/min)

Date	Day	Vol. (mL)	[CN] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [†]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
8-Aug	0	48	488		10014	1.3%	0.00	0.0%	3.73	b
9-Aug	1	1065	488	15.9	4141	12.8%	0.00	0.0%	3.98	p b
10-Aug	2	1070	488	1.2	941	15.4%	0.00	0.0%	4.20	c
11-Aug	3	1254	488	0.7	330	16.5%	0.00	0.0%	4.42	c
12-Aug	4	1290	488	0.0	124	16.9%	0.00	0.0%	4.61	c
13-Aug	5	1327	488	0.0	64	17.1%	0.00	0.0%	4.80	c
14-Aug	6	1275	488	0.0	29	17.2%	0.01	0.2%	5.14	c
15-Aug	7	1349	488	0.0	14	17.2%	0.04	0.6%	5.53	c
19-Aug	10	4190	488	0.0	45	17.7%	0.13	5.5%	6.39	c
22-Aug	14	4750	486	0.0	152	19.6%	0.15	12.1%	7.21	c
24-Aug	16	2640	486	0.0	192	20.9%	0.16	16.1%	7.37	c
27-Aug	19	4000	486	0.0	267	23.7%	0.15	21.7%	7.46	c
30-Aug	22	1222	486	0.0	284	24.6%	0.14	23.3%	7.43	c
2-Sep	25	2236	508	0.0	230	26.0%	0.14	26.2%	7.57	c
5-Sep	28	3795	508	0.0	272	28.7%	0.11	30.2%	7.67	c
8-Sep	31	3657	508	0.0	296	31.5%	0.11	34.0%	7.41	c
11-Sep	34	3930	508	0.0	316	34.7%	0.11	38.2%	7.53	c
14-Sep	37	3757	508	0.0	345	38.1%	0.10	41.7%	7.56	c
17-Sep	40	3358	492	0.0	359	41.3%	0.09	44.4%	7.74	c
20-Sep	43	3894	492	0.0	356	44.9%	0.09	47.6%	7.80	c
23-Sep	46	3639	492	0.0	326	48.0%	0.09	50.6%	7.53	c
26-Sep	49	3832	492	0.0	310	51.1%	0.09	53.7%	7.72	c

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #7 is 2569 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #7 is 0.716 ppm

Date	Day	Vol. (mL)	[CN] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rey of Cu [†]	[Au] (ppm)	%Rey of Au [§]	pH	color [†]
29-Sep	52	3660	492	0.1	295	53.9%	0.08	56.4%	8.25	p y
2-Oct	55	3975	492	1.0	249	56.5%	0.06	58.7%	8.12	y
5-Oct	58	3610	492	1.2	227	58.6%	0.06	61.1%	8.57	p y
8-Oct	61	3580	492	1.9	200	60.5%	0.05	62.9%	8.95	o
11-Oct	64	3307	492	1.2	175	62.0%	0.05	64.5%	9.08	o
14-Oct	67	2763	492	2.3	167	63.2%	0.05	65.7%	9.09	o
17-Oct	70	3460	489	2.4	151	64.5%	0.05	67.4%	9.38	o
20-Oct	73	3579	489	2.0	129	65.7%	0.04	68.6%	9.74	o
23-Oct	76	4050	489	2.7	113	66.9%	0.04	70.1%	9.76	o
26-Oct	79	3621	489	2.2	100	67.9%	0.03	70.9%	9.86	o
29-Oct	82	3768	489	1.4	93	68.8%	0.03	71.8%	9.89	o
1-Nov	85	3942	489	1.5	84	69.6%	0.03	72.7%	9.87	o
4-Nov	88	3755	489	2.0	83	70.5%	0.01	73.2%	9.88	o
7-Nov	91	3155	489	0.7	76	71.1%	0.01	73.5%	9.87	o
overflow	91	1689	489	1.6	55	71.3%	0.01	73.7%	9.87	o
10-Nov	94	3859	489	1.8	77	72.1%	0.01	74.0%	9.88	o
13-Nov	97	3961	489	2.0	71	72.8%	0.01	74.5%	10.00	o
16-Nov	100	3809	489	1.7	58	73.4%	0.01	74.9%	9.98	o
19-Nov	103	3734	489	1.3	52	73.9%	0.01	75.4%	10.03	o
22-Nov	106	4019	489	0.8	51	74.4%	0.01	75.9%	10.00	o
25-Nov	109	3959	489	1.3	48	74.9%	0.01	76.4%	10.04	o
28-Nov	112	3915	489	0.7	40	75.4%	0.01	76.8%	10.05	y
1-Dec	115	3907	489	0.5	38	75.7%	0.01	77.3%	10.09	y
4-Dec	118	4122	489	0.6	37	76.1%	0.01	77.8%	10.01	y

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #7 is 2569 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #7 is 0.716 ppm

Date	Day	Vol. (mL)	[CN ⁻] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [‡]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
7-Dec	121	3762	489	0.6	35	76.5%	0.01	78.3%	10.12	y
10-Dec	124	3798	489	0.9	34	76.8%	0.00	78.3%	10.02	p y
13-Dec	127	3917	489	0.5	33	77.2%	0.00	78.3%	10.11	p y
16-Dec	130	3981	489	0.5	32	77.5%	0.00	78.3%	10.13	p y
19-Dec	133	3986	489	0.3	31	77.8%	0.00	78.3%	10.01	p y
22-Dec	136	4088	489	0.6	30	78.1%	0.00	78.3%	10.10	p y
26-Dec	140	5085	489	0.4	29	78.5%	0.00	78.3%	10.08	p y
29-Dec	143	3771	489	0.4	28	78.8%	0.00	78.3%	10.07	p y
1-Jan	146	4253	496	0.6	28	79.1%	0.00	78.3%	10.13	p y
5-Jan	150	4753	496	0.4	26	79.4%	0.00	78.3%	10.04	p y
8-Jan	153	4051	496	0.4	26	79.7%	0.00	78.3%	10.08	p y
11-Jan	156	4078	496	0.6	26	80.0%	0.00	78.3%	10.10	p y

[†] Color legend: b: blue; p b: pale blue; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #7 is 2569 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #7 is 0.716 ppm

Table B-6: General results of column #8 (1000 ppm NaCN, Whole Telfer 'E' ore, 0.8698 mL/min)

Date	Day	Vol. (mL)	[CN] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [‡]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
8-Aug	0	8	966		14771	0.3%	0.00	0.0%	3.52	b
9-Aug	1	962	964	25.2	5698	13.7%	0.00	0.0%	3.84	p b
10-Aug	2	980	962	4.9	699	15.4%	0.00	0.0%	4.27	c
11-Aug	3	1250	960	0.0	215	16.0%	0.00	0.0%	4.50	c
12-Aug	4	1310	958	0.0	77	16.3%	0.00	0.0%	4.78	c
13-Aug	5	1358	956	0.0	26	16.4%	0.13	1.7%	5.56	c
14-Aug	6	1290	953	0.0	71	16.6%	0.29	5.4%	5.87	c
15-Aug	7	1396	951	0.0	187	17.2%	0.38	10.5%	6.17	c
19-Aug	10	4370	949	0.0	417	21.7%	0.28	22.4%	7.59	c
22-Aug	14	5030	947	0.0	527	28.2%	0.16	30.6%	7.79	c
24-Aug	16	2700	945	0.0	558	31.9%	0.15	34.6%	7.92	c
27-Aug	19	4270	943	0.0	547	37.6%	0.14	40.4%	7.81	c
30-Aug	22	3768	941	0.0	642	43.5%	0.14	45.5%	7.69	p y
2-Sep	25	3775	939	0.0	668	49.6%	0.14	50.7%	8.12	br
5-Sep	28	3925	934	0.0	518	54.6%	0.12	55.5%	7.66	br
8-Sep	31	3709	954	1.3	365	57.9%	0.12	60.0%	8.28	y
11-Sep	34	4069	952	5.7	325	61.2%	0.10	64.0%	9.48	y
14-Sep	37	3790	950	4.0	252	63.5%	0.09	67.3%	9.73	y
17-Sep	40	3336	948	3.1	224	65.3%	0.08	69.8%	9.85	y
20-Sep	43	3894	946	3.9	190	67.1%	0.06	72.2%	9.92	y
23-Sep	46	3540	944	3.3	151	68.5%	0.05	74.0%	10.03	y
26-Sep	49	3741	941	2.9	135	69.7%	0.05	75.8%	10.06	y

† Color legend: b: blue; p b: pale blue; br: brown; c: clear; o: orange; y: yellow; p y: pale yellow

‡ Calculated copper head grade of Telfer 'E' ore for column #8 is 2683 ppm

§ Calculated gold head grade of Telfer 'E' ore for column #8 is 0.663 ppm

Date	Day	Vol. (mL)	[CN] ⁻ ₀ (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [‡]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
29-Sep	52	3475	939	2.4	115	70.7%	0.03	76.7%	10.09	y
2-Oct	55	3772	937	1.7	104	71.6%	0.03	77.6%	10.14	y
5-Oct	58	3442	935	1.6	96	72.4%	0.03	78.5%	10.16	y
8-Oct	61	3595	933	1.6	88	73.2%	0.03	79.4%	10.18	y
11-Oct	64	3628	931	1.4	78	73.9%	0.01	79.8%	10.18	y
14-Oct	67	3540	929	1.4	72	74.5%	0.01	80.3%	10.16	y
17-Oct	70	3150	959	1.3	64	75.0%	0.00	80.3%	10.17	y
20-Oct	73	3763	959	1.2	58	75.6%	0.00	80.3%	10.23	y
23-Oct	76	3836	959	1.0	57	76.1%	0.00	80.3%	10.19	y
26-Oct	79	3477	959	1.0	55	76.6%	0.00	80.3%	10.21	y
29-Oct	82	3626	959	1.0	51	77.0%	0.00	80.3%	10.20	y
1-Nov	85	3695	959	0.9	45	77.4%	0.00	80.3%	10.19	y
4-Nov	88	3725	959	0.9	43	77.8%	0.00	80.3%	10.23	p y
7-Nov	91	3979	959	0.9	42	78.2%	0.00	80.3%	10.22	p y
10-Nov	94	4012	959	0.8	40	78.6%	0.00	80.3%	10.19	p y
13-Nov	97	4056	959	0.8	37	79.0%	0.00	80.3%	10.19	p y
16-Nov	100	3901	959	1.0	35	79.3%	0.00	80.3%	10.25	p y
19-Nov	103	3642	959	1.3	34	79.6%	0.00	80.3%	10.26	p y
22-Nov	106	4117	959	0.7	31	79.9%	0.00	80.3%	10.24	p y
25-Nov	109	4047	959	0.8	29	80.2%	0.00	80.3%	10.25	p y
28-Nov	112	4019	959	0.7	28	80.5%	0.00	80.3%	10.27	p y
1-Dec	115	3069	959	0.8	27	80.7%	0.00	80.3%	10.29	p y

[†] Color legend: b: blue; p b: pale blue; br: brown; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #8 is 2683 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #8 is 0.663 ppm

Table B-7: General results of column #9: 2000 ppm NaCN, Whole Telfer 'E' ore, 0.9283 mL/min)

Date	Day	Vol. (mL)	[CN] ⁻ _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [‡]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
8-Aug	0	47	1930		12966	1.6%	0.000	0.0%	3.49	b
9-Aug	1	1062	1925	16.5	3997	13.1%	0.000	0.0%	3.86	p b
10-Aug	2	1140	1919	0.0	371	14.2%	0.000	0.0%	4.52	p y
11-Aug	3	1345	1914	0.0	76	14.5%	0.363	4.2%	5.87	c
12-Aug	4	1380	1908	0.0	526	16.4%	0.575	10.9%	6.88	c
13-Aug	5	1358	1903	0.0	771	19.3%	0.388	15.4%	7.27	c
14-Aug	6	1375	1897	0.0	890	22.6%	0.363	19.7%	7.51	c
15-Aug	7	1452	1892	0.0	924	26.2%	0.338	23.9%	7.70	c
19-Aug	10	4540	1886	0.0	950	37.8%	0.288	35.0%	8.10	br
22-Aug	14	5180	1881	0.0	927	50.7%	0.250	46.1%	9.45	br
24-Aug	17	2800	1875	5.5	639	55.6%	0.200	50.8%	7.93	br
27-Aug	20	4350	1870	32.4	535	61.8%	0.175	57.3%	9.92	c
30-Aug	22	3895	1864	18.4	325	65.2%	0.125	61.5%	10.10	p y
2-Sep	25	3905	1859	11.2	258	68.0%	0.088	64.4%	10.19	y
5-Sep	28	4122	1850	8.1	201	70.2%	0.075	67.0%	10.22	y
8-Sep	31	4100	1902	6.7	163	72.0%	0.063	69.2%	10.21	y
11-Sep	34	4427	1900	5.3	139	73.6%	0.038	70.7%	10.26	y
14-Sep	37	4240	1898	4.9	115	75.0%	0.025	71.6%	10.25	y
17-Sep	40	3782	1896	4.4	104	76.0%	0.025	72.4%	10.29	y
20-Sep	43	4310	1894	4.6	94	77.1%	0.025	73.3%	10.30	y
23-Sep	46	4040	1892	4.0	75	77.9%	0.025	74.2%	10.37	p y
26-Sep	49	4240	1889	3.7	70	78.7%	0.025	75.1%	10.34	p y

[†] Color legend: b: blue; p b: pale blue; br: brown; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #9 is 2460 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #9 is 0.777 ppm

Date	Day	Vol. (mL)	[CN ⁻] _o (ppm)	[Fe] (ppm)	[Cu] (ppm)	%Rcy of Cu [†]	[Au] (ppm)	%Rcy of Au [§]	pH	color [†]
29-Sep	52	4070	1887	3.7	61	79.4%	0.025	75.9%	10.36	p y
2-Oct	55	4390	1885	3.0	55	80.0%	0.013	76.4%	10.38	p y
5-Oct	58	4020	1883	2.9	50	80.6%	0.013	76.9%	10.38	p y
8-Oct	61	4177	1881	3.0	46	81.1%	0.013	77.3%	10.39	p y
11-Oct	64	4279	1879	2.9	42	81.6%	0.013	77.8%	10.33	p y
14-Oct	67	1470	1877	4.5	53	81.8%	0.013	78.0%	10.35	p y
17-Oct	70	4457	2024	4.1	50	82.4%	0.000	78.0%	10.34	p y
20-Oct	73	4057	2024	3.4	36	82.8%	0.000	78.0%	10.37	p y
23-Oct	76	3836	2024	3.1	34	83.1%	0.000	78.0%	10.35	p y
26-Oct	79	3752	2024	3.1	32	83.5%	0.000	78.0%	10.41	p y

[†] Color legend: b: blue; p b: pale blue; br: brown; c: clear; o: orange; y: yellow; p y: pale yellow

[‡] Calculated copper head grade of Telfer 'E' ore for column #9 is 2460 ppm

[§] Calculated gold head grade of Telfer 'E' ore for column #9 is 0.777 ppm

Table B-8: Percentage of cyanide consumed for each column

Day	Column #6	Day	Column #7	Day	Column #8	Day	Column #9
3	100.0%	3	100.0%	0	100.0%	0	100.0%
7	100.0%	7	100.0%	5	100.0%	1	100.0%
10	100.0%	10	100.0%	16	100.0%	2	100.0%
16	100.0%	16	100.0%	22	100.0%	3	100.0%
25	100.0%	25	100.0%	28	100.0%	4	100.0%
34	100.0%	34	100.0%	31	89.2%	5	100.0%
43	100.0%	43	100.0%	34	76.5%	6	100.0%
52	100.0%	52	70.0%	37	63.6%	7	100.0%
58	95.0%	64	50.5%	40	48.3%	10	100.0%
64	88.0%	73	49.3%	43	45.6%	14	97.9%
79	70.0%	85	36.5%	46	39.7%	16	72.7%
91	63.5%	100	30.9%	49	36.6%	19	48.8%
109	52.7%	109	25.1%	52	31.1%	22	46.4%
121	47.7%	121	23.4%	55	27.3%	25	36.0%
133	48.7%	133	21.1%	58	25.1%	28	26.8%
143	48.5%	143	22.9%	61	24.6%	31	15.9%
162	42.0%	156	20.1%	64	24.4%	34	14.5%
181	38.7%			103	12.6%	37	15.7%

Table B-9: Concentration of thiocyanate in the effluent

Day	Column #7 (mol/L)	Day	Column #8 (mol/L)	Day	Column #9 (mol/L)
4	0.00000	3	0.00000	2	0.00000
5	0.00000	4	0.00000	3	0.00371
6	0.00000	5	0.00127	4	0.00524
7	0.00052	16	0.00157	7	0.00366
10	0.00138	19	0.00164	10	0.00353
14	0.00126	28	0.00179	31	0.00198
22	0.00085	31	0.00162	61	0.00070
40	0.00073	82	0.00087		
61	0.00070				
97	0.00069				

Appendix C. FORTRAN program listing for the general heap leaching model

The appendix C presents the FORTRAN Visual Workbench V. 1.00 program listing for the general heap leaching model as described in section 5. Each subroutine contains a heading which describe its role and define its main variables or arguments. Some short comments are also added into the listing on which the line is identified by the letter C.

The program listing is presented in two parts with their respective subroutines in the following order. Even though it is included in the general heap leaching model, the speciation model is placed alone because it can be run independently.

1. General heap leaching model

Program GENERAL
Subroutine PASS
Subroutine DISTRIB
Subroutine SUBREV
Subroutine CHARAC
Subroutine WRITEF
Function SRK
Function ZERO

2. Speciation model

Program SPECIATION
Subroutine SPEC
Subroutine COEFF
Subroutine PRECIP
Subroutine UTIL
Subroutine DATAOUT
Subroutine GAUSS

Program GENERAL

```
C-----
C Copyright 1998 Francois Coderre
C
C This program calculates the general heap leaching model in the
C present study of cyanidation of cupriferous gold ores.
C
C The bulk representing the flowing liquid and the reservoir
C representing the stagnant liquid are calculated sequentially
C at each increment of depth in the column. The speciation
C subroutine is also applied to each fluid element.
C
C The subroutines UTIL and CHARAC defines the constant values and the
C initial conditions for the heap. The subroutine PASS executes the
C model. Finally, the subroutine WRITEF opens, initializes and closes
C data files.
C-----
C
C PROGRAM GENERAL
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C
C CALL UTIL
C CALL CHARAC
C CALL WRITEF (1)
C CALL WRITEF (2)
C CALL PASS
C CALL WRITEF (5)
C STOP
C END
```

Subroutine PASS

```

C-----
C Copyright 1998 Francois Coderre and David G. Dixon
C
C The subroutine PASS is the core of the heap leaching model.
C It executes all the kinetic reactions in both the bulk and
C the reservoir and allows the speciation subroutine to calculate
C the equilibria in each fluid element. This procedure is performed
C for each depth and time increments.
C
C More details on this subroutine are presented in section 5.
C-----
C
C SUBROUTINE PASS
C
C IMPLICIT REAL*8 (A-H,O-Z)
C DIMENSION C(8),CF(8),CFOLD(8),CB(8,160),CSTOCK(8),CR(8,100)
C DIMENSION P(4),PB(4,160),PR(4,160),SB(160),SC(160)
C DIMENSION ANU(8,3),R(4),CNFB(160),CNFR(160),PHB(160),PHR(160)
C DIMENSION RRFAC(8),RBFAC(8),DIFFR(8),DIFFB(8)
C COMMON /COLUMN/TA,TM,PHI,NL,CSTOCK,P3INIT,P4INIT
C COMMON /RATE/ANU,AKA,AKB,AKC,CUFAC,AUFAC,PHIB,PHIC
C EXTERNAL SRK, ZERO
C
C CALL WRITEF(3)
C DO 11 L=1,NL
C   SB(L) = 1.
C   SC(L) = 1.
C   PB(1,L) = 0.
C   PB(2,L) = 0.
C   PB(3,L) = P3INIT
C   PB(4,L) = P4INIT
C   PR(1,L) = 0.
C   PR(2,L) = 0.
C   PR(3,L) = P3INIT
C   PR(4,L) = P4INIT
11 CONTINUE
C STOI = ANU(4,1)/ANU(1,1)
C NGM = NL/20 - 1
C NG1 = (2**NGM)
C NG2 = (2**NGM-1)
C TIME = -TA*PHI
C N1 = 1
C NTOT = 0
100 WRITE(*,*)'Enter the number of time increments, NT:'
C READ(*,*)NT
C NTOT = NTOT + NT
C DO 10 J=N1,NTOT
C   IF(J.LE.NL) THEN
C     DT = TA*PHI/NL
C     LL = J
C   ELSE
C     LL = NL
C     DT=TA/10.d0
C   ENDIF
C   TIME = TIME+DT
C   DO 1 I=1,8
C     CF(I) = CSTOCK(I)
C     IF(J.EQ.1) THEN
C       CR(I,1) = CF(I)
C       CB(I,1) = CF(I)
C     ENDIF
1 CONTINUE

```

Subroutine PASS (cont.)

```

DO 2 L=1,LL
  IF(J.EQ.L) CNFR(L) = CR(4,L)
  POXCU = ZERO(CNFR(L))/(ZERO(CR(1,L))+ZERO(CNFR(L)))
  POXCN = 1.D0 - POXCU
  R(1) = AKA*(ZERO(CR(1,L))*POXCU + STOI*ZERO(CNFR(L))*POXCN)
  R(2) = AKB*AUFAC*CNFR(L)*SB(L)**PHIB
  R(3) = AKC*CUFAC*CNFR(L)*SC(L)**PHIC
  SUMR = R(1) + R(2) + R(3)
  RATIO = 1.D0
90  I=0
  DO 7 I=1,8
    RC = 0.
    DO 4 K=1,3
      RC = RC + ANU(I,K)*R(K)
4    CONTINUE
    DIFFR(I)=(RC-(CR(I,L)-CB(I,L))/(PHI*TM))*DT
    RRFAC(I)=CR(I,L)+RATIO*DIFFR(I)
    IF (RRFAC(I).LE.0.D0 .AND. I.NE.7) THEN
      RATIO = CR(I,L)*0.99D0/(DIFFR(I))
      GOTO 90
    ENDIF
7    CONTINUE
    DO 3 I=1,8
      CR(I,L)=RRFAC(I)
      C(I) = CR(I,L)
      IF(I.LE.4) P(I) = PR(I,L)
3    CONTINUE
    CALL DISTRIB(C,P,CNFR(L),PHR(L))
    DO 9 I=1,8
      CR(I,L) = C(I)
      IF(I.LE.4) PR(I,L) = P(I)
      CFOLD(I) = CF(I)
9    CONTINUE
    IF(J.EQ.L) CNFB(L) = CB(4,L)
    POXCU = ZERO(CNFB(L))/(ZERO(CB(1,L))+ZERO(CNFB(L)))
    POXCN = 1.D0 - POXCU
    R(4)=AKA*(ZERO(CB(1,L))*POXCU+STOI*ZERO(CNFB(L))*POXCN)
    RATIO = 1.D0
95  I=0
    DO 8 I=1,8
      RC=ANU(I,1)*R(4)
      DIFFB(I)=(RC-(CB(I,L) - CR(I,L))/TM)*TA/NL
      RBFAC(I)=CF(I) + RATIO*DIFFB(I)
      IF (RBFAC(I).LE.0.D0 .AND. I.NE.7) THEN
        RATIO = CF(I)*0.99D0/(DIFFB(I))
        GOTO 95
      ENDIF
8    CONTINUE
    DO 5 I=1,8
      CF(I)=RBFAC(I)
      CB(I,L) = (CFOLD(I) + CF(I))/2.D0
      C(I) = CB(I,L)
      IF(I.LE.4) P(I) = PB(I,L)
5    CONTINUE
    CALL DISTRIB(C,P,CNFB(L),PHB(L))
    DO 6 I=1,8
      CB(I,L) = C(I)
      IF(I.LE.4) PB(I,L) = P(I)
      IF(L.EQ.J .AND. L.NE.NL) THEN
        CB(I,L+1) = CF(I)
        CR(I,L+1) = CF(I)
      ENDIF
6    CONTINUE

```

Subroutine PASS (cont.)

```

SB(L) = SRK(SB(L),AKB*CNFR(L),PHIB,DT)
SC(L) = SRK(SC(L),AKC*CNFR(L),PHIC,DT)
IF(L.EQ.LL) THEN
50  FORMAT(F7.1,2X,8E9.3,F7.2)
    WRITE(11,50)TIME,(CB(I,L),I=1,8),10.D0**(-PHB(L))
    WRITE(12,50)TIME,(CR(I,L),I=1,8),10.D0**(-PHB(L))
    WRITE(13,50)TIME,(PB(I,L),I=1,4),PHB(L)
    WRITE(14,50)TIME,(PR(I,L),I=1,4),SB(L),SC(L),PHR(L)
ENDIF
2  CONTINUE
WRITE(*,51) TIME,J,PHB(LL)
51  FORMAT('+' At time 'F7.1,' ('I3,') ', Bulk pH = 'F8.4)
55  FORMAT(F7.1,20E9.3,F9.4)
    WRITE(15,55)TIME,(CB(1,L*NG1-NG2),L=1,20),PHB(LL)
    WRITE(16,55)TIME,(CR(1,L*NG1-NG2),L=1,20),PHR(LL)
    WRITE(17,55)TIME,(CNFB(L*NG1-NG2),L=1,20),PHB(LL)
    WRITE(18,55)TIME,(CNFR(L*NG1-NG2),L=1,20),PHR(LL)
    WRITE(19,55)TIME,(CB(2,L*NG1-NG2),L=1,20),PHB(LL)
    WRITE(20,55)TIME,(CR(2,L*NG1-NG2),L=1,20),PHR(LL)
    WRITE(21,55)TIME,(PB(1,L*NG1-NG2),L=1,20),PHB(LL)
    WRITE(22,55)TIME,(PR(1,L*NG1-NG2),L=1,20),PHR(LL)
    WRITE(23,55)TIME,(PB(3,L*NG1-NG2),L=1,20),PHB(LL)
    WRITE(24,55)TIME,(PR(3,L*NG1-NG2),L=1,20),PHR(LL)
    WRITE(25,55)TIME,(PHB(L*NG1-NG2),L=1,20)
    WRITE(26,55)TIME,(PHR(L*NG1-NG2),L=1,20)
10  CONTINUE
    WRITE(*,*) 'Do you want to continue? (1=yes,2=no)'
    READ(*,*) IREP
    IF(IREP.EQ.1) THEN
        N1 = NTOT+1
        GOTO 100
    ELSE IF(IREP.EQ.2) THEN
        GOTO 200
    ENDIF
C
200 RETURN
END

```

Subroutine DISTRIB

```

C-----
C  Copyright 1998 Francois Coderre
C
C  The subroutine DISTRIB initialize the seven total concentrations
C  for speciation calculation.
C  1:Cu(II) 2:Cu(I) 3:Cu(I) 4:CN(-) 5:CNO(-) 6:CNS(-) 7:OH(-)
C
C  Arguments:
C  CONC  Aqueous species matrix (1:Cu(II) 2:Cu(I) 3:Cu(I) 4:CN(-)
C        5:CNO(-) 6:CNS(-) 7:OH(-)) for any depth increment L
C  PREP  Reversible precipitates matrix (1:CuCN, 2:CuCN and 3:Cu(OH)2)
C        for any depth increment L
C  L     Depth increment
C-----
C
C  SUBROUTINE DISTRIB (CONC,PREP,CNF,PH)
C
C  IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C  DIMENSION CONC(8),PREP(4),GUESS(27),X(27)
C
C  COMMON /INITIAL/ COH0,CCN0,CCUI0,CCUII0,CAU0,
C  +             COCN0,CSCN0,CSO40,ALPHA
C
C  CCUII0=CONC(1)+PREP(3)+PREP(4)
C  CCUI0=CONC(2)+PREP(1)
C  CAU0=CONC(3)+PREP(2)
C  CCN0=CONC(4)+PREP(1)+PREP(2)
C  COCN0=CONC(5)
C  CSCN0=CONC(6)
C  COH0=CONC(7)+2.D0*PREP(3)
C  CSO40=CONC(8)+PREP(4)
C  ALPHA=1.D0
C  IPREC=1
C  DO I=1,27
C    GUESS(I)=10.d0
C  ENDDO
C  CALL SPEC (ITER,X,GUESS,IPREC)
C  CALL SUBREV (X,CONC,PREP,CNF)
C  PH=-DLOG10(DEXP(X(11)))
C
C  RETURN
C  END

```


Subroutine SUBREV

```

C-----
C Copyright 1998 Francois Coderre
C
C The subroutine SUBREV separates the SPEC subroutine results into
C aqueous CONC and solid precipitates PREP.
C
C Arguments:
C X Log(concentration) vector
C PREP Reversible precipitates matrix (1:CuCN, 2:Cu(OH)2 and 3:Cu(OH)2)
C for any depth increment L
C CONC Aqueous species matrix (1:Cu(II) 2:Cu(I) 3:Cu(I) 4:CN(-)
C 5:CNO(-) 6:CNS(-) 7:OH(-)) for any depth increment L
C CNF Total free cyanide concentration (i.e. [CN-] + [HCN])
C-----
C
C SUBROUTINE SUBREV (X,CONC,PREP,CNF)
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C COMMON /STOCK/ CNACNPPM,PHINIT
C COMMON /IPRECIP/ ICUCN,IAUCN,ICUOH2,ICUSO4
C COMMON /AQUEOUS/ CUCNAQ,AUCNAQ,CUOH2AQ,CUSO4AQ
C DIMENSION CONC(8),PREP(4),X(27)
C
C Assess precipitation of CuOH2 and define new values for CONC(1)
C
C CUIITO=DEXP(X(13))+DEXP(X(15))+DEXP(X(16))+DEXP(X(20))
C + 2.D0*DEXP(X(17))+2.D0*DEXP(X(18))+3.D0*DEXP(X(19))
C + DEXP(X(27))
C IF (ICUOH2.EQ.1) THEN
C CONC(1)=CUIITO+DEXP(X(14))
C PREP(3)=0.D0
C ELSE IF (ICUOH2.EQ.2) THEN
C CONC(1)=CUIITO+CUOH2AQ
C PREP(3)=DEXP(X(14))
C ENDIF
C
C Assess precipitation of CuCN and define new values for CONC(2)
C
C CUITO=DEXP(X(2))+DEXP(X(3))+DEXP(X(4))+DEXP(X(5))
C IF (ICUCN.EQ.1) THEN
C CONC(2)=CUITO+DEXP(X(1))
C PREP(1)=0.D0
C ELSEIF (ICUCN.EQ.2) THEN
C CONC(2)=CUITO+CUCNAQ
C PREP(1)=DEXP(X(1))
C ENDIF
C
C Assess precipitation of AuCN and define new values for CONC(3)
C
C AUTO=DEXP(X(9))+DEXP(X(10))
C IF (IAUCN.EQ.1) THEN
C CONC(3)=AUTO+DEXP(X(8))
C PREP(2)=0.D0
C ELSE IF (IAUCN.EQ.2) THEN
C CONC(3)=AUTO+AUCNAQ
C PREP(2)=DEXP(X(8))
C ENDIF
C
C Assess aqueous cyano-species according to CuCN(s) and/or AuCN(s)
C for CONC(4)
C
C CUCNY=2.D0*DEXP(X(2))+3.D0*DEXP(X(3))+4.D0*DEXP(X(4))

```

Subroutine SUBREV (cont.)

```

+   +2.D0*DEXP(X(9))
CNF=DEXP(X(6))+DEXP(X(7))
IF ((ICUCN.EQ.1).AND.(IAUCN.EQ.1)) THEN
  CONC(4)=CUCNY+CNF+DEXP(X(1))+DEXP(X(8))
ELSE IF ((ICUCN.EQ.1).AND.(IAUCN.EQ.2)) THEN
  CONC(4)=CUCNY+CNF+DEXP(X(1))+AUCNAQ
ELSE IF ((ICUCN.EQ.2).AND.(IAUCN.EQ.1)) THEN
  CONC(4)=CUCNY+CNF+CUCNAQ+DEXP(X(8))
ELSE IF ((ICUCN.EQ.2).AND.(IAUCN.EQ.2)) THEN
  CONC(4)=CUCNY+CNF+CUCNAQ+AUCNAQ
ENDIF
C
C   Assess aqueous cyanate and thiocyanate species
C
CONC(5)=DEXP(X(21))+DEXP(X(22))
CONC(6)=DEXP(X(23))+DEXP(X(24))
C
C   Assess aqueous hydroxi-species according to CuOH2(s)
C   for CONC(7)
C
OHTO=DEXP(X(13))+DEXP(X(12))
+   +3.D0*DEXP(X(15))+4.D0*DEXP(X(16))
+   +DEXP(X(17))+2.D0*DEXP(X(18))+4.D0*DEXP(X(19))
HTO=+DEXP(X(7))+DEXP(X(11))+DEXP(X(22))+DEXP(X(24))+DEXP(X(26))
IF (ICUOH2.EQ.1) THEN
  CONC(7)=OHTO-HTO+2.D0*DEXP(X(14))
ELSE IF (ICUOH2.EQ.2) THEN
  CONC(7)=OHTO-HTO+2.D0*CUOH2AQ
ENDIF
C
C   Assess aqueous sulfate species
C
SO4TO=DEXP(X(25))+DEXP(X(26))
IF (ICUSO4.EQ.1) THEN
  CONC(8)=SO4TO+DEXP(X(27))
  PREP(4)=0.D0
ELSE IF (ICUSO4.EQ.2) THEN
  CONC(8)=SO4TO+CUSO4AQ
  PREP(4)=DEXP(X(27))
ENDIF
C
RETURN
END

```

Subroutine CHARAC

```

C-----
C   Copyright 1998 Francois Coderre
C
C   The subroutine defines all the constants necessary for the column
C   leaching calculation program.
C
C   All units in centimeter-minute-gram
C-----
SUBROUTINE CHARAC
C
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION P(4),CSTOCK(8),ANU(8,3)
  COMMON /STOCK/CNACNPPM,PHINIT
  COMMON /COLUMN/TA,TM,PHI,NL,CSTOCK,P3INIT,P4INIT
  COMMON /RATE/ANU,AKA,AKB,AKC,CUFAC,AUFAC,PHIB,PHIC
  DATA (ANU(I,1),I=1,8)/-2.,2.,0.,-1.,1.,0.,-2.,0./
  DATA (ANU(I,2),I=1,8)/0.,0.,1.,0.,0.,0.,1.,0./
  DATA (ANU(I,3),I=1,8)/0.,2.,0.,-1.,0.,1.,2.,0./

  OPEN (UNIT = 2,FILE = 'INITDATA.TXT',STATUS = 'OLD')
  READ(2,*)
  READ(2,*)
  READ(2,*)
  READ(2,*)CNACNPPM,PHINIT
  WMOLNACN = 22.9898D0 + 12.01115D0 + 14.0067D0
  CNACN0 = CNACNPPM/(WMOLNACN*1000.D0)

  READ(2,*)
  READ(2,*)
  READ(2,*)
  READ(2,*)AKA,AKB,AKC,PHIB,PHIC

  READ(2,*)
  READ(2,*)
  READ(2,*)
  READ(2,*)COLDIA,COLZ,W_ORE,NL
  COLAREA = 3.1416*COLDIA**2.D0/4.D0
  COLVOL = COLAREA*COLZ

  READ(2,*)
  READ(2,*)
  READ(2,*)
  READ(2,*)FLOWQ,EPSB,EPSR,AKM
  US = FLOWQ/COLAREA

  READ(2,*)
  READ(2,*)
  READ(2,*)
  READ(2,*)G_CU,FCUSO4,FCUOH2,FCUS,G_AU

  WMOLCU = 63.546D0
  WMOLAU = 196.967D0

  ENDFILE(UNIT = 2)
  CLOSE(UNIT = 2)

C   Calculation of leaching parameters

  TA = EPSB*COLZ/US
  TM = EPSR/AKM
  PHI = EPSR/EPSB
  RHO_ORE = W_ORE/COLVOL
  CUFAC = G_CU*RHO_ORE*1000.D0/(WMOLCU*EPSR)

```

Subroutine CHARAC (cont.)

```
AUFAC = G_AU*RHO_ORE*1000.D0/(WMOLAU*EPSR)
P3INIT = FCUOH2*CUFAC*PHI/(1. + PHI)
P4INIT = FCUSO4*CUFAC*PHI/(1. + PHI)

C   Stock solution concentrations

SMALL = 1.D-10
CSTOCK(1) = SMALL
CSTOCK(2) = SMALL*1.D-1
CSTOCK(3) = SMALL*1.D-5
CSTOCK(4) = CNACN0
CSTOCK(5) = SMALL*1.D-3
CSTOCK(6) = SMALL*1.D-2
CSTOCK(7) = 10.D0**(PHINIT - 14.D0)
CSTOCK(8) = SMALL*1.D-4
DO 2 I=1,4
  P(I) = 0.D0
2  CONTINUE
CALL DISTRIB(CSTOCK,P,CNF,PH)
PHINIT = PH

RETURN
END
```

Subroutine WRITEF

```

C-----
C  Copyright 1998 Francois Coderre
C
C  The subroutine WRITEF opens, initializes and closes result files
C-----
C
C  SUBROUTINE WRITEF (IWRITE)
C
C  IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
COMMON /STOCK/ CNACNPPM,PHINIT
COMMON /COLUMN/TA,TM,PHI,NL,CSTOCK,P3INIT,P4INIT
C
C  IF (IWRITE.EQ.1) THEN
      OPEN (UNIT=11,FILE='CONC_B.TXT',STATUS='OLD')
      OPEN (UNIT=12,FILE='CONC_R.TXT',STATUS='OLD')
      OPEN (UNIT=13,FILE='PREP_B.TXT',STATUS='OLD')
      OPEN (UNIT=14,FILE='PREP_R.TXT',STATUS='OLD')
      OPEN (UNIT=15,FILE='CUII_B.TXT',STATUS='OLD')
      OPEN (UNIT=16,FILE='CUII_R.TXT',STATUS='OLD')
      OPEN (UNIT=17,FILE='CN_B.TXT',STATUS='OLD')
      OPEN (UNIT=18,FILE='CN_R.TXT',STATUS='OLD')
      OPEN (UNIT=19,FILE='CUI_B.TXT',STATUS='OLD')
      OPEN (UNIT=20,FILE='CUI_R.TXT',STATUS='OLD')
      OPEN (UNIT=21,FILE='CUCN_B.TXT',STATUS='OLD')
      OPEN (UNIT=22,FILE='CUCN_R.TXT',STATUS='OLD')
      OPEN (UNIT=23,FILE='CUOH2_B.TXT',STATUS='OLD')
      OPEN (UNIT=24,FILE='CUOH2_R.TXT',STATUS='OLD')
      OPEN (UNIT=25,FILE='PH_B.TXT',STATUS='OLD')
      OPEN (UNIT=26,FILE='PH_R.TXT',STATUS='OLD')
      DO J=11,26
        WRITE (J,60) 'Stock cyanide concentration: ',CNACNPPM
        WRITE (J,61) 'Stock initial pH before NaCN: ', PHINIT
      ENDDO
60    FORMAT (/A,F10.1)
61    FORMAT (A,F10.3/)
      ENDIF
C
C  IF (IWRITE.EQ.2) THEN
      WRITE (11,64) 'TIME ', 'Cu(II)', 'Cu(I)', 'Au(I)', 'CN(-)',
+      'OCN(-)', 'SCN(-)', 'OH(-)', 'SO4', 'pH'
      WRITE (12,64) 'TIME ', 'Cu(II)', 'Cu(I)', 'Au(I)', 'CN(-)',
+      'OCN(-)', 'SCN(-)', 'OH(-)', 'SO4', 'pH'
      WRITE (13,65) 'TIME ', 'CuCN', 'AuCN', 'Cu(OH)2', 'CuSO4'
      WRITE (14,65) 'TIME ', 'CuCN', 'AuCN', 'Cu(OH)2', 'CuSO4',
+      'Au(s)', 'Cu2S'
64    FORMAT (3X,A,3X,A,4X,A,3X,A,4X,A,4X,A,3X,A,4X,A,4X,A,6X,A)
65    FORMAT (3X,A,3X,A,4X,A,5X,A,3X,A,4X,A,4X,A)
      ENDIF
C
C  IF (IWRITE.EQ.3) THEN
      WRITE(15,*) ' COPPER(II) IN THE BULK'
      WRITE(16,*) ' COPPER(II) IN THE RESERVOIR'
      WRITE(17,*) ' CYANIDE IN THE BULK'
      WRITE(18,*) ' CYANIDE IN THE RESERVOIR'
      WRITE(19,*) ' COPPER(I) IN THE BULK'
      WRITE(20,*) ' COPPER(I) IN THE RESERVOIR'
      WRITE(21,*) ' CuCN(s) IN THE BULK'
      WRITE(22,*) ' CuCN(s) IN THE RESERVOIR'
      WRITE(23,*) ' Cu(OH)2(s) IN THE BULK'
      WRITE(24,*) ' Cu(OH)2(s) IN THE RESERVOIR'
      WRITE(25,*) ' pH IN THE BULK'
      WRITE(26,*) ' pH IN THE RESERVOIR'

```

Subroutine WRITEF (cont.)

```
      DO I=15,26
        WRITE(I,*)
        WRITE(I,40) (L,L=1,20)
      ENDDO
40    FORMAT(5X,100I9,' PH')
      ENDIF
C
      IF (IWRITE.EQ.4) THEN
        DO I=11,26
          WRITE (I,*)
        ENDDO
      ENDIF
C
      IF (IWRITE.EQ.5) THEN
        DO I=11,26
          ENDFILE (UNIT=I)
          CLOSE (UNIT=I)
        ENDDO
      ENDIF
C
      RETURN
      END
```

Function SRK

```

C-----
C Copyright 1998 David G. Dixon
C
C This function SRK runs a Runge-Kutta for the calculation of the
C extraction (1-X) of a solid S. The differential equation is
C      SRK = Df/DT = - F*S**P
C-----
C
C FUNCTION SRK(S,F,P,DT)
C
C IMPLICIT REAL*8 (A-H,O-Z)
C IF(S.EQ.0.) GOTO 200
C F1 = -F*S**P
C Y = S + 0.5*DT*F1
C IF(Y.LT.0.) GOTO 100
C F2 = -F*Y**P
C Y = S + 0.5*DT*F2
C IF(Y.LT.0.) GOTO 100
C F3 = -F*Y**P
C Y = S + DT*F3
C IF(Y.LT.0.) GOTO 100
C F4 = -F*Y**P
C SRK = S + DT*(F1 + 2.*F2 + 2.*F3 + F4)/6.
C IF(SRK.LE.0.) SRK = 0.
C GOTO 200
100 SRK = 0.
C
200 RETURN
END

```

Function ZERO

```

C-----
C Copyright 1998 Francois Coderre
C
C This function initializes any negative or zero number to 1.d-20.
C This function is used to error-proof the speciation subroutine.
C-----
C
C FUNCTION ZERO(DUMMY)
C IMPLICIT REAL*8 (A-H,O-Z)
C
C IF (DUMMY.LE.0.D0) THEN
C PRINT *, 'A LITTLE ZERO HERE!', DUMMY
C PRINT *, ''
C ZERO = 1.D-20
C ELSE
C ZERO = DUMMY
C ENDIF
C RETURN
C END

```

Program SPECIATION

```

C-----
C  Copyright 1998 Francois Coderre
C
C  This program calculates the speciation distribution of three
C  metals: Cu(I), Cu(II) and Au(I) in cyanide solution based on
C  thermodynamic calculations.
C
C  This program will be inserted in the general heap leaching model
C  in the present study of cyanide leaching of cupriferous gold ores.
C  The solution chemistry of the leaching process is defined with
C  reference to both computational and experimental results. The
C  competition of cyanide complexation of gold and especially copper
C  during the cyanide leaching is particularly considered.
C-----
C
C  PROGRAM SPECIATION
C
C  IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C  DIMENSION X(27),GUESS(27)
C
C  COMMON /INITIAL/ COH0,CCN0,CCUI0,CCUII0,CAU0,COCN0,
+      CSCN0,CSO40,ALPHA
C
C  CALL UTIL
C
5  OPEN (UNIT=15,FILE='C:\FRANCOIS\CUAUOSC\SPECDATA.TXT',
+      STATUS='OLD')
    READ (15,*)
    READ (15,*)
    READ (15,*) COH0,CCN0,CCUI0,CCUII0,CAU0,COCN0,CSCN0,CSO40
    ENDFILE (UNIT=15)
    CLOSE (UNIT=15)
    ALPHA=1.0D0
C
C  The guess values represent the initial solution values set for
C  the Newton's method algorithm.
C
    DO J=1,27
        GUESS(J)=-0.5D0
    ENDDO
C
C  Set precipitation indice to 1 (no precipitation)
C
    IPREC=1
C
    CALL SPEC (ITER,X,GUESS,IPREC)
    CALL DATAOUT (ITER,X)
C
    PRINT *, 'Do you want to try again (YES=1, NO=2)'
    READ (*,*) IREP
    IF (IREP.EQ.1) THEN
        GOTO 5
    ELSE IF (IREP.EQ.2) THEN
        GOTO 10
    ENDIF
C
10 STOP
    END

```


Subroutine SPEC

```

C -----
C Copyright 1998 Francois Coderre
C
C This subroutine uses Newton's algorithm to solve speciation program
C
C Arguments:
C ITER Number of iterations required to solve the speciation program
C for the given set of initial conditions
C X Log(concentration) vector
C GUESS Initial solution values
C IPREC Precipitation condition index
C -----
C
C SUBROUTINE SPEC (ITER,X,GUESS,IPREC)
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C DIMENSION X(27),DX(27),A(27,28),COND(16,4),GUESS(27)
C
C COMMON /IPRECIP/ ICUCN,IAUCN,ICUOH2,ICUSO4
C COMMON /INITIAL/ COH0,CCN0,CCUI0,CCUII0,CAU0,
C + COCN0,CSCN0,CSO40,ALPHA
C COMMON /UTILMATRIX/ A,COND
C
C DATA N /27/
C
C NP=N+1
C
C Main DO-loop
C
C 5 DO 30 JTER=1,100
C IF (IPREC.GT.17) IPREC=1
C
C Set all initial log(concentration) values
C
C DO J=1,27
C X(J)=GUESS(J)
C ENDDO
C
C Set current precipitation indice
C
C ICUCN=COND(IPREC,1)
C IAUCN=COND(IPREC,2)
C ICUOH2=COND(IPREC,3)
C ICUSO4=COND(IPREC,4)
C
C Newton's algorithm starts here
C
C 7 DO 20 ITER=1,1000
C
C Initialize both maximum values of vectors X and DX to zero
C
C DIFMAX=0.D0
C XMAX=0.D0
C
C Initialize all non-numerical values of augmented coefficient
C matrix A and solve numerically using Gauss elimination method.
C
C CALL COEFF (X,N,NP,A)
C CALL GAUSS (A,N,N,NP,DX,RNORM,IERROR)
C
C Calculate new log(concentration) vector X and its maximum value

```

Subroutine SPEC (cont.)

```

C
      DO 10 I=1,N
        X(I)=X(I)+ALPHA*DX(I)
        DIFMAX=DMAX1(DIFMAX,DABS(DX(I)))
        XMAX=DMAX1(XMAX,DABS(X(I)))
10      CONTINUE
C
C      Evaluate convergence parameter and evaluate precipitation conditions
C
      ERR=DIFMAX/XMAX
      CALL PRECIP (X,IFINISH,ERR,IPREC,ITER)
C
C      IFINISH=1 Convergence is attained and set of precipitates is correct
C      IFINISH=2 Continue computation with new precipitate indice IPREC
C      IFINISH=3 Convergence is not attained, continue computation
C
15      IF (IFINISH.EQ.1) THEN
        ICUCN=COND(IPREC,1)
        IAUCN=COND(IPREC,2)
        ICUOH2=COND(IPREC,3)
        ICUSO4=COND(IPREC,4)
        GOTO 40
      ELSEIF (IFINISH.EQ.2) THEN
        IPREC=IPREC+1
        GOTO 30
      ELSEIF (IFINISH.EQ.3) THEN
        GOTO 20
      ENDIF
20      CONTINUE
30      CONTINUE
40      RETURN
C
      END

```

Subroutine COEFF

```

C -----
C Copyright 1998 Francois Coderre
C
C The subroutine COEFF assign and evaluate the non-numeric coefficients
C to the augmented coefficient matrix A.
C
C Arguments:
C X Log(concentration) vector
C N First (row) dimension of A in calling program
C NP Second (column) dimension of A in calling program
C A Augmented coefficient matrix
C -----
C
C SUBROUTINE COEFF (X,N,NP,A)
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C DIMENSION X(N),A(N,NP)
C
C COMMON /IPRECIP/ ICUCN,IAUCN,ICUOH2,ICUSO4
C COMMON /INITIAL/ COH0,CCN0,CCUI0,CCUII0,CAU0,
C + COCN0,CSCN0,CSO40,ALPHA
C COMMON /AQUEOUS/ CUCNAQ,AUCNAQ,CUOH2AQ,CUSO4AQ
C
C REAL*8 KCUCN1,KCUCN2,KCUCN3,KCUCN4
C COMMON /K_CUCN/ KCUCN1,KCUCN2,KCUCN3,KCUCN4
C REAL*8 KAUCN1,KAUCN2
C COMMON /K_AUCN/ KAUCN1,KAUCN2
C REAL*8 KW,KHCN,KHOCN,KHSCN
C COMMON /K_OTHER/ KW,KHCN,KHOCN,KHSCN
C REAL*8 KCUOH1,KCUOH2,KCUOH3,KCUOH4,KCU2OH,KCU2OH2,KCU3OH4
C COMMON /K_CUOH/ KCUOH1,KCUOH2,KCUOH3,KCUOH4,KCU2OH,KCU2OH2,KCU3OH4
C REAL*8 KHSO4,KCUSO4
C COMMON /K_SO4/ KHSO4,KCUSO4
C
C Mass balance equations for [Cu+]new (Jacobian matrix)
C [Cu+]old = [Cu+]new + [CuCN] + [Cu(CN)2] + [Cu(CN)3] + [Cu(CN)4]
C
C A(6,1)=DEXP(X(1))
C A(6,2)=DEXP(X(2))
C A(6,3)=DEXP(X(3))
C A(6,4)=DEXP(X(4))
C A(6,5)=DEXP(X(5))
C DO I=6,27
C A(6,I)=0.D0
C ENDDO
C
C Mass balance equations for [CN-]old (Jacobian matrix)
C [CN-]old = [CN-]new + [CuCN] + 2[Cu(CN)2] + 3[Cu(CN)3] + 4[Cu(CN)4]
C + [HCN] + [AuCN] + 2[Au(CN)2]
C
C A(7,1)=DEXP(X(1))
C A(7,2)=2.D0*DEXP(X(2))
C A(7,3)=3.D0*DEXP(X(3))
C A(7,4)=4.D0*DEXP(X(4))
C A(7,5)=0.D0
C A(7,6)=DEXP(X(6))
C A(7,7)=DEXP(X(7))
C A(7,8)=DEXP(X(8))
C A(7,9)=2.D0*DEXP(X(9))
C DO I=10,27
C A(7,I)=0.D0

```

Subroutine COEFF (cont.)

```

ENDDO
C
C   Mass balance equations for [Au+]new (Jacobian matrix)
C   [Au+]old = [Au+]new + [AuCN] + [Au(CN)2]
C
DO I=1,7
  A(10,I)=0.D0
ENDDO
A(10,8)=DEXP(X(8))
A(10,9)=DEXP(X(9))
A(10,10)=DEXP(X(10))
DO I=11,27
  A(10,I)=0.D0
ENDDO
C
C   Mass balance equations for [H-OH] (Jacobian matrix)
C   -[OH-]old = -[OH-]new + [HCN] + [HOCN] + [HSCN] + [H] + [HSO4] - [CuOH] - 2[Cu(OH)2]
C   - 3[Cu(OH)3] - 4[Cu(OH)4] - [Cu2OH] - 2[Cu2(OH)2] - 4[Cu3(OH)4]
C
DO I=1,6
  A(11,I)=0.D0
ENDDO
A(11,7)=DEXP(X(7))
A(11,8)=0.D0
A(11,9)=0.D0
A(11,10)=0.D0
A(11,11)=DEXP(X(11))
A(11,12)=-DEXP(X(12))
A(11,13)=-DEXP(X(13))
A(11,14)=-2.D0*DEXP(X(14))
A(11,15)=-3.D0*DEXP(X(15))
A(11,16)=-4.D0*DEXP(X(16))
A(11,17)=-DEXP(X(17))
A(11,18)=-2.D0*DEXP(X(18))
A(11,19)=-4.D0*DEXP(X(19))
A(11,20)=0.D0
A(11,21)=0.D0
A(11,22)=DEXP(X(22))
A(11,23)=0.D0
A(11,24)=DEXP(X(24))
A(11,25)=0.D0
A(11,26)=DEXP(X(26))
A(11,27)=0.D0
C
C   Mass balance equations for [Cu2+]new (Jacobian matrix)
C   [Cu2+]old = [Cu2+]new + [CuOH] + [Cu(OH)2] + [Cu(OH)3] + [Cu(OH)4]
C   + 2[Cu2OH] + 2[Cu2(OH)2] + 3[Cu3(OH)4] + [CuSO4]
C
DO I=1,12
  A(20,I)=0.D0
ENDDO
A(20,13)=DEXP(X(13))
A(20,14)=DEXP(X(14))
A(20,15)=DEXP(X(15))
A(20,16)=DEXP(X(16))
A(20,17)=2.D0*DEXP(X(17))
A(20,18)=2.D0*DEXP(X(18))
A(20,19)=3.D0*DEXP(X(19))
A(20,20)=DEXP(X(20))
DO I=21,26
  A(20,I)=0.D0
ENDDO

```

Subroutine COEFF (cont.)

```

A(20,27)=DEXP(X(27))
C
C   Mass balance equations for [OCN]new (Jacobian matrix)
C   [OCN-]old = [OCN-]new +[HOCN]
C
DO I=1,20
  A(21,I)=0.D0
ENDDO
A(21,21)=DEXP(X(21))
A(21,22)=DEXP(X(22))
DO I=23,27
  A(21,I)=0.D0
ENDDO
C
C   Mass balance equations for [SCN]new (Jacobian matrix)
C   [SCN-]old = [SCN-]new +[HSCN]
C
DO I=1,22
  A(23,I)=0.D0
ENDDO
A(23,23)=DEXP(X(23))
A(23,24)=DEXP(X(24))
DO I=25,27
  A(23,I)=0.D0
ENDDO
C
C   Mass balance equations for [SO4(2-)]new (Jacobian matrix)
C   [SO4(2-)]old = [SO4(2-)]new +[HSO4-] +[CuSO4]
C
DO I=1,24
  A(27,I)=0.D0
ENDDO
A(27,25)=DEXP(X(25))
A(27,26)=DEXP(X(26))
A(27,27)=DEXP(X(27))
C
C   Summation DO-Loop for Right-hand-side equations f6, f7, f10, f11, f20
C
DUMMY1=0.D0
DUMMY2=0.D0
DUMMY3=0.D0
DUMMY4=0.D0
DUMMY5=0.D0
DUMMY6=0.D0
DUMMY7=0.D0
DUMMY8=0.D0
DO I=1,27
  DUMMY1=A(6,I)+DUMMY1
  DUMMY2=A(7,I)+DUMMY2
  DUMMY3=A(10,I)+DUMMY3
  DUMMY4=A(11,I)+DUMMY4
  DUMMY5=A(20,I)+DUMMY5
  DUMMY6=A(21,I)+DUMMY6
  DUMMY7=A(23,I)+DUMMY7
  DUMMY8=A(27,I)+DUMMY8
ENDDO
C
C   Right-hand-side equations (Jacobian matrix)
C
A(1,28)=-X(3)+X(2)+X(6)+KCUCN3
A(2,28)=-X(4)+X(3)+X(6)+KCUCN4
C

```

Subroutine COEFF (cont.)

```

C   A(3,28) equations showed in ICUCN precipitation condition
C   A(4,28) equations showed in ICUCN precipitation condition
C
C   A(5,28)=-X(7)+X(11)+X(6)+KHCN
C   A(6,28)=-1.D0*DUMMY1+CCUI0
C   A(7,28)=-1.D0*DUMMY2+CCN0
C
C   A(8,28) equations showed in IAUCN precipitation condition
C   A(9,28) equations showed in IAUCN precipitation condition
C
C   A(10,28)=-1.D0*DUMMY3+CAU0
C   A(11,28)=-1.D0*DUMMY4-COH0
C   A(12,28)=-X(11)-X(12)+KW
C
C   A(14,28) equations showed in ICUOH2 precipitation condition
C
C   A(13,28)=-X(13)-X(11)+X(20)+KCUOH1
C   A(15,28)=-X(15)-3.D0*X(11)+X(20)+KCUOH3
C   A(16,28)=-X(16)-4.D0*X(11)+X(20)+KCUOH4
C   A(17,28)=-X(17)-X(11)+2.D0*X(20)+KCU2OH
C   A(18,28)=-X(18)-2.D0*X(11)+2.D0*X(20)+KCU2OH2
C   A(19,28)=-X(19)-4.D0*X(11)+3.D0*X(20)+KCU3OH4
C   A(20,28)=-1.D0*DUMMY5+CCUI0
C   A(21,28)=-1.D0*DUMMY6+COCN0
C   A(22,28)=-X(22)+X(21)+X(11)+KHOCN
C   A(23,28)=-1.D0*DUMMY7+CSCN0
C   A(24,28)=-X(24)+X(23)+X(11)+KHSCN
C   A(25,28)=-X(26)+X(25)+X(11)+KHSO4
C
C   A(26,28) equations showed in ICUSO4 precipitation condition
C
C   A(27,28)=-1.D0*DUMMY8+CSO40
C
C   If CuCN precipitates (ICUCN=2), the Jacobian matrix is slightly
C   modified
C
C   IF (ICUCN.EQ.2) THEN
C       CUCNAQ=10.D0**(-9.D0)
C       A(3,1)=0.D0
C       A(4,1)=0.D0
C       A(3,28)=-X(2)+DLOG(CUCNAQ)+X(6)+KCUCN2
C       A(4,28)=-DLOG(CUCNAQ)+X(5)+X(6)+KCUCN1
C       A(6,28)=A(6,28)-CUCNAQ
C       A(7,28)=A(7,28)-CUCNAQ
C   ELSEIF (ICUCN.EQ.1) THEN
C       A(3,1)=-1.D0
C       A(4,1)=1.D0
C       A(3,28)=-X(2)+X(1)+X(6)+KCUCN2
C       A(4,28)=-X(1)+X(5)+X(6)+KCUCN1
C   ENDIF
C
C   If AuCN precipitates (IAUCN=2), the Jacobian matrix is slightly
C   modified
C
C   IF (IAUCN.EQ.2) THEN
C       AUCNAQ=10.D0**(-14.D0)
C       A(8,8)=0.D0
C       A(9,8)=0.D0
C       A(8,28)=-X(9)+DLOG(AUCNAQ)+X(6)+KAUCN2
C       A(9,28)=-DLOG(AUCNAQ)+X(10)+X(6)+KAUCN1
C       A(7,28)=A(7,28)-AUCNAQ
C       A(10,28)=A(10,28)-AUCNAQ

```

Subroutine COEFF (cont.)

```

ELSEIF (IAUCN.EQ.1) THEN
  A(8,8)=-1.D0
  A(9,8)=1.D0
  A(8,28)=-X(9)+X(8)+X(6)+KAUCN2
  A(9,28)=-X(8)+X(10)+X(6)+KAUCN1
ENDIF
C
C If CuOH2 precipitates (ICUOH2=2), the Jacobian matrix is slightly
C modified
C
IF (ICUOH2.EQ.2) THEN
  CUOH2AQ=10.D0**(-7.5D0)
  A(14,14)=0.D0
  A(14,28)=-DLOG(CUOH2AQ)-2.D0*X(11)+X(20)+KCUOH2
  A(11,28)=A(11,28)+2.D0*CUOH2AQ
  A(20,28)=A(20,28)-CUOH2AQ
ELSEIF (ICUOH2.EQ.1) THEN
  A(14,14)=1.D0
  A(14,28)=-X(14)-2.D0*X(11)+X(20)+KCUOH2
ENDIF
C
C If CuSO4 precipitates (ICUSO4=2), the Jacobian matrix is slightly
C modified
C
IF (ICUSO4.EQ.2) THEN
  CUSO4AQ=1.D0
  A(26,27)=0.D0
  A(26,28)=-DLOG(CUSO4AQ)+X(25)+X(20)+KCUSO4
  A(27,28)=A(27,28)-CUSO4AQ
  A(20,28)=A(20,28)-CUSO4AQ
ELSEIF (ICUSO4.EQ.1) THEN
  A(26,27)=1.D0
  A(26,28)=-X(27)+X(25)+X(20)+KCUSO4
ENDIF
C
RETURN
END
C

```

Subroutine PRECIP

```

C-----
C Copyright 1998 Francois Coderre
C
C The subroutine PRECIP evaluates whether there are precipitates given
C the computed concentrations.
C
C Arguments:
C X Log(concentration) vector
C IFINISH =1 Convergence is attained and set of precipitates is correct
C =2 Continue computation with new precipitate indice IPREC
C =3 Convergence is not attained, continue computation
C ERR convergence parameter (=DIFMAX/XMAX)
C IPREC Precipitation indice
C ITER Number of iterations
C-----
C
C SUBROUTINE PRECIP (X,IFINISH,ERR,IPREC,ITER)
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C DIMENSION X(27),A(27,28),COND(16,4),CONDX(4)
C
C REAL*8 KCUCNSP,KAUCNSP,KCUOH2SP,KCUSO4SP
C COMMON /K_SP/ KCUCNSP,KAUCNSP,KCUOH2SP,KCUSO4SP
C COMMON /UTILMATRIX/ A,COND
C DATA EPS /1.D-10/
C
C Let the precipitation indice at 1 (no precipitation) for 10
C iterations to find most exact precipitation indice rapidly.
C
C IF (ITER.LE.10) THEN
C IFINISH=3
C RETURN
C ENDIF
C
C In the vicinity of ERR=1.0, overflow often occur. No convergence
C is sure to happen. New precipitation indice is set.
C
C IF ((ERR.GE.0.99D0).AND.(ERR.LE.1.01D0)) THEN
C IFINISH=2
C RETURN
C ENDIF
C
C Calculate precipitation conditions for CuCN, AuCN and Cu(OH)2
C Based on ICUCN, IAUCN, ICUOH2 system (=1:aqueous; =2:solid)
C
C PRECUCN=DEXP(X(5))*DEXP(X(6))
C PREAUCN=DEXP(X(10))*DEXP(X(6))
C PRECUOH2=DEXP(X(20))*(DEXP(X(12))**2.D0)
C PRECUSO4=DEXP(X(27))
C
C IPRECOLD=IPREC
C
C IF (PRECUCN.LE.KCUCNSP) THEN
C CONDX(1)=1
C ELSE
C CONDX(1)=2
C ENDIF
C
C IF (PREAUCN.LE.KAUCNSP) THEN
C CONDX(2)=1
C ELSE

```


Subroutine PRECIP (cont.)

```

      CONDX(2)=2
    ENDIF
C
    IF (PRECUOH2.LE.KCUOH2SP) THEN
      CONDX(3)=1
    ELSE
      CONDX(3)=2
    ENDIF
C
    IF (PRECUSO4.LE.KCUSO4SP) THEN
      CONDX(4)=1
    ELSE
      CONDX(4)=2
    ENDIF
C
C   Define new precipitation indice IPREC
C
    DO I=1,16
      IF ((COND(I,1).EQ.CONDX(1))
+ .AND. (COND(I,2).EQ.CONDX(2))
+ .AND. (COND(I,3).EQ.CONDX(3))
+ .AND. (COND(I,4).EQ.CONDX(4))) THEN
        IPREC=I
      ENDIF
    ENDDO
C
C   Evaluate convergence, if ERR less than EPS, convergence is attained
C   Otherwise, new precipitation indice is set
C   If ITER equals 1000, no convergence is attained, IPREC is changed
C
    IF (ERR.LE.EPS) THEN
      IF ((COND(IPRECOLD,1).EQ.CONDX(1))
+ .AND. (COND(IPRECOLD,2).EQ.CONDX(2))
+ .AND. (COND(IPRECOLD,3).EQ.CONDX(3))
+ .AND. (COND(IPRECOLD,4).EQ.CONDX(4))) THEN
        IFINISH=1
      ELSE
        IFINISH=2
      ENDIF
    ELSEIF (ITER.EQ.1000) THEN
      IFINISH=2
    ELSE
      IFINISH=3
    ENDIF
C
    RETURN
  END

```

Subroutine UTIL

```

C-----
C Copyright 1998 Francois Coderre
C
C The subroutine UTIL defines all constant values of the program and
C retrieves numerical data from different files in specific directory.
C a) Numeric matrix A: "CUAUCNIN.TXT"
C b) Precipitation conditions: "PR8COND.TXT"
C-----
C
C SUBROUTINE UTIL
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C DIMENSION A(27,28),B(27,28),COND(16,4)
C
C REAL*8 KCUCN1,KCUCN2,KCUCN3,KCUCN4
C COMMON /K_CUCN/ KCUCN1,KCUCN2,KCUCN3,KCUCN4
C REAL*8 KAUCN1,KAUCN2
C COMMON /K_AUCN/ KAUCN1,KAUCN2
C REAL*8 KW,KHCN,KHOCN,KHSCN
C COMMON /K_OTHER/ KW,KHCN,KHOCN,KHSCN
C REAL*8 KCUOH1,KCUOH2,KCUOH3,KCUOH4,KCU2OH,KCU2OH2,KCU3OH4
C COMMON /K_CUOH/ KCUOH1,KCUOH2,KCUOH3,KCUOH4,KCU2OH,KCU2OH2,KCU3OH4
C REAL*8 KHSO4,KCUSO4
C COMMON /K_SO4/ KHSO4,KCUSO4
C REAL*8 KCUCNSP,KAUCNSP,KCUOH2SP,KCUSO4SP
C COMMON /K_SP/ KCUCNSP,KAUCNSP,KCUOH2SP,KCUSO4SP
C COMMON /UTILMATRIX/ A,COND
C
C Dissociation constants for cyano-complexes. Data retrieves from
C FLYNN, C.M. and HASLEM, S.M, Bureau of Mines, IC9429, 1995, p. 148
C ZHANG, Yu et al., Hydrometallurgy, Vol. 46, 1997, pp. 256-258
C
C KCUCN1=DLOG(10.D0**(10.4D0))
C KCUCN2=DLOG(10.D0**(11.2D0))
C KCUCN3=DLOG(10.D0**(5.30D0))
C KCUCN4=DLOG(10.D0**(1.50D0))
C
C KAUCN1=DLOG(10.D0**(18.0D0))
C KAUCN2=DLOG(10.D0**(19.0D0))
C
C KW=DLOG(10.D0**(-14.D0))
C KHCN=DLOG(10.D0**(9.21D0))
C KHOCN=DLOG(10.D0**(3.47))
C KHSCN=DLOG(10.D0**(1.6))
C
C KCUOH1=DLOG(10.D0**(-7.97D0))
C KCUOH2=DLOG(10.D0**(-16.24D0))
C KCUOH3=DLOG(10.D0**(-26.62D0))
C KCUOH4=DLOG(10.D0**(-39.70D0))
C KCU2OH=DLOG(10.D0**(-6.71D0))
C KCU2OH2=DLOG(10.D0**(-10.55D0))
C KCU3OH4=DLOG(10.D0**(-20.95D0))
C
C KHSO4=DLOG(10.D0**(1.99D0))
C KCUSO4=DLOG(10.D0**(2.30D0))
C
C KCUCNSP=10.D0**(-19.5D0)
C KAUCNSP=10.D0**(-32.0D0)
C KCUOH2SP=10.D0**(-19.3D0)
C KCUSO4SP=10.D0**(0.D0)
C

```

Subroutine UTIL (cont.)

```

C   Fill augmented coefficient matrix A with numerical values
C
  OPEN (UNIT=8,FILE='C:\FRANCOIS\CUAUOSCN\COEFF01.TXT',
+   STATUS='OLD')
  DO I=1,19
    READ (8,*) (B(I,J),J=1,27)
  ENDDO
  DO J=1,27
    DO I=1,5
      A(I,J)=B(I,J)
    ENDDO
    DO I=6,7
      A(I+2,J)=B(I,J)
    ENDDO
    DO I=8,15
      A(I+4,J)=B(I,J)
    ENDDO
    A(22,J)=B(16,J)
    A(24,J)=B(17,J)
    A(25,J)=B(18,J)
    A(26,J)=B(19,J)
  ENDDO
  ENDFILE (UNIT=8)
  CLOSE (UNIT=8)
C
C   Fill precipitation conditions matrix COND
C   Based on ICUCN, IAUCN, ICUOH2 system (=1:aqueous; =2:solid)
C
  OPEN (UNIT=5,FILE='C:\FRANCOIS\CUAUOSCN\PR16COND.TXT',
+   STATUS='OLD')
  DO I=1,16
    READ (5,*) (COND(I,J),J=1,4)
  ENDDO
  ENDFILE (UNIT=5)
  CLOSE (UNIT=5)
C
  RETURN
  END

```

Subroutine DATAOUT

```

C-----
C Copyright 1998 Francois Coderre
C
C The subroutine DATAOUT prints the results of the program SPECIATION
C in the file "RESULTS.TXT" and calculates the error of each functions
C evaluated.
C
C Arguments:
C ITER Number of iterations required to solve the speciation program
C for the given set of initial conditions
C X Log(concentration) vector
C-----
C
C SUBROUTINE DATAOUT (ITER,X)
C
C IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C DIMENSION X(27)
C
C COMMON /IPRECIP/ ICUCN,IAUCN,ICUOH2,ICUSO4
C COMMON /INITIAL/ COH0,CCN0,CCUI0,CCUII0,CAU0,
C + COCN0,CSCN0,CSO40,ALPHA
C COMMON /AQUEOUS/ CUCNAQ,AUCNAQ,CUOH2AQ,CUSO4AQ
C
C REAL*8 KCUCN1,KCUCN2,KCUCN3,KCUCN4
C COMMON /K_CUCN/ KCUCN1,KCUCN2,KCUCN3,KCUCN4
C REAL*8 KAUCN1,KAUCN2
C COMMON /K_AUCN/ KAUCN1,KAUCN2
C REAL*8 KW,KHCN,KHOCN,KHSCN
C COMMON /K_OTHER/ KW,KHCN,KHOCN,KHSCN
C REAL*8 KCUOH1,KCUOH2,KCUOH3,KCUOH4,KCU2OH,KCU2OH2,KCU3OH4
C COMMON /K_CUOH/ KCUOH1,KCUOH2,KCUOH3,KCUOH4,KCU2OH,KCU2OH2,KCU3OH4
C REAL*8 KHSO4,KCUSO4
C COMMON /K_SO4/ KHSO4,KCUSO4
C REAL*8 KCUCNSP,KAUCNSP,KCUOH2SP,KCUSO4SP
C COMMON /K_SP/ KCUCNSP,KAUCNSP,KCUOH2SP,KCUSO4SP
C
C Sum of similar species for percentage calculations
C
C CNTO=DEXP(X(6))+DEXP(X(7))+DEXP(X(1))+2.D0*DEXP(X(2))
C + 3.D0*DEXP(X(3))+4.D0*DEXP(X(4))+DEXP(X(8))+2.D0*DEXP(X(9))
C
C CUITO=DEXP(X(1))+DEXP(X(2))+DEXP(X(3))+DEXP(X(4))+DEXP(X(5))
C
C CUIITO=DEXP(X(13))+DEXP(X(14))+DEXP(X(15))+DEXP(X(16))
C + 2.D0*DEXP(X(17))+2.D0*DEXP(X(18))+3.D0*DEXP(X(19))
C + DEXP(X(20))+DEXP(X(27))
C
C AUTO=DEXP(X(8))+DEXP(X(9))+DEXP(X(10))
C
C SO4TO=DEXP(X(25))+DEXP(X(26))+DEXP(X(27))
C
C OPEN (UNIT=6,FILE='C:\FRANCOIS\CUAUOSCN\RESULTS.TXT',
C + STATUS='OLD')
C
C Print results for initial and final pH
C
C WRITE (6,*)
40 WRITE (6,50) ITER
50 FORMAT (//IX,'Solution vector after',I5,' iterations: '/')
WRITE (6,55) -DLOG10(1.D-14/COH0)

```

Subroutine DATAOUT (cont.)

```

55  FORMAT (7X,'Initial pH= ',F16.10)
    WRITE (6,60) -DLOG10(DEXP(X(11)))
60  FORMAT (10X,'Final pH= ',F16.10)
C
C  Print results for CN, HCN, cyanate species and initial CN
C
    WRITE (6,62) DEXP(X(6)),KCUCN3-X(3)+X(2)+X(6)
62  FORMAT (10X,'FREE CN= ',G16.5,2X,'ERROR ON F1',D16.6)
    WRITE (6,64) DEXP(X(7)),KCUCN4-X(4)+X(3)+X(6)
64  FORMAT (9X,'FREE HCN= ',G16.5,2X,'ERROR ON F2',D16.6)
    WRITE (6,114) DEXP(X(21))
114  FORMAT (7X,'OCN(-)(aq)= ',G16.5)
    WRITE (6,116) DEXP(X(22)),KHOCN-X(22)+X(21)+X(11)
116  FORMAT (9X,'HOCN(aq)= ',G16.5,2X,'ERROR ON F22',D16.6)
    WRITE (6,118) DEXP(X(23))
118  FORMAT (7X,'SCN(-)(aq)= ',G16.5)
    WRITE (6,120) DEXP(X(24)),KHSCN-X(24)+X(23)+X(11)
120  FORMAT (9X,'HSCN(aq)= ',G16.5,2X,'ERROR ON F24',D16.6)
    WRITE (6,65) CNTO
65  FORMAT (7X,'Initial CN= ',G16.5)
C
C  Print results for cyano-cuprous species and initial Cu(I)
C
    WRITE (6,*)
    IF (ICUCN.EQ.1) THEN
        WRITE (6,66)
    ELSEIF (ICUCN.EQ.2) THEN
        WRITE (6,67)
    ENDIF
66  FORMAT (9X,'CuCN does not precipitate')
67  FORMAT (9X,'CuCN precipitates')
    WRITE (6,*)
C
    WRITE (6,68) DEXP(X(1)),KCUCN2-X(2)+X(1)+X(6)
68  FORMAT (11X,'CU(CN)= ',G16.5,2X,'ERROR ON F3',D16.6)
    WRITE (6,70) DEXP(X(2)),KCUCN1-X(1)+X(5)+X(6)
70  FORMAT (10X,'CU(CN)2= ',G16.5,2X,'ERROR ON F4',D16.6)
    WRITE (6,72) DEXP(X(3)),KHCN-X(7)+X(11)+X(6)
72  FORMAT (10X,'CU(CN)3= ',G16.5,2X,'ERROR ON F5',D16.6)
    WRITE (6,74) DEXP(X(4))
74  FORMAT (10X,'CU(CN)4= ',G16.5)
    WRITE (6,76) DEXP(X(5))
76  FORMAT (10X,'CU(+) = ',G16.5)
    WRITE (6,78) CUITO
78  FORMAT (4X,'Initial CU(I)= ',G16.5)
C
C  Print results for hydroxi-cupric species and initial Cu(II)
C
    WRITE (6,*)
    IF (ICUOH2.EQ.1) THEN
        WRITE (6,80)
    ELSEIF (ICUOH2.EQ.2) THEN
        WRITE (6,81)
    ENDIF
80  FORMAT (9X,'Cu(OH)2 does not precipitate')
81  FORMAT (9X,'Cu(OH)2 precipitates')
    WRITE (6,*)
C
    WRITE (6,88) DEXP(X(13)),KCUOH1-X(13)-X(11)+X(20)
88  FORMAT (12X,'CUOH+= ',G16.5,2X,'ERROR ON F13',D16.6)
    WRITE (6,90) DEXP(X(14)),KCUOH2-X(14)-2.D0*X(11)+X(20)
90  FORMAT (10X,'CU(OH)2= ',G16.5,2X,'ERROR ON F14',D16.6)

```

Subroutine DATAOUT (cont.)

```

WRITE (6,92) DEXP(X(15)),KCUOH3-X(15)-3.D0*X(11)+X(20)
92 FORMAT (10X,'CU(OH)3= ',G16.5,2X,'ERROR ON F15',D16.6)
WRITE (6,94) DEXP(X(16)),KCUOH4-X(16)-4.D0*X(11)+X(20)
94 FORMAT (10X,'CU(OH)4= ',G16.5,2X,'ERROR ON F16',D16.6)
WRITE (6,96) DEXP(X(17)),KCU2OH-X(17)-X(11)+2.D0*X(20)
96 FORMAT (12X,'CU2OH= ',G16.5,2X,'ERROR ON F17',D16.6)
WRITE (6,98) DEXP(X(18)),KCU2OH2-X(18)-2.D0*X(11)+2.D0*X(20)
98 FORMAT (9X,'CU2(OH)2= ',G16.5,2X,'ERROR ON F18',D16.6)
WRITE (6,100) DEXP(X(19)),KCU3OH4-X(19)-4.D0*X(11)+3.D0*X(20)
100 FORMAT (9X,'CU3(OH)4= ',G16.5,2X,'ERROR ON F19',D16.6)
WRITE (6,102) DEXP(X(20))
102 FORMAT (9X,'CU(2+)= ',G16.5)
WRITE (6,103) CUIITO
103 FORMAT (3X,'Initial CU(II)= ',G16.5)
C
C Print results for cyano-aurous species and initial Au(I)
C
WRITE (6,*)
IF (IAUCN.EQ.1) THEN
WRITE (6,104)
ELSEIF (IAUCN.EQ.2) THEN
WRITE (6,105)
ENDIF
104 FORMAT (9X,'AuCN does not precipitate')
105 FORMAT (9X,'AuCN precipitates')
WRITE (6,*)
C
WRITE (6,106) DEXP(X(8)),KAUCN2-X(9)+X(8)+X(6)
106 FORMAT (11X,'AU(CN)= ',G16.5,2X,'ERROR ON F8',D16.6)
WRITE (6,108) DEXP(X(9)),KAUCN1-X(8)+X(10)+X(6)
108 FORMAT (10X,'AU(CN)2= ',G16.5,2X,'ERROR ON F9',D16.6)
WRITE (6,110) DEXP(X(10))
110 FORMAT (11X,'AU(+)= ',G16.5)
WRITE (6,112) AUTO
112 FORMAT (4X,'Initial AU(I)= ',G16.5)
C
C Print results for cupric-sulfate species and initial SO4(2-)
C
WRITE (6,*)
IF (ICUSO4.EQ.1) THEN
WRITE (6,124)
ELSEIF (ICUSO4.EQ.2) THEN
WRITE (6,125)
SO4TO=SO4TO+CUSO4AQ
ENDIF
124 FORMAT (9X,'CuSO4 does not precipitate')
125 FORMAT (9X,'CuSO4 precipitates')
WRITE (6,*)
C
WRITE (6,126) DEXP(X(25)),KHSO4-X(26)+X(25)+X(11)
126 FORMAT (11X,'SO4(2-)= ',G16.5,2X,'ERROR ON F25',D16.6)
WRITE (6,128) DEXP(X(26)),KCUSO4-X(27)+X(25)+X(20)
128 FORMAT (10X,'HSO4(-)= ',G16.5,2X,'ERROR ON F26',D16.6)
WRITE (6,130) DEXP(X(27))
130 FORMAT (11X,'CUSO4= ',G16.5)
WRITE (6,132) SO4TO
132 FORMAT (4X,'Initial SO4(2-)= ',G16.5)
C
ENDFILE (UNIT=6)
CLOSE (UNIT=6)
RETURN
END

```

Subroutine GAUSS

```

C-----
C  Copyright 1998 Francois Coderre
C
C  The subroutine GAUSS uses Gauss elimination with partial
C  pivot selection to solve simultaneous linear equations of
C  the form  $[A]\{X\}=\{C\}$ .
C
C  Arguments:
C    A  Augmented coefficient matrix containing all coefficients
C        and R.H.S. constants of equations to be solved.
C    N  Number of equations to be solved
C    NDR First (row) dimension of A calling program
C    NDC Second (column) dimension of A calling program
C    X  Solution vector
C    IERROR Error flag
C        =1 Successful Gauss elimination
C        =2 Zero diagonal entry after pivot selection
C    RNORM Measure of size of residual vector  $\{C\}-[A]\{X\}$ 
C-----
C
C  SUBROUTINE GAUSS (A,N,NDR,NDC,X,RNORM,IERROR)
C  IMPLICIT REAL*8 (A-H,O-Z), INTEGER (I-N)
C  DIMENSION A(NDR,NDC),X(N),B(50,51)
C
C  Define rows and columns indicator variables
C
C  NP=N+1
C  NM=N-1
C
C  Set up working matrix B
C
C  DO 20 I=1,N
C    DO 10 J=1,NP
C      B(I,J) = A(I,J)
C    CONTINUE
C  20 CONTINUE
C
C  Carry out elimination process N-1 times
C
C  DO 70 K=1,NM
C    KP=K+1
C
C    Search for largest coefficient in column K, rows K through N
C    IPIVOT is the row index of the largest coefficient
C
C    BIG=ABS(B(K,K))
C    IPIVOT=K
C    DO 30 I=KP,N
C      AB=ABS(B(I,K))
C      IF (AB.GT.BIG) THEN
C        BIG=AB
C        IPIVOT=I
C      ENDIF
C    CONTINUE
C
C    Interchange rows K and IPIVOT if IPIVOT.NE.K
C
C    IF (IPIVOT.NE.K) THEN
C      DO 40 J=K,NP
C        TEMP=B(IPIVOT,J)
C        B(IPIVOT,J)=B(K,J)

```

Subroutine GAUSS (cont.)

```

        B(K,J)=TEMP
40      CONTINUE
        ENDIF
C
C      Check diagonal element for zero entry
C      B(K,K)=0 causes an abnormal return with IERROR=2
C
        IF (B(K,K).EQ.0.D0) THEN
            IERROR=2
            RETURN
        ENDIF
C
C      Eliminate B(I,K) from rows K+1 through N
C
        DO 60 I=KP,N
            QUOT=B(I,K)/B(K,K)
            B(I,K)=0.D0
            DO 50 J=KP,NP
                B(I,J)=B(I,J)-QUOT*B(K,J)
50      CONTINUE
60      CONTINUE
70      CONTINUE
C
C      Check last diagonal element for zero entry
C      B(N,N)=0 causes an abnormal return with IERROR=2
C
        IF (B(N,N).EQ.0.D0) THEN
            IERROR=2
            RETURN
        ENDIF
C
C      Back substitute to find solution vector
C
        X(N)=B(N,NP)/B(N,N)
        DO 90 I=NM,1,-1
            SUM=0.D0
            DO 80 J=I+1,N
                SUM=SUM+B(I,J)*X(J)
80      CONTINUE
            X(I)=(B(I,NP)-SUM)/B(I,I)
90      CONTINUE
C
C      Calculate norm of residual vector, C-A*X
C      Normal return with IERROR=1
C
        RSQ=0.D0
        DO 110 I=1,N
            SUM=0.D0
            DO 100 J=1,N
                SUM=SUM+A(I,J)*X(J)
100     CONTINUE
            RSQ=RSQ+(A(I,NP)-SUM)**2.D0
110    CONTINUE
        RNORM=SQRT(RSQ)
        IERROR=1
        RETURN
        END

```