THE CYANIDE HEAP LEACHING
BEHAVIOR OF CUPRIFEROUS GOLD ORES

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

Department of Metals and Materials Engineering

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
December 2002

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Date _January 3rd, 03_

ABSTRACT

To develop a fundamental understanding of cyanide heap leaching of low-grade gold ores, with significant copper mineralization, two sets of column leach tests were operated under two different leaching solutions. In one set, four 1.5 m tall column tests were leached with sodium cyanide solution. In the second set, another four columns were leached with solutions of cyanocuprate complexes in the absence of free cyanide. Each set was run for a period of up to 200 days. The behavior of individual species, were investigated for the purpose of developing reliable rate parameters for the mathematical model.

Significant amount of weak acid soluble copper minerals was discharged from the ore, simply by pre-rinsing with water. The cyanide leaching is shown to occur in different stages with remarkable characteristics as follows:

(a) Significant decrease in the pH at the beginning of the cyanide column leach tests;

(b) Reductive dissolution of the remaining WAS copper salts and dissolution of copper sulfide minerals, from the first day of the experiment;

(c) Dissolution of gold from the first stage while no free cyanide is present in the solution;

(d) The occurrence of two distinct peaks in copper concentration, first as the result of leaching of labile copper sulfides and second as the result of redissolution of copper cyanide precipitates;

(e) Free cyanide breakthrough in the effluent, which is accompanied by the appearance of dissolved iron.

The second set of column leach tests showed that the leaching of gold with a solution of cyanocuprate complex and in the absence of free cyanide is accessible with rate parameters comparable to leaching with cyanide. It is also concluded that some of the copper minerals can be leached in the absence of free cyanide. Iron does not show any dissolution in cyanocuprate leaching systems.

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List of abbreviations and acronyms

AAS   Atomic absorption spectrometry

AVR   Acidification-volatilization-reneutralization

ICP   Induction couple plasma

MMAT   Metals and Materials Engineering

MMPE   Mining and Mineral Processing Engineering

PSD   Particle size distribution

UBC   University of British Columbia

WAS   Weak acid soluble

XRD   X-ray diffraction

Acknowledgments

The author wishes to thank many people for providing the resources needed to complete this thesis. First and foremost, I would like to thank my family for all the support, which I have received from them. I would like to thank Dr. David G. Dixon for his constant encouragement and support. Working with him has been a great honor for me.

The author would also like to thank the students, faculty and staff of the MMAT department of UBC for all their helps, ideas and friendships. I would particularly like to thank Dr. Berend Wassink and Samuel Borolorunuro for their help throughout the experimental work and technical assistance for the potentiometric titration analysis, atomic absorption analysis, cyanide titration and cyanide waste treatment. The help of Shawn Crego, Ross McLeod and Carl Ng with the construction of the stands and columns for the column leaching tests is also gratefully acknowledged.

The author would also like express sincere thanks to the Mining and Mineral Process Engineering Department of UBC for use of their equipment for crushing, grinding and splitting of ore samples, to Chem Met consultants Inc. and International Plasma Laboratory for the chemical analysis.

My gratitude extends to the Newcrest Mining Ltd., Telfer Gold Mine (Perth, Australia), which has been provided the funding and the ore material for this research.

1 Introduction

Gold has been the most sought after of metals throughout human history. It was likely one of the first metals recognized by early humans and it's novelty, utility and rarity helped it to become a highly valued material.

Generally, gold occurs in nature in the metallic state, and may range from large nuggets to very small particles called invisible gold. The extraction treatment of this metal is strongly dependent on different factors, some of the most important of which are:

1. The size of the gold particles.

2. The physical/ chemical nature of other minerals associated with gold.

3. The gold grade of the ore along with the current gold price.

The size of gold particles can determine the amenability of the ore to gravity separation/concentration methods, while the physical/chemical properties of the minerals in the ore may have a critical influence on selecting a pretreatment process as well as the complexing agent used in the leaching process, as well as in the process design for recovering gold from complex solutions. Finally a combination of the current gold price and the gold grade of the ore will determine if it is economically feasible to treat a gold deposit, and imposes a variety of limitations on the design of treatment processes for any particular deposit.

Heap leaching is the most commonly applied method for low grade and high tonnage ore deposits. By opening up vast reserves of low–grade ores to economic exploitation, heap leaching has made a significant and lasting impact, and has probably contributed more

than any other technology to the surge in gold production for the past twenty years (Fleming, 1998). At the same time several copper–gold ore deposits have been discovered in different places around the world. The presence of copper minerals affects gold cyanidation mainly by increasing the consumption of cyanide, and by decreasing the carbon loading capacity for precious metals. Although several other lixiviants for gold treatment processes have been introduced and thoroughly researched and tested over the years, the cyanide process is almost impossible to beat, both technically and economically.

Therefore, it is perfectly comprehensible why having a clear understanding of the behavior of different species, especially gold and copper, in these leaching systems is important.

The goal of this project is to develop a fundamental understanding of cyanide heap leaching of low–grade gold ores with significant copper mineralization, in order to facilitate the optimum design of heaps for rapid gold extraction and minimum consumption of cyanide. For doing this a comprehensive set of the kinetic data of different species in cyanide column leaching experiments, under different cyanide concentrations, must be prepared to validate future mathematical modeling work on cyanide heap leaching of cupriferous gold ores. The valuable experiences of previous research, particularly that of Mr. Francois Coderre, former M.A.Sc. student in the MMAT Department of the University of British Columbia, have been considered precisely and those experiments were modified wherever applicable. Throughout this thesis, the experiments done by Mr. Coderre are called phase I. In phase II, similar experiments to phase I have been conducted, with modified techniques and after eliminating the weak acid soluble copper from the ore.

Considering the ability of copper–cyanide complex solutions to dissolve gold particles, another set of column leaching experiments called phase III has been run with the purpose of collecting the kinetic data and investigating of the behavior of different species in this new system to be used in future modeling work.

2 Literature review

2.1 Gold and it's history

Gold was used and valued by ancient people who formed it into a variety of objects. There was no need for comprehensive knowledge of mining and metallurgy to have gold, as it could be found in the native state as nuggets, big enough to be collected by panning and other direct mining practices.

With improvement of chemical knowledge over the ages, the alchemists decided to find an easier process to have this precious metal: transmutation of base metals into gold. Although it never happened, it had major influences on the improvement of the science of chemistry. In the beginning of the ninth century, Jabir Ibn Hayyan discovered aqua regia and it's ability to dissolve gold. However, it never found an industrial application. After the discovery of chlorine in 1774 by Carl Wilhelm Scheele, it was noted that chlorine has the ability to attack all metals including gold. Almost one century after that, in 1851, chlorine found it's first application in the extraction of gold from its ores. Chlorination was the major method for gold ore treatment for almost forty years, until the discovery of the cyanidation process by John Steward MacArthur in 1887. This new process enjoyed immediate industrial success in New Zealand in 1889 and in South Africa in 1890 (Habashi, 1987). Cyanidation has been the standard method for gold extraction for more than one century and remained essentially unchanged until late 1960s. It generally consisted of the following procedures:

1. Milling the ore and leaching in cyanide solution.

2. Solid–liquid separation, washing the solid residues as efficiently as possible.

3. Treating the pregnant solution by zinc cementation to recover the precious metals.

Although this process was highly economical and efficient for most ore bodies, it had some limitations depending to the mineralogical properties of the ore. The cutoff grade for most gold mines was 2 – 3 ppm leachable gold in the ore, even while the gold price had strongly increased. Low grade ore bodies, refractory ores, the presence of other cyanide consumers and preg–robbing minerals in the ore have been the major problems of the cyanidation process, which new technologies have tried to address during the past thirty years. Heap leaching and carbon–based adsorption processes are two of the most important innovations in gold industry. Also development of pre–treatment technologies from roasting to pressure leaching and biooxidation have made it possible to process refractory gold ores with cyanidation.

There have been many serious attempts by researchers to find alternative reagents for cyanide that would be more environmentally friendly, faster, and less affected by interfering ions. Table 1 presents other leaching systems for gold, (Woodcock, 1988). Some of these reagents, especially thiourea and thiosulfate, have been found to be very strong substitutes for cyanide, but in general each one has its own disadvantages. Table 2 gives the potential application of leaching reagents for gold. Generally being more expensive, having faster degradation rates and yielding less stable gold complexes than to $Au(CN)_2^-$ are the most serious disadvantages of the alternative reagents tested. In addition, as shown in Table 2-1, oxygen is not a suitable oxidant for gold in some of these situations, and therefore a more expensive oxidant is required.

Table 2-1 Leaching systems for gold (J. T. Woodcock, 1988)

Leaching Reagent	Oxidant used	Gold complex in solution	General condition
Alkaline Systems			
Cyanide	O_2	$Au(CN)_2^-$	pH >10
Ammonia–Cyanide	O_2	$Au(CN)_2^-$	pH >10
Organic Nitriles	O_2	$Au(CH(CN)_2)_2^-$	pH >7
Alpha–hydoxynitriles	O_2	$Au(CN)_2^-$	pH >10
Calcium Cyanamide	O_2	$Au(NCN)_2^{3-}$	pH >10
Alkali Cyanoform	O_2	$Au(C(CN)_3)_2^-$	pH >10
Neutral System			
Thiosulfate	O_2	$Au(S_2O_3)_2^{3-}$	pH > 7, 60°C
Bromocyanide	Br CN	$Au(CN)_2^-$	pH 7
Bromine	Br_2	$AuBr_4^-$	pH 7
Acid Systems			
Chlorine (aqueous)	Cl_2	$AuCl_4^-$	pH < 2, Cl^-
Ferric Chloride	Fe^{3+}	$AuCl_4^-$	pH < 2, Cl^-
Aqua Regia	HNO_3	$AuCl_4^-$	pH < 0, Cl^-
Thiocyanate	Fe^{3+}, H_2O_2	$Au(SCN)_4^-$	pH < 3
Thiourea	Fe^{3+}, H_2O_2	$Au(NH_2(SNH_2)_2^+$	pH 1–2

Table 2-2 – Properties and applications of leaching reagents for gold
(T. V. Subrahmanyam et al., 1988)

Leaching Reagent	Properties and applications
Alkaline Systems	
Cyanide	Universally used
Ammonia-Cyanide	Used for oxidized gold-copper ores but not persisted with.
Organic Nitriles	Malanonitrile and alpha-hydroxynitrile are less toxic than cyanide; expensive and slower leachants; function in alkaline or near neutral solutions; malanonitrile is claimed to be more effective than cyanide at pH 7–8 and may be effective on some base metal ores.
Alpha-hydroxynitriles	Function by slow hydrolysis in alkaline solution releasing cyanide ions and the parent ketone. The slow release of cyanide may be effective in dissolving gold while minimizing side reactions with other minerals.
Calcium Cyanamide and Alkali Cyanoform	Hydrolyse in alkaline solutions to form stable low toxicity carbanions, capable of complexing gold;
Neutral System	
Thiosulfate	Is non–toxic and inexpensive; no commercial scale ore operations are reported. Neutral thiosulfate solutions dissolve gold slowly from various products; a mild oxidant and elevated temperature are needed; copper additions accelerate the dissolution rate.
Bromocyanide	Expensive; provides both oxidant and complexing reagent; has been used on sulphotelluride ores to dissolve gold.
Bromine	Leaches gold as well as platinum at acid, neutral or alkaline pH; faster leaching kinetics when a protonic cation (NH_4^+) and an oxidant are added; among the disadvantages are the high reagent costs and the need for reagent recovery and regeneration.

Acid Systems	
Chlorine (aqueous)	Gold and silver are leached rapidly at acid pH. Acidified chlorine was found to be worth testing for ores containing less than 0.5% sulphur, beyond which level chlorine consumption is high. High reaction rates achieved when gold is oxidized to Au(III) state and complexed with chlorine, bromide or iodide, although these reagent combinations are aggressive to other minerals and materials of construction.
Thiocyanate	Can be used in conjunction with Fe (III) at pH 2 to dissolve gold and uranium. Gold and unused thiocyanate can be recovered by ion exchange.
Thiourea	Low toxicity and dissolves gold readily (leach rates of 256 mg Au/cm^2/hr, i.e. more than 100 times that of gold in an 0.1% NaCN solution); suffers from high reagent consumption which is caused by oxidation degradation; addition of SO_2 is claimed to minimize oxidative degradation. However, it has also been reported that minimal amounts of thiourea were saved at the expense of substantial quantities of sulphide, oxidant and acid. Thiourea also reacts readily with copper.

2.2 Gold and its minerals

Gold is located in the IB group of the periodic table of elements along with silver and copper; therefore, they have similar electronic structures, with a single 's' electron outside a filled 'd' electron orbital. But contrary to copper and silver which occur mainly as sulfide minerals, gold has a tendency to occur as the native element or alloyed with other metals such as silver. Its principal oxidation states are +1 (aurous) and +3 (auric). The average abundance of gold in the earth's crust is 0.005 g/t, less for limestone and granite-rhyolite, 0.003 g/t, and more for sedimentary rocks, 0.03 g/t (Boyle, 1987).

Silver and copper are the most abundant metals associated with gold mineralogicaly or as alloys. Arsenopyrite, pyrite and chalcopyrite are minerals which gold is usually associated with, either as very small inclusions or as ionic substitutions (Paterson, 1990). Other metals which are commonly found in gold ores are As, Sb, Bi, Fe, Pb and Zn (Yannopoulos, 1990). Copper minerals come only after pyrite and arsenopyrite as the primary host metals sulfide minerals associated with gold. Most copper deposits were found to contain gold to more or less extent (Deng Tong et al., 1995). Other important gold minerals are gold tellurides, which are usually found in ores in association with native gold and other sulfides. The most common gold tellurides are calaverite ($AuTe_2$) and sylvanite ([Au,Ag] Te_4). Table 2-3 presents a list of gold minerals, reported by Boyle in 1979. Most common naturally occurring gold minerals and some of their properties were listed by Marsden et al. (1992) and are presented in Table 2-4.

Table 2-3 – List of gold minerals (R. W. Boyle, 1979)

Native elements, alloys and metallic compounds			
Gold	Au	Platinum gold	(Au, Pt)
Electrum	(Au, Ag)	Bismuthian gold	(Au, Bi)
Cuproaride	(Au, Cu)	Gold Amalgam	Au_2Hg_3 (?)
Porpezite	(Au, Pd)	Maldonite	Au_2Bi
Rhodite	(Au, Rh)	Auricuprite	$AuCu_3$
Iridic gold	(Au, Ir)	Palladium cuproauride	$(Cu, Pd)_3Au_2$
Tellurides:			
Calaverite	$AuTe_2$	Muthmannite	$(Ag,Au)Te_2$
Krennerite	$(Au,Ag)Te_2$	Sylvanite	$(Au,Ag)Te_4$
Montbrayite	$(Au,Sb)_2Te_3$	Kostovite	$AuCuTe_4$
Petzite	Ag_3AuTe_2	Nagyagite	$Pb_5Au(Te,Sb)_4S_{5-8}$
Sulphide	Uytenbogaardtite	Ag_3AuS_2	
Antimonide	Aurostibite	$AuSb_2$	
Selenide	Fischessetite	Ag_3AuSe_2	

Table 2-4 – Most common naturally occurring gold minerals (Marsden et al., 1992)

Gold Minerals	Formula of Minerals	Au content, (%)	Specific gravity, (g/cm^3)	Moh's hardness	Colour
Native gold	Au	>75	16–19.3	2.5–3.0	Deep yellow
Electrum	(Au, Ag)	45–75	13.16	2.0–2.5	pale Yellow
Calaverite	$AuTe_2$	39.2–42.8	9.2	2.5–3.0	White or creamy yellow
Krenerite	Au_4AgTe_{16}	30.7–43.9	8.6	2.5	Creamy white
Sylvanite	$AuAgTe_4$	24.2–29.9	8.2	1.5–2.0	Creamy white
Montbroyite	Au_2Te_3	38.6–44.3	9.9	2.5	Creamy white
Petzite	Ag_3AuTe_2	19.0–25.2	9.1	2.5	Creamy white white violet tint
Hessite	Ag_2Te	4.7	8.4	2.5–3.0	Greyish white
Nagyagite	$Au(Pb,Sb,Fe)_8(S,Te)_{11}$	7.4–10.2	7.5	1.5	Creamy white
Kostovite	$CuAuTe_4$	25.2	No data	2.0–2.5	White but tarnishes pink
Aurostibnite	$AuSb_2$	43.5–50.9	9.9	3.0	Grey white
Maldonite	Au_2Bi	64.5–65.1	15.5	1.5–2.0	

2.3 Gold ore classifications

There are different methods for classifying gold ores, depending on the ore characteristics, which are used for this purpose. Marsden et al. (1992) used mineralogical and formation characteristics of gold ores and classified them as follows:

1. Primary ores

2. Secondary materials

Gold ores associated with oxidized, silver–rich, iron sulfides, arsenic sulfides, copper sulfides, antimony sulfides, tellurides and carbonaceous minerals are sub–divisions of the primary ores, while gravity concentrates, flotation concentrates, tailings, refinery materials and recycled gold are known as secondary materials in this classification method. Another method for classification of gold ores is based on the required mineralogical method for processing of these gold sources. Subrahmanyam et al. (1988) classified gold ores in three main divisions using this method and presented the following categorization:

1. Ores containing free gold.

2. Non-refractory gold ores or readily leachable ores.

3. Refractory ores.

LaBrooy et al. (1994) used a similar method and presented the following categories:

1. Free-milling

    a. Oxide

    b. Sulfide

2. Complex

    a. Cyanide consuming

    b. Oxygen consuming

    c. Preg-robbing

3. Refractory

    a. Highly refractory

    b. Semi refractory

"Free milling" covers those ores which respond very well to conventional cyanidation leaching, with more than 90% of their gold content being recoverable in 20–30 hrs at a particle size P_{80} of 75 µm. When a gold ore demands inordinately large amounts of cyanide or oxygen to give acceptable gold recoveries, it is called a complex ore. Finally, refractory ores are those which yield low gold recoveries in the conventional cyanidation process. Most of the time, the term "refractory" is used for both the latter types of ore (Hoan, 1998). Usually in refractory ores, the host rock contains high concentration of sulfides such as pyrite and arsenopyrite, which are inert to cyanide attack and gold particles are encapsulated within their matrices (Fleming, 1998). Also, the presence of minerals which consume cyanide, and the presence of carbonaceous materials in the ore, which are able to reabsorb the gold after it has been exposed to cyanide leach liquor, can be the other sources of refractoriness. If a gold ore contains gold particles encapsulated in sulfide minerals and also contains graphitic carbon, it is called a double refractory ore (Fleming, 1998).

2.4 Treatment of gold ores

Procedures for treating gold ores vary markedly from mine to mine based on the chemical and physical properties of any particular ore deposit. The commonly used extraction processes for treatment of gold ores include (Bhappu, 1990):

1. Gravity concentration (using jigs, tables, spirals, Reichert cone, etc.).

2. Amalgamation (with mercury)

3. Flotation (as free particles or contained in base metal sulfide concentrates)

4. Pyrometallurgy (in the smelting and refining of base metal ores and concentrates)

5. Hydrometallurgy (direct cyanidation, cyanidation with carbon adsorption, heap leaching, and chlorination–leach)

6. Combination methods (gravity or flotation concentration followed by cyanidation or roasting of flotation concentrates followed by cyanidation)

In this thesis, treatment operations of the low–grade ores and copper bearing gold ores are considered particularly.

2.4.1 Low–grade gold deposits

Low–grade ore deposits must be addressed with a process which incurs low capital and operating costs. Heap leaching is most commonly applied to low grade and high tonnage ores; the ore may be run–of–mine or crushed to a size as fine as 10 mm (Subrahmanyam et al., 1988). Heap leaching consists of piling ore to a given height, usually 10–20 m, on a gently sloping impermeable bed, and spraying dilute reagent solution onto the top of the heap. The concentration of the cyanide solution is usually 0.5–1.0 g/L NaCN at pH of 10–11 and the application rate is 6 $L/hr/m^2$ of heap surface (Subrahmanyam et al., 1988).

While the leachant solution flows down through the heap, it dissolves the gold, then the pregnant solution is directed to the impervious pad at the bottom of the heap and flaws to a collection pond. After that, the leaching solution, which usually contains less than 1–2 ppm gold is sent to carbon adsorption columns to recover gold, although some mines use zinc cementation for this purpose. In the next step, the cyanide concentration of the solution is adjusted and the leachant is recycled to the leaching circuit again. The recycling is continued until the pregnant solution from the bottom of the heap shows a gold concentration less than 0.05–0.1 ppm (Fleming, 1998 and Subrahmanyam, 1988). Heap leaching is very low cost and flexible, can be used for both small- (<200 t/day) and large–scale (50000 t/day) operations. It is possible to operate with costs as low as $1 to $2 per ton.

The major drawback of this process is its low extraction, usually about 60–75%. In general, to have successful heap leaching, the gold–bearing ore must be porous and contain fine–sized clean gold particles (Yannopoulos, 1990). Dorey et al., 1988, has reported the following specific characteristics for an ore to be amenable to heap leaching:

1. Content of extremely small or flattened gold particles

2. Porous and permeable host rock

3. Absence of refractory, carbonaceous, or preg–robbing materials (which handicap the gold leaching)

4. Absence of cyanicides (materials consuming cyanide)

5. Absence of fines and/or clays that impede uniform cyanide solution percolation (agglomeration is required with excessive fines and clays)

6. Absence of acid–forming constituents (which cause high consumption of cyanide or lime)

2.4.2 Treatment of copper gold ores

The presence of copper in a gold ore causes several problems because of high solubility of these minerals in cyanide solution. High cyanide consumption is the major problem in these situations. Usually the cut–off grade for direct cyanidation is 0.5% copper for oxidized and 1% for sulfide gold ores; above these, the cyanide consumption is intolerable (LaBrooy, 1992). High loadings of copper on carbon in carbon adsorption columns and retarding the gold adsorption process are other major problems caused by the presence of copper minerals in a gold ore. There have been extensive attempts by researchers to find ways to deal with these kinds of minerals. Muir et al. (1989) reported the following options as identified and tested methods for treating copper–gold minerals:

1. Flotation to produce a high-grade copper-gold concentrate for smelting.

2. Separation of a low copper fraction (<0.5% Cu) and processing by conventional cyanidation and C.I.P.

3. Selective pre-leaching of high copper fractions (>1% Cu).

4. Selective leaching of gold by using mixed cyanide reagents or alternative reagents.

Several other options have been added to this list during the past few years, and the different aspects of these methods are summarized in the following sections.

2.4.2.1 Flotation of high grade copper gold concentrate

The purpose of this method is to obtain a copper concentrate with a high gold grade to sell directly to smelters. After smelting this concentrate, the gold is extracted form the anode slimes of copper electro–refining. This is the simplest and most economic method for gold ores containing high copper concentrations. This process is widely used and gold recoveries of 50–93% have been achieved (LaBrooy, 1992). A concentrate assaying 25.7% copper and 109 g/t gold, produced by Newmont Ltd in Australia at their Telfer mine, and another concentrate assaying 22.0% copper and 300 g/t gold, produced by BHP Gold Ltd at their Brown's Creek Mine, are two examples of this process (Muir et al., 1989).

One drawback of this method is that it may take months before the gold value is realized and it is possible that significant amounts of gold may be left in low–grade copper tailings.

This method is not as simply applicable for oxidized or transition ores. The controlled potential sulfidization pretreatment may be able to produce an acceptable flotation concentrate in such cases.

2.4.2.2 Direct cyanidation

If the copper content of ore is not sufficient to be recovered as a concentrate, other methods must be considered. Direct cyanidation can have different aspects as following:

- Direct cyanidation with the purpose of selective leaching of gold

The major object of any selective leaching approach is to choose a reagent which is selective for gold over copper minerals, or to choose reagent mixtures and conditions which render the copper minerals insoluble.

- K process

This method, developed and patented by Kaljas Pty Ltd, was claimed to be selective for leaching gold from metallic copper or oxidized copper ores (Sehic, 1988). In this process a combination of bromine reagents at a neutral pH are used, which result in rapid dissolution of gold, passivation of copper metals, and inhibition of copper oxide dissolution.

The advantage of this method is relatively low bromine consumption, related to cyanide consumption. The process seems to be limited to oxidized copper minerals because of reactivity of the bromine with sulfides (Muir, 1989).

- Leaching with Thiourea

The use of thiourea to extract gold from sulfide concentrates has been investigated by numerous researchers. Selective leaching of gold by thiourea is limited to chalcopyrite concentrates because of reactivity of thiourea with other copper minerals. Also, copper(II) is known to catalyze the oxidation and decomposition of thiourea to formamidine disulfide, cyanamide and sulfur (Deschenes and Ghali, 1988).

- Ammonia–Cyanide mixtures

Research on the ammonia-cyanide leach system has indicated that gold is leached and recovered while most of the copper is left in the tailings. This process has the advantage of lower cyanide consumption (Muir et al., 1989 and 1995). It is based on the formation

of a copper–ammonia–cyanide complex which can dissolve gold in the absence of oxygen, and with minimal dissolution of copper.

The formation of the copper–ammonia–cyanide complex $Cu(NH_3)_2(CN)_2$ requires reagent additions in the weight ratios suggested by the formula.

2.4.2.3 Direct cyanidation followed by CN⁻, Cu recovery processes

- The AVR process

The earliest experience of the mining industry with cyanide recovery from tailings was the AVR process, which involves acidification, volatilization and reneutralization. The acidification of gold plant tailings is done with sulfuric acid to lower the pH to less than 7, usually to pH 3 to 5. This causes free cyanide and weakly complexed cyanides (complexes of Zn, Cd, Ni and Cu) to be converted to HCN, which is subsequently volatilized and directed to a lime slurry or caustic solution to be converted back to free cyanide ions. When there is a high concentration of copper cyanide complex in the tailings, incomplete recovery of cyanide occurs.

$$Cu(CN)_3{}^{2-} + H_2SO_4 \rightarrow CuCN + 2\,HCN + SO_4{}^{2-}$$
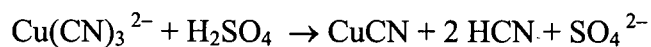
Therefore, this has several drawbacks. For example, only 67% of the available cyanide is recovered, also the copper product is not valuable because of the cyanide attached to it and also it is not environmentally safe for final discharge (Fleming, 1988).

- The MNR process

In this method, sulfide ions are added to the cyanide solution as well as acid.

$$2\,Cu(CN)_3{}^{2-} + S^{2-} + 3\,H_2SO_4 \rightarrow Cu_2S + 6\,HCN + 3\,SO_4{}^{2-}$$
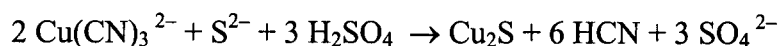
Using this process, all the cyanide associated with copper is recovered and recycled. Also, the acid consumption is less than the AVR process, and the copper sulfide product is readily recovered (Fleming, 1988). High sulfide consumptions and difficulty in filtering or processing the slimy precipitate have been reported as problems of this technique (Muir, 1989).

- The Augment Process

The Augment process recovers copper cyanide and free cyanide directly from solution or pulps by ion exchange (Fleming et al., 1995). It is claimed that this process enjoys the following advantages over the AVR and MNR processes:

- The sulfuric acid never is exposed to the tailings, so acid consumption is stochiometric.

- The process is safer.

- Copper is recovered as cathode metal.

2.4.2.4 Other methods

The Sceresini process suggests selective elution of copper with cold caustic cyanide solution from carbon adsorption columns. This process is followed by cyanide recovery by acidification and precipitation of copper as copper sulfide or sulfate (LaBrooy, 1992).

In another process suggested by Muir et al. (1989), copper is selectively stripped from carbon by washing with cold 5% NaCN solution in a pre–elution step to desorb copper as higher copper–cyanide complexes without desorbing gold. The basis of this method is that carbon strongly adsorbs monovalent cyanide complexes, but has only a weak affinity

for multi–charged complexes (Tsuchide et al., 1984). A process was tested by Tong et al. (1995).

To remove copper selectively from a cupriferous gold concentrate, the Oxygenated chloride-leaching process uses oxygen in the presence of chloride to oxidize mineral sulfides to sulfur thereby releasing their metal values into solution. This process is claimed to be feasible for extracting copper under rather mild conditions and to leave pyrite intact (Deng et al., 1995).

2.5 Chemistry background

2.5.1 Form of cyanide

The cyanide ion is isoelectronic with carbon monoxide and molecular nitrogen. The C and N atoms are triply bonded. In aqueous solutions, cyanide ion hydrolyzes to form hydrogen cyanide with a $pK_a = 9.21$ at $25°$ C. Since HCN gas is a deadly toxin, cyanide must be used in alkaline solutions. Aqueous cyanide can be oxidized to cyanogen, $(CN)_2(g)$, or cyanate, CNO^-, according to the following reactions:

$$(CN)_2 \text{ (g)} + 2\text{ H}^+ + 2\text{ e}^- \rightarrow 2\text{ HCN} \qquad E° = +0.37 \text{ V}$$

$$OCN^- + 2\text{ H}^+ + 2\text{ e}^- \rightarrow CN^- + H_2O \qquad E° = -0.14 \text{ V}$$

$$OCN^- + H_2O + 2\text{ e} \rightarrow CN^- + 2\text{ OH}^- \qquad E° = -0.98 \text{ V}$$

$$2\text{ HCNO} + 2\text{ H}^+ + 2\text{ e}^- \rightarrow (CN)_2 \text{ (g)} + H_2O \qquad E° = +0.33 \text{ V}$$
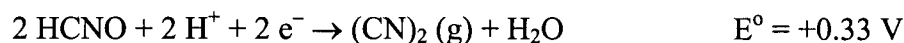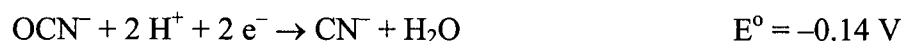
Cyanogen gas is soluble in water. Calculations on the stability of the cyanide–water system show that the most stable form of cyanide in the water stability region is cyanate. However, the fact that cyanide is stable in aqueous solution indicates that the kinetics of the oxidation of cyanide to cyanate and/or cyanogen is very slow if no catalyst is present (Wang, 1990).

2.5.2 Free cyanide

Free cyanide is either the uncomplexed cyanide ion, CN^-, and molecular hydrogen cyanide, HCN. They are related by the acid dissociation of HCN:

$$HCN \quad \leftrightarrow \quad CN^- + H^+ \qquad\qquad pK_a = 9.21$$

The concentration of free cyanide is the sum of the CN^- and HCN concentrations. The proportions of free cyanide in the CN^- and HCN forms as a function of pH at $25°$ C and

zero ionic strength is shown in Figure 2–1. As it can be seen in this figure, CN^- is the predominant species at pH above 9.2.
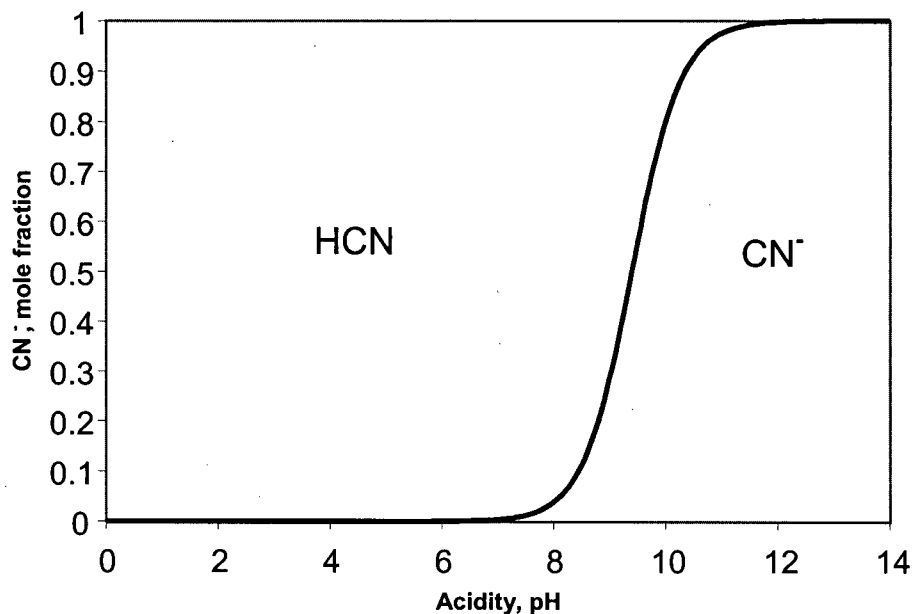
Figure 2-1 Equilibrium distribution diagram for free cyanide versus pH 25°C and zero ionic strength

2.5.3 Oxidation reactions

Free CN^- and SCN^- can be oxidized by many oxidants, such as hydrogen peroxide (H_2O_2), ozone (O_3), hypochlorite (ClO^-), or peroxomonosulfate (HSO_5^-). Sulfur species such as elemental sulfur, polysulfides, and thiosulfate ($S_2O_3^{2-}$) oxidize CN^- to SCN^-. Strong oxidants such as O_3 also oxidize species such as NCO^-, in which the bound nitrogen is oxidized to N_2.

The possible oxidation reaction products of cyanide are shown schematically in Figure 2-2.

Figure 2-2 Oxidation of free cyanide

$$C_2N_2$$

Fe^{3+}
Cu^{2+}

H_2O_2, O_3, HSO_5^- Cl_2, HClO, NH_2Cl

NCO$^-$ ◄————————— CN$^-$ —————————► ClCN

S(s)
S_x^{2-}
$S_2O_3^{2-}$

SCN$^-$
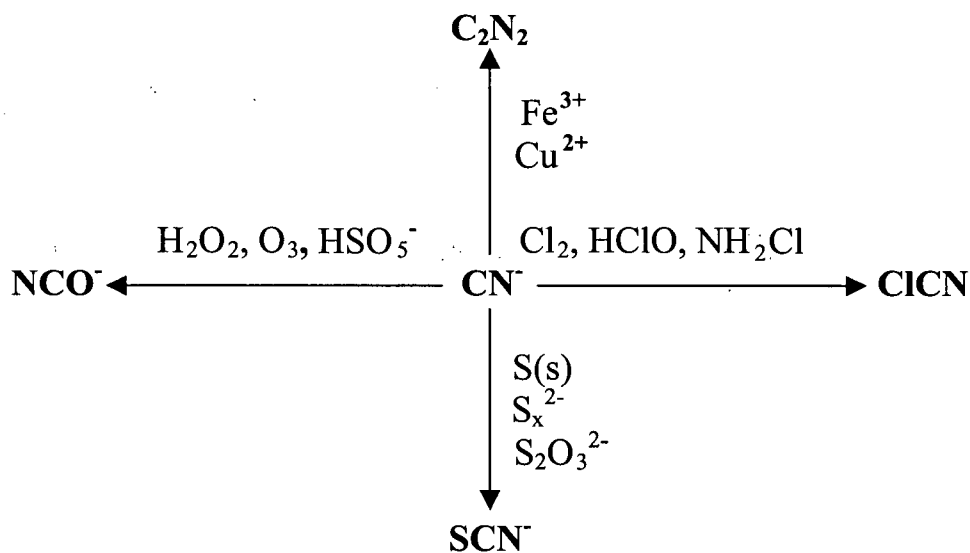
2.5.4 Complexed cyanide

Cyanide bound to metal ions is referred to as complexed cyanide. Complexed cyanide may occur as solids $M(CN)^q(s)$ or dissolved species $[M(CN)_p]^{q-p}$ (aq), where M^{q+} represents any metal ion of charge or oxidation state +q. Metal cyanide complexes can be divided to three major groups.

- WAD or weak acid dissociable complexes, which are rapidly and completely decomposed by acids, e.g. Zn, Cd, and Ni cyanide complexes.

- Partially WAD cyanide complexes. Examples of this group are Cu, Ag, Au and Hg cyanide complexes.

- Non–WAD cyanide complexes, which are resistant to decomposition by acids. Examples of this group are iron and cobalt cyanide complexes.

2.5.5 Gold dissolution in cyanide

The Pourbaix diagram for the stability of gold in water is presented in Figure 2-3. This diagram indicates that metallic gold is be more stable than gold oxide compounds and gold ions under the conditions for stability of water. The gold metal has no coexistence boundaries with the gold oxides within the water boundaries. Therefore, the oxides would not be produced directly from the metal by oxidation in water.
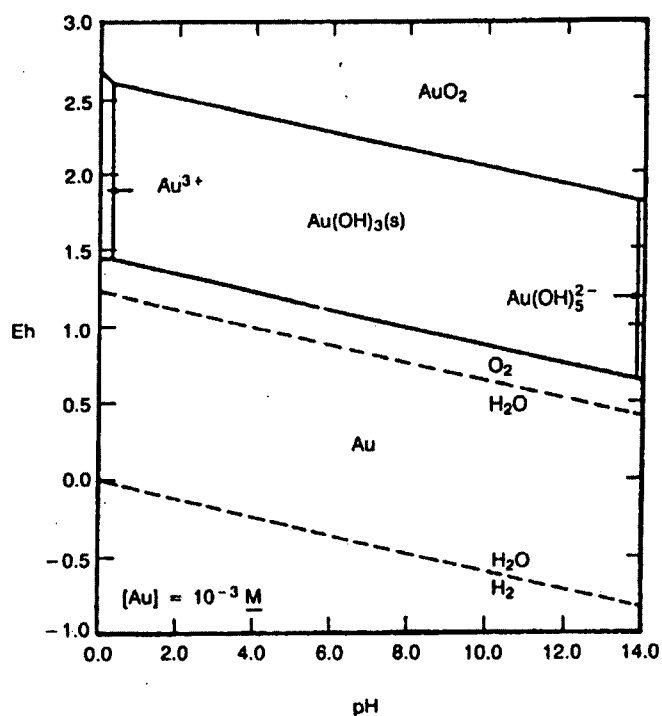
Figure 2-3 Pourbaix diagram for the Au–H_2O System

The dissolution of gold by oxidation only can be achieved in the presence of a complexing agent, such as cyanide ion CN^-, to produce the complex $Au(CN)_2^-$, which remains in solution (Pourbaix, 1966). The dissolution of gold by cyanide was known as early as 1783 by Scheele, one year after he discovered the blue gas which we now know to be HCN. The dissolution reaction of gold in cyanide was studied by numerous

chemists of the time such as Bagration in Russia, Elsner in Germany and Faraday in England (Habashi, 1987). Elsner in 1846 recognized that atmospheric oxygen was essential for the dissolution of gold in cyanide solutions and proposed the following equation as the governing reaction:

$$4\ Au + 8\ NaCN + O_2 + H_2O \rightarrow 4\ NaAu(CN)_2 + 4\ NaOH$$
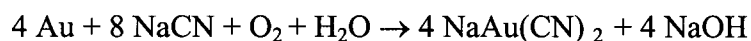
In 1896, Bodlander discovered that hydrogen peroxide was formed as an intermediate product during this reaction and suggested that gold dissolution proceeded through two steps and proposed the following equations (Haque et al., 1992):

$$2\ Au + 4\ NaCN + O_2 + 2H_2O \rightarrow 2\ NaAu(CN)_2 + 2\ NaOH + H_2O_2$$

$$2\ Au + 4\ NaCN + H_2O_2 \rightarrow 2\ NaAu(CN)_2 + 2\ NaOH$$
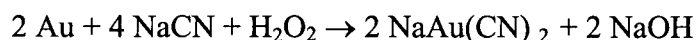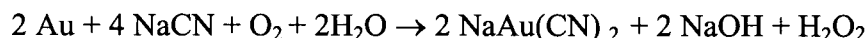
Summation of these two gives Elsner's equation again.

Almost 100 years after Elsner's suggestion for the concept of the reaction between gold and cyanide, Boonstra in 1943 recognized an electrochemical behavior for this reaction in which dissolved oxygen is reduced to H_2O_2 or OH^-. Subsequently, this concept was accepted by many researchers and the following equations are a simplified representation of the electrochemical mechanism of gold cyanidation (Haque et al., 1992):

Anodic reactions:

$$2\ Au \rightarrow 2\ Au^+ + 2\ e^-$$

$$\underline{2\ Au^+ + 4\ CN^- \rightarrow 2\ Au(CN)_2^-}$$

$$2\ Au + 4\ CN^- \rightarrow 2\ Au(CN)_2^- + 2\ e^-$$

Cathodic reactions:

$$\tfrac{1}{2}\ O_2 + 2\ e^- \rightarrow O^{2-}$$

$$\underline{H_2O + O^{2-} \rightarrow 2\ OH^-}$$

$$H_2O + \tfrac{1}{2}\ O_2 + 2\ e^- \rightarrow 2\ OH^-$$
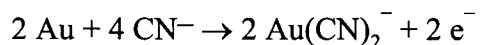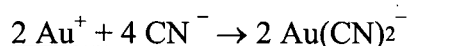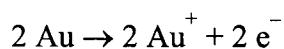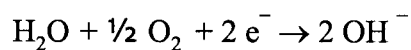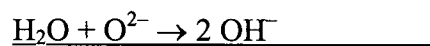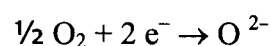
Summation of the above equations again results in Elsner's equation.

Figure 2-4 presents the Pourbaix diagram for the stability of gold in cyanide solution. As can be seen, the presence of cyanide opens a new window of stability within the stability region of water in which gold will form the dicyanoaurate complex, $Au(CN)_2^-$. The formation of this complex is the basis of the dissolution of gold in cyanide systems.
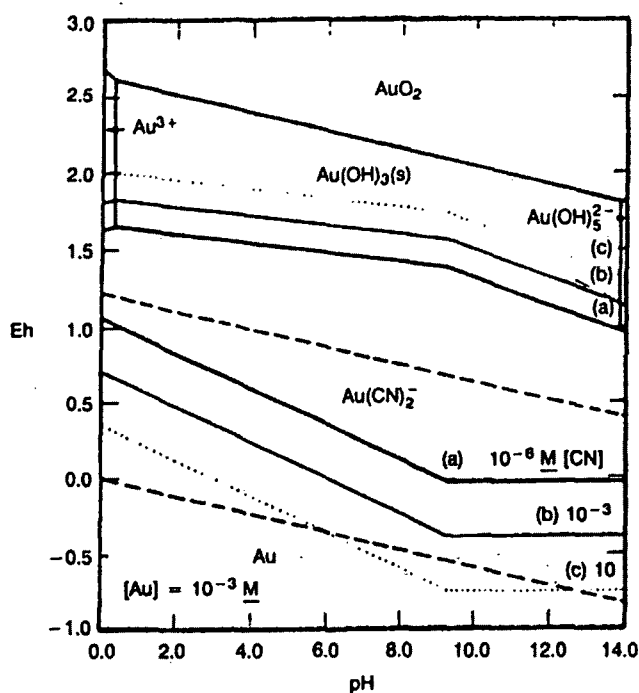
Figure 2-4 Pourbaix diagram for the Au–CN–H₂O System

From the above figure, it is clear that the solubility region of gold as $Au(CN)_2^-$ extends in both acidic and basic medium, but generally cyanidation is conducted in the pH range of 10 to 12 because of the high pK_a value of HCN and its extreme toxicity.

The speciation diagram for the gold-cyanide-water system shows that the precipitation of dicyanoaurate to the cuprous cyanide salt can occur upon decreasing the pH of the

system. This diagram also shows that the precipitation of gold as AuCN(s) is strongly

dependent on the mole ratio of gold to cyanide.
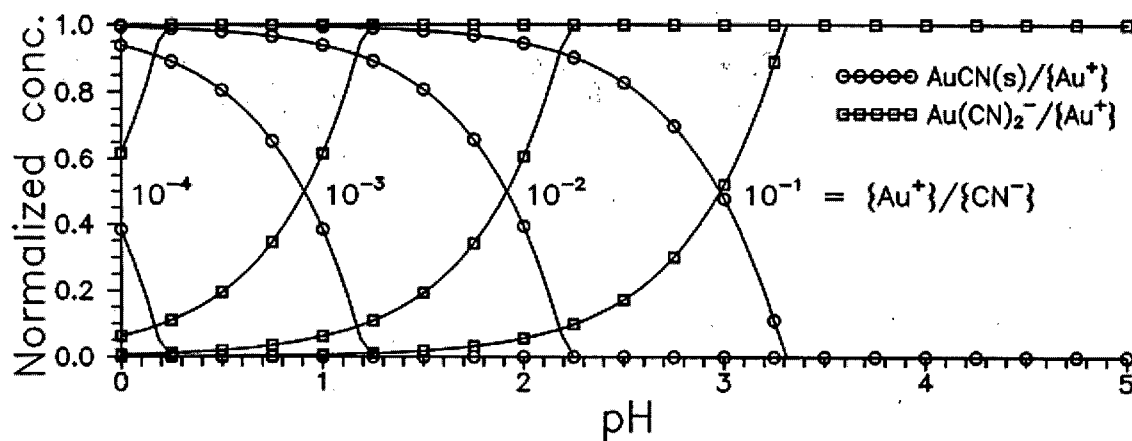
Figure 2-5 Speciation diagram for the Au(I) –CN–H₂O system at four different {CN⁻} / {Au⁺} ratios (Coderre and Dixon, 1999)

2.5.6 Interference of other components on the gold cyanidation

The presence of other components such as Ag, Cu, Fe, Ni, Co, Hg, Pb, As, S and Sb in

gold ores is common. Some of these elements have various degrees of oxidation and

some of them form stable complexes with cyanide and are considered as cyanide

consumers or cyanicides. The presence of some of these elements with high stability

constants leads to high consumption of cyanide and oxygen. In addition, their presence

creates difficulties for solution purification and the control of cyanide levels in the

effluent solutions for disposal (Haque, 1992). There are small differences in the

thermodynamic data on the stability constants of metal cyanocomplexes in the literature.

Data from three different sources (Haque, 1992; Rees et al., 1999 and Adams, 2001) are

presented in Table 2-5. The log β values are stability constants for the complexation

reactions with cyanide: $\qquad M^{y+} + n\, CN^- \Leftrightarrow M(CN)_n^{\,(n-y)-}$

Table 2-5 Stability constants for some of the metal cyanide complexes

Metal Ion	Complex	Stability Constant log β		
		Haque, 1992	Rees et al., 1999	Adams, 2001
Co^{3+}	$Co(CN)_6^{3-}$	64.0		64.0
Fe^{3+}	$Fe(CN)_6^{3-}$	43.6	43.6	43.9
Fe^{2+}	$Fe(CN)_6^{4-}$	35.4	35.4	36.9
Hg^{2+}	$Hg(CN)_4^{2-}$	41.5		
Au^+	$Au(CN)_2^-$	38.3	39.3	36.6
Cu^+	$Cu(CN)_4^{3-}$	30.3	23.1	27.9
Cu^+	$Cu(CN)_3^{2-}$		21.66	26.8
Cu^+	$Cu(CN)_2^-$		16.26	21.7
Ag^+	$Ag(CN)_3^{2-}$			21.8
Ag^+	$Ag(CN)_2^-$	21.1	20.48	20.9
Zn^{2+}	$Zn(CN)_4^{2-}$	16.7	19.62	21.57
Zn^{2+}	$Zn(CN)_3^-$			16.68
Zn^{2+}	$Zn(CN)_2$			11.02
Zn^{2+}	$ZnCN^+$			5.34
Ni^{2+}	$Ni(CN)_4^{2-}$	31.3	30.22	31.1
Ni^{2+}	$Ni(CN)_3^-$			22.0
Ni^{2+}	$Ni(CN)_2$			14.0
Ni^{2+}	$NiCN^+$			7.0

2.5.7 Copper dissolution in cyanide

Copper (II) is reduced to copper (I) and oxidizes cyanide rapidly to cyanogen (Coderre and Dixon, 1999). Thermodynamically, this reaction is favored, regardless of the form of the species involved. Eventually, cyanogen will disproportionate to cyanate and cyanide, directly or indirectly.

$$\{Cu^{2+}\} + 2\ \{CN^-\} \rightarrow 2\ \{Cu^+\} + (CN)_2$$

$$(CN)_2 + 2\ \{OH^-\} \rightarrow \{CN^-\} + \{OCN^-\} + H_2O$$
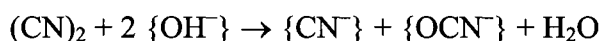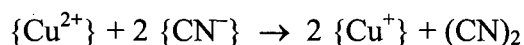
Subsequently copper (I) forms a range of cyanocuprate complexes as the following (the free energies from Rees et al., 1999):

$$Cu^+ + CN^- \Leftrightarrow CuCN\downarrow$$

$$CuCN + CN^- \Leftrightarrow Cu(CN)_2^- \qquad\qquad \Delta G_r^0 = 2.24\ kJ/mol$$

$$Cu(CN)_2^- + CN^- \Leftrightarrow Cu(CN)_3^{2-} \qquad\qquad \Delta G_r^0 = 20.29\ kJ/mol$$

$$Cu(CN)_3^{2-} + CN^- \Leftrightarrow Cu(CN)_4^{3-} \qquad\qquad \Delta G_r^0 = 19.24\ kJ/mol$$
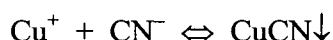
Vukcevic (1996) has compared the free energies of these reactions with the reaction of gold with free cyanide as follows:

$$2\ Au + 4\ CN^- + \tfrac{1}{2}\ O_2 \Leftrightarrow 2\ Au(CN)_2^- + 2\ OH^- \qquad \Delta G = -46.86\ kcal/mol$$
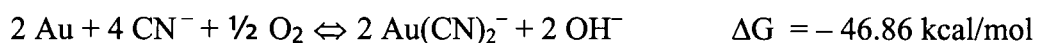
for copper (I) in cyanide solution:

Species	CuCN	$Cu(CN)_2^-$	$Cu(CN)_3^{2-}$	$Cu(CN)_4^{3-}$
ΔG kcal/mol	25.88	83.11	129.90	180.71

Comparing these data, it can be concluded that when copper is present in a gold-cyanide system, $Cu(CN)_2^-$, with its more negative ΔG value than $Au(CN)_2^-$, is favored thermodynamically. Also, it is important to notice that the copper concentration in solution is typically much higher than gold, and that copper cyanidation is faster.

There are numerous studies confirming that cuprocyanide complexes are responsible for leaching of gold in the absence of free cyanide in solution, as the following reactions show (Vukcevic, 1996):

$$Au + 2\ Cu(CN)_4^{3-} + \tfrac{1}{4}\ O_2 + \tfrac{1}{2}\ H_2O \Leftrightarrow Au(CN)_2^- + 2\ Cu(CN)_3^{2-} + OH^-$$

$$\Delta G = -46.86\ kcal/mol$$

$$2\ Au + 4\ Cu(CN)_3^{2-} + \tfrac{1}{2}\ O_2 + H_2O \Leftrightarrow 2\ Au(CN)_2^- + 4\ Cu(CN)_2^- + 2\ OH^-$$

$$\Delta G = -69.32\ kcal/mol$$

$$Au + Cu(CN)_2^- + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \Leftrightarrow Au(CN)_2^- + Cu^+ + OH^-$$
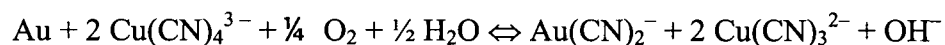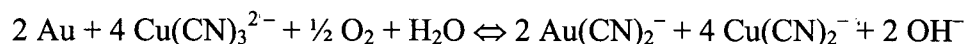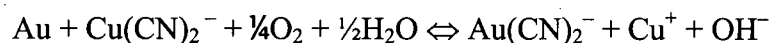
$$\Delta G = -48.89\ kcal/mol$$

The formation of $Cu(CN)_2^-$ is favored at pH less than 6 and at very low cyanide concentrations. This is the least stable copper–cyanide complex. Perhaps the most important characteristic of this component in the gold extraction process is its adsorption onto activated carbon.

The $Cu(CN)_4^{3-}$ species is preferred at high pH, high cyanide concentrations and in the presence of hypersaline solutions (Lukey et al., 1999). However this tetracyano complex, is quite weak ($K_{4,3} = 0.02$), it will dissolve gold via dissolution of its fourth CN^- until the ratio of CN^-:Cu falls to 3:1. Muir et al. (1989) reported that the rate of gold dissolution

under this condition would be only about half of the rate with sodium cyanide. In 1991, LaBrooy et al. measured the rates of leaching of a gold rotating disc in pure NaCN, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ solutions at pH 10.5 in some experiments and compared them as a function of the total cyanide present. They found that the results of these comparisons were strongly depending on the total cyanide. In solutions with less concentration of total cyanide, NaCN had the highest dissolution rate, however in solutions with high concentrations of total cyanide, >1 g/L, $Cu(CN)_4^{3-}$ had the highest dissolution rate.

$Cu(CN)_3^{2-}$ is the predominant cyanocuprate complex (Hedley et al., 1958; Penneman et al., 1956; Lower et al., 1965; Haque, 1992). This complex also is a suitable lixiviant for gold, albeit slower than free cyanide. The lower adsorption of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ on to activated carbon accounts for the use of high cyanide solution concentrations to improve the selectivity of gold over copper when this process is used for gold extraction from pregnant solutions.

The presence of each of these copper and cyanide components are dependent on the pH of the system and the mole ratio of cyanide to copper as shown in Figure 2-6.
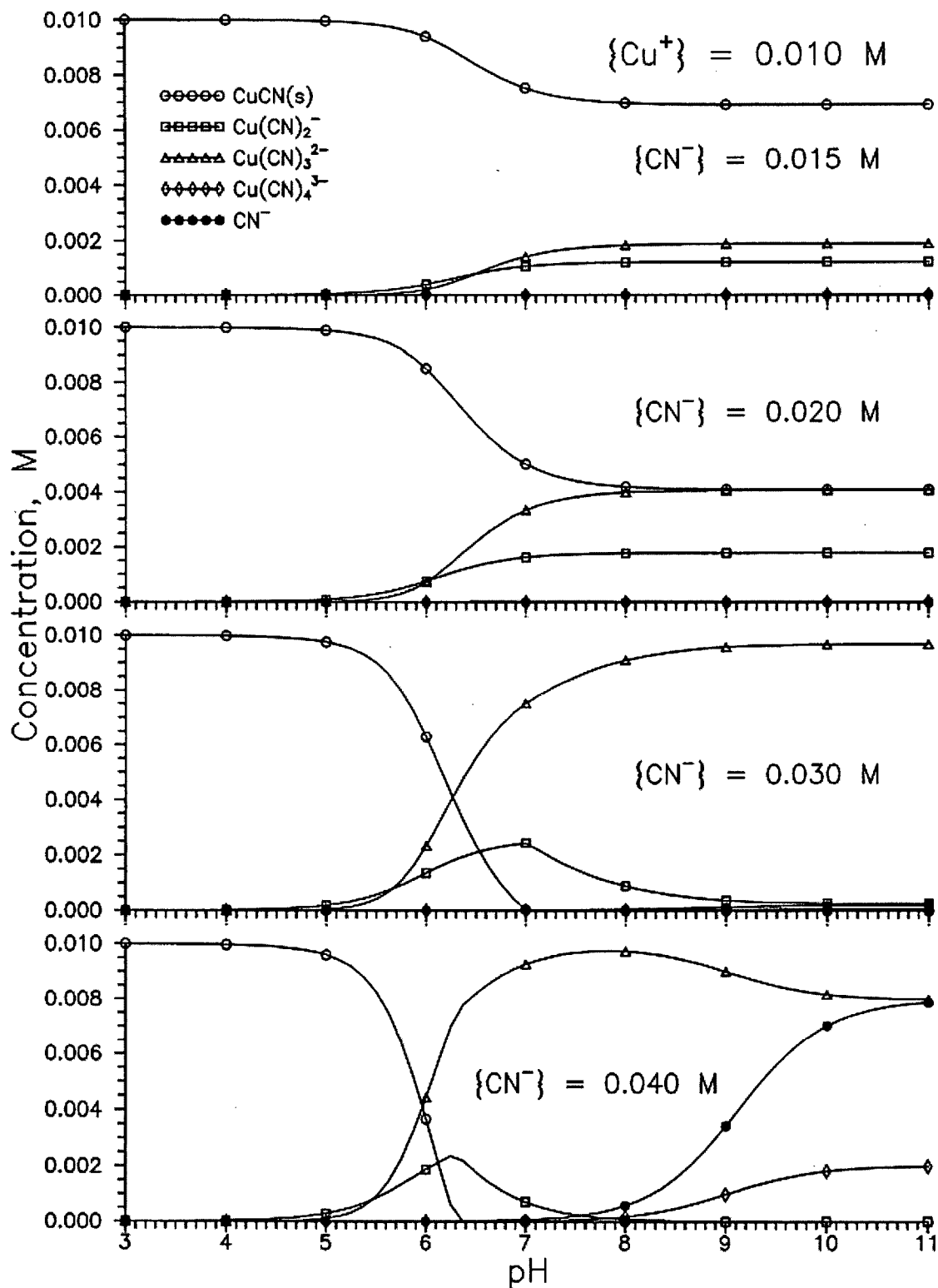
Figure 2-6 Speciation diagrams for the Cu(I) –CN–H₂O system at four different {CN⁻}/ {Cu⁺} ratios (Coderre and Dixon, 1999)

2.5.8 Dissolution of copper minerals in cyanide solutions

Experiments on artificial ores conducted by Leaver and Woolf (1931) showed that most copper minerals are highly soluble in cyanide solutions. In their case, the leaching period was twenty-four hours (Shantz, 1976). Later experiments on copper minerals by Hedley and Tabachnick in 1958 showed that the dissolution of copper minerals in cyanide solution is a function of temperature, Table 2-6.

Table 2-6 Solubility of copper minerals in cyanide solutions
(Leaver et al., 1931; Hedley et al., 1958)

Mineral	Formula	Extraction (%)[a]	Total dissolved copper (%) [b]	
			23°C	45°C
Azurite	$2Cu(CO)_3.Cu(OH)_2$	100	94.5	100
Malachite	$Cu(CO)_3.Cu(OH)_2$	100	90.2	100
Chalcocite	Cu_2S	100	90.2	100
Native copper	Cu	100	90	100
Cuprite	Cu_2O	100	85.5	100
Bornite	$FeS.2Cu_2S.CuS$	94	70	100
Enargite	$2CuS.As_2S_5$	98.9	65.8	75.1
Tetrahedrite	$4Cu_2S.Sb_2S_3$	40.3	21.9	43.7
Chrysocolla	$CuSiO_3$	16.9	11.8	15.7
Chalcopyrite	$CuFeS_2$	8.4	5.6	8.2

[a] Data from Leaver and Woolf (1931)

[b] Data after Hedley and Tabachnick (1958)

Investigations of Lower and Booth in 1965 showed that the extent of copper extraction is dependent on the ratio of cyanide to copper in solution, Table 2-7. They found that the rates of copper extraction from the minerals tested increase in the order of bornite, covellite, chalcocite and malachite.

Table 2-7 Solubility of copper minerals in cyanide solutions (Lower et al., 1965) [a]

Mineral	Cyanide ratio [b]	Extraction (% Cu)	Cyanide consumption g NaCN/ g Cu Extracted
Chalcocite	1.37	54.4	0.13
Chalcocite	2.76	92.6	0.15
Cuprite	1.88	82.7	0.18
Cuprite	4.94	96.6	0.11
Malachite	2.01	76.9	0.42
Malachite	2.04	78	0.41
Malachite	2.31	88.1	0.4
Malachite	4.48	99.7	0.42
Azurite	3.62	91.8	0.55
Covellite	1.96	53.2	0.53
Covellite [c]	5.15	95.6	0.46
Chalcopyrite [d]	2.79	5.8	0.82
Bornite [c]	5.13	96	0.69

[a] Data after Lower and Booth (1965) generated by leaching at room temperature for 6 hrs
[b] Cyanide ratio is expressed as grams NaCN per gram of contained copper
[c] Four-hour leach in this test only
[d] – 325 mesh mineral used in this test

Hence, it may be concluded that:

- All copper minerals are readily leachable in cyanide solutions with the exception of chrysocolla and chalcopyrite;

- Oxide minerals are more cyanide–soluble than sulfides when low cyanide to copper ratios are adopted;

- A lower cyanide consumption is noticed for copper (I) minerals compared to copper(II) minerals.

Generally, cyanocuprate complexes and soluble sulfide (S^{2-}) are the products of the reaction of cyanide with copper sulfide minerals, however the chemistry behind these reactions is different for different minerals. Cyanidation of copper(II) minerals requires reduction of cupric to cuprous and cyanide will be oxidized to cyanate during this reaction. Therefore, the consumption of cyanide is higher in this case.

Cyanide forms strong complexes with copper and therefore is energetic enough to break sulphide lattices without oxidation. Therefore, for copper (I) complexes such as chalcocite the cyanidation reactions can proceed without any redox reaction:

$$Cu_2S + 6\,CN^- \rightarrow 2\,Cu(CN)_3{}^{2-} + S^{2-}$$

$$Cu_2S + 8\,CN^- \rightarrow 2\,Cu(CN)_4{}^{3-} + S^{2-}$$

$$Cu_2S + 9\,CN^- + 0.5\,O_2 \rightarrow 2\,Cu(CN)_4{}^{3-} + SCN^- + 2\,OH^-$$
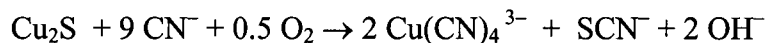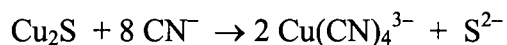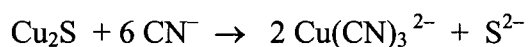
These reactions proceed at a rapid rate and without the requirement for oxygen.

In the case of cupric minerals, copper dissolves as the cuprous complex and in doing so, oxidizes cyanide to cyanogen, which ultimately converts to cyanate. This reaction results

in increased cyanide usage and therefore, increased cyanide loss. The following equations are suggested by W.H. Jay (2000) for copper (II) minerals.

$$2\ CuCO_3 + 7\ CN^- + 2\ OH^- \rightarrow 2\ Cu(CN)_3{}^{2-} + 2\ CO_3{}^{2-} + CNO^- + H_2O$$

$$2\ CuCO_3 \bullet Cu(OH)_2 + 13.5\ CN^- \rightarrow 3\ Cu(CN)_4{}^{3-} + 1.5\ CNO^- + 1.5\ CO_3{}^{2-} + H_2O$$

$$CuCO_3 \bullet Cu(OH)_2 + 9\ CN^- \rightarrow 2\ Cu(CN)_4{}^{3-} + CNO^- + CO_3{}^{2-} + H_2O$$

$$2\ CuS + 7\ CN^- + 2\ OH^- \rightarrow 2\ Cu(CN)_3{}^{2-} + 2\ S^{2-} + CNO^- + H_2O$$

$$2\ CuS + 10\ CN^- + 0.5\ O_2 + H_2O \rightarrow 2\ Cu(CN)_4{}^{3-} + 2\ SCN + H_2O$$

$$2\ CuO + H_2O + 9\ CN^- \rightarrow 2\ Cu(CN)_4{}^{3-} + CNO^- + 2\ OH^-$$

$$2\ CuFeS_2 + 19\ CN^- + 2\ OH^- \rightarrow 2\ Cu(CN)_3{}^{2-} + 4\ S^{2-} + CNO^- + 2\ Fe(CN)_6{}^{4-} + H_2O$$
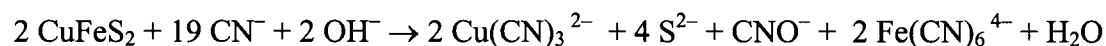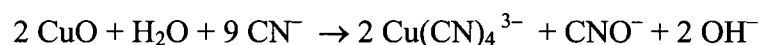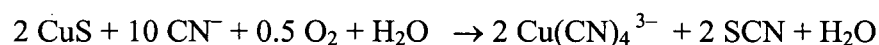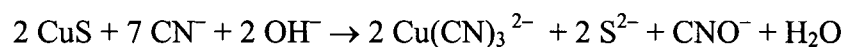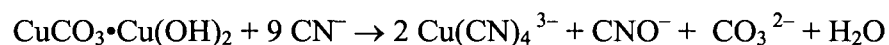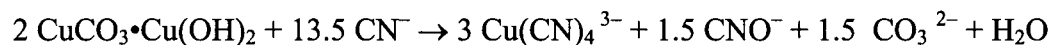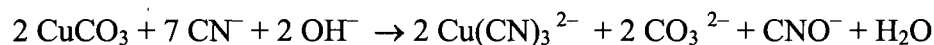
Kakovskii et al., 1964, investigated the dissolution of cupric sulfide in cyanide solution, which gave very interesting results. They found that the dissolution of simple sulfides of copper occurs in different ways in the presence and in the absence of oxygen. Particularly, they found that the dissolution of cupric(II) sulfide involves the simultaneous occurrence of two competing reactions:

$$2\ CuS + 8\ CN^- + O_2 + 2\ H_2O \rightarrow 2\ Cu(CN)_3{}^{2-} + 2\ S^0 + (CN)_2 + 4\ OH^-$$

$$2\ CuS + 7\ CN^- \rightarrow 2\ Cu(CN)_3{}^{2-} + S^{2-} + CNS^-$$
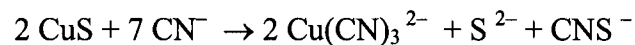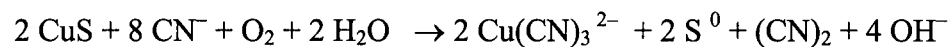
They discovered that in the presence of oxygen both reactions might take place. The share of each of these in the overall dissolution process is determined by the concentration of dissolved oxygen. The more oxygen available in the solution, the greater the relative quantity of cupric sulfide dissolved according to the first reaction, and vice versa.

2.5.9 Sulfur in cyanide solution

Sulfide is one of the reaction products of sulfide minerals with cyanide. Since the cyanidation process operates under an oxidizing atmosphere, the produced sulfide ion may be oxidized in the following sequence: $S^{2-} \rightarrow S_2^{2-} \rightarrow S_2O_3^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$

For example, consider the formation of thiosulfate:

$$2\ S^{2-} + 2\ O_2 + H_2O \rightarrow S_2O_3^{2-} + 2\ OH^-$$
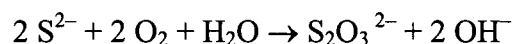
and the formation of sulfate:

$$S_2O_3^{2-} + 2\ OH^- + 2\ O_2 \rightarrow 2\ SO_4^{2-} + H_2O$$
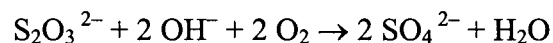
The extent of sulfide oxidation is limited more by kinetics than by thermodynamics (Zhang et al., 1997). Furthermore, sulfide ion may react with cyanide in the presence of oxygen to form thiocyanate, which generally known as follows:

$$S^{2-} + CN^- + \tfrac{1}{2}\ O_2 \rightarrow CNS^- + 2\ OH^-$$
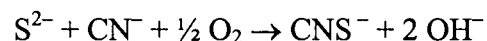
It will be discussed later in this section that the chemistry of formation of thiocyanate is not as simple as the above equation. Formation of thiocyanate is one of the important sources of cyanide loss during cyanidation of sulfide-bearing gold minerals. In addition to all the above chemical transformations, sulfide ion may form a protective coating on the surface of gold particles and therefore retard the cyanidation process. Therefore, cyanide consumption, excess oxygen demand and surface passivation are three major problems created by sulfide ions in a cyanidation circuit.

Because of the important role of copper sulfide minerals in the cyanidation chemistry of the ore which was used in this project, the actions of sulfide ions in cyanide systems are

discussed in more details here. According to the investigation done by Luthy et al. (1979) on sulfur-cyanide interactions, there are two predominate pathways for the formation of thiocyanate from reactions of cyanide with oxidation products of sulfide:

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^-$$

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^-$$
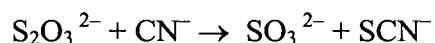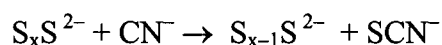
Their kinetic investigation showed that the rate of production of thiocyanate from polysulfides is at least three orders of magnitude faster than the other pathway, depending on pH. However, the specific weight of the first reaction in the overall thiocyanate formation depends upon the presence of polysulfide in the system, which depends upon the formation of polysulfide from the oxidation of monosulfide. The maximum formation of polysulfide occurs in the pH range of 6.5–8. A high ratio of S_{tot}^{2-}/O_2 is required for oxidation of sulfide to polysulfide. At pH greater than 8.5, thiosulfate is the main product, regardless of the ratio of S_{tot}^{2-}/O_2; some sulfite (SO_3^{2-}) may form and may be slowly oxidized to sulfate, or sulfite may react with the sulfur on polysulfides to form thiosulfate.
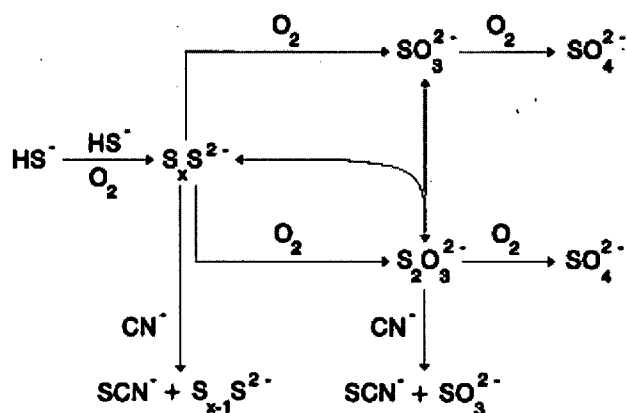
Figure 2-7 Possible reactions of cyanide with reduced sulfur species in aqueous solution to yield thiocyanate (Luthy et al., 1979)

Dixon and Coderre (1999) summarized the above results as follows:

Sulfide minerals will decompose in cyanide solution under atmospheric conditions and:

- Produce primarily bisulfide ions, with thiosulfate and traces of sulfite and sulfate under alkaline conditions.

- Produce primarily bisulfide ions, with a mixture of thiocyanate and thiosulfate under neutral conditions.

However, it seems, because the reaction of cyanide and thiosulfate is one of the two predominant pathways for the formation of thiocyanate, therefore the production of thiocyanate must be considered in both alkaline and neutral conditions.

In addition to the above reactions, sulfide may undergo oxidation by dissolved oxygen and may produce or consume hydrogen ions, depending on the products and other conditions as follows (Chen et al., 1972):

$$2HS^- + O_2 + 2H^+ \rightarrow 2H_2O + 2S^0$$

$$2\,HS^- + 2\,O_2 \rightarrow H_2O + S_2O_3{}^{2-}$$

$$2\,HS^- + 4\,O_2 \rightarrow 2\,SO_4{}^{2-} + 2\,H^+$$
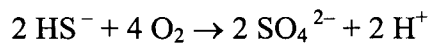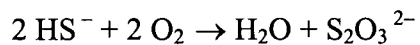
Also, considering the suggestion of Kakovskii et al. (1964) about the different pathways for the dissolution of copper sulfide in cyanide solution in the presence and absence of oxygen, this can be a source of formation of sulfur in the system. In this case, polysulfide ions, $S_x{}^{2-}$, may be formed through the interaction of sulfur and an aqueous solution of sulfide.

$$HS^- + (x{-}1)\,S^0 \rightarrow S_x{}^{2-} + H^+ \qquad (x\ can\ be\ 2\text{–}5)$$
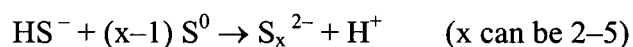
pK values for the above equation have been reported by Maronny (1959) as follows:

$$pK_2 = 12.16 \quad pK_3 = 10.85 \quad pK_4 = 9.86 \quad pK_5 = 9.18$$

At pH greater than 6, $S_4{}^{2-}$ and $S_5{}^{2-}$ are the dominant polysulfide species.

2.6 Column leaching tests, phase I

A kinetic and thermodynamic model of cyanide heap leaching of cupriferous gold ores was developed by Francois Coderre under the supervision of Professor David Dixon in the Department of Metals and Materials Engineering at the University of British Columbia. In that project four short cyanide column tests along with four taller column tests were conducted on a cupriferous gold ore sample. The concentrations of cyanide solutions were adjusted to 200, 500, 1000 and 2000 ppm NaCN. No pretreatment was done to the ore. Sampling of effluent solutions was done regularly and the samples then were analyzed for gold, copper, free cyanide and pH. Some of the samples were analyzed for iron and thiocyanate content. The results of four tall column experiments are shown in Figure 2-8 to Figure 2-11.

Based on these results, they suggested that the cyanide leaching occurs in four distinct stages as follows:

1. Reductive dissolution of Cu(II) salts, during which copper and gold precipitate as cyanide salts, and no gold appears in the column effluent.

2. Re–dissolution of the copper and gold cyanide precipitates.

3. Leaching of copper sulphide minerals and elemental gold.

4. Free cyanide breakthrough in the effluent, which is accompanied by the appearance of dissolved iron from the redissolution of metal hexacyanoferrates.
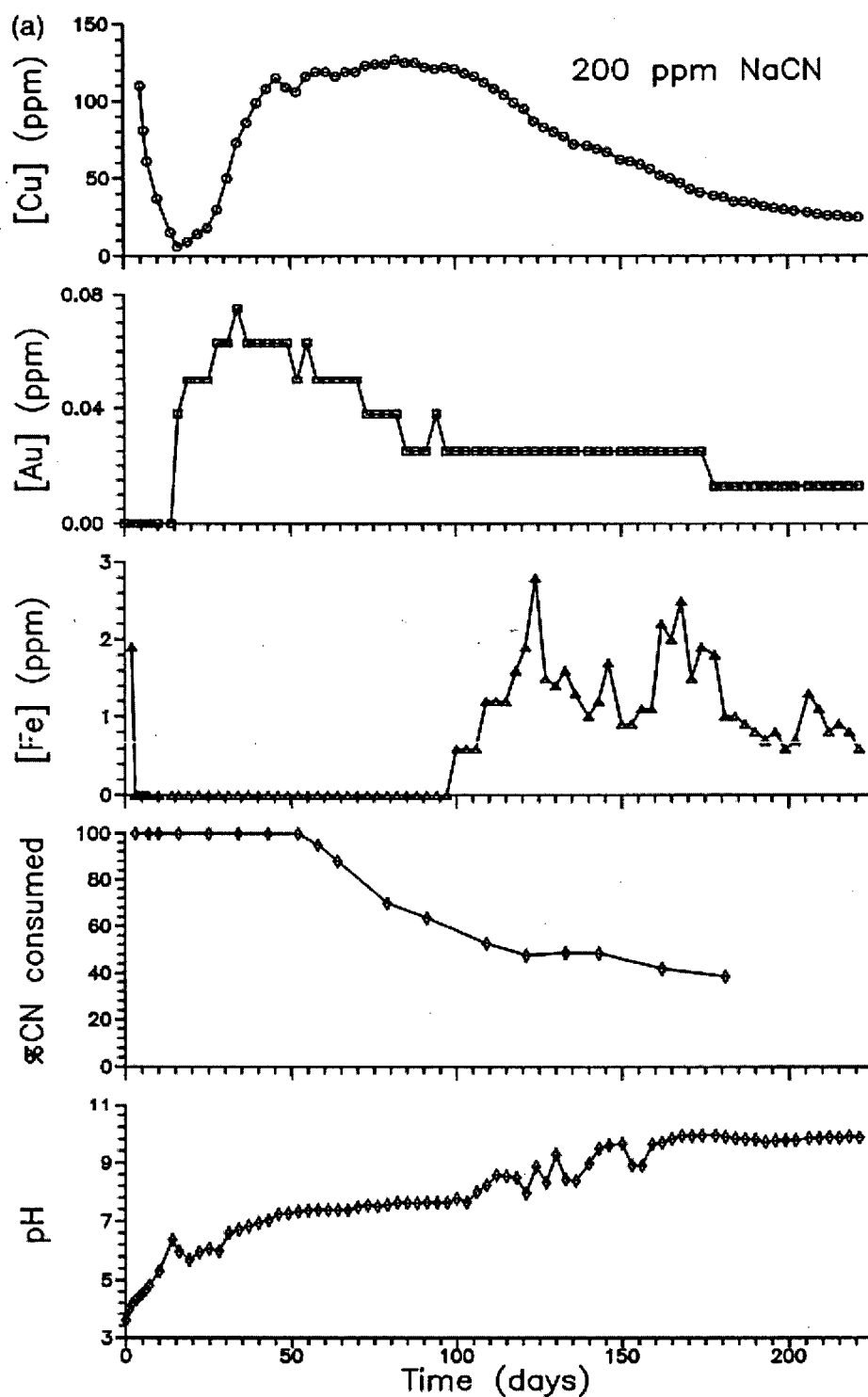
**Figure 2-8 Results of column leaching tests with 200 ppm NaCN, phase I
(Coderre et al., 1999)**
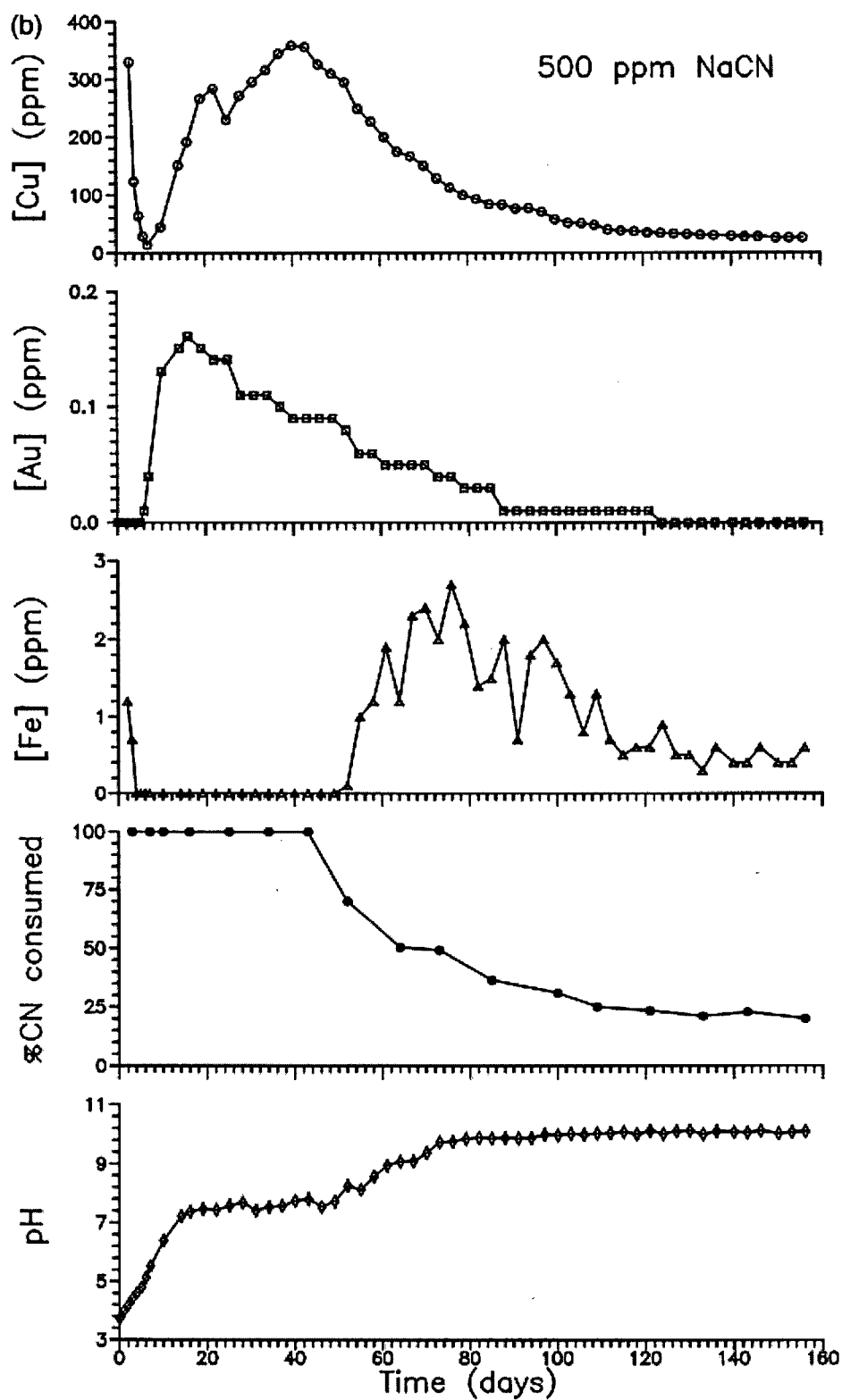
Figure 2-9 Results of column leaching tests with 500 ppm NaCN, phase I (Coderre et al., 1999)
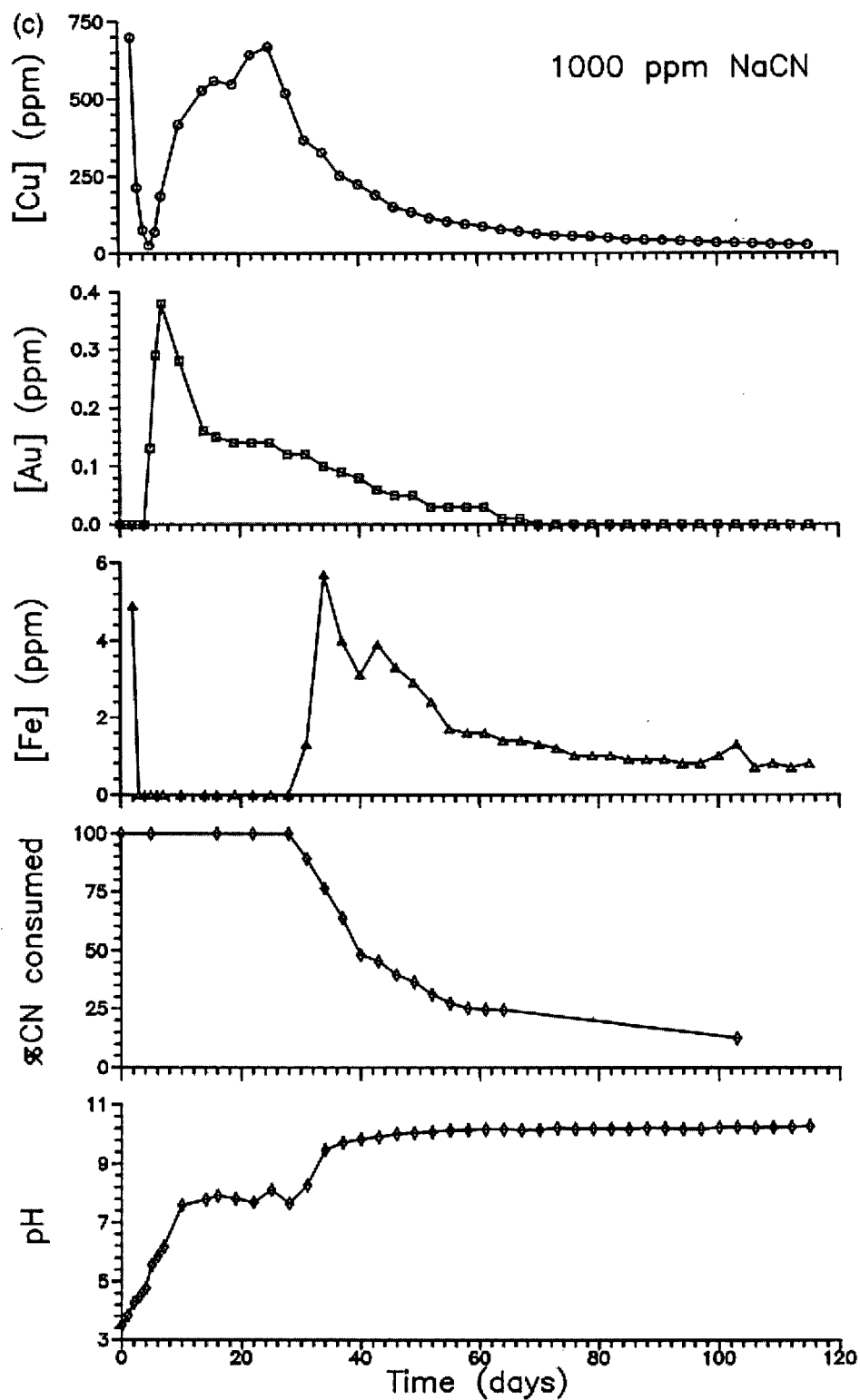
Figure 2-10 Results of column leaching tests with 1000 ppm NaCN, phase I (Coderre et al., 1999)
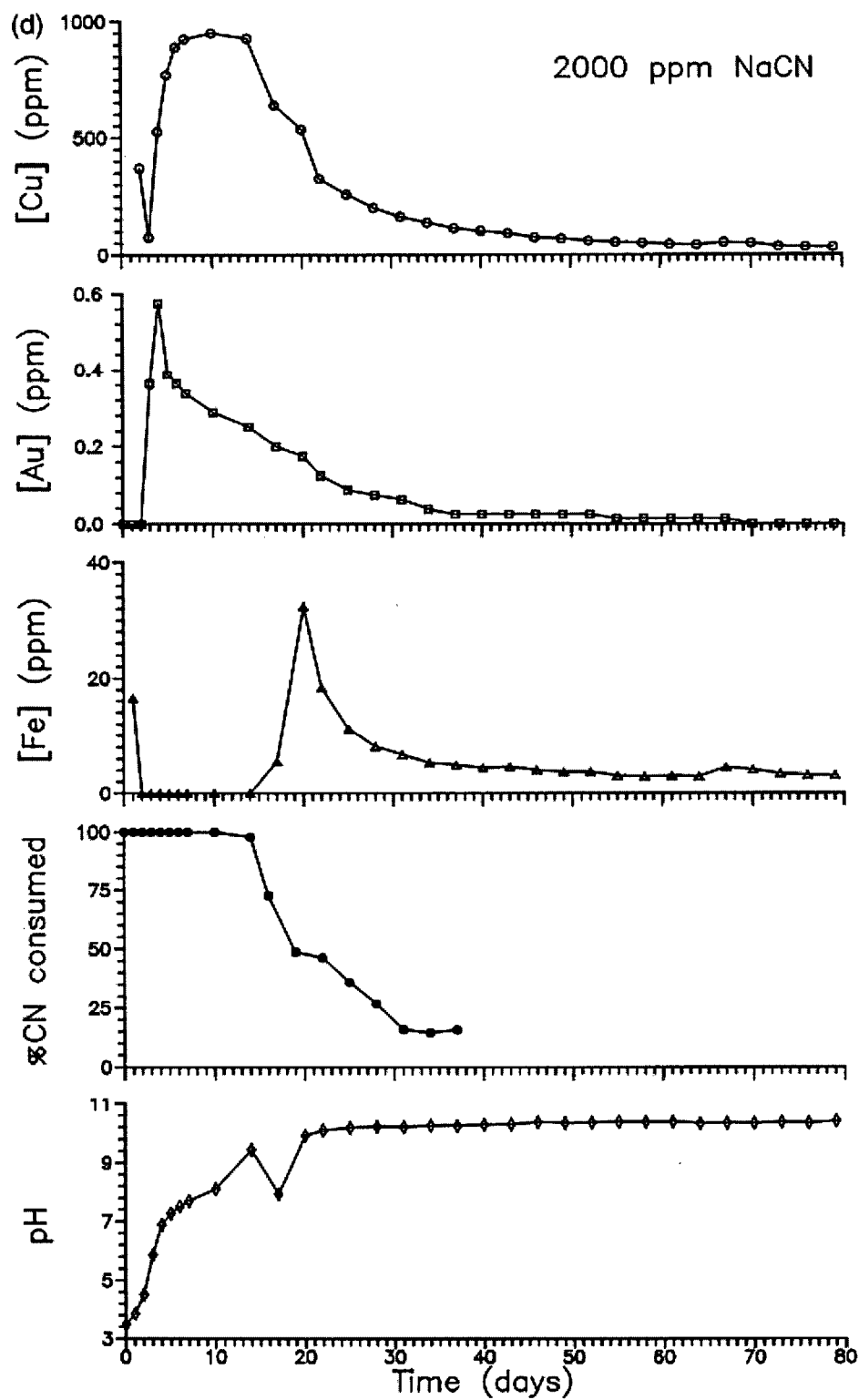
Figure 2-11 Results of column leaching tests with 2000 ppm NaCN, phase I (Coderre et al., 1999)

3 Materials and experimental procedures

A complete description of the physical and mineralogical properties of the ore and also experimental parameters/procedures, which have been used in this project, will be presented in this Chapter.

To obtain the most consistency and also to have comparable results with the phase I of this project, it has been tried to keep experimental parameters for phase II and phase III same as the ones for phase I, as much as it was possible. Although because of some safety issues and also tending to have more accurate results, small changes in some procedures have been applied. The materials and reagents, which have been used throughout this project, are listed in Table 3-1.

3.1 The ore

The ore, which have been used throughout this project, is known as Telfer ore composite 'E', a cupriferous gold ore which were provided by Robert Dunne of Newcrest Co. in phase one. The general mineralogical description of this ore and specific details on copper mineralogy are presented in this section.

3.1.1 General mineralogical description

The mineralogical analysis of the ore, done by Wolfgang Baum at the Pittsburgh Mineral & Environmental Technology laboratories (PMET) shows Telfer ore composite 'E' consists of a siliceous/ quartz-rich, sericitic rock material which contains elevated amounts of pyrite and iron oxide/hydroxides with minor amount of jarositic material. In

addition minor amounts of manganese oxides (about 3 Vol. %) and traces of copper-bearing clay as well as traces of malachite has been reported. The results of the microscopic modal analysis by PMET are presented in the following, Table 3-2.

The x-ray diffraction analysis of the ore performed in the XRD laboratory of the MMAT department of UBC is presented in Figure 3-1.

Table 3-1 List of reagent s used in phase II and III

Chemical reagent/Material	Used in	Manufacturer / Provider
The ore, Telfer composite E	Column Leaching tests	Telfer Mines, Australia
Sodium Cyanide, NaCN	Column Leaching tests Phase II	Anachemia Granular, assay 95% min.
Copper (I) Cyanide, CuCN	Column Leaching tests Phase III	Aldrich Chemical Company Assay 99% min.
Sodium Hydroxide, NaOH	Column Leaching tests Phase II- III	Fisher Chemicals Solid, Pellets
Silver Nitrate, $AgNO_3$	Cyanide Titration	Fisher Chemicals
Formalin Solution	Total Cyanide recovery	Solution 37%
p-Dimethylqminobenzal-rhodanine - Indicator	Cyanide Titration	0.1 g in 100ml Acetone
Methyl red Indicator	Total Cyanide recovery	Baker's Chemical 1 g/L ethanol, 95%
Sulfamic Acid, NH_2SO_3H	Total Cyanide recovery	Fisher Chemicals
Acetate Buffer	Total Cyanide recovery	54 g NaO_2CCH_3 + 100 mL Glacial acetic acid, to 1 L
Sodium Hypochlorate, Bleach	Waste cyanide solution Destruction procedure	Applied chemical technologies Solution 12%

Table 3-2 The results of the microscopic modal analysis of the ore

Mineral	Concentration (Vol. %)
Gangue (with inclusions of iron oxides, pyrite and traces of copper sulfides)	80.00
Iron oxides/hydroxides	8.60
Pyrite	6.52
Manganese oxides	2.33
Covellite/ Chalcocite	2.00
Copper-stained clay	0.50
Native copper (partially oxidized into iron oxides and chalcocite)	0.03
Malachite	0.02
Chalcopyrite	<0.01
Total	100.00
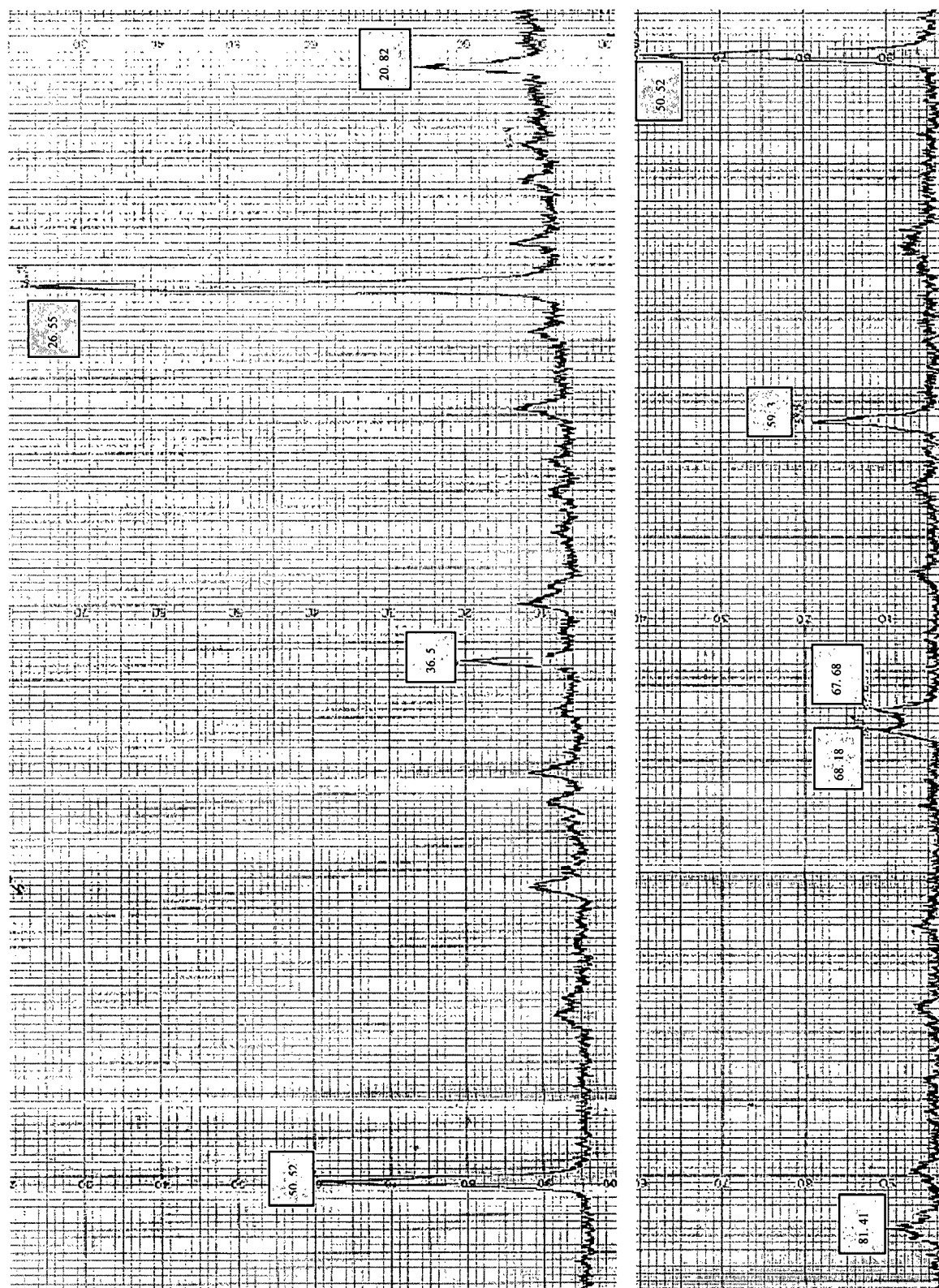
Figure 3-1 X-ray diffraction analysis of Telfer ore composite 'E'

The results of partial elemental analysis of the ore for gold, copper and iron, which have been done several times by different analyzers throughout the phase I to phase III, are given in . The comprehensive data from each analyzer is presented in appendix A. The consistency of these results between different analyzers may present the homogenously sampling and accuracy of those results. The presented results for Au and Fe in Table 3-3 are the mean values of the results in appendix A.

Table 3-3 Partial elemental analysis of the ore

Au (ppm)	Cu (%)	Fe (%)	Ag (ppm)	S_{total} (%)	S^{2-} (%)
0.61	0.258	6.49	0.80	2.58	2.48

3.1.2 Copper mineralogy

According to PMET report the major copper-bearing minerals are secondary copper sulfides (i.e. covellite and lesser amount of chalcocite). Both of these minerals are replacing pyrite (rimming and fracture-related replacement). About 20% of the pyrite particles contain oxidation channels, which are filled with a mixture of copper-bearing iron oxides and ultra fine covellite and chalcocite, which exhibits signs of bacterial oxidation.

The secondary copper sulfides also occur as ultra fine (<20 micron) inclusions within iron oxides/hydroxides. Further, there are minor amounts of relatively coarse-grained covellite (+/- 260 micron in diameter). 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 <10 micron to 200 micron. Finally, there are ultra fine (<20 micron) inclusions of chalcopyrite within the pyrite and traces of malachite. Gold particles were not observed.

It is indicated that the iron oxide/hydroxides contain trace amounts of copper originating from the pyrite and native copper replacement as well as the association with the secondary copper sulfides.

From this result it can be concluded the majority of the copper minerals present will be amenable to cyanide leaching. It is also viable to conclude that a cyanide lixiviant may solubilize some of the copper associated with the iron oxidation minerals. Also it is predictable the cyanicidal characteristics of the copper minerals may increase in a finely crushed heap feed.

Further individual analysis at PMET for the covellite and chalcocite concentrations in the Telfer Composite 'E' samples is presented in Table 3-4. It is pertinent to consider that most of covellite occurring as replacement rims around larger pyrite particles is intimately admixed with fine gangue (which appear to be slime coatings). This mineralogical feature could result in slower cyanide dissolution rates of the covellite.

Table 3-4 The result of individual analysis of the ore by PMET

Minerals	Concentration (Vol. %)
Covellite	1.7
Chalcocite	0.3

3.2 Experimental procedure

The remaining sample from phase I has been used for both phase II and phase III. The original sample had been provided by Telfer mine, which was a 700 kg sample of the Telfer composite 'E' ore. This sample was screened to remove all material not passing one inch. Then the coarse material was crushed in a gyratory crusher to reduce the size to minus one inch. After mixing of both parts, the whole material was coned, quartered, split and placed in plastic bags for storage. The same procedure of sample preparing used for phase II and phase III and eight homogeneous batches of 15 kg sample prepared and used in column leaching tests. The ore density was measured at 2.59 g/cm^3.

3.2.1 Sampling/ Reducing samples to testing size

Different procedures have been used for sampling of the materials depending to the samples sizes. Because of the importance of these procedures, these techniques are described in details in Appendix G. In general the main idea always is to have a homogeneous sample for column leach tests and/or for chemical analysis of the untreated or treated samples.

3.2.2 Particle size distribution (PSD)

Particle size is a very important factor in determining the rate of leaching. To predict the overall reaction rate for a particle assembly we must know:

1. A certain rate at which a particle of a certain size will react.

2. The fraction of particle assembly, which has this certain size.

In the following this size fractions have been represented mathematically through the use of probability density function and cumulative distribution function.

3.2.2.1 Procedure for determining the particle size distribution

A total amount of two kilograms sample, prepared using the quartering method, was treated for collecting the classifier data. First the whole material was screened with a 0.297-millimeter sieve and was divided to two sub-samples of fine and coarse material. Then each sub-sample was screened using a series of sieves in a Ro-Tap Sieve Shaker giving the results in Table 3-5.

Figure 3-2 and Figure 3-3 present the probability density function and cumulative distribution function of this material in discrete forms.

Table 3-5 Results of particle size distribution calculation

D (mm) passing size	Average (mm)	Mass (g)	% Total ore	F	μ	(D/μ-1)²	CV²
0.00	0.02	0	0.00%	0.00%	0.000	1.000	0.008
0.04	0.04	15.57	0.78%	0.78%	0.000	0.991	0.005
0.05	0.05	9.51	0.48%	1.26%	0.002	0.989	0.039
0.05	0.06	77.93	3.91%	5.17%	0.003	0.987	0.043
0.08	0.09	86.47	4.34%	9.51%	0.001	0.982	0.010
0.11	0.13	20.40	1.02%	10.54%	0.002	0.974	0.013
0.15	0.17	25.79	1.30%	11.83%	0.001	0.964	0.008
0.18	0.20	17.05	0.86%	12.69%	0.003	0.956	0.013
0.21	0.25	27.35	1.37%	14.06%	0.006	0.949	0.022
0.30	0.36	46.26	2.32%	16.39%	0.009	0.928	0.023
0.42	0.51	49.04	2.46%	18.85%	0.013	0.900	0.023
0.59	0.72	53.08	2.67%	21.51%	0.020	0.859	0.023
0.85	1.02	55.40	2.78%	24.30%	0.030	0.802	0.023
1.19	1.45	58.54	2.94%	27.24%	0.056	0.729	0.026
1.70	2.53	77.03	3.87%	31.10%	0.122	0.626	0.023
3.36	4.06	96.00	4.82%	35.92%	0.238	0.345	0.015
4.76	5.72	116.94	5.87%	41.80%	0.486	0.173	0.009
6.68	8.10	169.22	8.50%	50.29%	1.056	0.032	0.004
9.51	11.51	259.77	13.04%	63.34%	1.730	0.028	0.035
13.50	20.20	299.54	15.04%	78.38%	4.367	0.432	0.620
26.90		430.57	21.62%	100.00%		5.300	
		1991.46	**1.00**		**8.146**		**0.983**
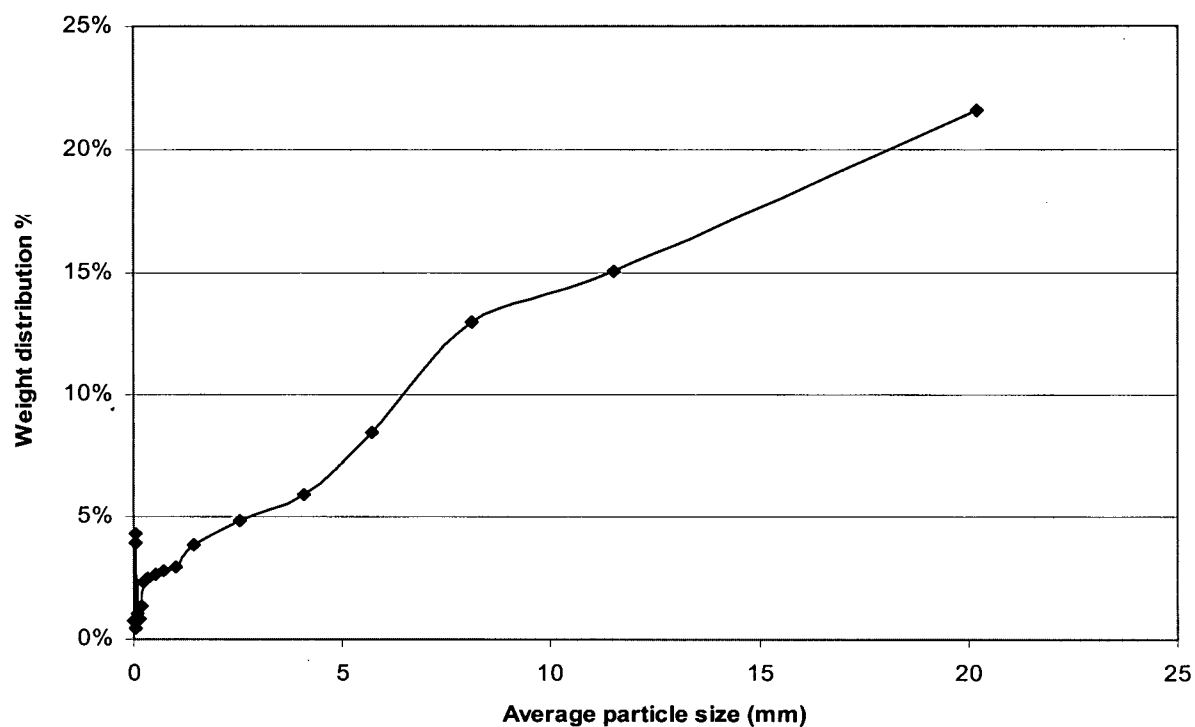
Figure 3-2 The discrete probability density function
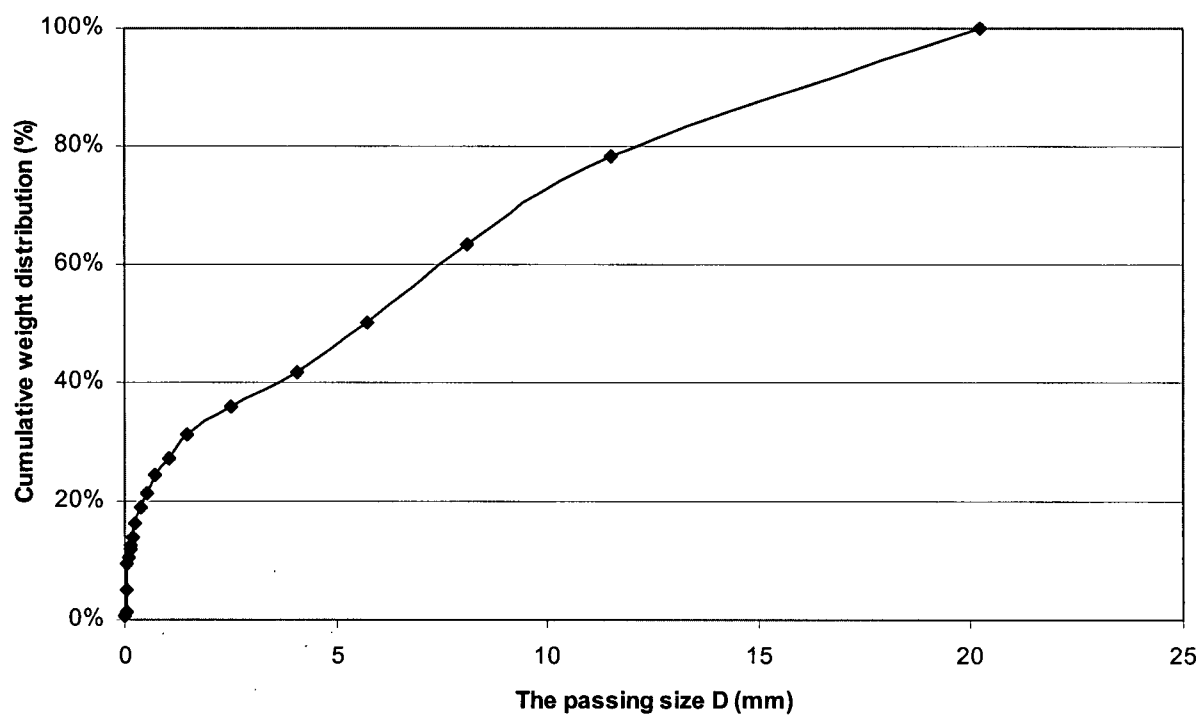
Figure 3-3 The discrete cumulative distribution function

In order to account for the distribution of particle sizes in the analysis of leaching experiments, it is convenient to work with one of the common normalized particle size distribution functions, such as the Gates-Gaudin-Schuhmann (GGS) distribution.

Table 3-6 shows the details for determining the parameter **m** from the coefficient of variation CV^2 of the particle size distribution. The normalizing size **D*** can be calculated from the parameter **m** and the mean or average particle size μ. Then the dimensionless particle size ζ can be calculated easily from the normalizing size and the arithmetic average size **D**.

Table 3-6 Calculation of the normalizing size D*

$CV^2 = 1/(m(m+2))$	m	$D^* = \mu(m+1)/m$
0.983	0.4203423	27.526
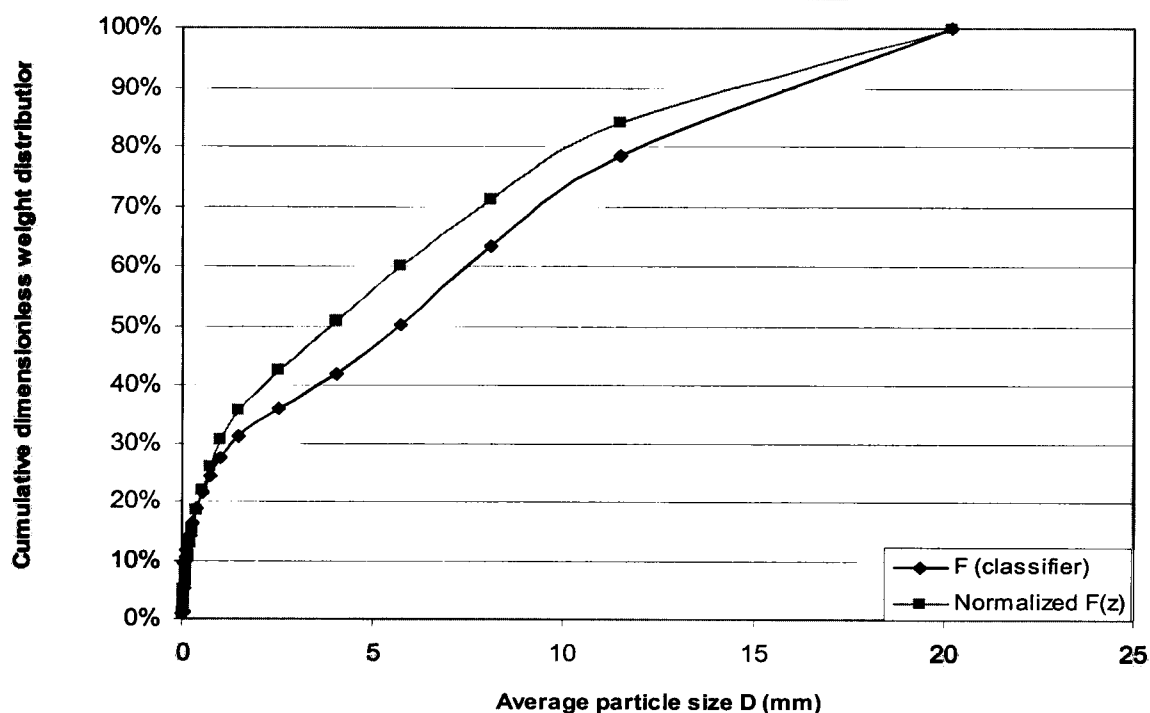
Figure 3-4 The comparison of the GGS cumulative distribution function with the experimental data cumulative distribution

Table 3-7 Calculation of the GGS cumulative distribution function

D average	$\zeta = D/D^*$	$f(\zeta) = m\zeta^{m-1}$	$F(\zeta) = \zeta^m$	Normalized $F_{GGS}(\zeta)$
0.019	0.001	28.569	0.047	0.009
0.042	0.002	18.164	0.065	0.021
0.049	0.002	16.497	0.070	0.033
0.064	0.002	14.131	0.078	0.048
0.091	0.003	11.560	0.090	0.064
0.128	0.005	9.455	0.105	0.084
0.165	0.006	8.161	0.116	0.105
0.195	0.007	7.408	0.125	0.128
0.254	0.009	6.363	0.139	0.154
0.357	0.013	5.217	0.161	0.183
0.506	0.018	4.265	0.186	0.218
0.722	0.026	3.469	0.216	0.257
1.020	0.037	2.839	0.250	0.303
1.445	0.052	2.320	0.290	0.357
2.530	0.092	1.677	0.367	0.424
4.060	0.147	1.275	0.447	0.506
5.720	0.208	1.045	0.517	0.601
8.095	0.294	0.854	0.598	0.711
11.505	0.418	0.697	0.693	0.839
20.200	0.734	0.503	0.878	1.000
			5.439	

3.2.3   Column leaching tests

Figure 3-5 The columns setup for phase II of the column leaching experiments

3.2.3.1   Introduction

A number of column leach tests, if run correctly, can generate sufficient data on the leaching characteristics of an ore to allow prediction of the extraction/time curves for different operating scenarios. The maximum particle size of the ore to be used in a column tests will influence both the weight of ore in the column and the time required to complete the column test. Larger particle sizes require larger sample weights and longer test times. Initial test work is most conveniently carried out on samples with a top size of

0.75 to 2 inches. If it is anticipated that the ore will be crushed before leaching then the particle sizes used in the column test should bracket the anticipated crush size. As the diameter of the test column should be at least 5 times (and preferably 6 or more times) the largest ore particle in the column, the test column should be 4 to 12 inches in diameter. The height of the column should be at least 5 times the column diameter but increasing the height to equal the anticipated height of the lift in the commercial heap is advisable.

3.2.3.2 Columns specifications

The purpose of this set of experiments was to collect kinetic information on the ore, under different influent concentrations. Four column tests have been run in each phase of these experiments. The 180 cm columns were made of rigid transparent acrylic with an inner diameter of 8.9 cm and an outer diameter of 10 cm. These columns were loaded with the 15.0 ± 0.05 kg Telfer composite 'E' ore, which have previously prepared as described in section 1.2.1 and Appendix G. Some glass wool was placed at the bottom of the column before loading, to prevent any losses of ore during the loading process and also to prevent clogging the effluent nozzle by fine materials. Also for having a homogenous spraying of influent solution, some other glass wool was placed on the top of the ore in each column.

3.2.3.3 The pumping system

To ensure the same irrigation rate for all the columns in each phase, a Masterflex peristaltic pump with four heads, Masterflex L/S, attached to it was used to feed the columns. The Irrigation rate in the range of 0.75- 0.95 mL/min was selected to be

comparable with the experiment characteristics of phase I. To avoid any cyanide hydrolyzes to hydrogen cyanide HCN, all the cyanide solutions were prepared and kept in a solution of sodium hydroxide with a pH of 10.5.

Tygon size 14, which is a thermoplastic, PVC-based material with plasticizer and can provide a flow rate in the range of 0.21- 130 mL/min was used for all the tubing in setting up the columns.

Table 3-8 The pumping system specifications

Pump	Type	Cat. No.	Flow rate* (ml/min)	Specification a	Specification b
	Variable speed	MR-07553-80	0.06 to 380	Speed range 1-100 (rpm)	Detached controller
Pump Head	Standard pump head	MR-07014-20	0.21-130	Thick wall/ CRS Rotor	Clear polycarbonate housing
Drive	Standard drive system	MR-07553-80	0.21 to 21	Speed range 1-100 (rpm)	No. of heads accepted 4
Tubing	Tygon	MR-06409-14	0.21 to 21	Inside diameter 1.6 (mm)	Maximum vacuum suction lift 660 mm Hg

3.2.3.4 Influent solution for phase II

In both phases II and III the stock solutions were prepared weakly to minimize the decreasing of the cyanide concentration due to destruction under radiation. The details of preparing the stock solutions are discussed later in this section, Figure 3-6. To reduce the effect of the radiation, the stock solution buckets were covered with aluminum shields.

In phase II the columns were leached with sodium cyanide solutions with four different nominal concentrations exactly same as what had been done in phase one.

prepare approximately 15 kg de-ionized water (solution A)

Prepare small volume of concentrated sodium hydroxide solution pH>12 (solution B)

Adjust the pH of solution A to 11.5 using solution B (solution C)

Take approximately one litter of solution C into a 2 liter erlyne (Solution D)

Add precisely appropriate amount of solid sodium cyanide to solution D, completely disolve it 2 gr NaCN for 200 ppm NaCN solution, 5 gr NaCN for 500 ppm NaCN solution 10 gr NaCN for 1000 ppm NaCN sol. and 20 gr NaCN for 2000 gr NaCN Sol. (solution E)

noting the weigh of empty bucket, Pour the solution E throughly into a 20 liter bucket, following the rinsing the erlyne completely with solution C (solution F)

Add enough amount of solution C to solution F to the final weigh of 10 kg Sodium Cyanide Solution, pH 11.5

Figure 3-6 The procedure for preparing the bulk influent solutions for the phase II

This time before starting the leaching experiment with cyanide, the columns were thoroughly pre-rinsed with de-ionized water to remove all the water-soluble copper minerals from the ore. The purpose of this was to eliminate the effects of such a copper minerals on the collected data during the main leaching processes. This pre-rinsing period

has been continued for tow weeks. Then for adjusting/ stabilizing the pH, the columns were rinsed with a 15 kg solution of sodium hydroxide with a pH of 11.5. The irrigation rate of all these process was 0.95 ml/min. The concentration of copper in the effluent solutions of all the columns dropped to less than 80 ppm.

All the bulk cyanide solutions were prepared using the de-ionized water, pH adjusted on 11.5 by sodium hydroxide before adding the sodium cyanide.

The complete characteristics of the column leaching tests in phase II have been presented in Table 3-9. As it can be seen in this table, because of using only one pump with four head for feeding the columns, the irrigation rates of the influent solutions in all of the columns have been the same, although the effluent solutions have had different flow rates, even in each column.

Table 3-9 Main characteristics of the column leaching tests in phase II

Columns	Column 1	Column 2	Column 3	Column 4
Leaching Solution	Cyanide Solution	Cyanide Solution	Cyanide Solution	Cyanide Solution
Nominal [NaCN] (ppm))	200	500	1000	2000
Nominal free [CN⁻] (ppm)	106	265	531	1062
Ore weight (kg) ± 0.05	15.0	15.0	15.0	15.0
Ore High (cm)	145	144	147	144
pH of the influent solution	11.5	11.5	11.5	11.5
Irrigation rate of the influent sol. (ml/min)	0.95	0.95	0.95	0.95
Irrigation rate of the effluent sol. (ml/min)	0.75-1.05	0.75-1.05	0.75-1.05	0.75-1.05
Flux (L/m².hr)	9.16	9.16	9.16	9.16

3.2.3.5 Influent solution for phase III

Figure 3-7 The columns setup for phase III of the column leaching experiments

The leaching experiments in this phase also were started with a pre-rinsing period with de-ionized water prior to the beginning of the main leaching experiment with tricyanocuprate complex solution. The purpose of this procedure was also to remove all the water-soluble copper minerals from the ore by thoroughly pre-rinsing the columns with de-ionized water. This process was continued for a period of three weeks. Then each

column was rinsed with a 15 kg solution of sodium hydroxide with a pH of 11.5 at the same irrigation rate of 0.95 ml/min to adjust/ stabilize the pH. The concentration of copper in the effluent solutions of almost all the columns dropped to less than 50 ppm. The leaching tests were started after these processes.

In phase III the columns were leached with a solution of copper (I) cyanide complex. According to what was discussed in chapter two of this thesis, the copper (I) cyanide complexes have the ability to leach gold. Based on experimental evidences, tricyanocuprate complex, $Cu(CN)_3{}^{2-}$, is the predominant complex among three copper (I) cyanide complexes. To have the appropriate concentration of the tricyanocuprate complex in the influent solution, for having a comparable results to phases one and two, it was tried to provide the same amount of free cyanide ion $(CN)^-$ as the driving force for leaching reaction, which here it can be called the equivalent free cyanide. To do so the following equations have been considered.

$$Au^0 + \tfrac{1}{4} O_2 + H^+ + 2\, Cu(CN)_3{}^{2-} \quad Au(CN)_2{}^- + Cu(CN)_2{}^- + \tfrac{1}{2}H_2O \qquad \textbf{Equation 3-1}$$

$$Cu(CN)_3{}^{2-} \quad Cu(CN)_2{}^- + CN^- \qquad \textbf{Equation 3-2}$$
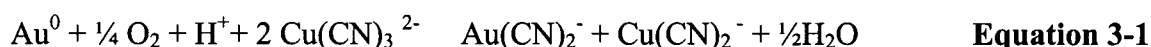
Table 3-10 describes the calculations for determining the amount of NaCN(s) and CuCN(s), which had to be used to prepare the tricyanocuprate complex solutions with the free cyanide ion concentrations equivalent to that for the previous phases of this project.

In this phase, pH of the solution was adjusted on 11.0 by sodium hydroxide before adding the copper (I) cyanide and sodium cyanide. Because of the difficulty of dissolving copper (I) cyanide in water, especially for columns 7 and 8, the procedure in

Figure 3-8 was used to prepare the bulk solutions of tricyanocuprate complex as stock influent solutions for phase III.

Table 3-10 Calculations for determining the amount of copper (I) cyanide and sodium cyanide, needed to prepare the tricyanocuprate complex solution with the equivalent free cyanide ion same as that for phase II.

Column numbers in phase II	Nominal [NaCN] (ppm)	Total NaCN in 10kg Solution (gr)	Total NaCN, CN- in 10kg (mol)	The equivalent Column number in phase 3	Total CN- for $Cu(CN)_3^{2-}$ to provide the equivalent free CN- in 10kg solution (mol)	The portion (2/3) of CN- which is provided by NaCN (mol)	The portion (1/3) of CN- which is provided by CuCN (mol)	Total NaCN needed for 10kg solution in phase 3 (gr)	Total CuCN needed for 10kg solution in phase 3 (gr)
	A	B	C	D	E	F	G	H	I
	A	$A*10^4/10^6$	$49.00721 * B$	D	$3 * C$	$2/3 * C$	$1/3 * C$	$49.00721 * F$	$89.5634 * H$
1	200	2	0.04	5	0.12	0.08	0.04	4	3.66
2	500	5	0.10	6	0.31	0.20	0.10	10	9.14
3	1000	10	0.20	7	0.61	0.41	0.20	20	18.28
4	2000	20	0.41	8	1.22	0.82	0.41	40	36.55

```
┌─────────────────────────────────────────────────────────────────────────────┐
│              prepare approximately 15 kg de-ionized water (solution A)        │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│            Prepare small volume of concentrated sodium hydroxide solution     │
│                             pH>12 (solution B)                                │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│                       Adjust the pH of solution A to 11.0                     │
│                              using solution B                                 │
│                               (solution C)                                    │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│      Take approximately one litter of solution A into a 2 liter erlyne (Solution D) │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│  Add precisely appropriate amount of solid sodium cyanide to solution D, and disolve it well │
│      4 gr NaCN for 200 ppm Eq. NaCN sol., 10 gr NaCN for 500 ppm Eq. NaCN sol. │
│   20 gr NaCN for 1000 ppm Eq. NaCN sol. and 40 gr NaCN for 2000 gr Eq. NaCN Sol. │
│                               (solution E)                                    │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│                              Heat the solution E                              │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│ Add precisely appropriate amount of solid copper cyanide to solution E, and completely disolve it │
│     3.65 gr CuCN for 200 ppm Eq. NaCN sol., 9.14 gr CuCN for 500 ppm Eq. NaCN sol. │
│  18.28 gr CuCN for 1000 ppm Eq. NaCN sol. and 36.55 gr CuCN for 2000 gr Eq. NaCN Sol. │
│                               (Solution F)                                    │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│                       noting the weigh of empty bucket                        │
│  Pour the solution F throughly into a 20 litter bucket, following the rinsing the erlyne │
│                         throughly with solution C                             │
│                               (solution G)                                    │
└─────────────────────────────────────────────────────────────────────────────┘
                                      │
┌─────────────────────────────────────────────────────────────────────────────┐
│   Add enough amount of solution C to solution G to the final weigh of 10 kg   │
│                       Tricyanocuprate Solution, pH 11                         │
└─────────────────────────────────────────────────────────────────────────────┘
```

Figure 3-8 The procedure for preparing the bulk influent solutions for the phase III

Table 3-11 presents main characteristics of the column leaching tests in phase III. Same as what have been seen for phase II, the irrigation rates of the influent solutions for all of the columns had the same value, but the flow rate of the effluent solutions even in each columns showed the daily variation.

Table 3-11 Main characteristics of the column leaching tests in phase III

Columns	Column 6	Column 7	Column 8	Column 9
Leaching Solution	$Cu(CN)_3^{2-}$	$Cu(CN)_3^{2-}$	$Cu(CN)_3^{2-}$	$Cu(CN)_3^{2-}$
Nominal [NaCN] (ppm))	400	1000	20000	40000
Nominal [CuCN] (ppm))	365	914	1828	3655
Equivalent free [CN-] (ppm)	106	265	531	1062
Ore weight (kg) ± 0.05	15.0	15.0	15.0	15.0
Ore High (cm)	143	146	144	147
pH of the influent solution	11.5	11.5	11.5	11.5
Irrigation rate of the influent sol. (ml/min)	0.95	0.95	0.95	0.95
Flow rate of the effluent sol. (ml/min)	0.75-1.05	0.75-1.05	0.75-1.05	0.75-1.05
Flux $(L/m^2.hr)$	9.16	9.16	9.16	9.16

3.2.3.6 Sampling/ analyses procedure

The effluent solutions were led to Erlenmeyer flasks that were placed at the bottom of each column, which were kept inside another 20 litter buckets to prevent any unpredicted spillage. The sampling was done daily at the beginning of the leaching tests, but when no considerable changes in concentration of the elements were noticed, the frequency of the sampling was reduced.

Immediately prior to sampling, the pregnant solution in each flask was stirred well for about five minutes to have a homogenous solution. Then the solution samples of 120 mL were removed from the effluent flasks and kept in sealed plastic bottles. After each sampling the rest of the effluent solutions were transferred from the flask to a waste solution bucket, for a subsequent cyanide waste treatment process. The samples then were stored in dark boxes in a cold place, to retard oxidation of cyanide and disintegration of the different cyanide complexes.

The pH of the samples were measured immediately after the sampling, using a conventional pH probe with a precision of 0.01. Ron Williams at Chem Met Consultants Inc. measured gold concentrations, by solid fire assay followed by atomic absorption spectrometry. Copper and iron concentrations were measured using atomic absorption spectrometry (AAS) to a precision of 0.01 ppm. When necessary, samples were diluted with a sodium cyanide solution with pH of 11.5.

The free cyanide concentrations of the samples were measured by silver nitrate titration using a precise automatic titrator. A potentiometric titration method was used to measure the thiocyanate concentration of the samples. Because of the importance of these techniques, more details are discussed about them in the following section.

3.2.3.7 Titration of free cyanide

A solution of silver nitrate with 0.025 M concentration is used as the titrant. The indicator, which is used in this method, is a solution of p-Dimethylaminobenzal-Rhodanine with a concentration of 0.1 g in 100 ml Acetone.

Depending to the concentration of free cyanide, 10 to 25 ml of the each solution is taken as the sample and is diluted with adding 50 ml de-ionized water in a 125 ml flask. Then three drops of indicator are added into the solution, and well mixed. This solution then is titrated with silver nitrate using an auto-burette. The end point in this condition is when the color changes from orange to pink. At this time, the volume of consumed silver nitrate solution is recorded and the free cyanide is calculated using the following formula.

$$\text{Free Cyanide (g/l)} = \frac{V_{AgNO3} * C_{AgNO3} * 26.018 * 2}{V_{sample}}$$

3.2.3.8 Potentiometric titration for thiocyanate

This method involves titrating the sample with silver nitrate solution while observing the potential difference between a double junction reference electrode and a silver electrode. When titrating thiocyanate, the cyanide is masked with a formalin solution (37%).

First a solution of silver nitrate with a concentration of 0.0250 M is prepared. The concentration of silver nitrate can be tested by titrating it with a sodium chloride solution. The automatic titrator has to be wash out completely with de-ionized water. In next step, the titrator pipette is filled with silver nitrate solution. In next step, 10 ml of the cyanide/ thiocyanate solution is taken as the sample and is placed in a 250 ml beaker, diluted to

about 125 ml with de-ionized water and treated with 5 ml of formalin to mask the cyanide. The mixture is stirred and allowed to stand for 10 minutes. Nitric acid (6 M, 5 ml) is added to give a total volume of 135 ml. Then two electrodes and the titrator burette are placed in the beaker and the initial potential of the solution is recorded. The silver nitrate is added to the solution slowly and the solution is mixed well with a magnetic stirrer, at the same time the voltage and the volume of silver nitrated are recorded frequently. When the potential begins to increase more rapidly, silver nitrate is added with a lower rate. With passing the sharp increase of the potential, experiment is done. Now a plot from the recorded data can be provided. The point, which has the maximum dE/dV value, is determining the end point, which E and V, respectively are presenting the solution potential and the volume of silver nitrate solution. Then the thiocyanate concentration is calculated using the following formula (Atkinson et al, 1982).

$$SCN^-(g/l) = \frac{V_{AgNO3} * C_{AgNO3} * 58.08}{V_{sample}}$$

3.2.4 Cyanide waste treatment

After preparing 120 mL samples, the rest of the effluent solutions should be treated to be safe enough for throwing away. For this purpose, all the cyanide in effluent solutions was oxidized to cyanate OCN^- and all the heavy metal ions (in our case copper ions) were precipitated as metal oxides. To do this excess amount of sodium hypochlorite solution (Bleach 12%) was used as the oxidizer.

$$OCl^- + H_2O + 2e^- \quad Cl^- + 2\ OH^-$$

$$CN^- + 2\ OH^- \quad OCN^- + H_2O + 2e^-$$

OVERALL: $\qquad\qquad CN^- + OCl^- \quad Cl^- + OCN^-$
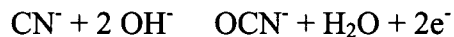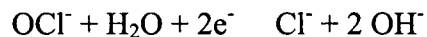
Therefore at least one mole OCl⁻ is needed for destruction of every mole of CN⁻. Table 3-12 shows the calculations for determining the amount of sodium hypochlorite solution, which was used for every one litter of each influent solution.

Cyanide waste solutions were stored in 20 litter buckets and inside the fume hood, before treating the waste solutions. The waste treatment procedures were done weekly also inside the fume hood. The oxidizer solution always should be added to the cyanide waste solutions very slowly while the whole solution was stirring. These solutions usually left to be well mixed over the night. In next step, after making sure that there is no cyanide left in the solutions, the pH of the solutions were adjusted to around 7.0, and then they were left quiet for another day for the metal oxides to precipitate and settle down. After that the solid and liquid parts were separated. The liquid part was safe to be thrown away and the solid phase was collected to be sent for subsequent heavy metals waste treatment.

Table 3-12 Calculations for determining the amount of required 12% sodium hypochlorite solution to oxidize the waste cyanide solutions

Column	1	2	3	4	5	6	7	8
Nominal [NaCN] ppm	200	500	1000	2000	400	1000	2000	4000
Nominal [CuCN] ppm	0	0	0	0	365	914	1828	3655
[CN] from NaCN mol/L	0.0041	0.0102	0.0204	0.0408	0.0082	0.0204	0.0408	0.0816
[CN] from CuCN mol/L	0	0	0	0	0.0041	0.0102	0.0204	0.0408
Total [CN] mol/L	0.0041	0.0102	0.0204	0.0408	0.0122	0.0306	0.0612	0.1224
Moles of OCl to oxidize each mole of CN	0.0041	0.0102	0.0204	0.0408	0.0122	0.0306	0.0612	0.1224
Using Double to ensure complete oxidation	0.0082	0.0204	0.0408	0.0816	0.0245	0.0612	0.1224	0.2449
Required bleach mol/L of CN solution	0.0082	0.0204	0.0408	0.0816	0.0245	0.0612	0.1224	0.2449
Noting bleach was 12% pure	0.0680	0.1700	0.3401	0.6802	0.2040	0.5102	1.0203	2.0405
Required bleach gr/L of CN solution	5.1	12.8	25.7	51.3	15.4	38.5	77.0	154.0

3.2.5 The treated ore

The treated ore contains valuable information for the head assay analysis, and also possible good information on the interactions of the leach solution with the ore at different heights of the columns.

For providing these data, the whole leached residual ore from each column was carefully emptied onto a brown paper, and was allowed to dry for 24 hours. The dried ore was then divided to five equal sections, approximately 3 kg each. Then each part was crushed and then well grounded using rod mills. Because the samples were changed to very fine powder, the following procedure was used to provide a small portion, 100 gr, of sample for gold and copper assays.

The whole powder was placed on a $1.1 \times 1.1 \, m^2$ brown paper on a flat surface. Then using a roller, the sample flattened to the shape of a rectangular. After that, the sample was mixed by lifting the opposite corner of the sheet. After repeating these steps several times, a flat surface of the powder was made again. Then using a spatula small portions of the sample were picked up, randomly form deferent places of the rectangular. Some photos of step by step of this procedure are presented in Figure 3-9.

The provided 100-gram samples from each section were sent for gold analysis by fire assay and copper analysis by strong HNO_3/ ClO_4 acid digestion.
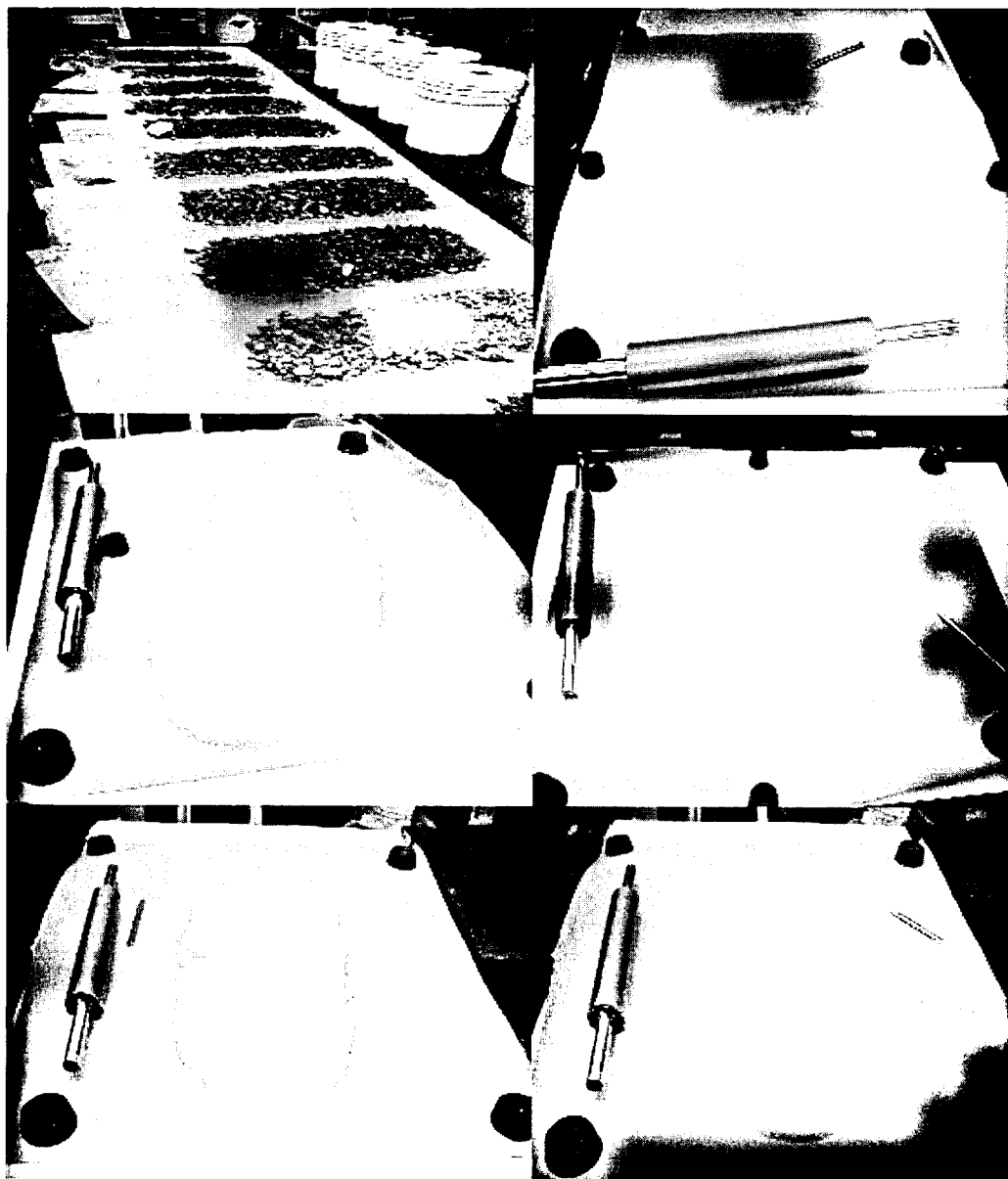
Figure 3-9 Drying and sampling of the leached residue materials

3.2.6 Safety issues

Because of the toxicity of the cyanide salts, taking adequate precaution on working with these chemicals and being familiar with safety practices are necessary.

Health hazards and safety precautions on this subject have been reviewed in details in Appendix B .The procedures, which experienced for avoiding any cyanide related hazard are discussed here.

All cyanides were stored in tightly closed, airtight containers fitted with covers. These containers were identified clearly as containing hazardous material. Any contact with acids or acid salts was carefully avoided, to prevent immediate generating of highly poisonous gaseous hydro cyanic acid. The laboratory in which these experiments have been done, always were kept well ventilated. All the tubing used for pumping the cyanide solutions to the leaching columns were suitably protected against leakage of those solutions.

For preparing sodium cyanide solutions, caustic was always added to the water before dissolving solid sodium cyanide. The objective was to obtain a pH of 11 or even higher and thereby create the protective alkalinity necessary to avoid hydrolysis and HCN evolution.

In case of solid cyanide spillage, it was swept up immediately with a brush and because it had become dirty and unusable, it was destroyed by an oxidation destruction process. The area was washed thoroughly with alkaline water. Liquid spills were neutralized with hypochlorite.

An automatic HCN alarm equipment was used occasionally. This equipment can continuously monitor the mill atmosphere and to provide an alarm output if the level of HCN exceeds a preset value.

The pH of the influent and effluent solutions was frequently measured with a standard pH electrode.

First aid supplies have been always located in the cyanide laboratory, and have been immediately accessible at all times.

4 Experimental results and discussion – phase II

4.1 Pre–rinsing period

The first effluent solution emerged 30 to 32 hours after starting the column experiments. Very high concentrations of copper in the effluent solutions during the first days of rinsing with de–ionized water were noticed from all of the columns. In Figure 4-1, time zero is the time of the first solution from each column. As was expected, the concentration curves all show very similar behavior for all four columns. At the end of the first week, the copper concentration dropped significantly to 105–215 ppm and copper dissolution continued with a gradual decrease in the dissolution rate. This process was continued for 21 to 23 days and at the end of this period, the effluent solutions had
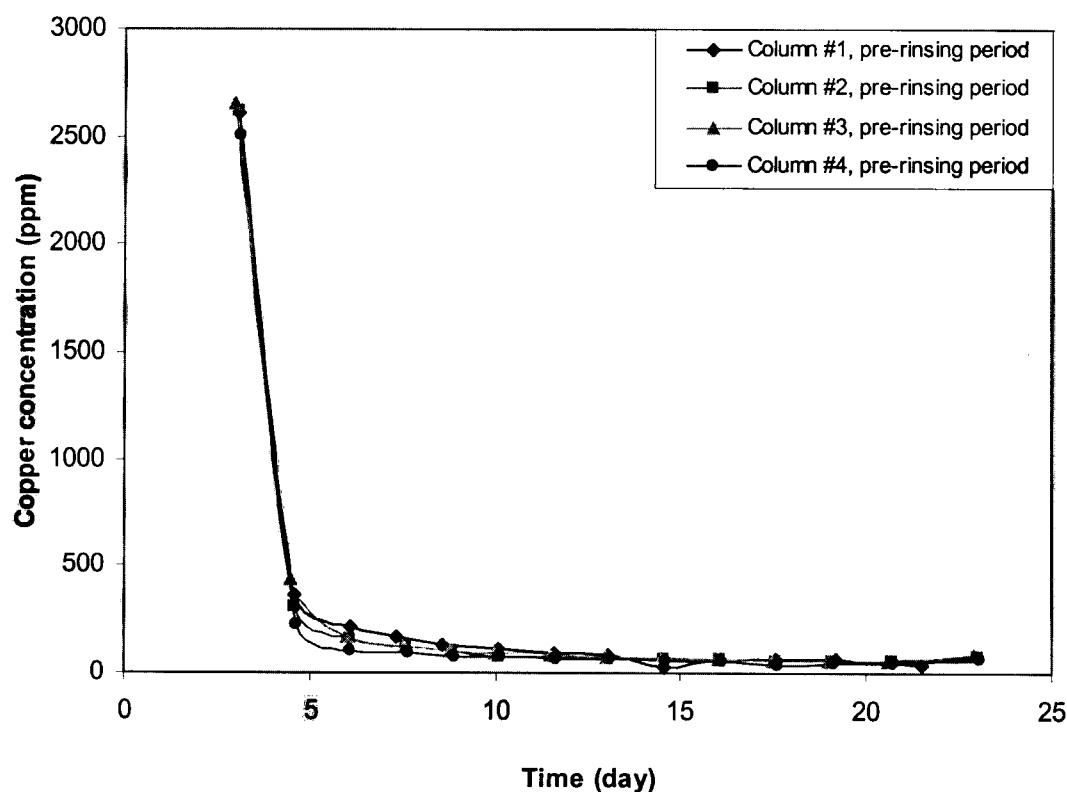
Figure 4-1 Copper concentration in pre–rinsing period

copper concentrations between 41 and 60 ppm.

As shown in Figure 4-2, the significant observation in this period was that 80 to 87 percent of the total water soluble copper was extracted in the first five days of the rinsing period. After five days, water-soluble copper minerals that were partly locked within other insoluble minerals, and other copper minerals with lower solubility in water, were dissolved. In any case, as shown in Figure 4-3, nearly 25 percent of the total copper in each column was removed with plain water. It bears notice that the extraction calculations were done based on the head copper grade, which was determined separately for each column at the end of the cyanide leaching process.
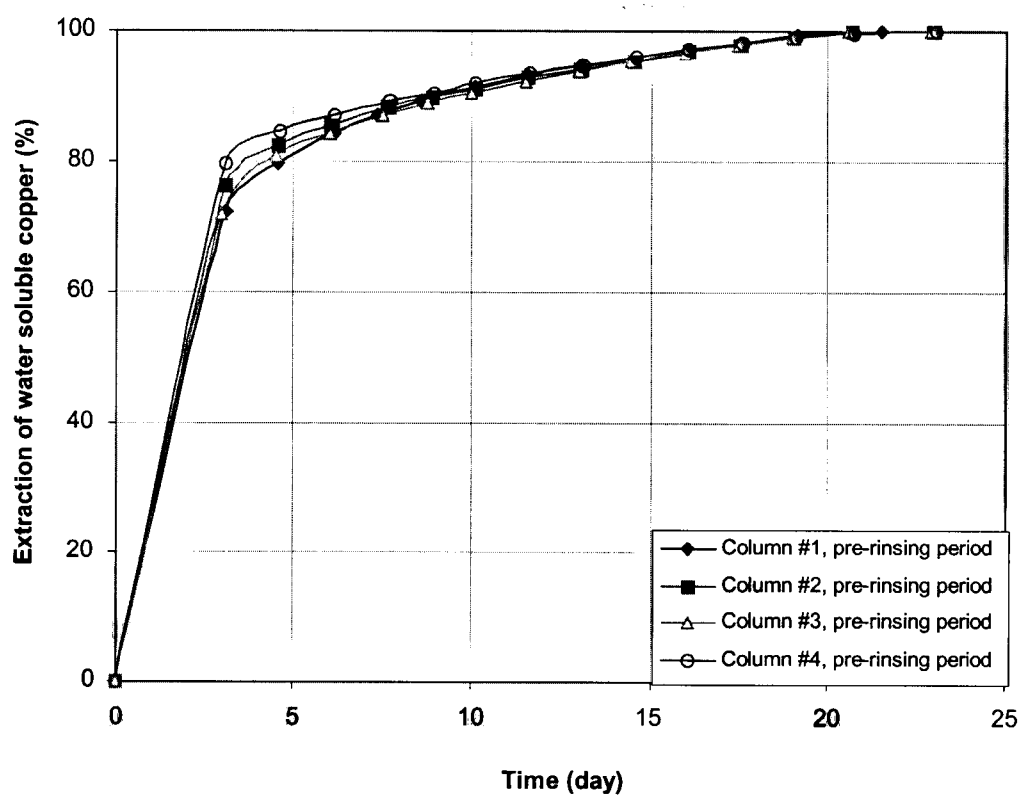
Figure 4-2 Extraction of water–soluble copper (%)

Although the influent solutions were pumped to the columns at the same flow rate, different flow rates were measured for the effluent solutions. This could have been due to a variety of factors which can affect the behavior of solution in a column, including influent nozzle characteristics, sample concentration in the column, sample size distribution, sample permeability, and the chemical nature of solutes in different sections of the column.
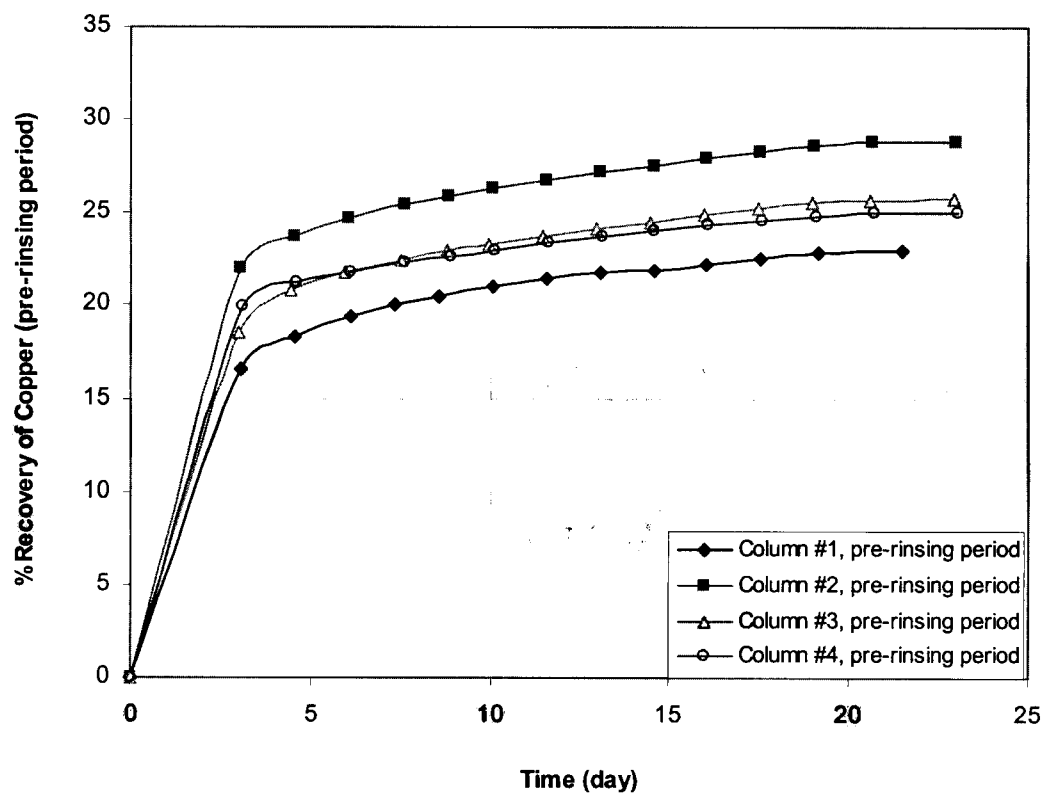
Figure 4-3 Extraction of copper, pre–rinsing period (%)

4.2 Cyanidation period

4.2.1 Presentation of the copper behavior

Effluent copper concentrations during cyanidation are presented in Figure 4-4. Because of the rapid changes in the behavior of copper during the first few days of leaching, an enlarged plot of this stage is presented in Figure 4-5, using a logarithmic scale for the time axis.

Three different leaching behaviors of copper are identified from the concentration curves. As shown in Figure 4-5, the first stage begins with a copper concentration between 63 and 90 ppm for different columns, which rapidly decreases to approximately 20 ppm but only for columns 1, 2 and 3, and not for column 4. However, as shown in Table 4-1, the duration of this stage differs between columns, as follows:

The duration of stage one for Column 1 > Column 2 > Column 3 > Column 4

Table 4-1 General observations of the first stage of copper concentration curves

Column Number	1	2	3	4
Nominal [NaCN] (ppm)	200	500	1000	2000
[Cu] (ppm) at first sampling (after 40 hrs)	73	90	77	63
[Cu] (ppm) at beginning of labile copper sulfide leaching	17	20	19	63
Time at which labile copper sulfide leaching begins (days)	9	4.2	2.7	<1.7
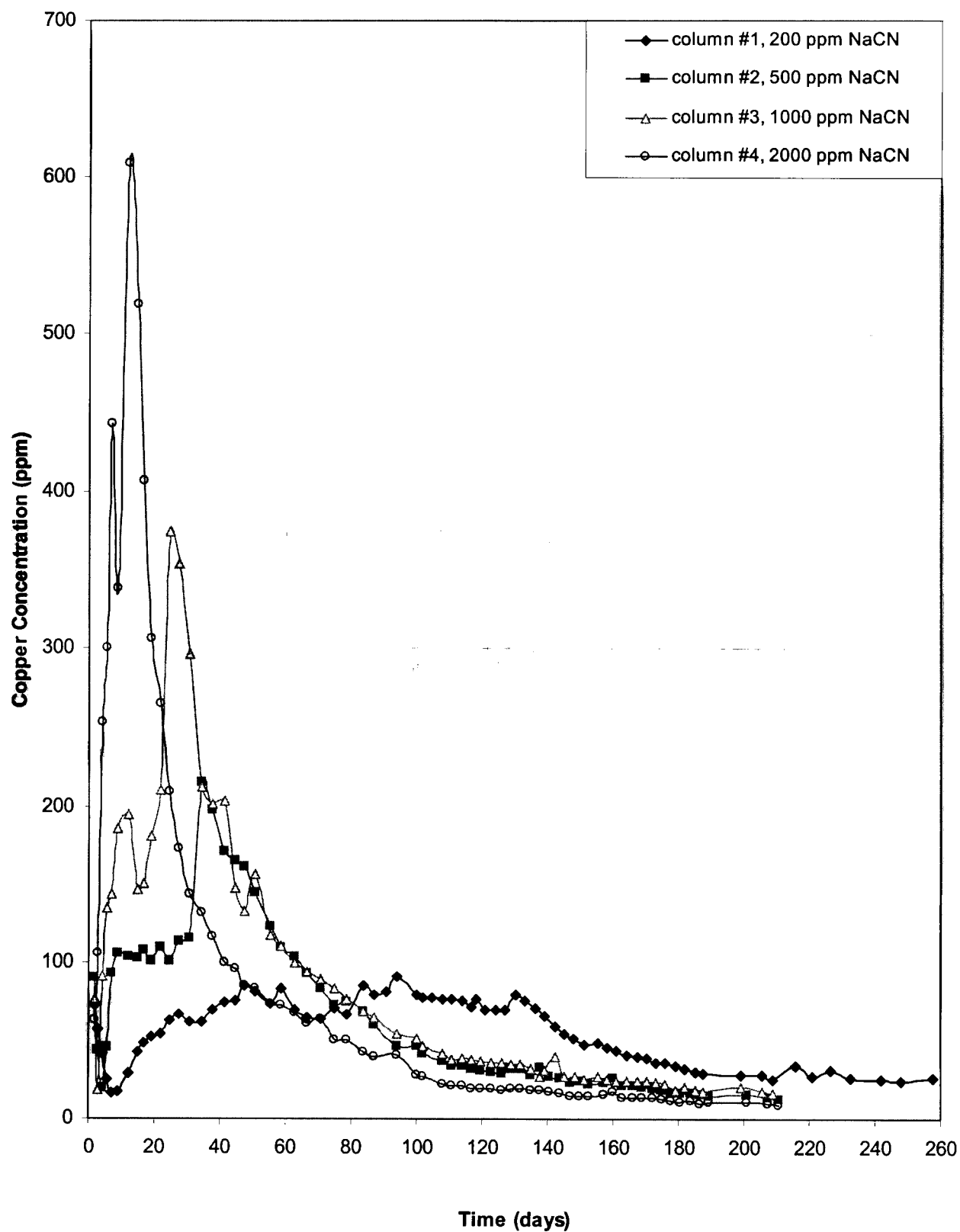
Figure 4-4 Copper concentration (ppm)
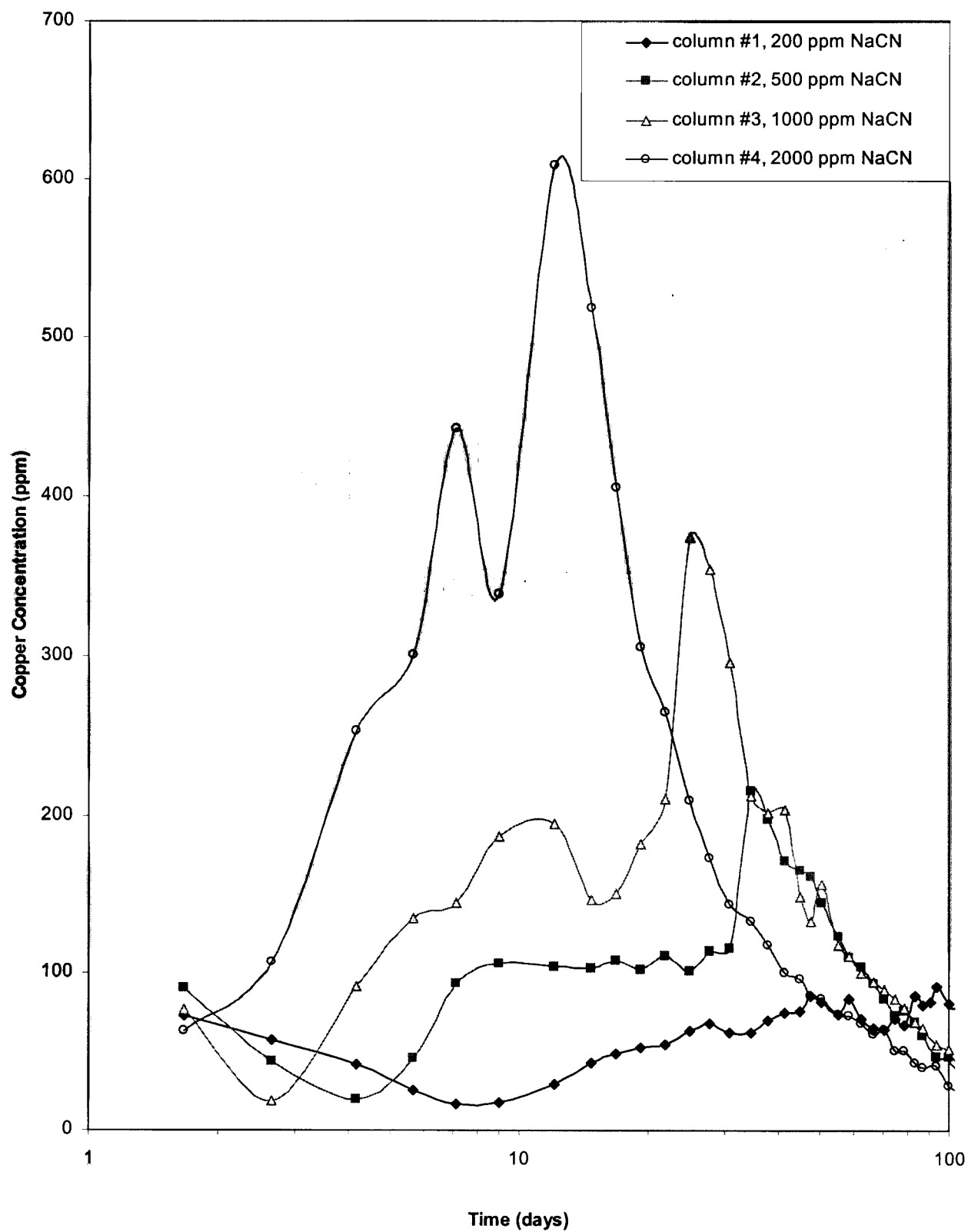
Figure 4-5 Copper concentration in logarithmic scale

It is remarkable that the columns with the lower cyanide concentrations have higher copper concentrations in each sampling period in this stage, except for column 4, which is in a transition from stage one to stage two during the first sampling period.

The dissolution of the remaining WAS (weak acid soluble) copper minerals occurs during this stage and the curves in Figure 4-5 represent the depletion of these minerals. This behavior can be described as the reduction of Cu(II) by cyanide and the subsequent precipitation of CuCN(s), which is highly dependent upon cyanide concentration and pH:

$$2\{Cu^{2+}\} + 4\{CN^-\} \rightarrow 2CuCN(s) + (CN)_2$$
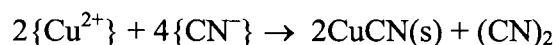
The important aspects of the copper concentration curves during the second stage of leaching are summarized in Table 4-2. This stage represents the leaching of labile copper sulfides, such as covellite and chalcocite. Interesting aspects of the copper leaching behavior during this period can be summarized as follows:

1- At the end of the dissolution of WAS copper minerals in stage one, copper concentrations go through a minimum and then increase rapidly, showing two distinct peaks in most of the effluent copper concentration curves.

2- The time for the beginning of which stage is inversely proportional to the influent cyanide concentration.

3- The peak copper concentrations are proportional to the cyanide concentrations of the influent solutions.

4- For columns with higher cyanide concentrations, these peaks occur at earlier times.

5- The time delays between the first peak and second peak are larger in columns with less cyanide.

6- Copper concentrations decline rapidly beyond the second peaks.

7- The intensity of this decline represents a sharper drop in the columns with higher influent cyanide concentrations.

Table 4-2 General observations on the second stage of the copper concentration curves

Column Number	1	2	3	4
Nominal [NaCN] (ppm)	200	500	1000	2000
[Cu] (ppm) at first peak	85	108–110	195	443
[Cu] (ppm) at second peak	92	212	375	608
Time at which the first peak happens (days)	47.7	16.8–21.8	12.1	7.2
Time at which the second peak happens (days)	93.8	34.6	24.9	12.1
Delay between the first and second peaks (days)	46.1	12.8–17.8	12.8	4.9

Stage three of these concentration curves begins with a rapid decrease in copper concentration and appears as a long tail, gradually decreasing to the end of the experiment.

Compared with experimental data from phase I of the project, the following results are noticeable:

1. The duration of stage one, and the amounts of the copper extracted during this stage, are much smaller in phase II.

2. The copper concentrations during the first stage of phase II are much smaller.

3. The copper concentrations at the first and second peaks are smaller in phase II.

4. The first and second peaks are much more distinct in phase II.

5. A comparison of the columns with 200 ppm cyanide concentration in phase I and phase II shows the same decrease of 26 ± 1 % for the copper concentration at both the first and second peaks.

6. Comparisons of the columns with 500, 1000 and 2000 ppm cyanide concentration in phase I and phase II show that the copper concentrations at the first peaks have been decreased 19 ± 2 % more than the second peaks.

Therefore, one can conclude that one of the sources of copper for the first and second peak was significantly decreased in phase II, probably as a result of the decrease in amount of CuCN precipitates available for redissolution.

Table 4-3 Comparisons of some characteristics of the first and second stages for phase I and phase II

Column Number	1	2	3	4
Nominal [NaCN] (ppm)	200	500	1000	2000
Max. [Cu] at the beginning of stage one phase I (ppm)	798	941	699	371
Max. [Cu] at the beginning of stage one phase II (ppm)	73	90	77	63
Min. [Cu] at the end of stage one phase I (ppm)	6	14	26	76
Min. [Cu] at the end of stage one phaseII (ppm)	17	20	19	63
Time duration of stage one phase I (days)	16	7	5	3
Time duration of stage one phase II (days)	9	4.2	2.7	>1.7
[Cu] (ppm) at first peak in phase I	115	284	558	950
[Cu] (ppm) at first peak in phase II	85	110	195	443
Relative decrease in [Cu] in first peak (%)	**26%**	**61%**	**65%**	**53%**
[Cu] (ppm) at second peak in phase I	127	359	668	950
[Cu] (ppm) at second peak in phase II	92	212	375	608
Relative decrease in [Cu] in second peak	**27%**	**41%**	**44%**	**36%**

In phase II, most of the WAS minerals were removed during pre-rinsing. The dissolution of refractory copper minerals, mainly chalcocite and covellite encapsulated in ferruginous bio–oxidation products or siliceous gangue materials may describe the behavior of copper during the third stage of the effluent copper concentration curves.
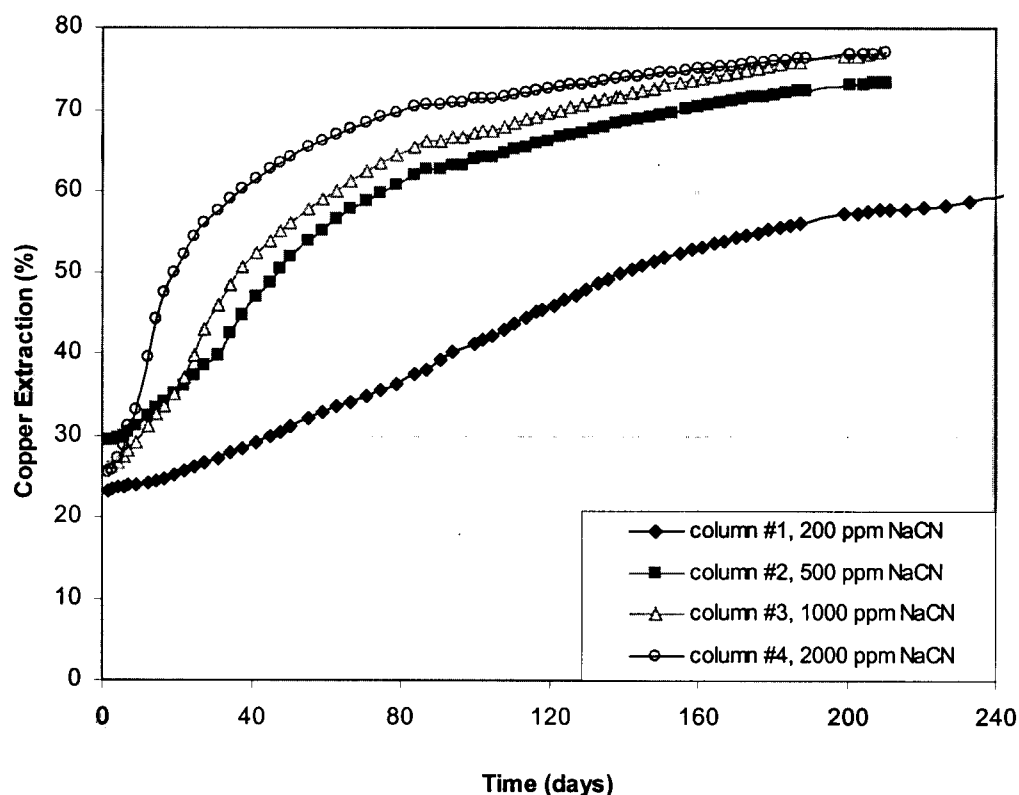
Figure 4-6 Copper Extraction (%)

Copper extraction curves during cyanidation are presented in Figure 4-6. At 500, 1000 and 2000 ppm NaCN concentrations, approximately 75% of the total copper was leached from each column, but at 200 ppm NaCN only 60% was recovered after 250 days. Results from the high NaCN columns suggest that nearly 65% of the total copper is in the form of labile copper sulfide minerals and WAS copper minerals.

As explained previously, the leached ore was emptied from each column carefully and then separated into five equal sections numbered consecutively from top to bottom. After drying, crushing and fine grinding, the samples were well mixed and a small homogeneous portion of each was sent for copper and gold assays.

The results of these analyses are presented in Figure 4-7. For calculating the copper head grade, it was necessary to determine:

1- The amount of copper discharged during pre-rinsing.

2- The amount of copper leached during cyanidation.

3- The amount of copper which remained in the leached residue.

The copper assay results of each section and relevant calculations are presented in Table 4-4. The details and calculations of the total amount of copper in each section are presented in Appendix C. It is important to note that the copper recovered from pre-rinsing and cyanidation were extracted from the total 15 kg ore sample in each column. However, due to the loss of leached residue during crushing and grinding, the amount of un-leached copper is different from that calculated in Tables C-1 to C-4 in Appendix C. Therefore, for an accurate value of the residual copper, a correction factor must be applied, as presented in Table C-5 in Appendix C.

Table 4-4 represents the calculations for determining the Cu head grades in columns 1 to 4. From this table, the average copper head grade for this ore was determined to be 2433 ppm. This value was initially measured as 2580 ppm by others, and as 2562 ppm using the same procedure during phase I of the project. Figure 4-7 presents the average copper grades of the leached ore in the different column sections.

Table 4-4 Determining the copper head grade in phase II

Column Number	1	2	3	4
Nominal [NaCN] ppm	200	500	1000	2000
Column Leach test period (day)	258	210	210	210
Net Copper Leached in Prewash (mg)	9.479	9.337	9.479	8.903
Net Copper Leached in Cyanide column leach (g)	15.537	14.450	18.867	18.449
Net Copper in residual ore (g)	16.187	8.604	8.467	8.203
Total net Copper (g)	41.203	32.391	36.813	35.554
Weight of ore in column (g)	15000	15000	15000	15000
Calculated Head Copper grade (ppm)	2747	2159	2454	2370
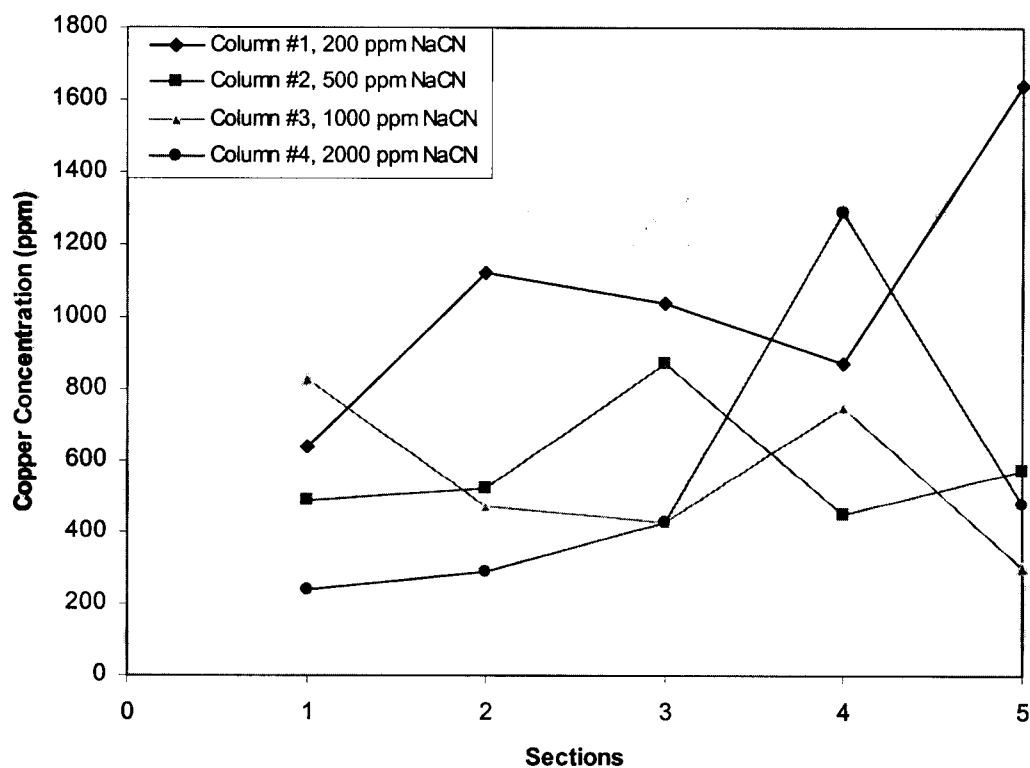
Figure 4-7 Copper grades in leached residue as a function of height

4.2.2 The gold leaching behavior

Figure 4-8 shows the effluent gold concentrations in phase II. Comparing these results with phase I, no significant delay in gold leaching behavior is observed here, except briefly in column 1 with 200 ppm NaCN.

Each gold concentration curve shows a distinct peak during the early stage of the experiment, except column one, which has more of a plateau instead of a peak.

From the gold extraction curves in Figure 4-9, it appears that more than 65% of the gold in this ore is easily leachable with cyanide and the remaining 35% represents more refractory gold, which is responsible for the long tails in the gold concentration curves in Figure 4-8. In addition, as shown in Figure 4-9, the leaching behavior of gold is strongly dependent on the cyanide concentration of the influent solution. In column 4, with 2000 ppm nominal NaCN concentration, 60% gold extraction was obtained after only 22 days, compared with 38, 67 and 170 days respectively for columns 3, 2 and 1. A very interesting observation can be made by comparing the gold and copper extraction curves.
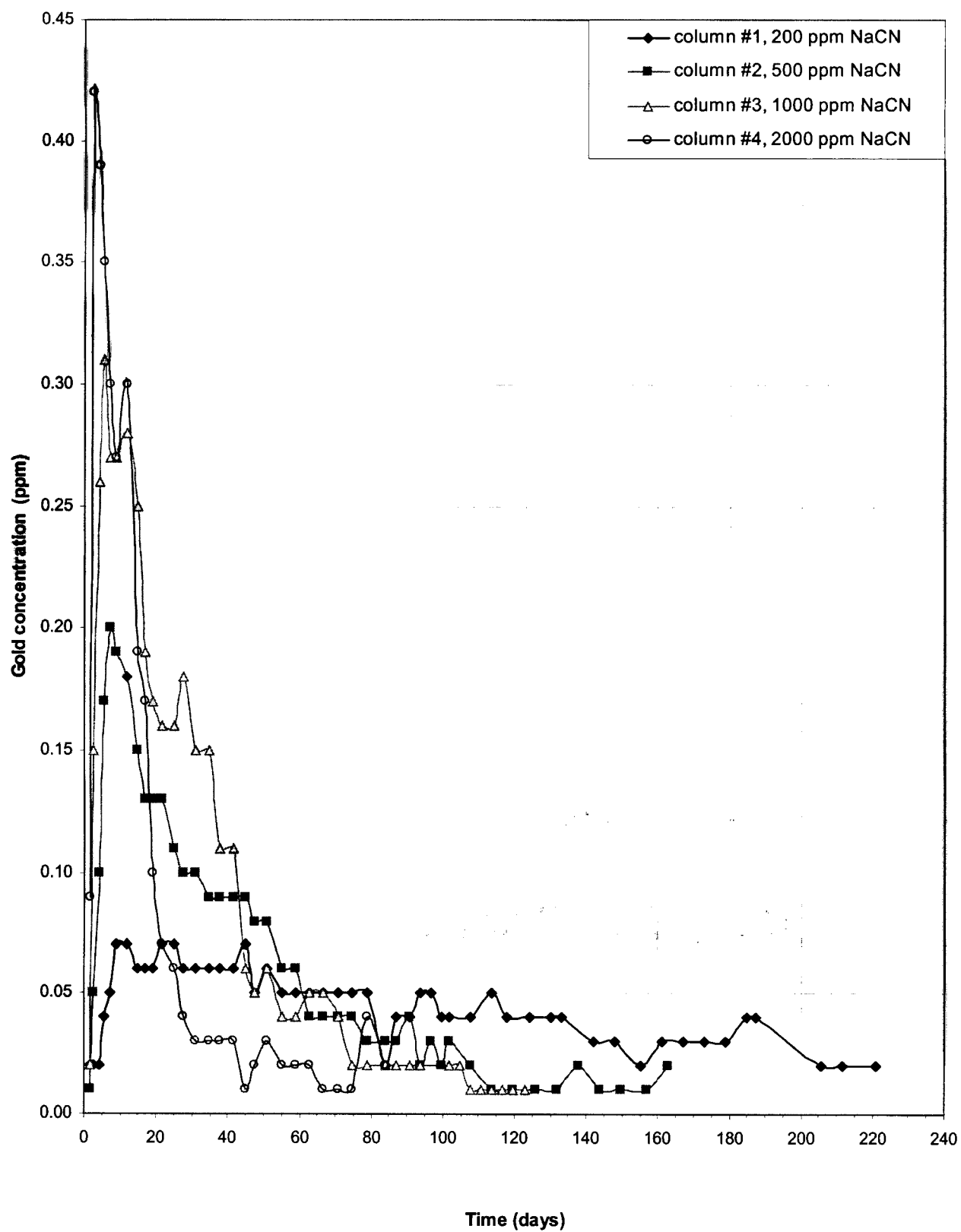
Figure 4-8 Gold concentration in effluent solutions, phase II

This clearly shows that gold follows copper extraction curves in both dissolution of labile copper sulfides and refractory copper minerals. Therefore, one can conclude that gold particles in this ore are completely associated with copper sulfide minerals. This is the exact result achieved in phase I, with a minor difference at the beginning of the experiments. In phase I, somehow because of the high concentration of the WAS copper minerals in the ore at the onset of cyanidation, there was a more intense drop in the effluent pH and a larger extent of subsequent CuCN(s) precipitation. Moreover, because of the low pH some of the gold had precipitated as AuCN(s). Both of these precipitates redissolved later when the pH increased. This effect is largely absent from phase II because of the pre-rinsing.
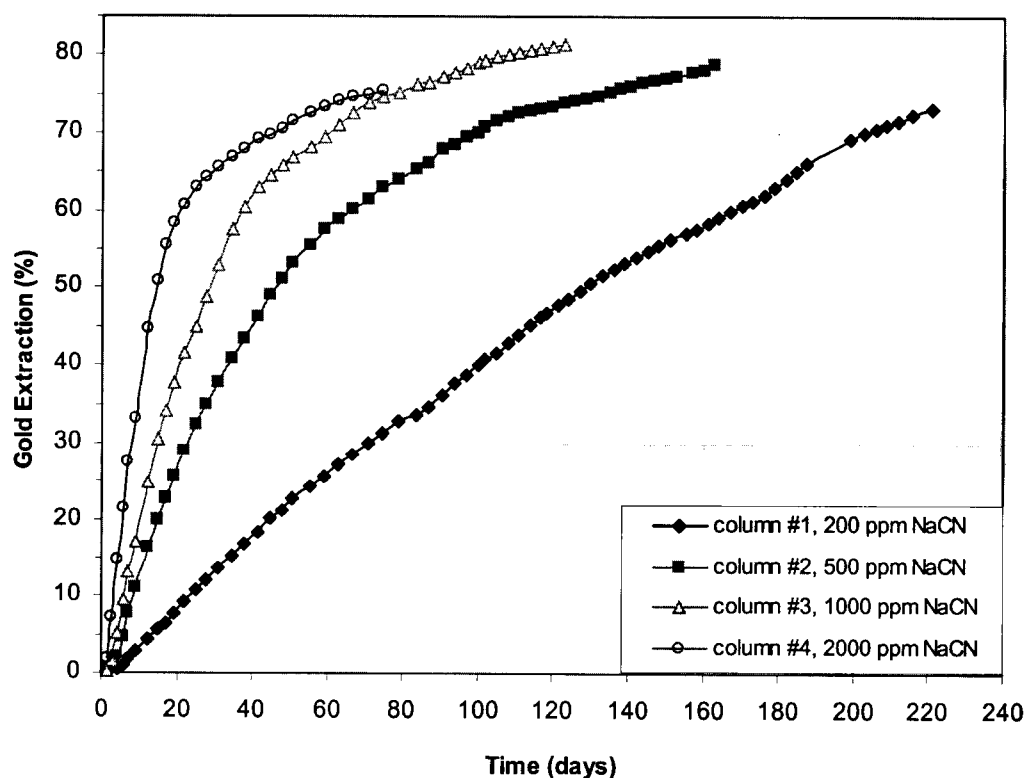
Figure 4-9 Gold extraction with cyanide solution, phase II (%)

4.2.2.1 Gold head grade

The results of gold assays on the leached residue for different column sections are presented in Figure 4-10. Further details and calculations of the total amount of gold in each section are presented in Tables D–1 to D–4 in Appendix D. In addition, the calculation for determining the correction factor to eliminate the error due to residual ore losses during crushing and grinding is given in Table D-5 in Appendix D.
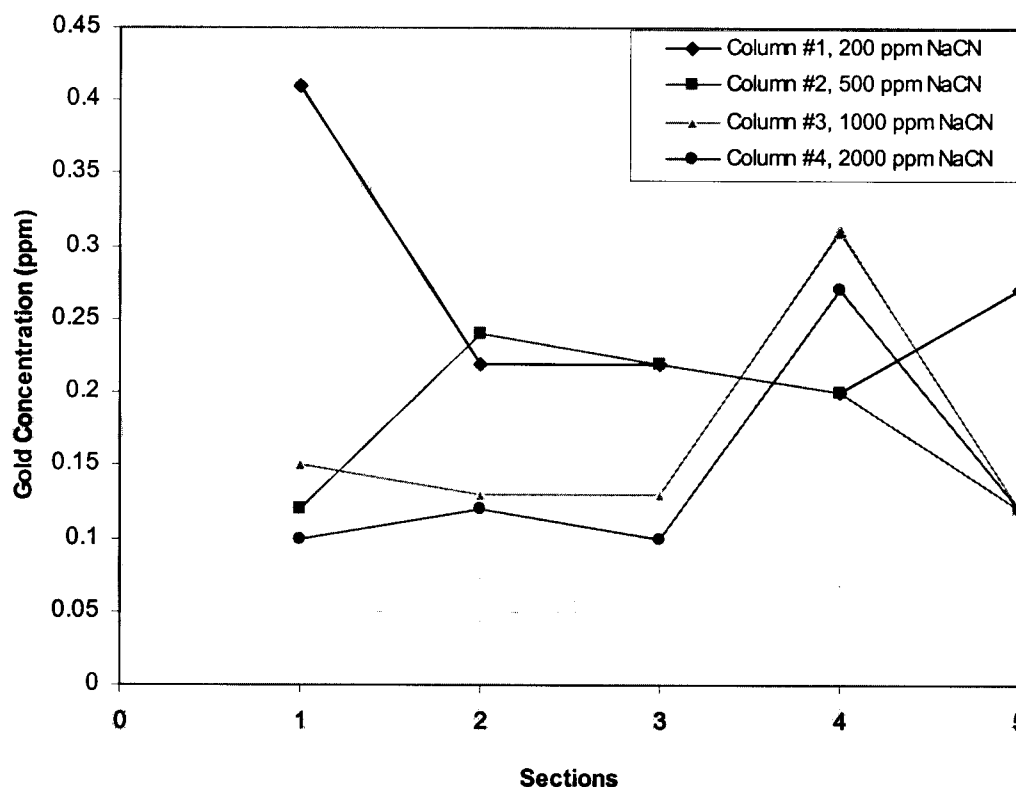
Figure 4-10 Gold grades in leached residue, phase II

The gold head grade can be calculated by determining the total gold leached during cyanidiation and the total gold remaining in the leached residue. This is shown in Table 4-5, and gives an average gold head grade of 0.85 ppm. This value was initially measured at 0.58 ppm by fire assay of samples of untreated ore and 0.72 ppm by a similar

procedure in phase I of the project. An explanation for the considerable difference of the calculated head gold grade of column 4 with the other columns can be that the column 4 was leached for only up to 80 days, therefore as it can bee seen a much smaller amount of gold was leached from this column and as a consequence the possibility of an error such a nugget error in the assaying of the leached residue ore is higher.

Table 4-5 Determining the gold head grade, Phase II

Column Number	1	2	3	4
Nominal [NaCN] ppm	200	500	1000	2000
Column Leach test period (day)	258	210	210	210
Net Gold Leached in Cyanide column leach (mg)	10.754	9.823	11.422	7.681
Net Gold in residual ore (mg)	3.954	2.660	2.592	2.133
Total net Gold (mg)	14.708	12.483	14.014	9.814
Weight of ore in column (mg)	15000	15000	15000	15000
Calculated Head Gold grade (ppm)	0.98	0.83	0.93	0.65

4.2.3 The pH variation

The variation of pH in the effluent solution has a very critical role in the complexation behavior of gold and copper. Effluent pH data are presented in Figure 4-11, and can be summarized as follows:

1. The very low pH of the first effluent samples depends on the influent cyanide concentration. Columns with lower cyanide concentrations show lower initial pH values.

2. The pH rapidly increases to a maximum value which is higher in columns with higher cyanide concentrations.
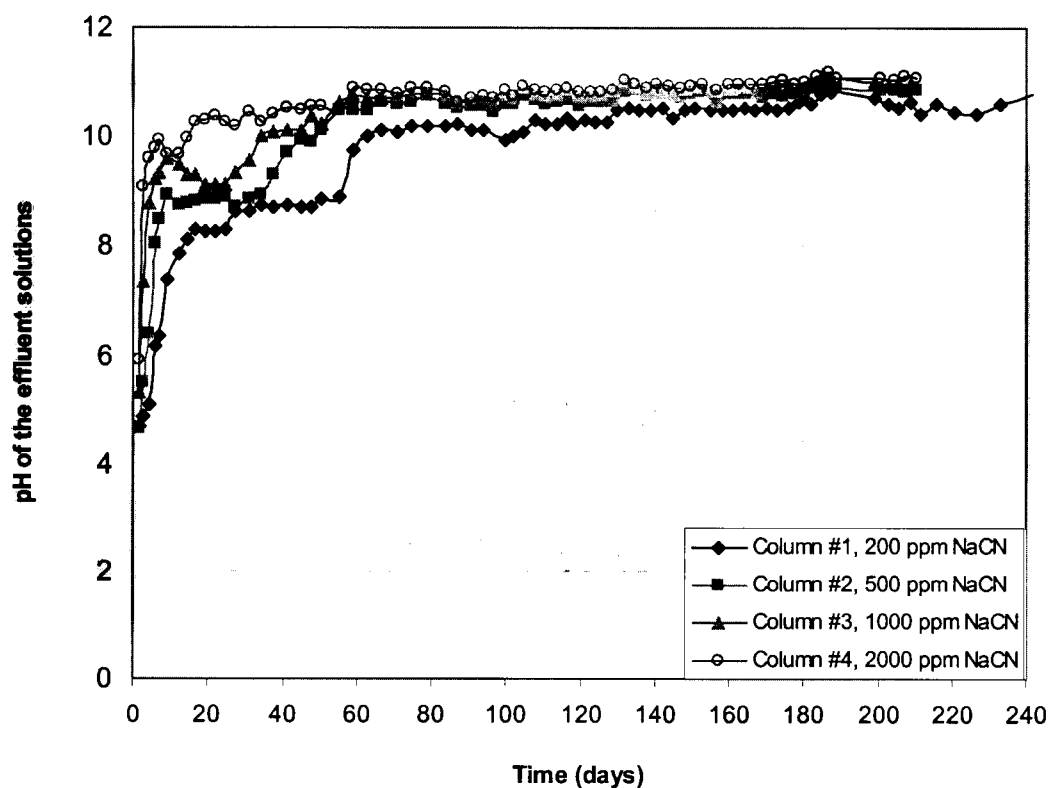
Figure 4-11 pH of the effluent solution, phase II

3. This is followed by a short decrease in pH and then a plateau. This period is shorter for columns with more cyanide.

4. Next comes another rapid increase in pH followed by some irregular behavior, with the pH eventually stabilizing at a final value which is higher at higher cyanide concentrations.

The importance of these pH variations becomes clearer when compared with the behavior of copper in the effluent, as shown in Figure 4-12 and Figure 4-13. Some interesting aspects of this comparison are listed in Table 4-6.

Table 4-6 Some important aspects of the comparison of pH and [Cu] curves.

Column Number	1	2	3	4
Nominal cyanide concentration (ppm)	200	500	1000	2000
pH of the first sample	4.68	4.65	5.32	5.89
pH at the end of the first rapid increase	8.29	8.92	9.59	9.94
Time of the end of the first rapid increase in pH (days)	16.8	9.0	9.0	7.2
Time of the first peak in [Cu] curve (days)	Not clear	9.0	12.1	7.2
Time of the end of the plateau on pH curve (days)	Not clear	34.6	24.9	12.1
Time of the rapid decrease on [Cu] curve (days)	130.1	34.6	24.9	12.1
The average of the final stabilized pH (± 0.05)	10.67	10.85	10.95	11.05

Figure 4-12 Comparison of pH and [Cu] results for columns #1 and #2
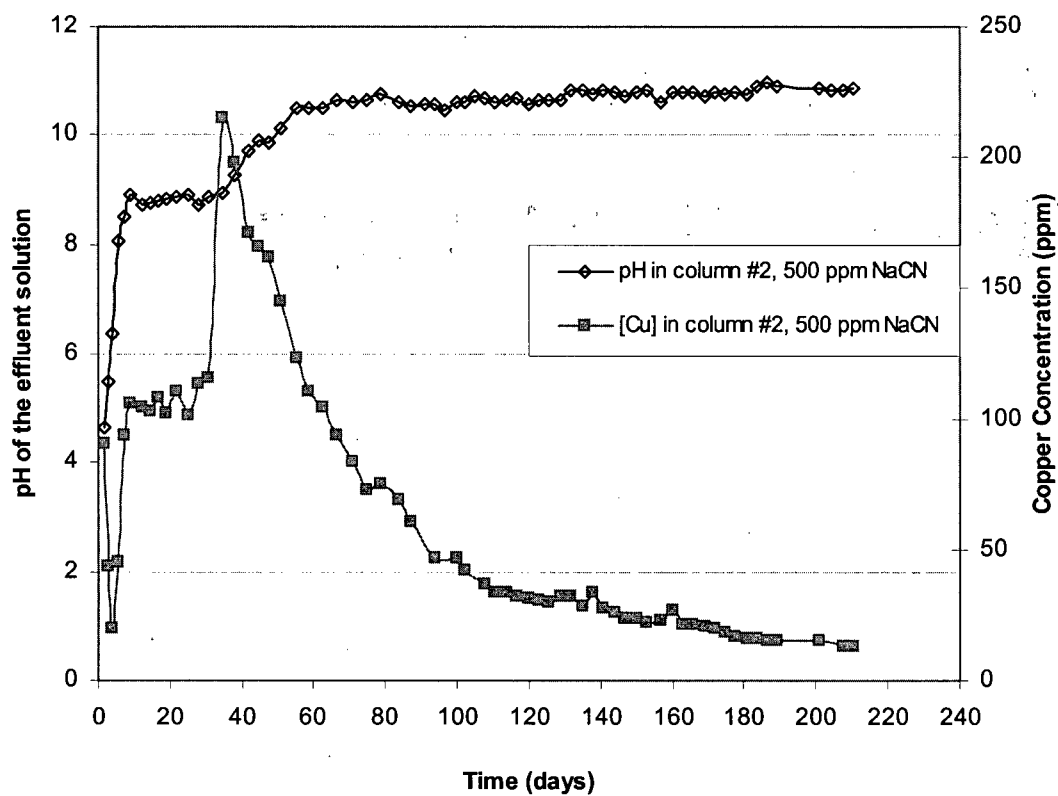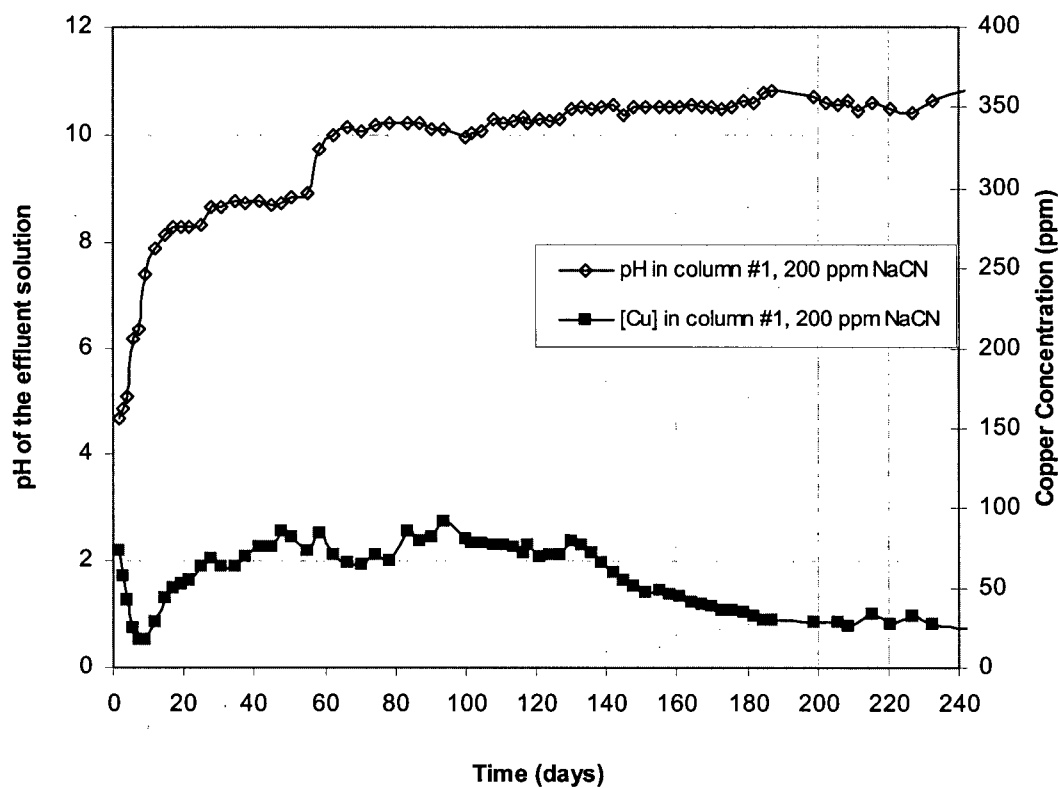
Figure 4-13 Comparison of pH and [Cu] results for columns #3 and #4
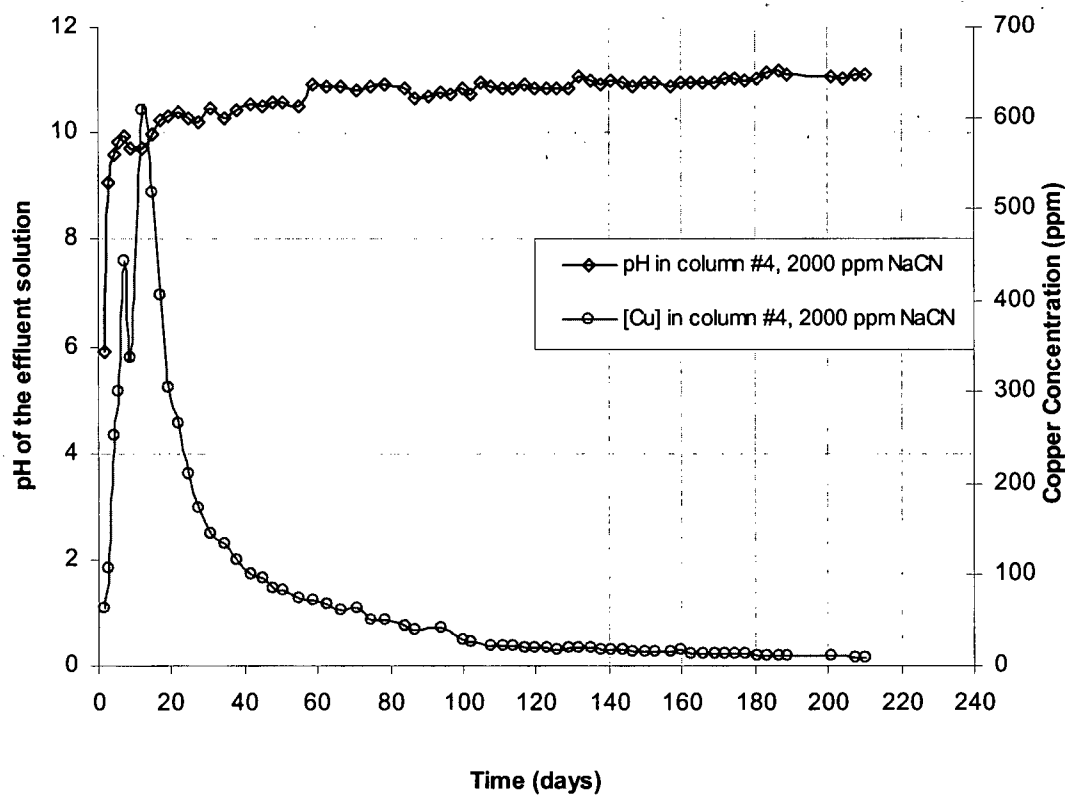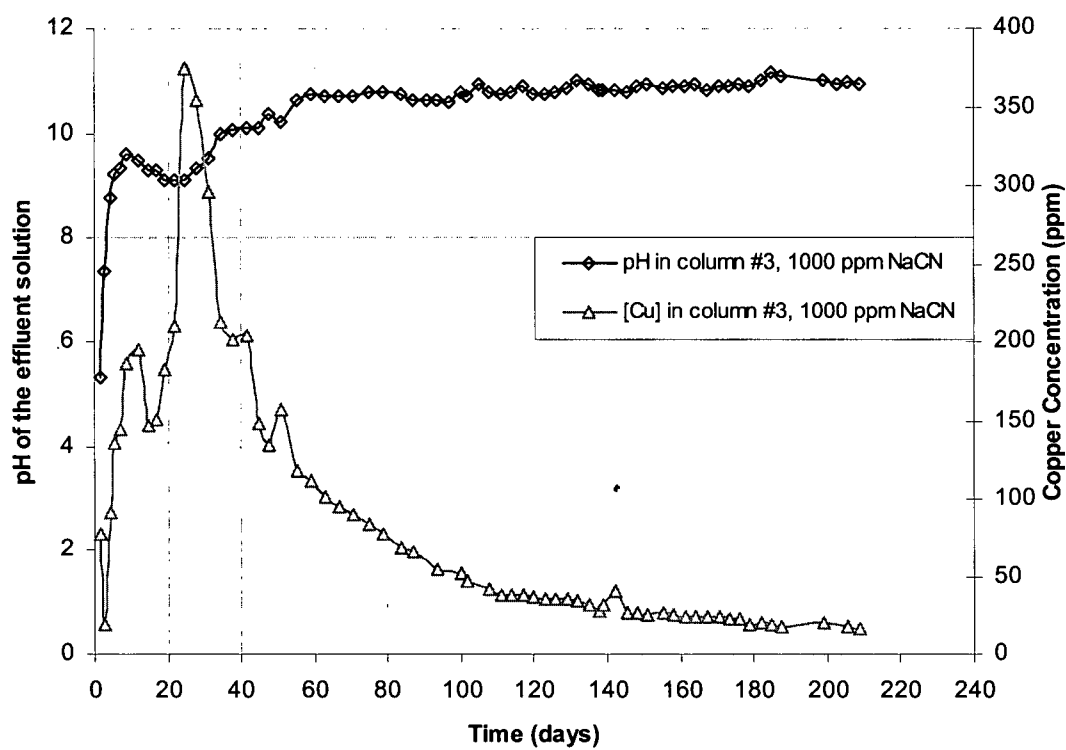
Figure 4-12, Figure 4-13 and Table 4-6 show a very strong relationship between pH and copper concentration in the effluent. In some stages, pH affects the behavior of copper and of subsequent reaction products, but some other times the hydroxide ion content of the system varies because of a chemical reaction involving a specific type of copper mineral, specifically covellite.

It should be noted that a solution of sodium hydroxide with a pH of 11 was passed through the columns to stabilize the pH prior to cyanidation. However, as in phase I of the project, the pH of the effluent solution decreased markedly as soon as cyanide solution was introduced.

Some examples of reactions involving copper, cyanide and hydroxide ion or hydrogen ion, which show how each one can affect the other, are as follows:

- Dissolution of copper in cyanide solutions can give the di–, tri–, and tetracyanocuprate (I) complexes and copper cyanide precipitate, the amount of each of which is dependent on the cyanide/copper ratio and the pH of the solution.

- Decomposition of copper(I) cyanocomplexes to CuCN(s) consumes hydrogen ion:

$$Cu(CN)_3^{2-} + 2\,H^+ \rightarrow\ CuCN(s) + 2HCN$$

- Oxidation of cyanide to cyanogen with copper(II) and the following hydrolysis reactions (Coderre and Dixon, 1999):

$$2\,\{Cu^{2+}\} + 2\,\{CN^-\} \rightarrow\ 2\,\{Cu^+\} + (CN)_2$$

$$(CN)_2 + \{OH^-\} \rightarrow \{NCCONH^-\}$$

$$\{NCCONH^-\} + \{OH^-\} \rightarrow \{CN^-\} + \{OCN^-\} + H_2O$$
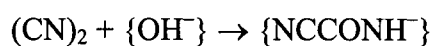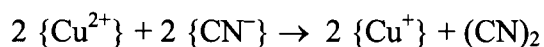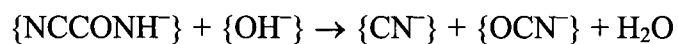
- Coderre and Dixon (1999) suggested the following equation for the reaction of covellite in a cyanide system, upon disproportionation of the cyanogen:

$$2\ CuS + \{CN^-\} + 2\{OH^-\} \rightarrow 2\ \{Cu^+\} + 2\ \{S^{2-}\} + \{OCN^-\} + OH^-$$
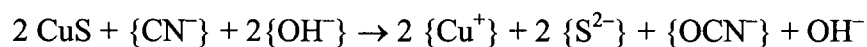
Copper(I) minerals have no direct effect on the pH, but S^{2-} which is a product of the reactions of copper sulfides with cyanide, goes into solution as bisulfide HS^-, and thereby affects on the pH.

4.2.4 Free cyanide concentration in the effluent solution

Free cyanide concentrations in the effluent are presented in Figure 4-14. The complete depletion of free cyanide can be observed in the first stage of all four columns, although it takes a longer time for columns with less cyanide to show any free cyanide in the effluent.
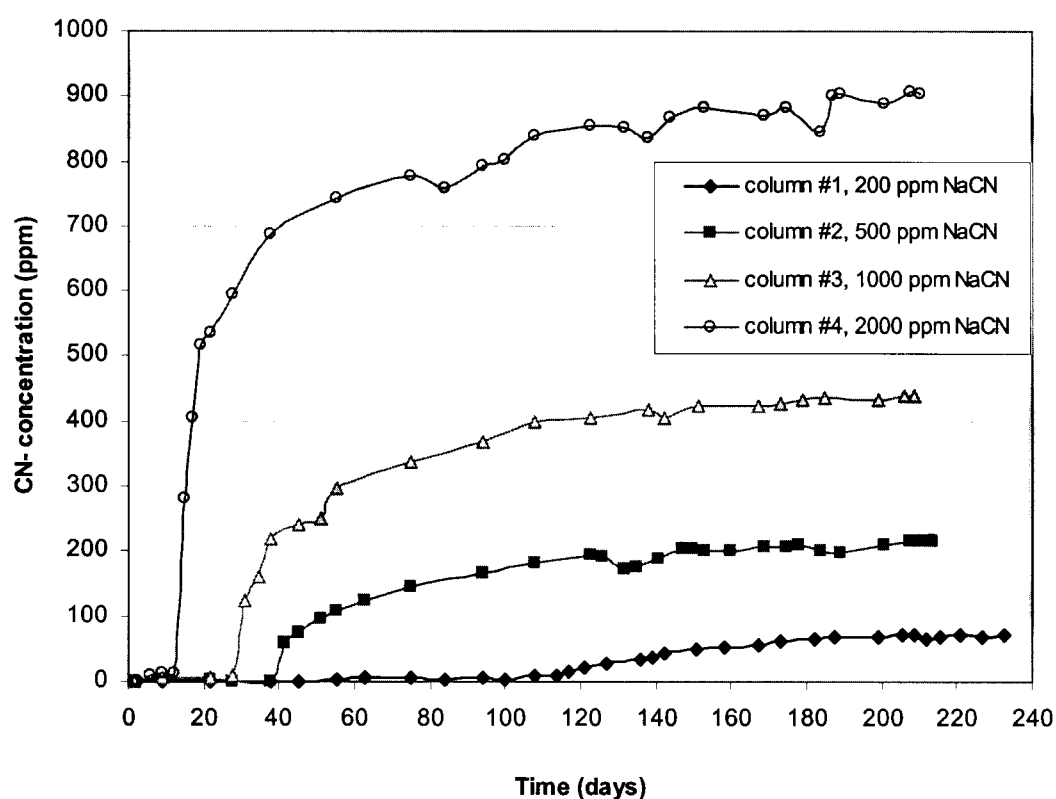
Figure 4-14 Free cyanide concentration in the effluent, phase II

The rapid increase of free cyanide concentration during the next stage, known as cyanide breakthrough, represents the strong depletion of rapidly cyanide-consuming minerals from the columns. Therefore, one would expect to see some corresponding change in the behavior of those minerals before the end of this rapid increase of free cyanide concentration in the effluent. This is clearer in columns with higher cyanide

concentrations, because more free cyanide is available everywhere inside the column to react with those minerals. For example, as shown in Figure 4-16, the end of these rapid changes in free cyanide concentration can be estimated to be day 19.1 for column 4 and day 37.8 for column 3. Therefore, we can investigate the behavior of the rapidly cyanide-consuming minerals by analyzing the copper behavior prior to these points without being too worried about interference from other minerals. In addition, by comparing the transition from complete depletion of free cyanide to the rapid increase of free cyanide with the copper concentration curves at those times, the following behavior can be suggested:

1. The dissolution of WAS copper minerals, labile copper sulfides and redissolution of copper cyanide precipitates occur with complete depletion of free cyanide.

2. While this continues, exactly after the sharp peak in the copper concentration curve, free cyanide will emerge in the effluent solution and the copper concentration will only decrease beyond that point. It should be noted that according to the speciation diagram for the Cu(I)-CN-H_2O system, Figure 2-6, no free cyanide exits in the solution as long as CuCN(s) is present. This suggests that the second peaks in the copper concentration curves must represent the redissolution of CuCN precipitates.

Changes in the slope of the free cyanide concentration curves at the end of the first rapid increase represent the activation of another cyanide consumer in the system. This will most probably be the refractory copper sulfide mineral, as can be seen most clearly in column 3 by noticing the changes in the copper concentration curve during this period,

Figure 4-16. Eventually, with depletion of those refractory copper minerals, the cyanide concentration curves show more stable concentrations in the effluent.

Finally, comparisons of the copper extraction curves and the cyanide concentration curves in Figure 4-17 and Figure 4-18, show the close relationship in the behavior of these two elements.

Figure 4-15 Comparison of [CN⁻] and copper conc. results for columns #1 and #2
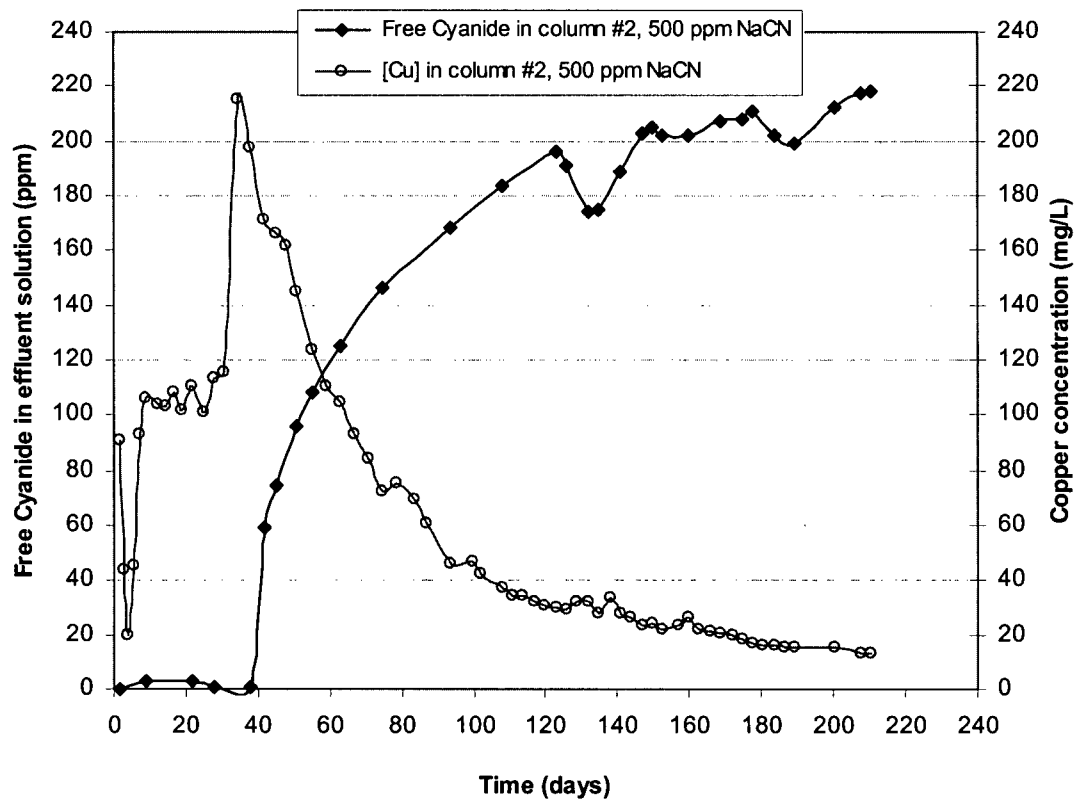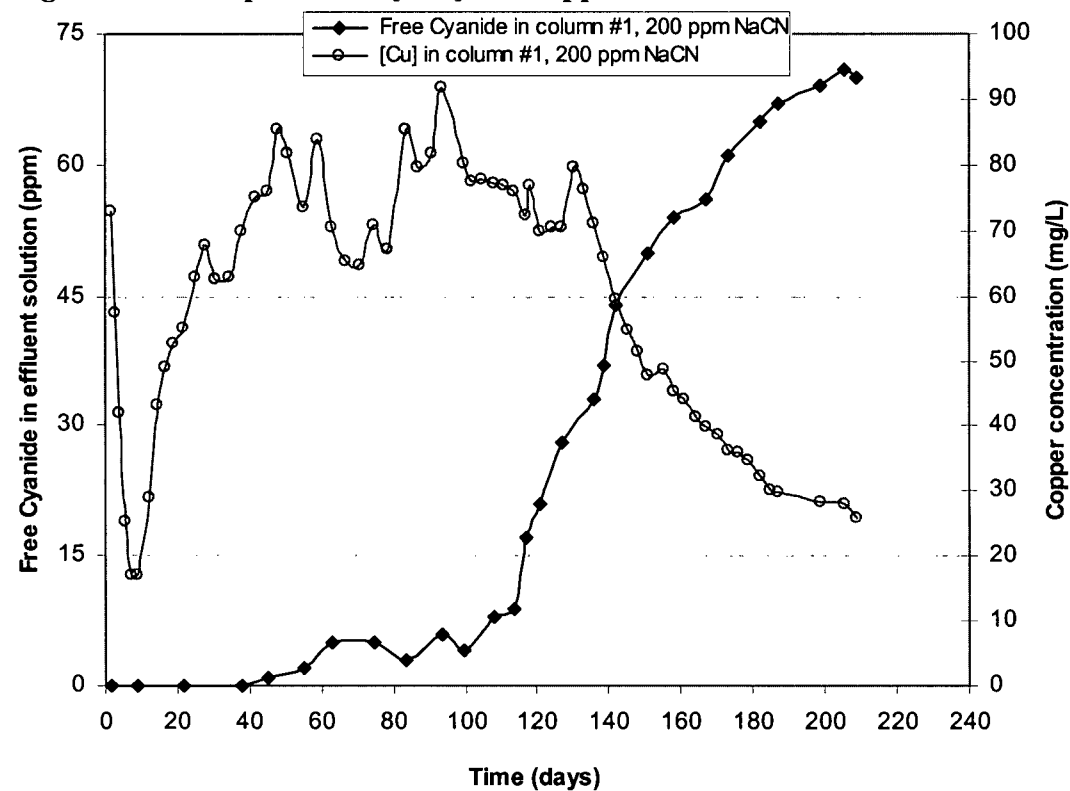
Figure 4-16 Comparison of [CN⁻] and copper conc. results for columns #3 and #4
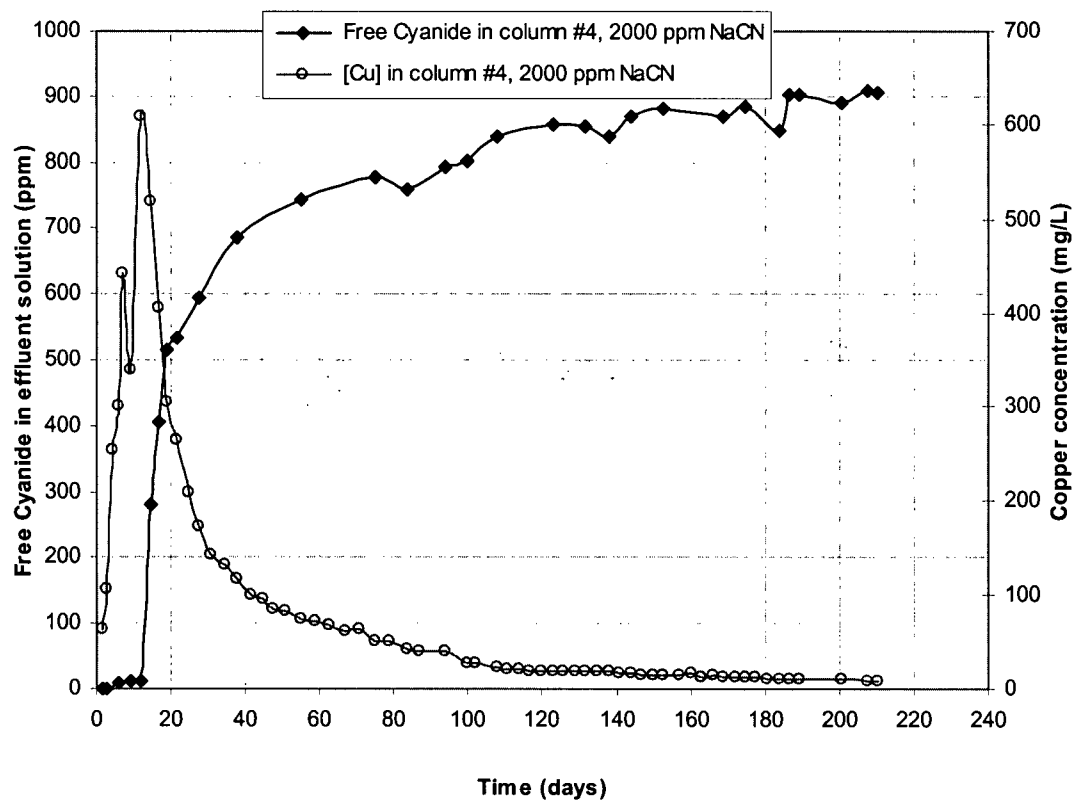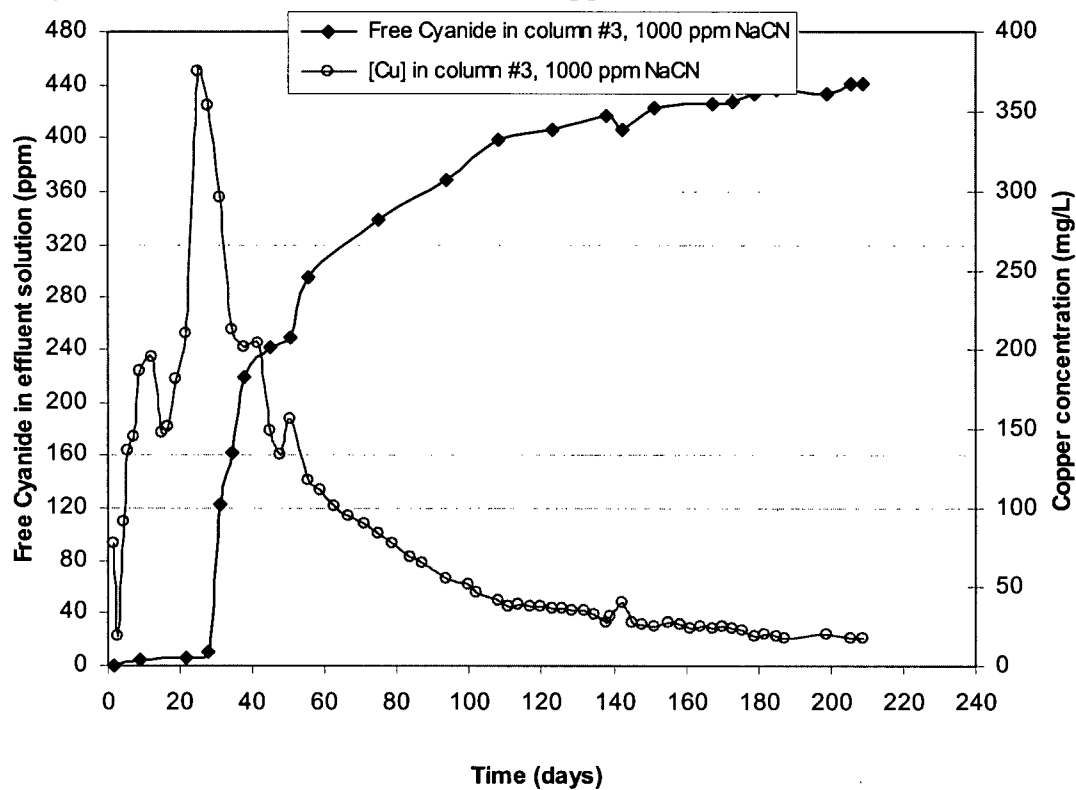
Figure 4-17 [CN⁻] and copper extraction results for columns #1 and #2
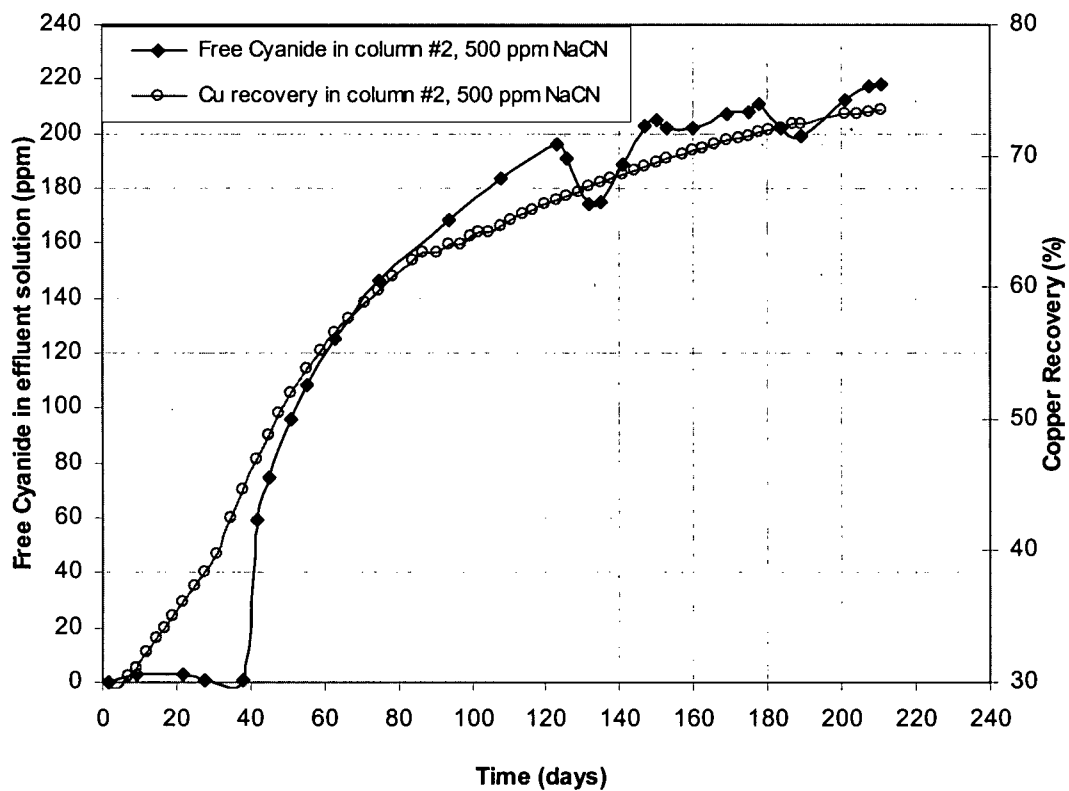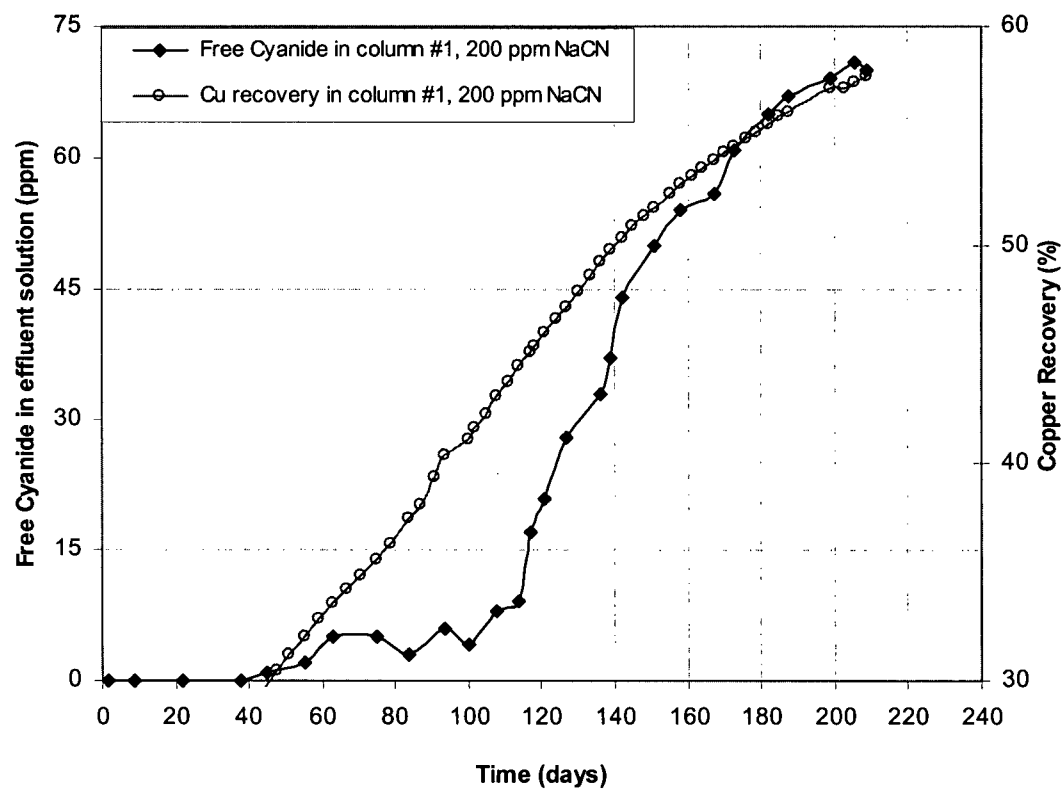
Figure 4-18 [CN⁻] and copper extraction results for columns #1 and #2
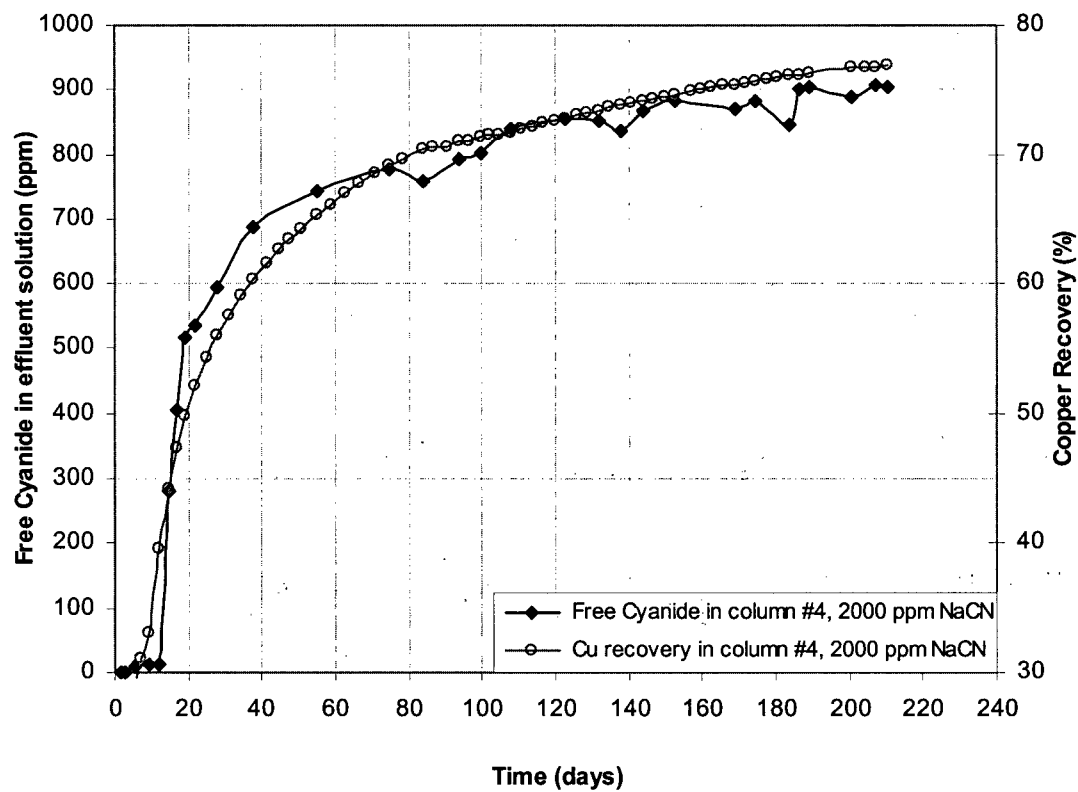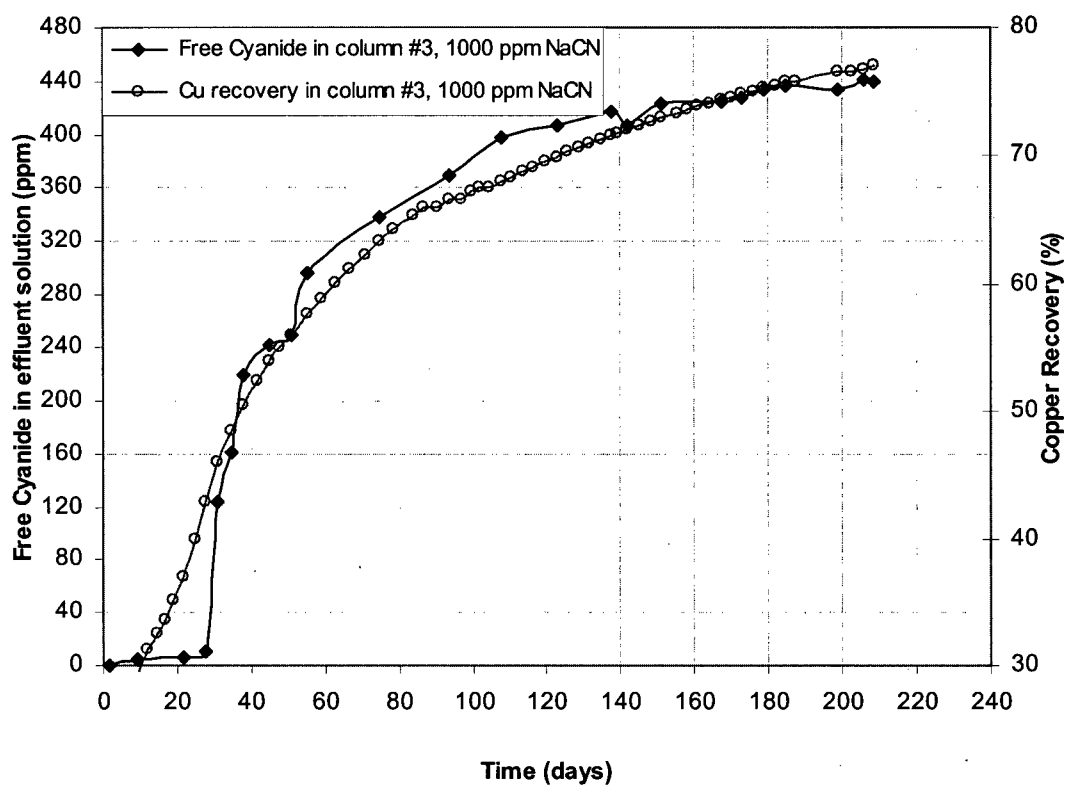
4.2.5 Thiocyanate in the effluent solution

The process of cyanidation is unfavorably affected by the presence of free sulfur or sulfide minerals in the ore. Cyanide will preferentially leach sulfide minerals and will react with sulfur to produce thiocyanate. These reactions will also enhance the oxidation of reduced sulfur species, increasing the requirement for lime addition to control the pH at a sufficient level to avoid the volatilization of hydrogen cyanide (HCN). Hence, cyanide can be lost through the formation of thiocyanate (SCN^-), and this can represent a major loss of cyanide in any ore which contains sulfide minerals.

The concentrations of thiocyanate in the column effluents are presented in Figure 4-19 and Figure 4-20. As shown, the concentration of thiocyanate is high when the free cyanide concentration in the effluent solution is very low and when the concentration of free cyanide increases the thiocyanate concentration decreases.

This behavior is in complete agreement with the copper concentration behavior and strongly shows how the presence of copper sulfide minerals has affected the cyanide behavior in the columns. In addition, a comparison between thiocyanate concentration and pH seems to explain the rapid decrease in pH at the beginning of the experiments.

Copper sulfide minerals such as covellite and chalcocite are readily soluble in cyanide solutions. In case of covellite, its reaction oxidizes cyanide to cyanogen and eventually cyanate, which consume two moles of hydroxide per mole of cyanogen. The sulfide goes into solution as HS^-, which increase pH by consuming the hydrogen ion. The sulfide ion may undergo oxidation, ultimately forming sulfite and sulfate, which strongly decrease the pH of the solution. Some of bisulfide ions are oxidized to polysulfides and thiosulfate

in the presence of oxygen, and both reactions consume hydrogen ion and therefore tend to increase the pH. At the same time, the influent solution is basic, and therefore also increases the pH. Therefore, it is understandable that the pH behavior is very complicated.

The thiocyanate concentration curves also represent another important aspect of the behavior of the copper sulfide minerals. Whereas it is very difficult to determine which copper in the effluent is from the dissolution of copper sulfide minerals, and which is from the redissolution of copper cyanide precipitates, the thiocyanate concentration can be a powerful tool for this purpose. The appearance of thiocyanate in the effluent solution from the first stage of all the column tests shows that in fact the dissolution of copper sulfide minerals began at the very beginning of the experiments. Also Figure 4-21 and Figure 4-22 clearly show that the peak of the thiocyanate concentration occurs exactly at the same time of the first peak of the copper concentration in all four columns. Therefore the first peak in copper concentration must represent the actual leaching of the copper sulfides.

The rapid decrease in thiocyanate concentration is remarkable because in those periods copper still shows a high concentration in all the columns. According to Coderre and Dixon (1999), a mixture of thiocyanate and thiosulphate would be expected in cyanide solution at lower pH, whereas mostly thiosulfate with traces of sulfite and sulfate would be expected under alkaline conditions.

Figure 4-19 [CN⁻] and [SCN⁻] results for columns #1 and #2
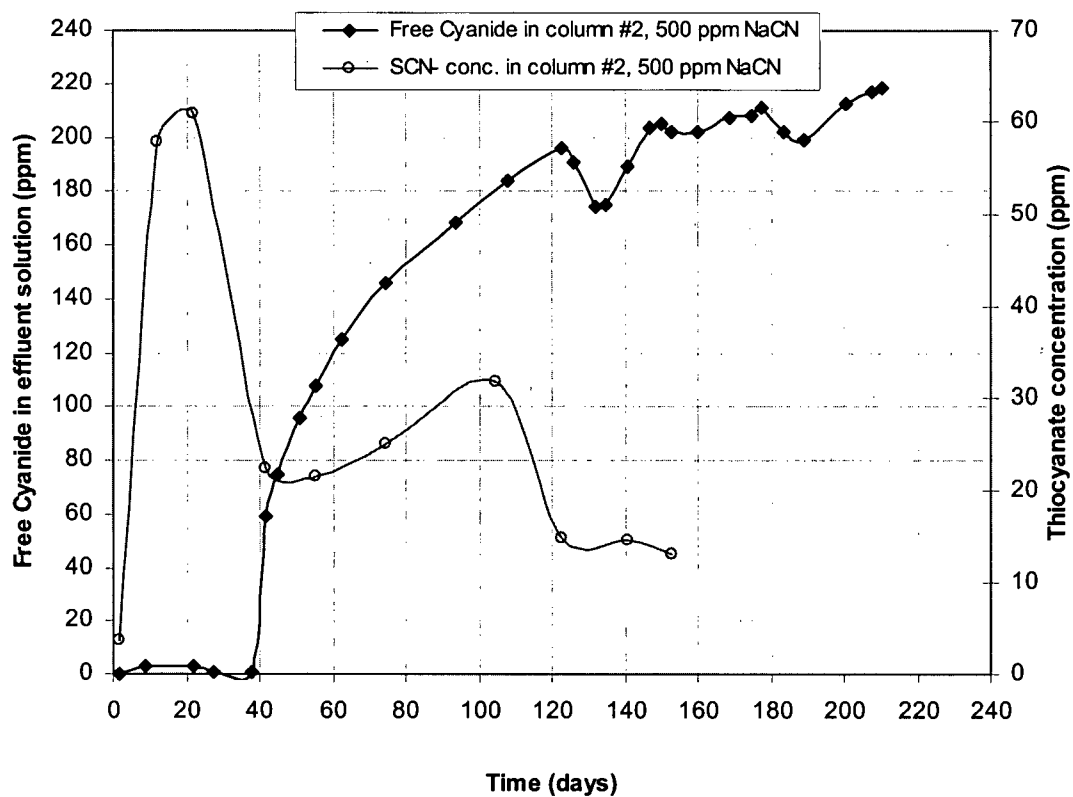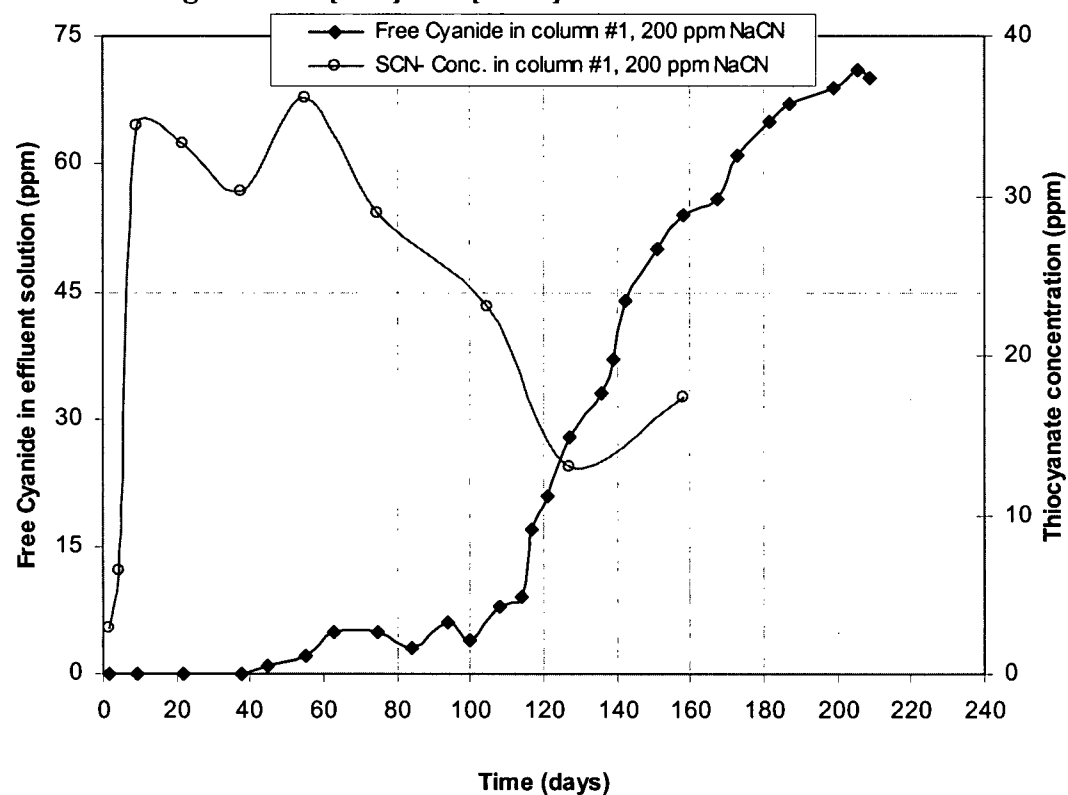
Figure 4-20 [CN⁻] and [SCN⁻] results for columns #3 and #4
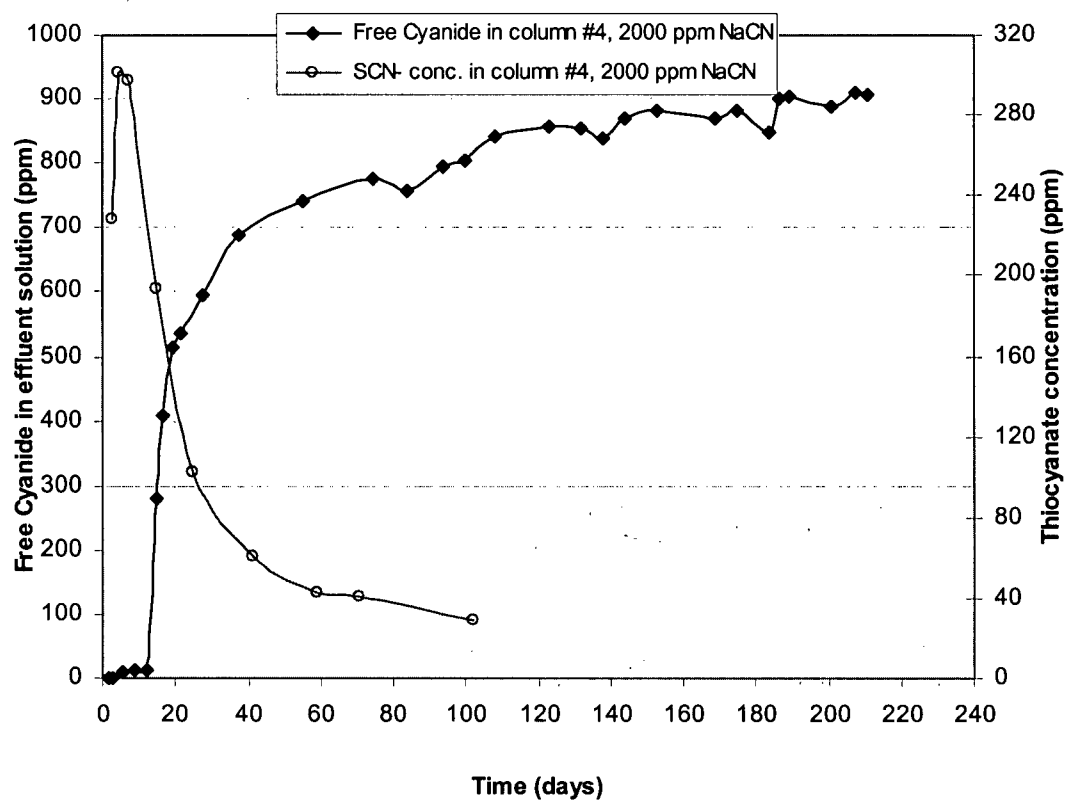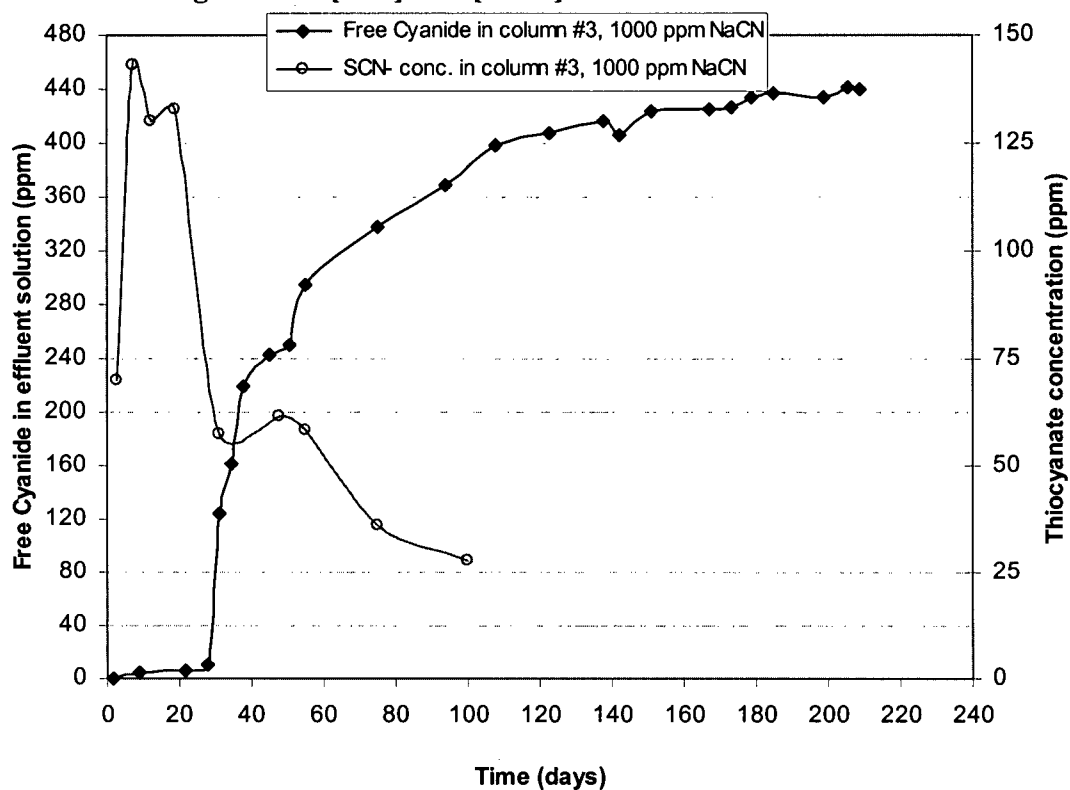
Figure 4-21 Comparison of [SCN⁻] and copper conc. results for columns #1 and #2
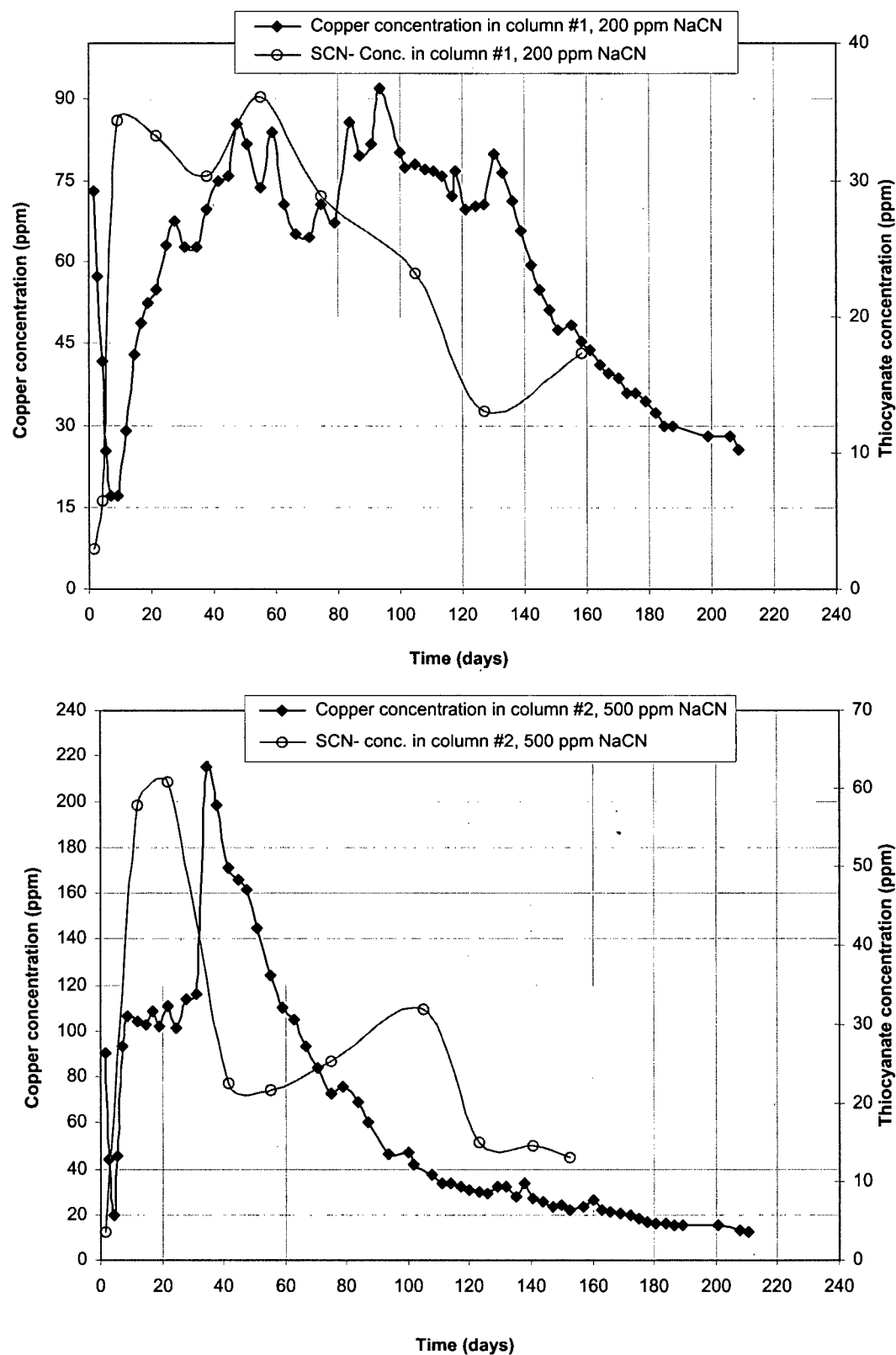
Figure 4-22 Comparison of [SCN⁻] and copper conc. results for columns #3 and #4
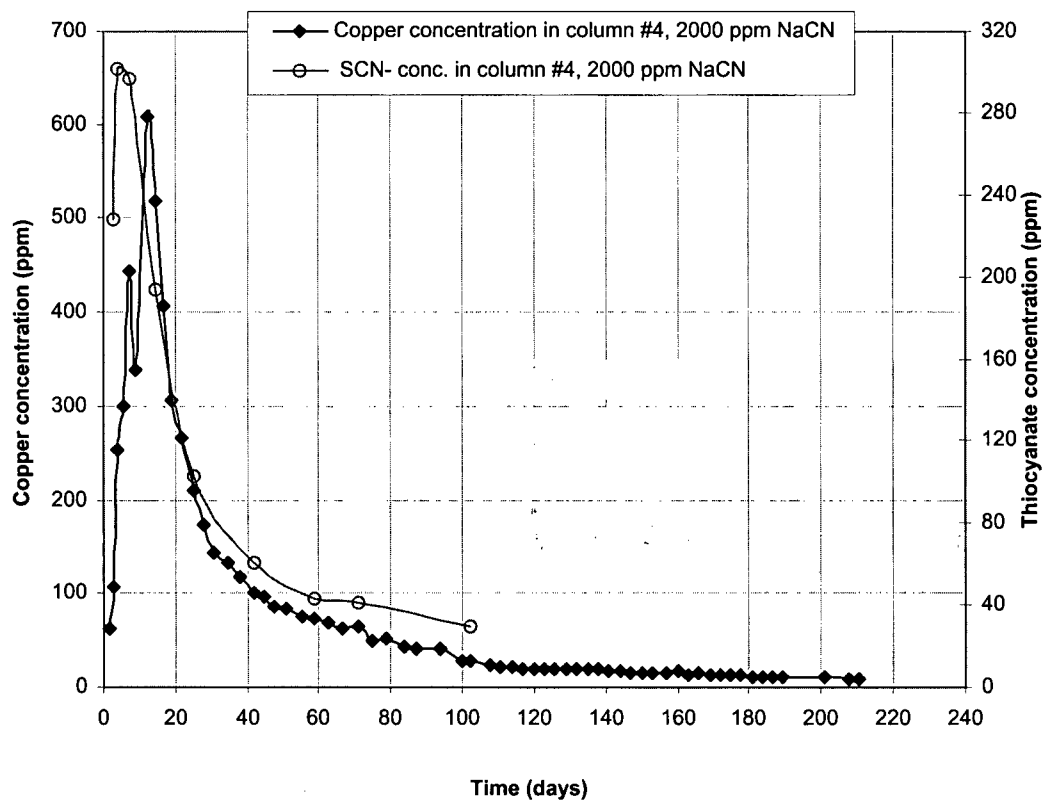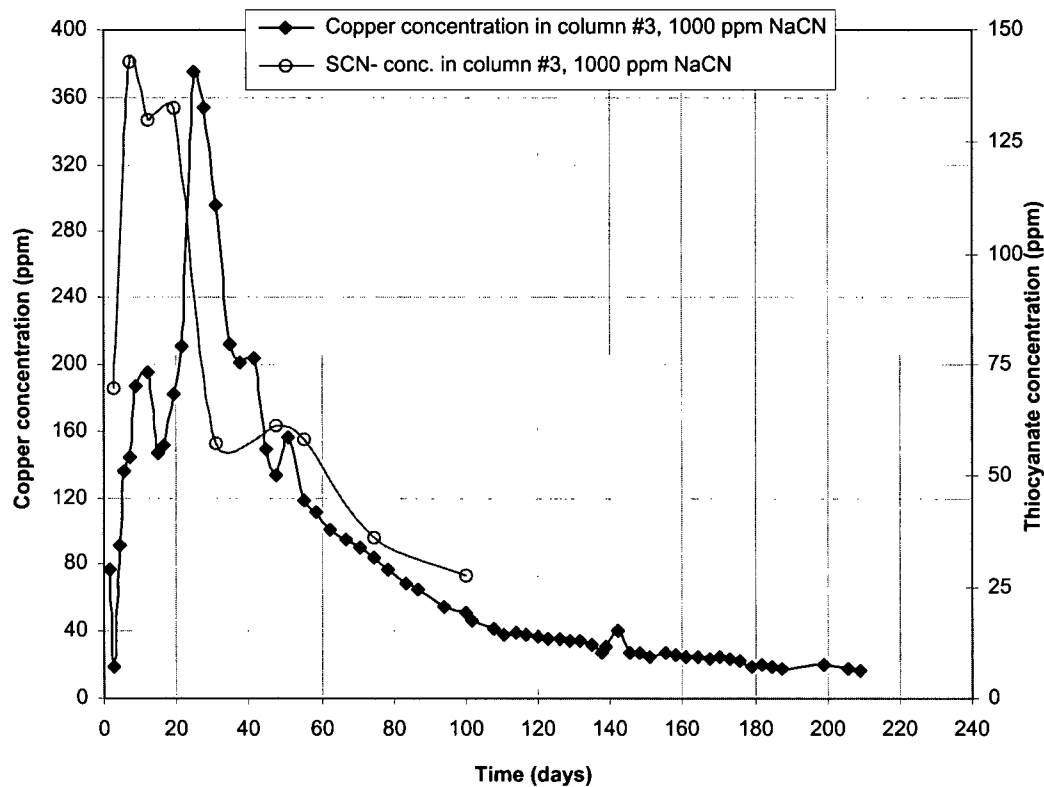
4.2.6 The iron behavior

The iron concentration curves in Figure 4-23 present very similar behavior to that seen during phase I, the only difference being that this time the concentrations of iron at peaks are generally smaller, except for column 3. General observations of the iron concentration curves and a comparison between these results and those from phase I are summarized in Table 4-7.

Table 4-7 General observations and a comparison of iron concentration curves in phases I and II

Column Number	1	2	3	4
Nominal cyanide concentration (ppm)	200	500	1000	2000
The lag time in phase I (days)	109	55	31	16
The lag time in phase II (days)	116.7	41.6	30.9	14.7
The Iron concentration at the peak in phase I (ppm)	2.8	2.7	5.7	32.4
The Iron concentration at the peak in phase II (ppm)	0.9	0.7	6.4	13.5
Average iron concentration after tail in phase I (ppm)	0.9	0.8	0.9	3.1
Average iron concentration after tail in phase II (ppm)	0.3	0.2	0.6	1.9

Clearly, some iron was dissolved during pre-rinsing, and this accounts for the discharge of less iron in phase II. Comparing the iron and free cyanide concentration curves, one can understand the behavior of iron in these systems. Such a comparison for each column is presented in Figure 4-24 and Figure 4-25. As shown in the figures, there is no trace of iron in the effluent solutions before cyanide breakthrough. However, after this point the

iron concentration suddenly increases to a maximum and then decreases with a long tail. The appearance of iron in the effluent corresponds exactly to the time of cyanide breakthrough in every column. Hence, one could use iron as an accurate indicator for determining the exact time of cyanide breakthrough. This is important, since determining the end point in cyanide titration with silver nitrate is always difficult due to the presence of cyanocuprate(I) complexes and other cyanide species, but determining iron by atomic absorption spectrometry is easy and accurate.
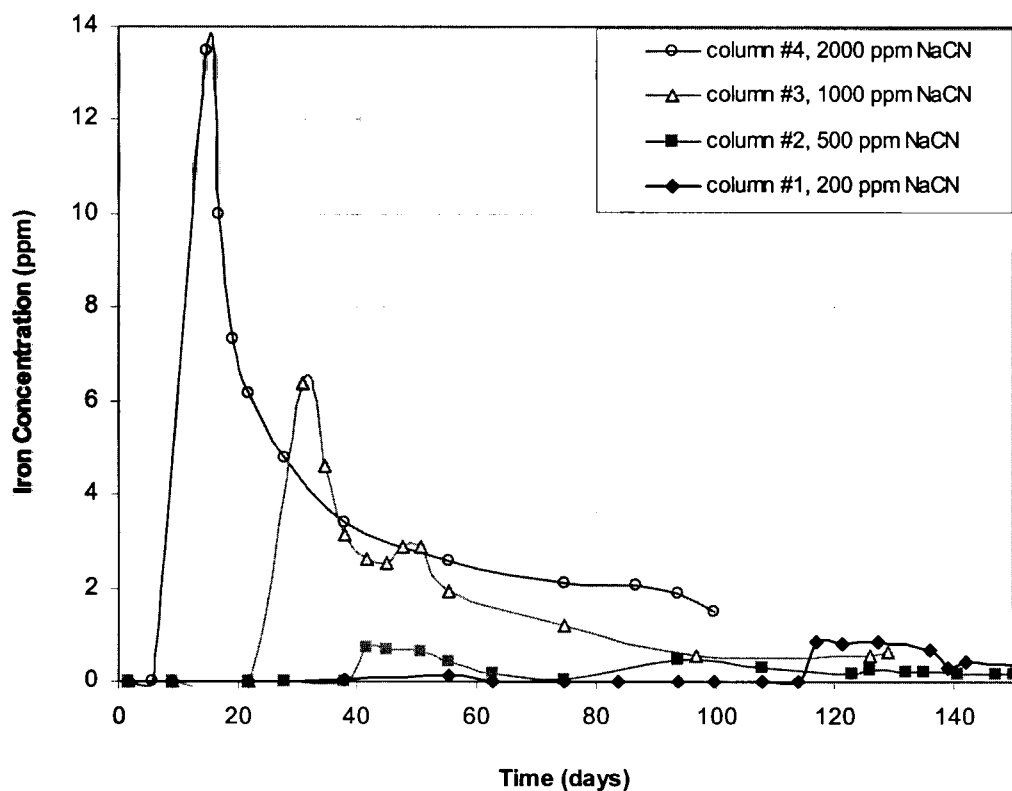
Figure 4-23 Iron concentration in the effluent solutions, phase II

Figure 4-24 Iron behavior and the free cyanide concentration, column #1 and #2
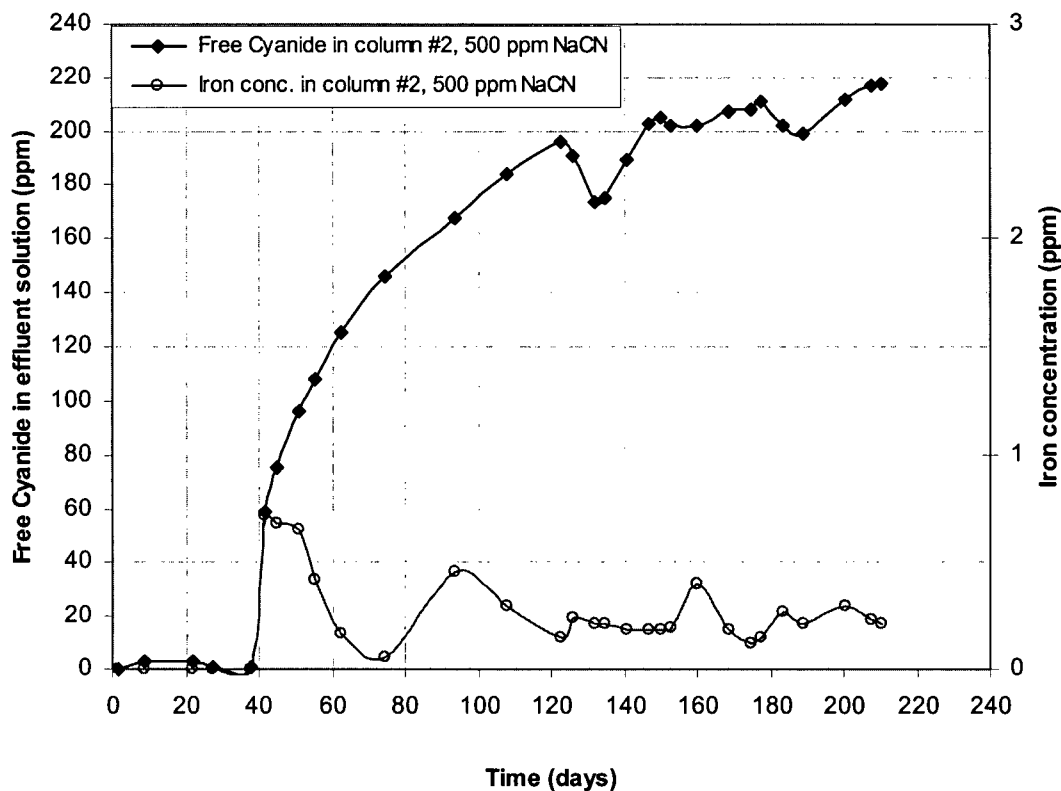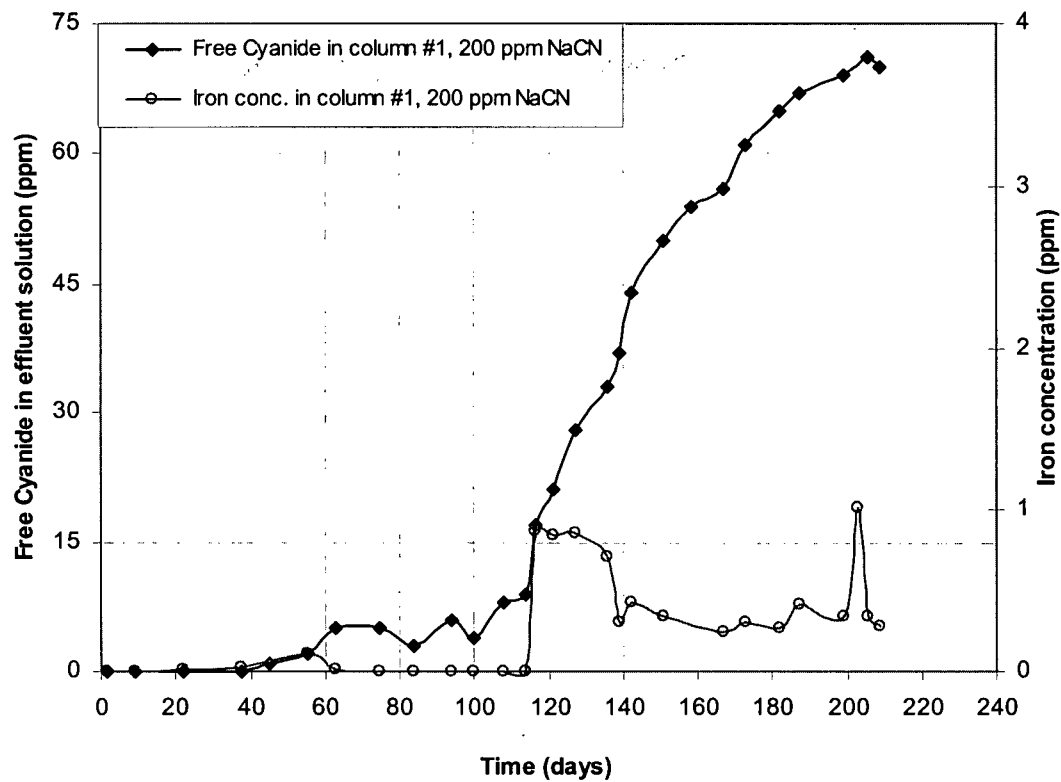
Figure 4-25 Iron behavior and the free cyanide concentration, column #3 and #4
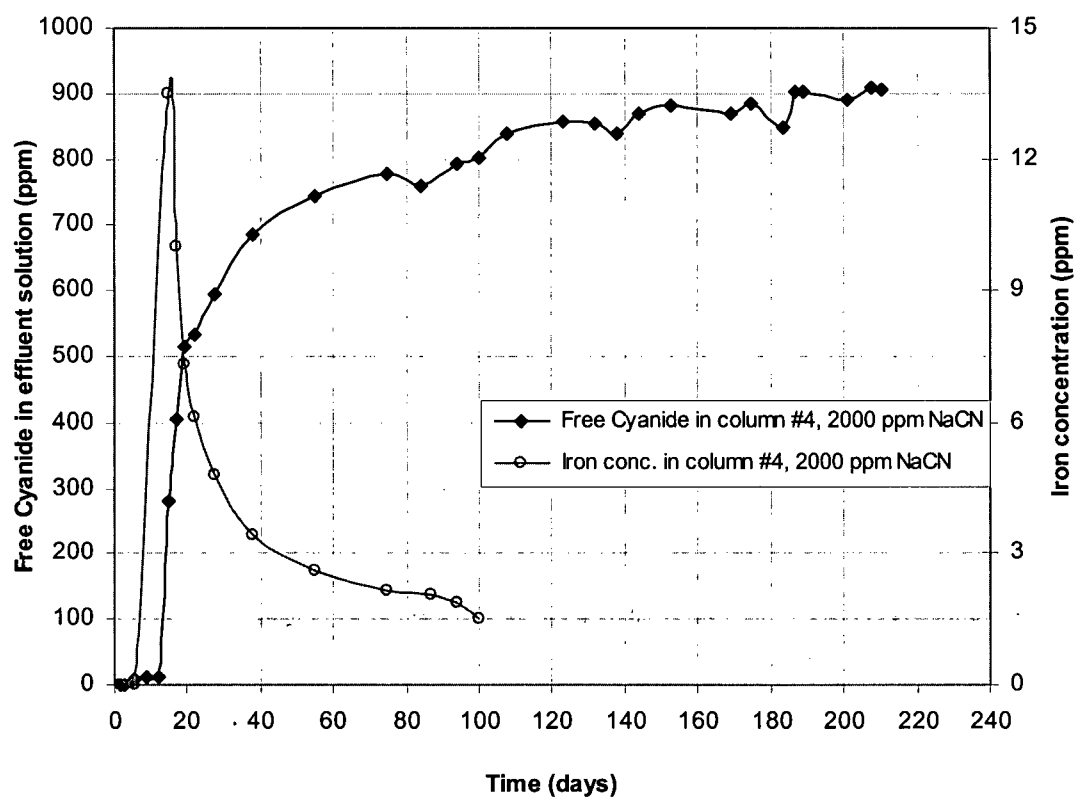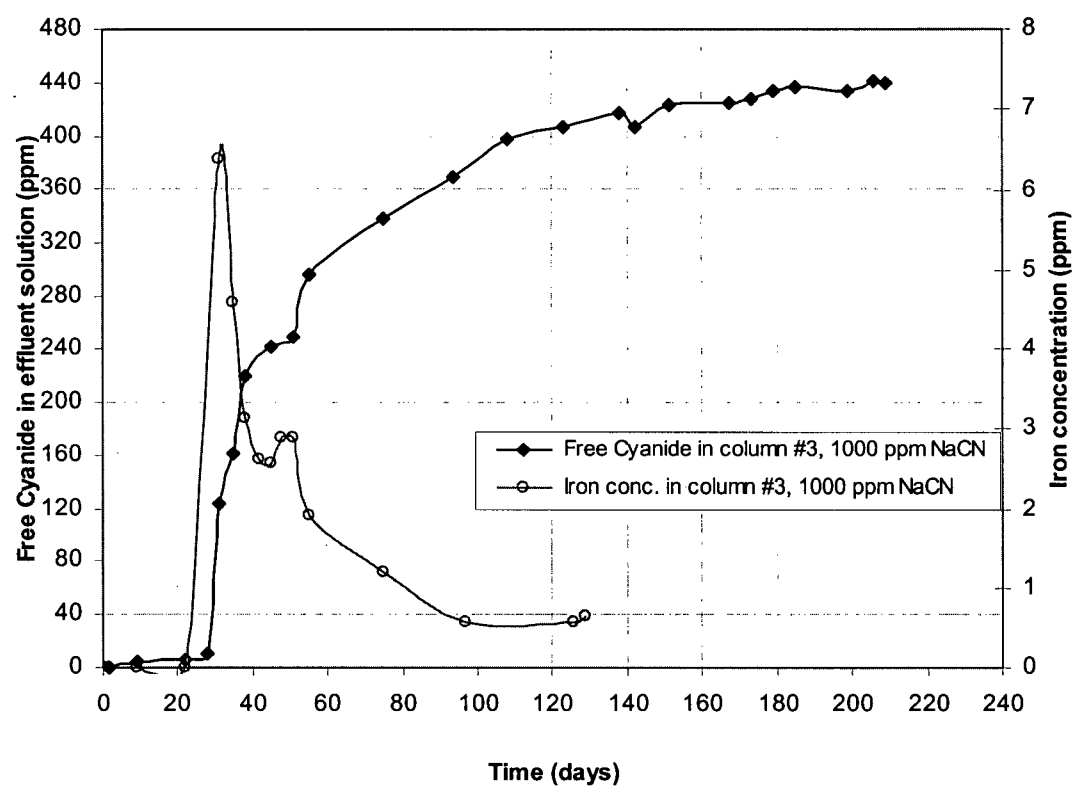
4.3 Conclusions

A considerable amount of copper as WAS copper minerals was excluded from the ore by pre-rinsing before cyanidation. At the onset of cyanidation, a remarkable decrease in the pH occurred. Given the high concentrations of thiocyanate in the effluent, the pH drop may be the result of dissolution of copper sulfide minerals in cyanide at the very beginning stages after running the cyanide in the columns. During this period the sulfide ion goes into solution first as HS^-, and subsequent oxidation forces the pH to decrease as follows:

$$2\,HS^- + 3\,H_2O \quad S_2O_3^{2-} + 8\,H^+ + 8\,e^- \quad \log K = -27.00$$

$$HS^- + 3\,H_2O \Leftrightarrow SO_3^{2-} + 7\,H^+ + 6\,e^- \qquad \log K = -37.28$$

$$HS^- + 4\,H_2O \Leftrightarrow SO_4^{2-} + 9\,H^+ + 8\,e^- \qquad \log K = -27.00$$
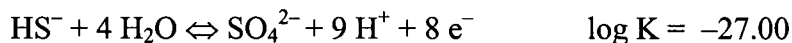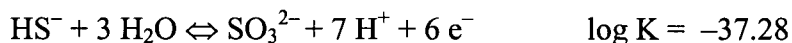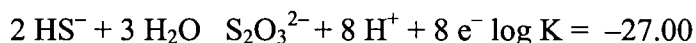
At the end of the pre-rinsing period, a solution of NaOH was passed through the columns. Also during the whole experiments, the pH of cyanide solutions was stabilized to higher that 10.5 with sodium hydroxide. The presence of copper sulfate minerals in the ore can be the source of $(OH)^-$ consumption and rapid decrease of the pH as follows:

$$CuSO_4 + 2NaOH \Leftrightarrow Cu(OH)_2 + Na_2SO_4$$
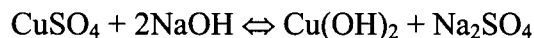
Because of the low pH at this time most of the reduced copper from the remaining WAS copper minerals and from the dissolution of copper sulfide minerals precipitates as $CuCN(s)$. With increasing pH, possibly mostly because of the oxidation of sulfide and the formation of thiosulfate and polysulfides which eventually leads to the formation of thiocyanate, the dissolution of labile copper sulfides continues with a higher rate and

finally creates the first peak in copper concentration curve. This implication is supported by the thiocyanate behavior. Redissolution of the copper cyanide precipitates, reaches a maximum at the second peak in the copper concentration curves. At this time, free cyanide becomes available in solution for dissolving other elements, and the first traces of iron are detected in the effluent.

Dissolution of gold began from the first day of cyanide leaching in all columns except column 1, which gave a lag time of 4.2 days before the appearance of gold in the effluent. Given that the pH ranged from 4.7 to 5.1 during that period, the precipitation of gold as $AuCN(s)$ seems unlikely. Regarding the low amount of cyanide in the influent solution for this column, the presence of thiocyanate in the effluent solution from the very first samples and the consuming of most of the cyanide by copper, the lack of available free cyanide may be the main reason for this lag time. Similar lag times were also noted in all four columns of phase I. It should be noted that the presence of gold in effluent solutions from very beginning of the leaching experiments, in the absence of free cyanide, suggests that gold was leached with cyanocuprate complexes.

5 Experimental results and discussions - phase III

5.1 Pre-rinsing period

As in phase II, the columns in phase III were pre-rinsed with de-ionized water for a period of one month. In the last week of pre-rinsing, the pH was adjusted to 11 to stabilize the pH prior to cyanidation.

The first droplets of effluent solution appeared after 36 hours with a color of dark blue. Effluent copper concentrations, shown in Figure 5-1, are more or less identical to those of phase II.
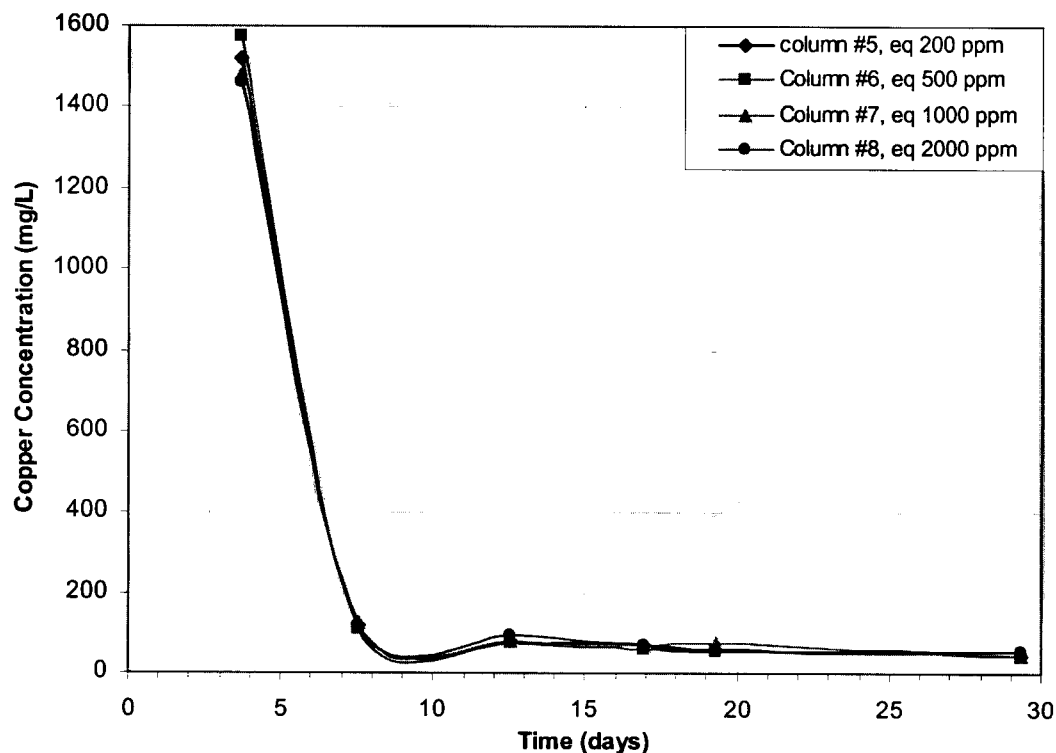
Figure 5-1 The copper concentration in pre-rinsing period, phase III

Pre-rinsing was halted once the copper concentration in all from all four columns fell to within 40 to 50 mg/L, which occurred after 29 days. Total amounts of 12.13, 12.11, 11.79 and 11.41 grams of copper were discharged respectively from columns 5, 6, 7 and 8. This compares with 9.38, 9.34, 9.48 and 8.91 grams of copper discharged from columns 1, 2, 3 and 4 in phase II after 21-23 days of rinsing. Copper extraction curves during pre-rinsing for phase III are presented in

Figure 5-2.
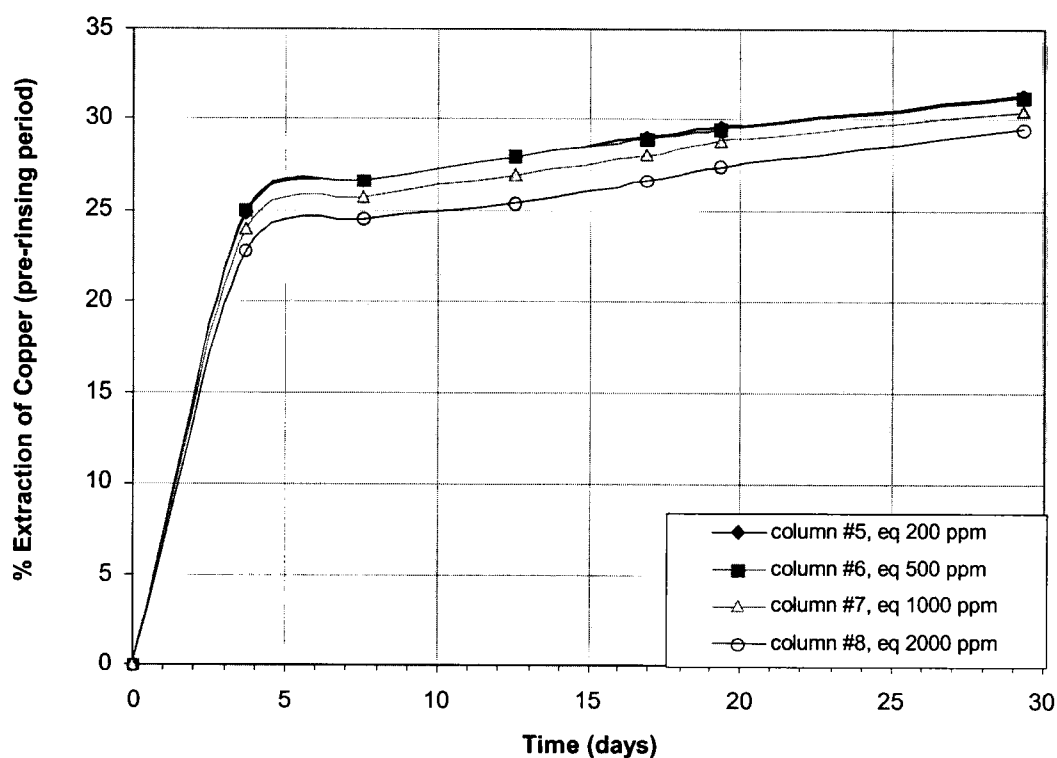
Figure 5-2 Copper extraction in pre-rinsing process (%), phase III

Because of the presence of large concentrations of copper cyanide complexes in the leaching solutions, the estimated value of copper head grade from the untreated ore, 2580 ppm, has been used in all copper extraction calculations. According to these, 29.5 to 31 percent of the total copper was removed during pre-rinsing. As shown in Figure 5-3, more than 80 percent of this water-soluble copper was removed in less than five days of rinsing.
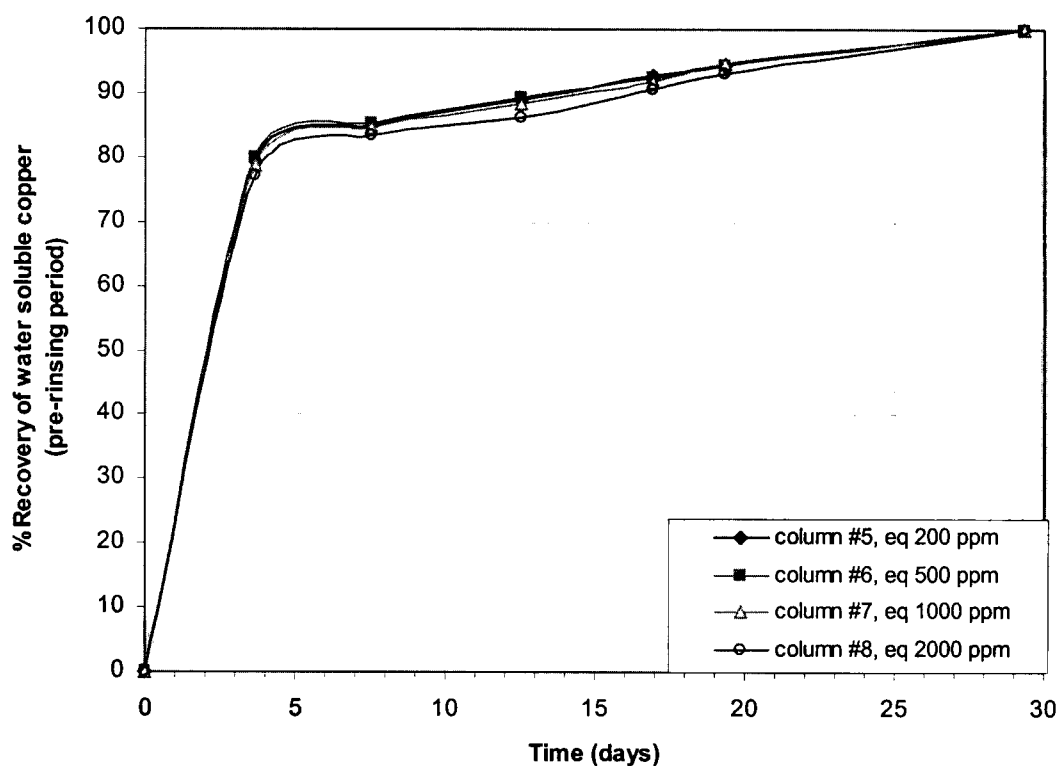
Figure 5-3 Water-soluble copper extraction in pre-rinsing period

5.2 Leaching with copper cyanide solutions

5.2.1 Presentation of the copper behavior

Because the leach solution lacked free cyanide, the copper shows an entirely different behavior from that observed in phase II, as shown in Figure 5-4. The influent solutions were prepared by dissolving a mixture of copper cyanide and sodium cyanide powders in de-ionized water at pH 11. Therefore, the influent solutions in this phase initially contained a high concentration of copper. Table 5-1 presents some aspects of the chemistry of the influent solutions. As shown in the table, a cyanide to copper mole ratio of three was maintained to insure the presence of predominantly the tricyanocuprate(I) complex.

The curves in Figure 5-4 begin with very low concentrations of copper, which rapidly increase during the first week of leaching. After six to eight days, the rapid increase ends and the concentrations continue to rise gradually. Eventually, the concentration curves pass through the value of the influent copper concentration and then try to stabilize somewhere above those concentrations. This behavior is nearly the same for all of the columns except column 8, which inexplicably shows frequent sharp changes. A number of samples from this column were sent to different analysts to determine if any major error was incurred during the first analysis, with similar results.
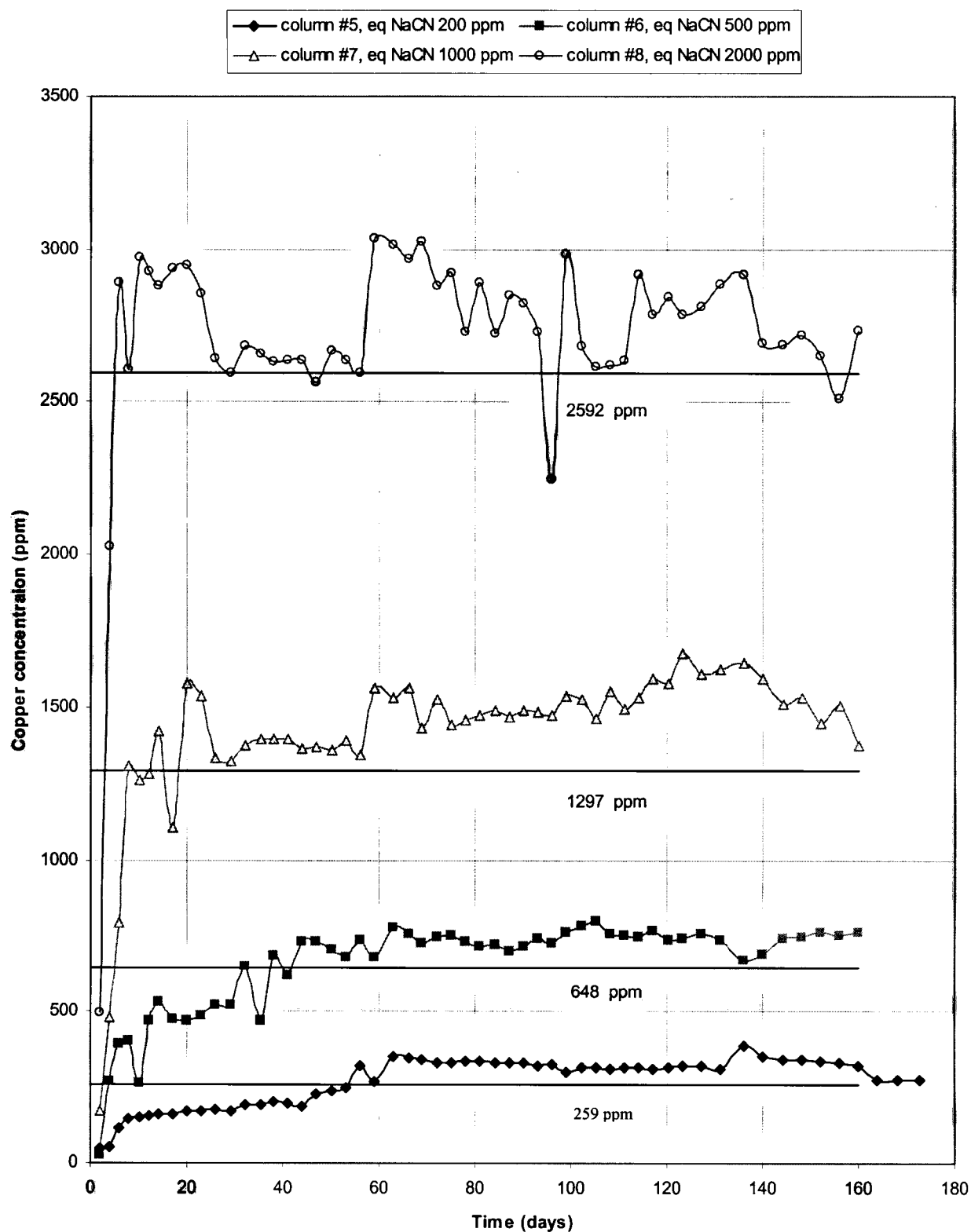
Figure 5-4 Copper concentrations of the effluent solutions, phase 3

Table 5-1 Some aspects of the influent solutions chemistry in phase 3

Column Number	5	6	7	8
Equivalent [NaCN] (ppm)	200	500	1000	2000
[NaCN] (ppm)	400	1000	2000	4000
[CuCN] (ppm)	364.7	914	1828	3653.3
Total [CN$^-$] (ppm)	318	796	1593	3185
Total [CN$^-$] as [NaCN] (ppm)	600	1500	3000	5999
[Cu$^+$] (ppm)	259	648	1297	2592
CN$^-$/Cu$^+$ mole ratio	3	3	3	3
PH	11.5	11.5	11.5	11.5

Copper extraction curves are presented in Figure 5-5. These curves continue from where the curves in Figure 2 left off. Time zero in this figure is the time of the first detection of column effluent. Copper introduced with the influent solution for each sample has been subtracted from the total copper. For this reason, these plots show a decrease during the early stages of leaching. This decrease is sharper but shorter lived at higher influent copper concentrations. This period takes 53, 35, 12 and 4 days respectively for columns 5, 6, 7 and 8. Then copper concentrations increase at a rate in proportion to the influent copper concentration. The remarkable aspect of the extraction curves is that even in this

case the copper is leached along with the gold, although the final extraction is very different between these columns. Columns 1 and 2 show final recoveries of 43 to 46 percent, while this value for columns 7 and 8 is equal to 120 percent, which is obviously in error. Upon close inspection of the data, and after conducting additional atomic absorption analysis, it was determined that two factors could be the source of error:

1. The actual concentrations of copper in the influent solutions may have been slightly higher than the calculated values. This could have occurred because of changes in the composition of the reagents, or by experimental error in preparing the influent solutions.

2. Noting the significant differences in the copper analysis results from different analysts, and considering the high stability of the cyanocuprate complexes, some errors in the copper analytical procedure could be the source of these errors.

Finally investigating the copper concentration curves and the copper extraction plots can suggest that, data that are more reliable have been gained in experiments on columns 5 and 6.
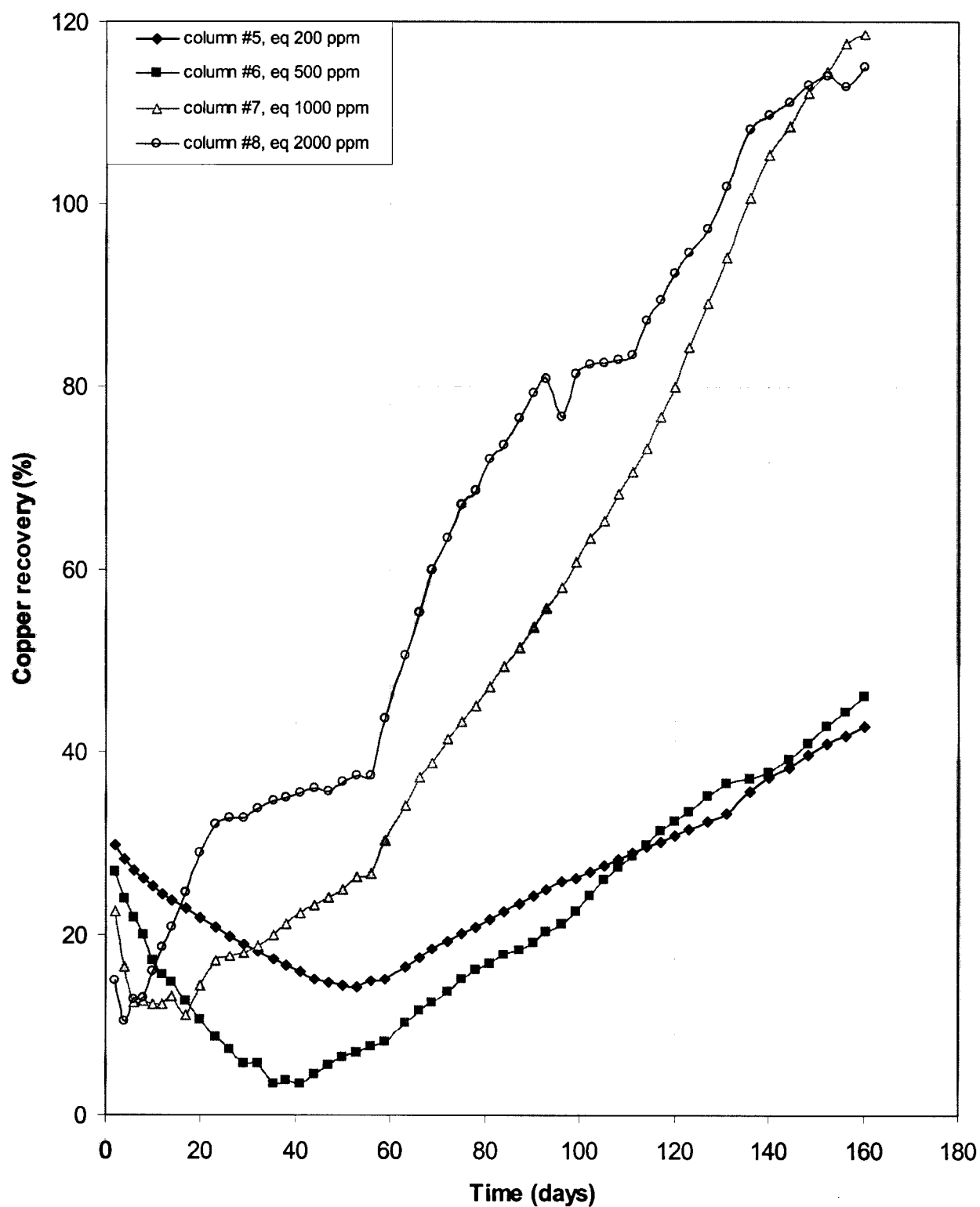
Figure 5-5 Copper extraction (%), phase 3

5.2.2 The behavior of gold

Figure 5-6 shows gold concentration in the effluent solutions in phase 3. Unlike copper, the gold curves are very smooth and easy to interpret. Some interesting aspects of these plots can be listed as follows:

1. Gold dissolution begins rapidly, with no lag time in all four columns.

2. Peaks in the gold concentration curves are observed at the beginning of the leaching process, and only in column 5 does this peak take place beyond the first data point.

3. The intensity of these peaks is related to the influent cyanocuprate concentration.

4. These curves continue with a downward tail until all the amenable gold in the columns is leached to a final detectable concentration of 0.01 mg/L.

The extraction curves in Figure 5-7 show that higher gold recoveries can be achieved in a shorter time with higher cyanocuprate concentrations. Gold recoveries of 60 to 75% were obtained in these experiments, although the times required for these recoveries are very different for the different columns. For instance, it took 160 days for column 5 to pass 60% extraction, while this value for columns 6, 7 and 8 was 108, 63 and 29 days, respectively. This compares to 168, 67, 38 and 21 days for columns 1, 2, 3, and 4, respectively.
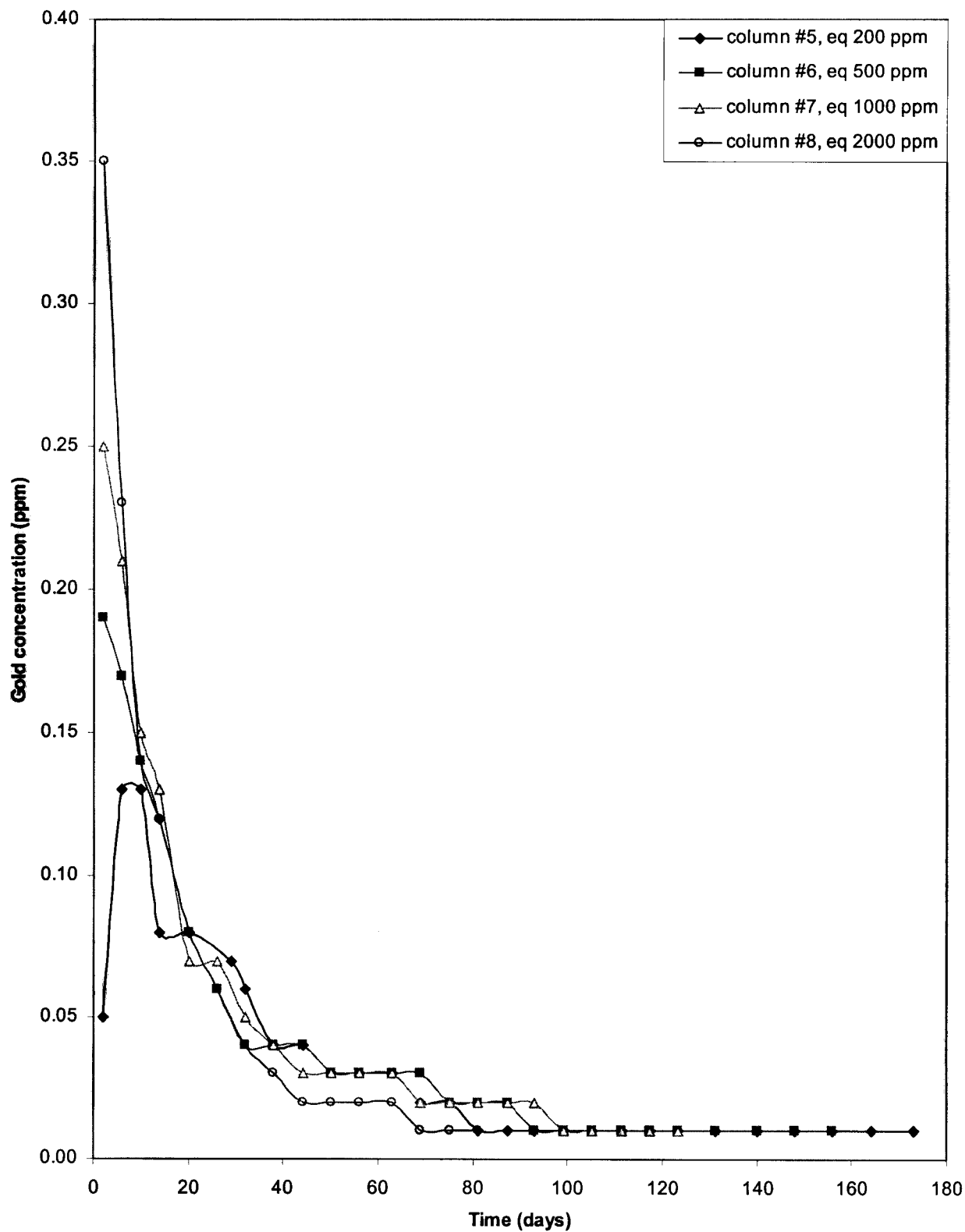
Figure 5-6 Gold concentration behavior, phase 3
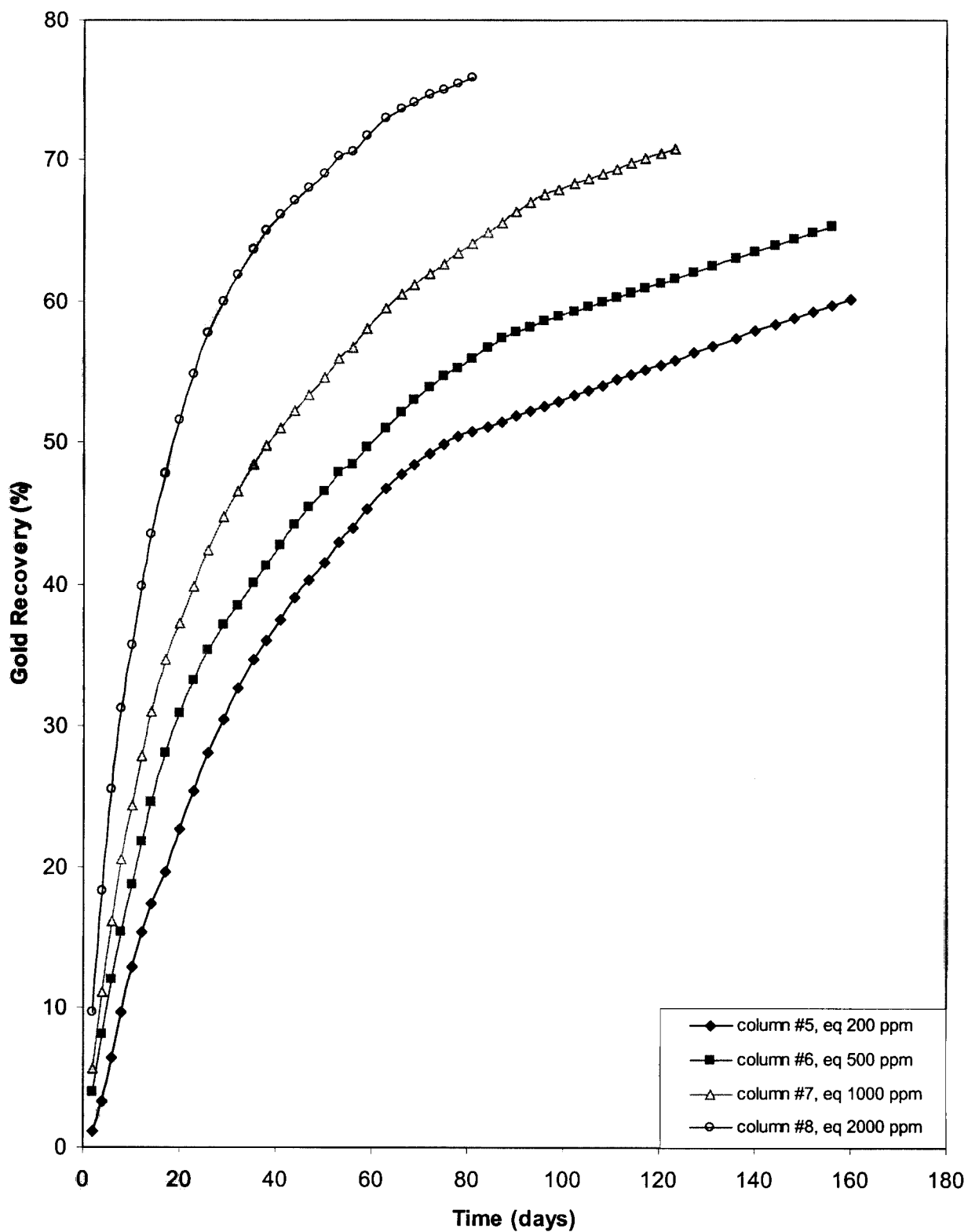
Figure 5-7 Gold extraction in phase 3

Therefore, it can be concluded that cyanide can dissolve gold faster than cyanocuprate complexes, and better recoveries can be achieved with cyanide solutions.

5.2.2.1 Gold head grade

At the end of the leaching experiments, as in phase II, the treated residues were divided into five sections and sent for analysis. Detailed analytical results are given in Appendix F. Figure 5-8 shows the gold concentration in each column section. In this figure it is perfectly clear that columns with higher cyanocuprate concentrations contained less residual gold.

By determining the total gold leached and the total gold remaining in the residue, it is possible to calculate the gold head grade. The details of these calculations are given in Table 5-2. According to these results, a value of 0.80 ppm has been determined for the average gold head grade. This value was determined to be 0.85 ppm in phase II.

Table 5-2 Determining the gold head grade in columns 5 – 8, Phase III

Column Number	5	6	7	8
Equivalent [NaCN] ppm	200	500	1000	2000
Column Leach test period (day)	180	160	160	160
Net Gold Leached in Cyanide column leach (mg)	7.450	8.587	8.663	7.521
Net Gold in residual ore (mg)	4.919	4.554	3.563	2.389
Total net Gold (mg)	12.369	13.141	12.227	9.910
Weight of ore in column (mg)	15000	15000	15000	15000
Calculated Head Gold grade (ppm)	0.82	0.88	0.82	0.66
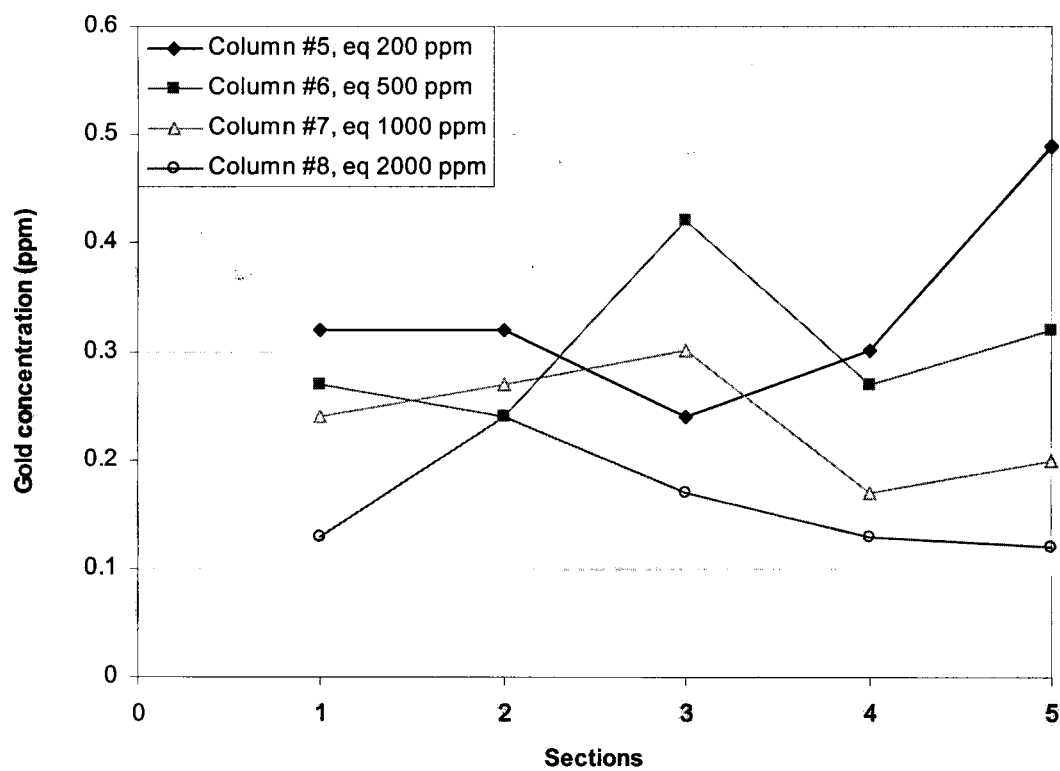
Figure 5-8 Gold grades in leached residual of ore, phase III

5.2.3 pH behavior of the effluent solution

Figure 5-9 presents the pH behavior of the effluent solutions. The general pH behavior in all of the columns can be summarized as follows:

1. As seen in phase II, a very sharp decrease in the pH of the effluent solutions was experienced for the first samples, compared to the pH of the influent solutions. Columns with lower cyanocuprate concentrations showed more intense decreases in pH.

2. The pH increases rapidly in subsequent samples, at a higher rate in columns with higher cyanocuprate concentrations.
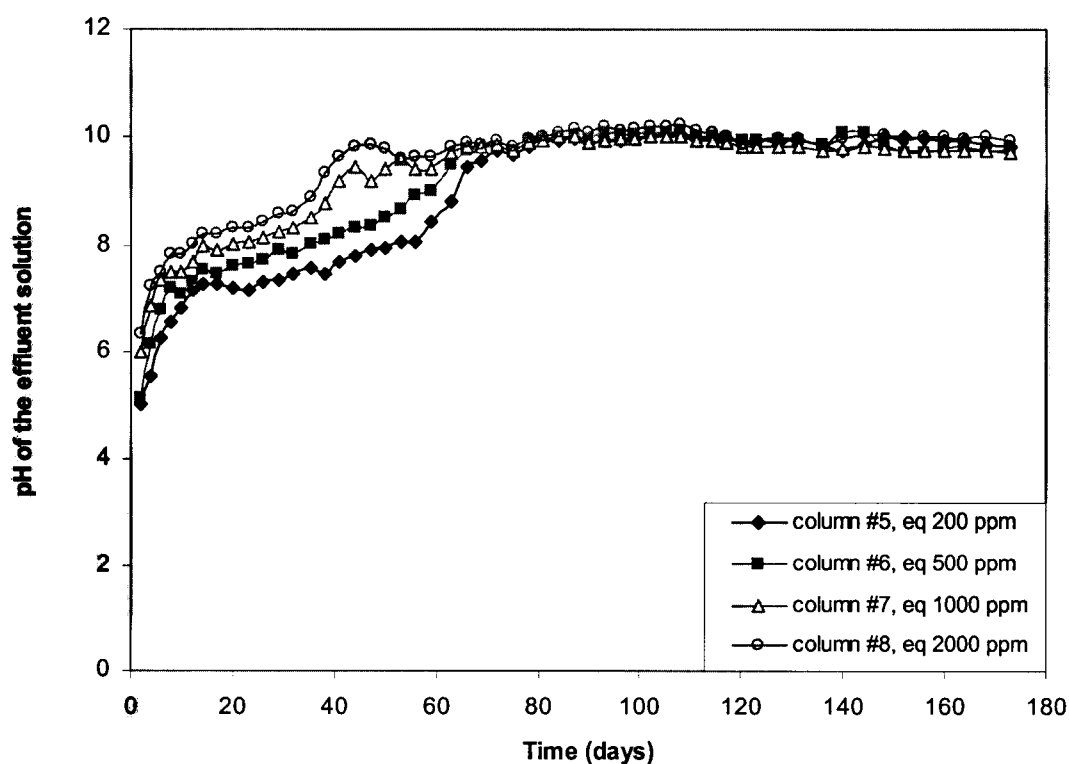
Figure 5-9 pH variation of the effluent solution in phase III

3. In next stage, the pH increases gradually for a longer time. This step is also shorter for columns with higher cyanocuprate concentrations.

4. Finally, another rapid increase in pH occurs, after which all of the columns approach approximately the same effluent pH.

Some of the interesting aspects of Figure 5-9 and some comparisons with the results from the phase II experiments are listed in Table 5-3. It should be noted that the pH of the influent solutions in this phase was adjusted to 11, while this value was 11.5 in phase II. It is also noted that although the pH of the influent solutions in this phase was lower,

Table 5-3 - Some of the selected aspects of the pH curves

Column Number	1	2	3	4
Equivalent NaCN concentration (ppm)	200	500	1000	2000
pH of the first sample, Phase II	4.68	4.65	5.32	5.89
pH of the first sample, Phase III	5.04	5.13	6.01	6.33
pH at the end of the first rapid increase, phase III	7.29	7.19	7.49	7.83
pH at the end of the gradual increase, Phase III	8.05	8.52	8.50	8.63
Time of the end of the gradual increase in pH (days)	56	50	35.3	32
pH at the end of the second rapid increase, phase III	9.44	9.75	9.44	9.83
The average final pH, phase III	9.89	9.93	9.79	9.97

the decrease in pH in the first samples is not as sharp as in phase II. The following reasons may be responsible for this:

1. Because a longer time was spent pre-rinsing phase III, more of the WAS copper minerals were dissolved from the columns. This would serve to increase the pH slightly in phase III.

2. The WAS copper minerals may also be less soluble in cyanocuprate solution than in cyanide solution.

Because of the high concentrations of copper in the influent solutions, it is very difficult to follow the actual copper dissolution behavior and the accompanying pH variations in every step of these experiments. However, Figure 5-10 and Figure 5-11 certainly indicate a close relationship between effluent copper concentration and effluent pH.

As was seen in Figure 5-4, the time required for the effluent solutions to achieve the influent copper concentrations differed for each column. However, the time required for filling the columns with influent copper solution and reaching a physical equilibrium in the absence of chemical reactions would be expected to be the same for each column. It is remarkable that the very low concentrations of copper in all of the columns at the beginning of the experiments occur during the first stage of pH variations as described above. It is clear that most of the copper from the influent solutions, and from the dissolution of copper minerals, precipitated in the columns at low pH. In the second stage of pH variations, with the influx of highly basic solution to the columns, the pH increases rapidly, and as a result:

1. Less copper cyanide is precipitated.

2. Some of the precipitated copper cyanides re-dissolve.

Figure 5-10 Comparison of pH and [Cu] of the effluent solutions, columns 5 & 6
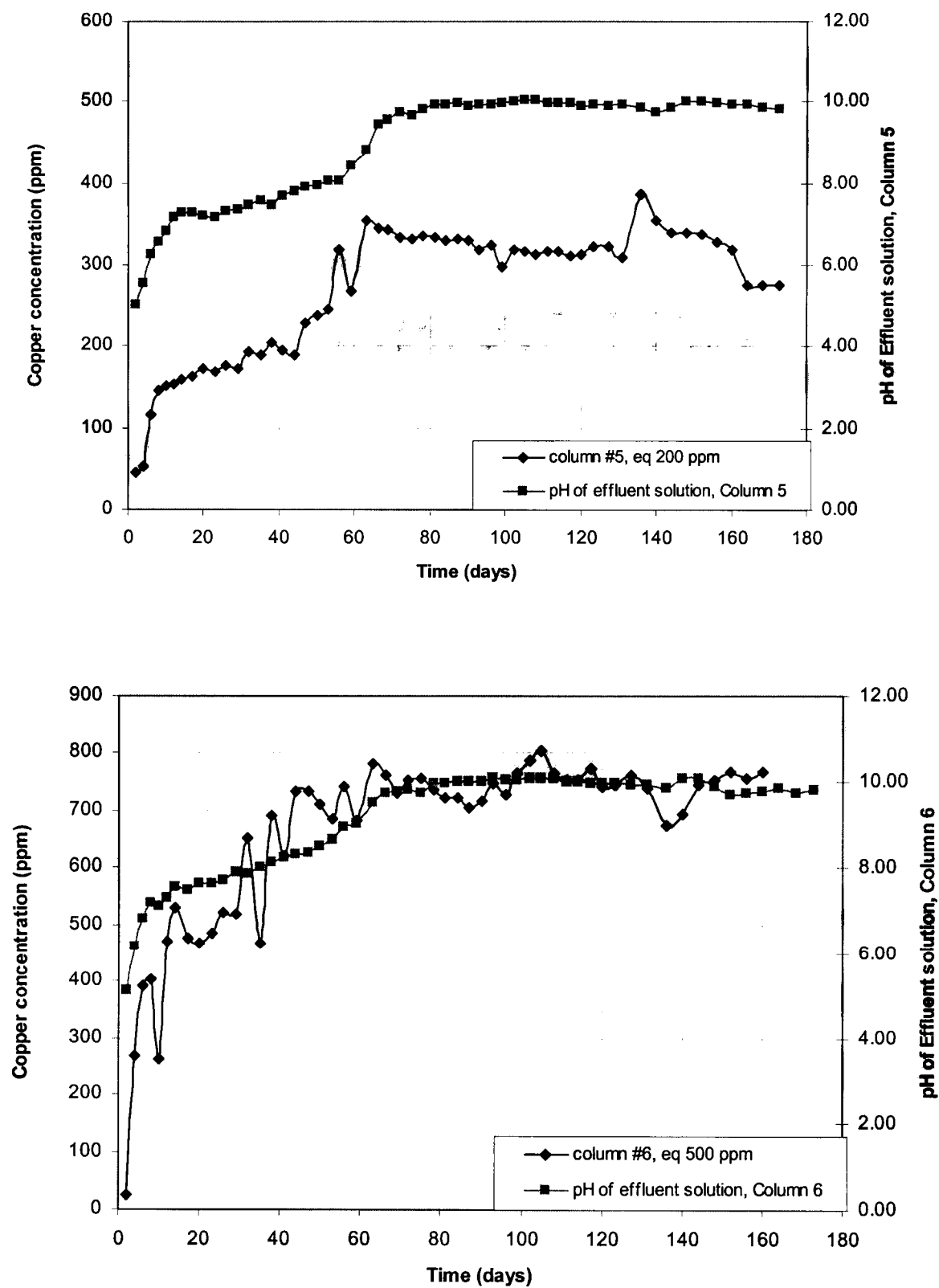
Figure 5-11 Comparison of pH and [Cu] of the effluent solutions, columns 7 & 8
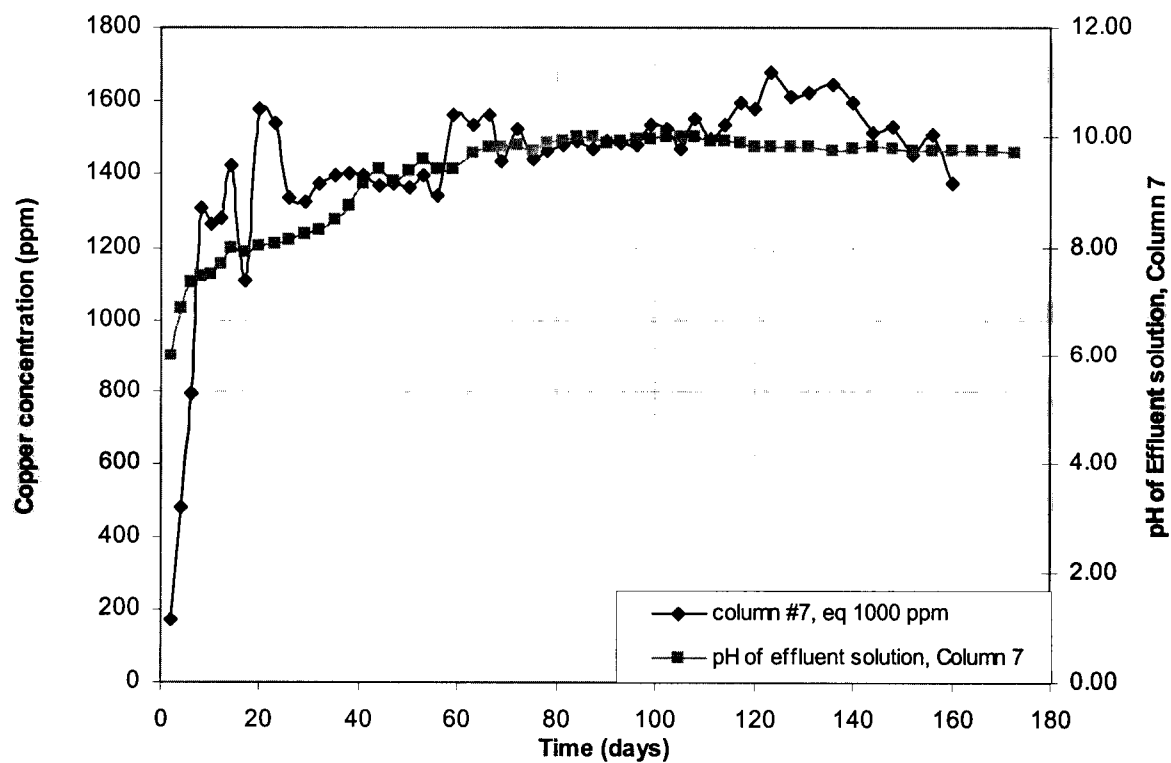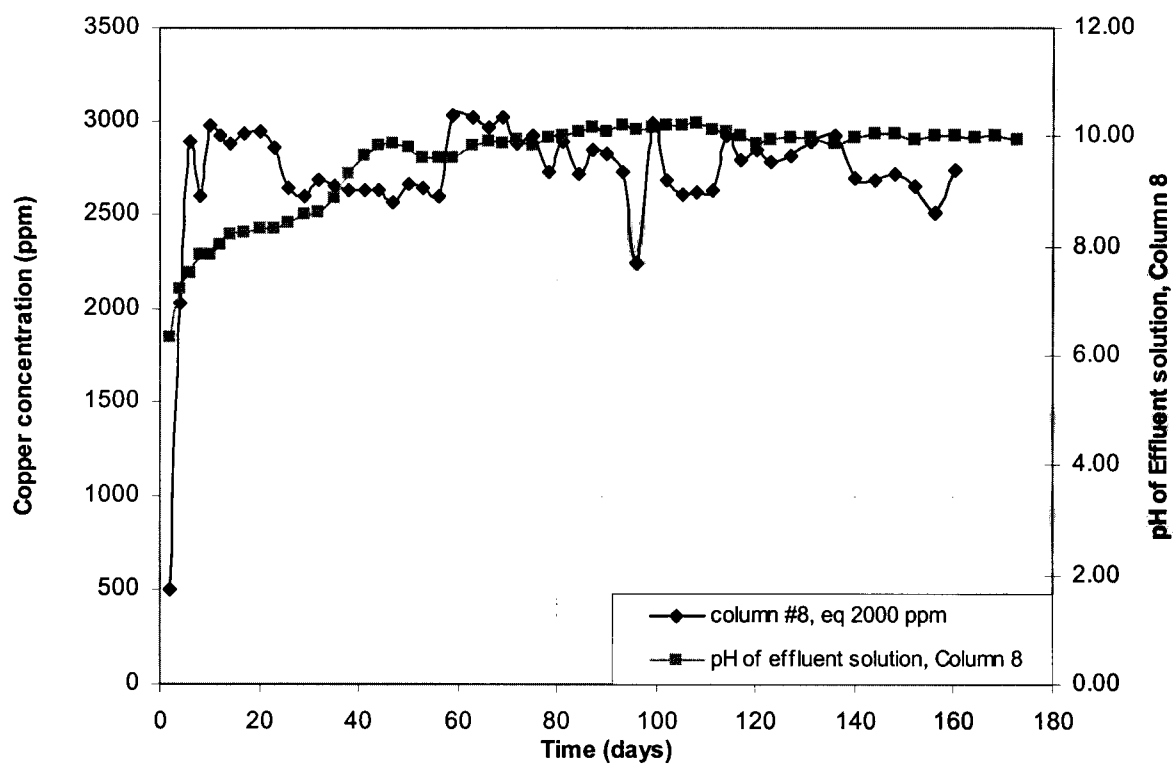
5.2.4   Free cyanide concentration in the effluent

Although the total cyanide concentration of the influent solutions in phase III was almost three times larger than in phase II, most of the cyanide was complexed with copper ions. Therefore, it was very difficult to analyze the effluent solutions for free cyanide concentration with acceptable error due to the interference of cyanocuprate complexes. The results of titration analyses of the effluent solutions for free cyanide concentration are shown in Figure 5-12. The similar behavior of these curves, albeit at different levels, is the remarkable aspect of these plots.

Comparing with the same curves from phase II, the following aspects are notable:

1. The maximum free cyanide concentrations are 10 to 25 times smaller in phase III.

2. Unlike in phase II, no lag time is noted at the beginning of the curves.

3. Also in contrast to phase II, the free cyanide concentrations never reach stable values.
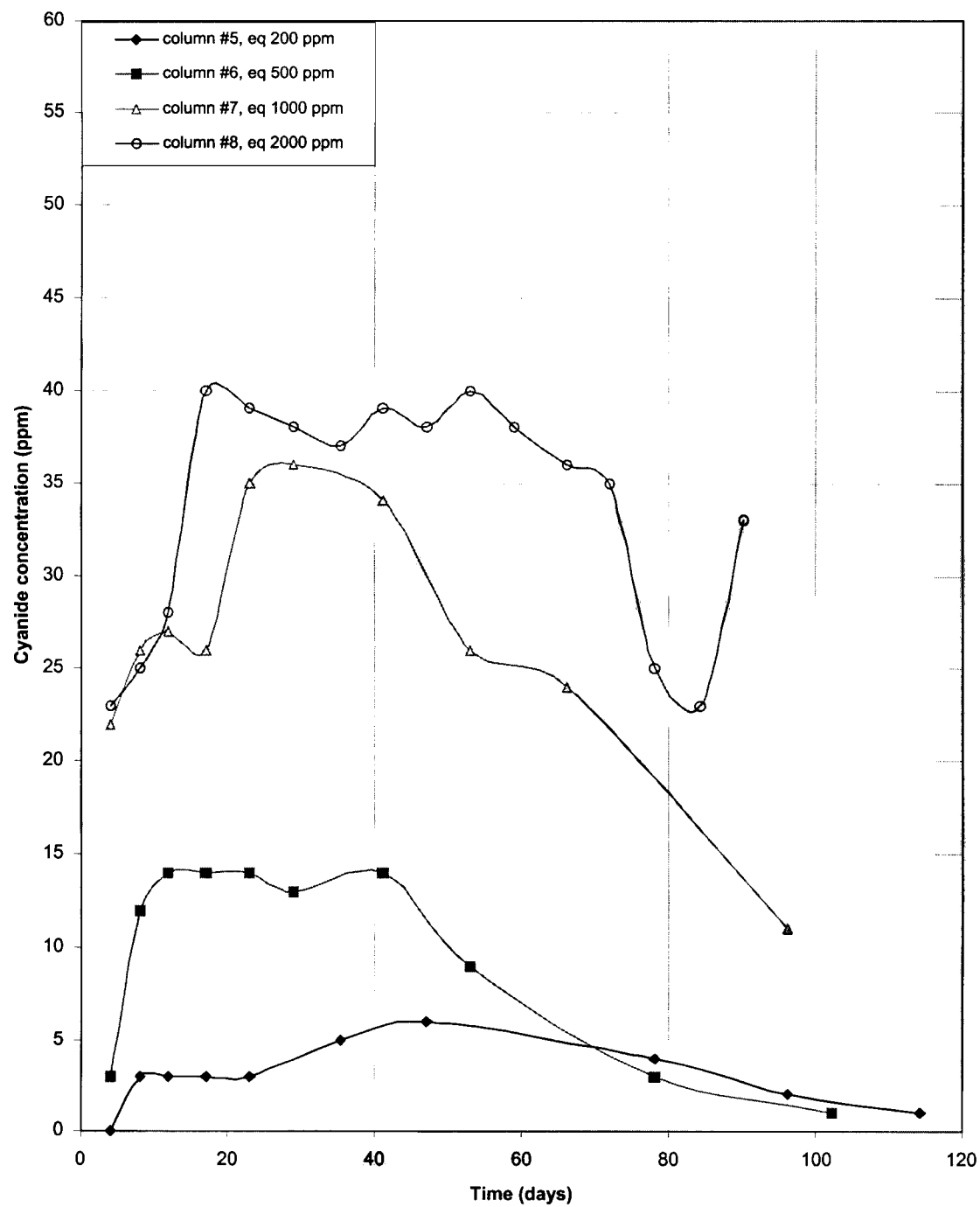
Figure 5-12 The approximate free cyanide concentrations in effluent solutions, phase III

5.2.5 Thiocyanate in the effluent solution

As explained in chapter 4, the presence of thiocyanate in the effluent solutions is the result of copper sulfide leaching or the reaction of sulfur with cyanide. Although it is believed that most of the cyanide in the influent solutions from phase III was in form of cyanocuprate complexes, the presence of thiocyanate ions was again detected, as shown in Figure 5-13 and Figure 5-14. Some of the interesting features of these figures can be summarized as follows:

1. The presence of thiocyanate ions at the beginning of all of the experiments shows that the dissolution of copper sulfide minerals must have occurred from the very early stages of these experiments.

2. The maximum thiocyanate concentrations in these experiments fall between 35 and 50 mg/L, and unlike in phase II, they seem to bear no relationship to the cyanide concentrations of the influent solutions.

3. The thiocyanate concentrations in phase III are 2 to 25 times smaller than in phase II.

4. As shown in these figures, the thiocyanate concentrations decline rapidly when the pH is increasing, tends to stabilize at high pH values.

It is important to note that thiocyanate is only one of the possible reaction products of sulfide mineral dissolution in cyanide systems, and primarily bisulfide ions, with some thiosulfate and polysulfides, can be the other products of such reactions, depending on the pH.

Figure 5-13 [SCN⁻] of the effluent solutions in phase III, columns 5 & 6
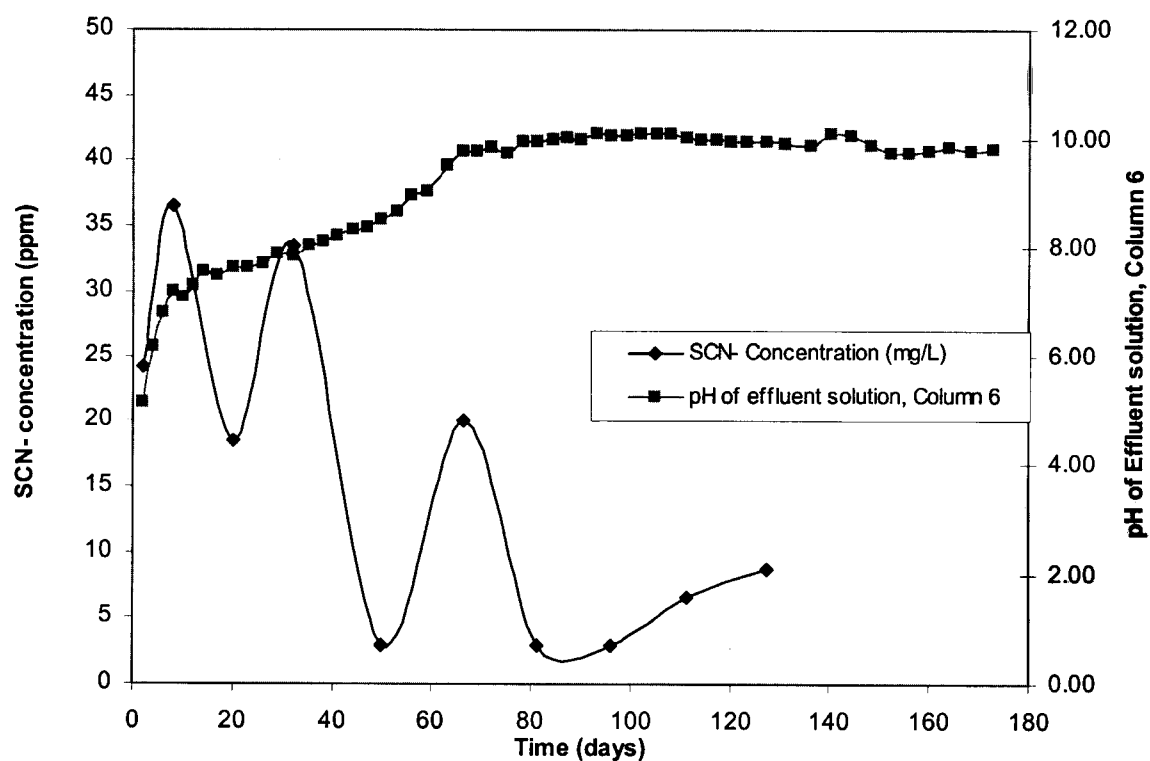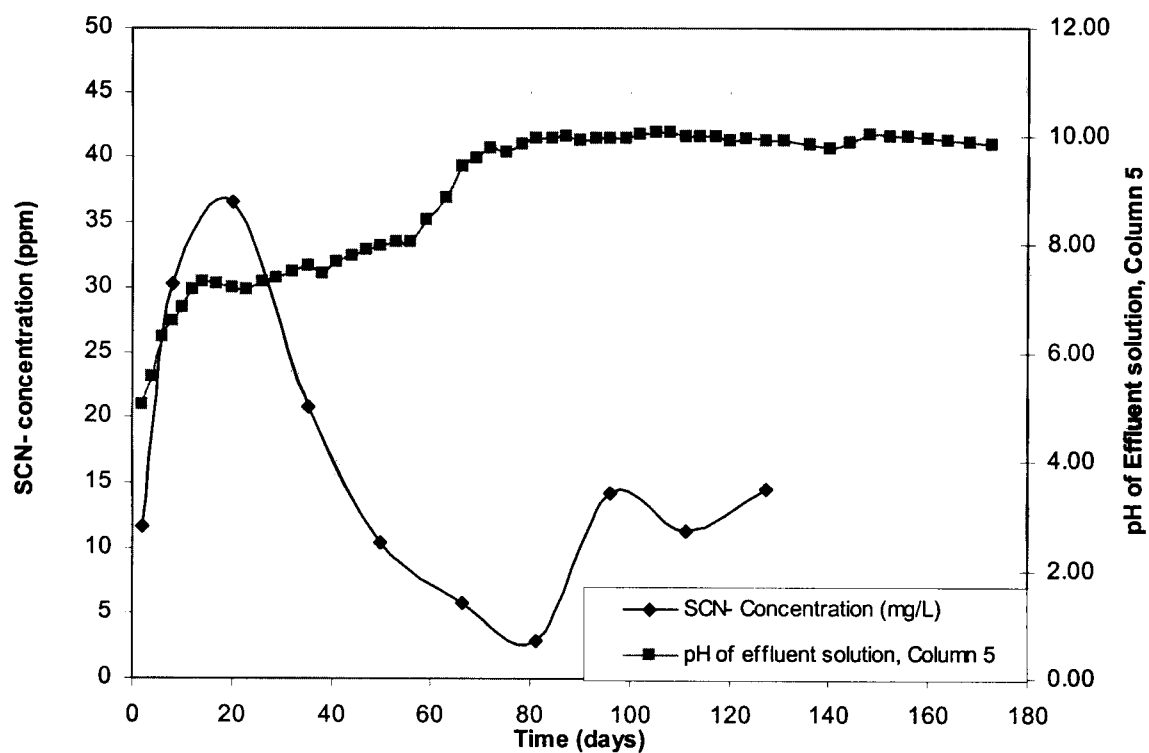
Figure 5-14 [SCN⁻] of the effluent solutions in phase III, columns 7 & 8
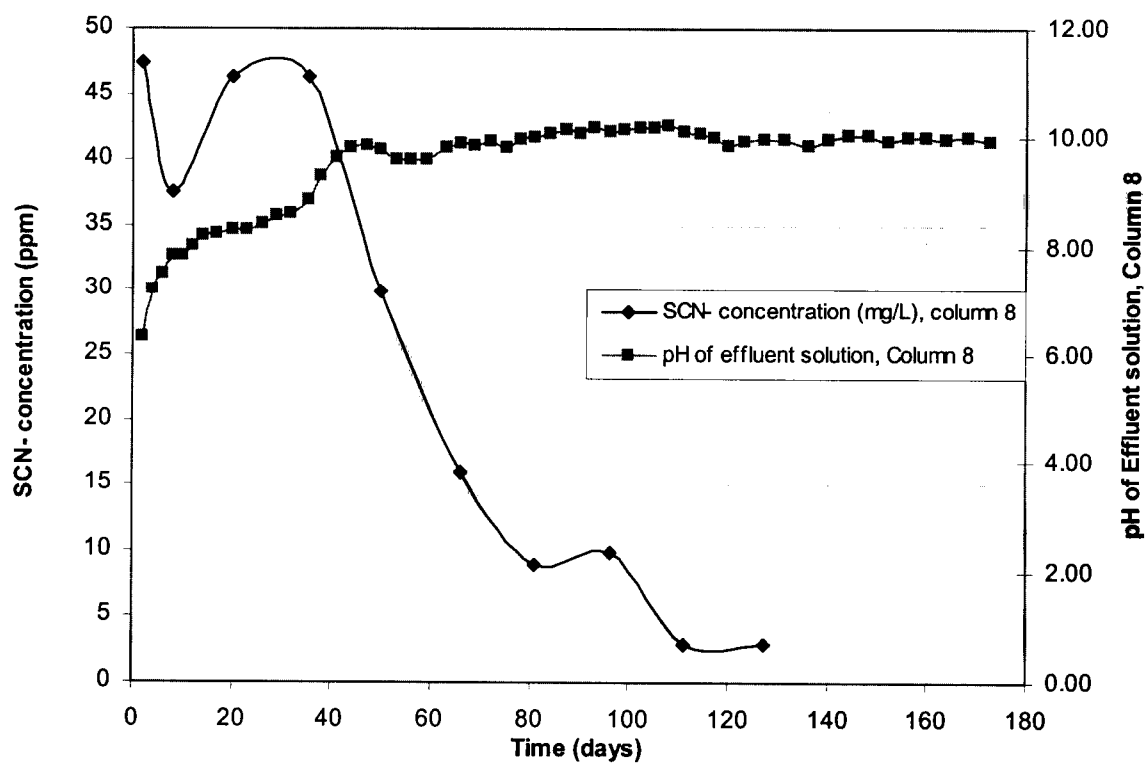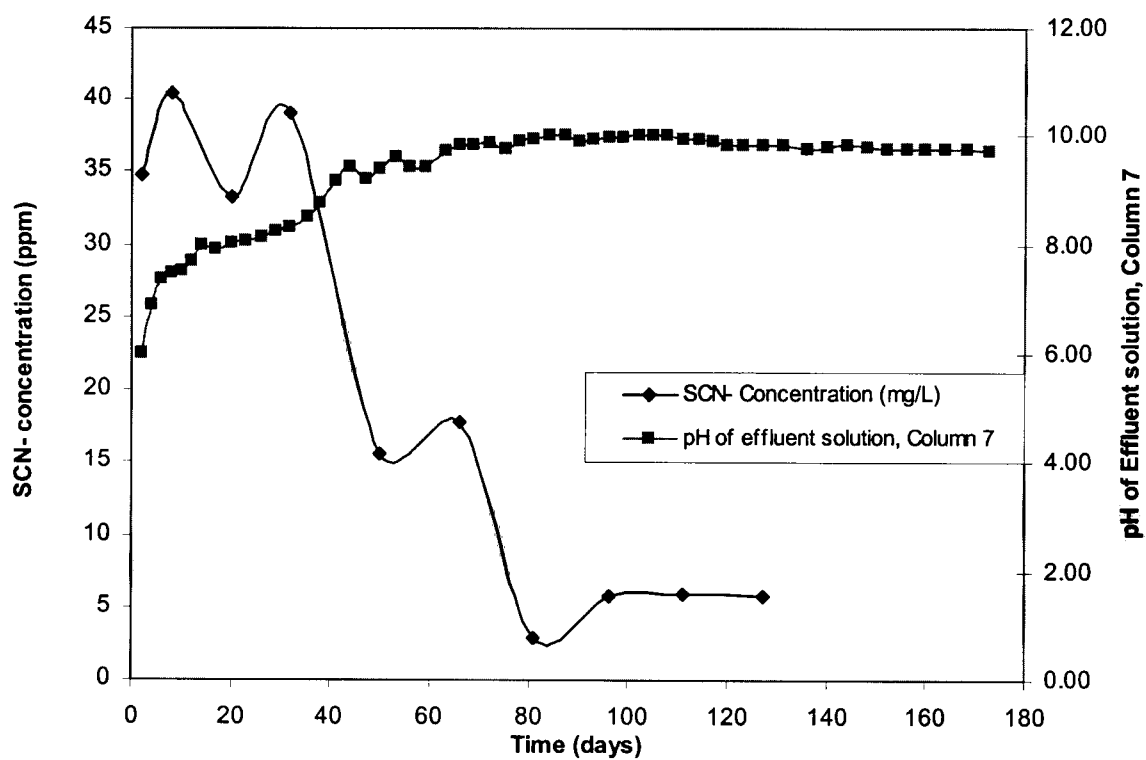
5.2.6 The behavior of iron

Unlike in phases I and II, the iron concentration curves do not display any particularly notable behavior in phase III, as shown in Figure 5-15. In previous phases it was experienced that iron dissolution occurred only after cyanide breakthrough. Considering the iron concentration curves in this phase, it can be suggested that iron does not have significant solubility in cyanocuprate solutions in the absence of free cyanide. Even in experiments with very high concentrations of cyanocuprate complexes, no considerable amount of iron was detected in the effluent solutions.

Iron at very low concentrations was detected in the effluent solutions from the first day of leaching, with no significant changes in concentration observed during the experiments.
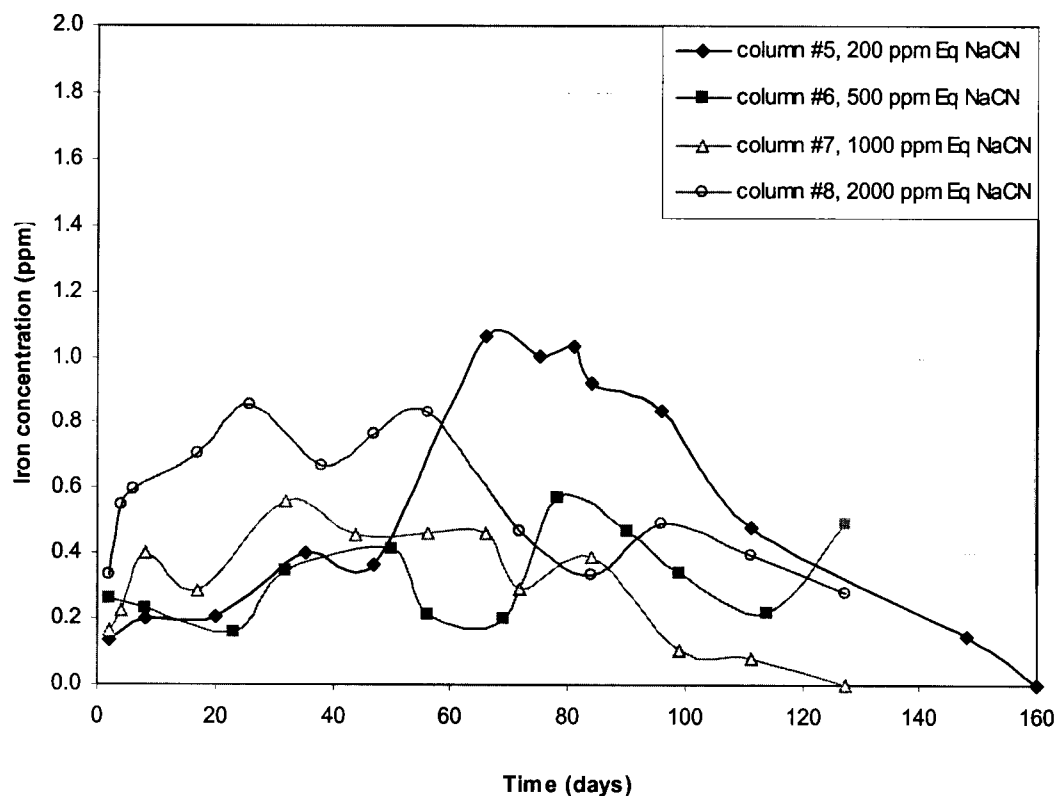
Figure 5-15 Iron concentration curves in phase III

5.3 Conclusion

Investigation of the copper concentration and copper extraction data in phase III suggests the occurrence of some error, particularly in columns 7 and 8. Although calculated copper recoveries are larger than expected, comparing them with the gold extraction curves and with the data provided in phase II presents some remarkable aspects, as shown in Figure 5-16 and Figure 5-17. In these figures, copper extraction has been calculated based on the copper content of the columns after pre-rinsing. In addition, in Figure 5-16 the copper contents of the influent solutions have been subtracted from the copper contents of each sample, and hence, there are some negative values in these extraction curves which are not shown in the figure.

Phase III has provided sufficient data to show that a solution of cyanocuprate complexes will dissolve a significant amount of copper from copper minerals, even in the predicted absence of free cyanide. However, as shown in Figure 5-16, before gold extraction reaches 60%, copper shows little if any extraction. In phase II at 60% gold extraction, 35 to 40% of the copper had been recovered.
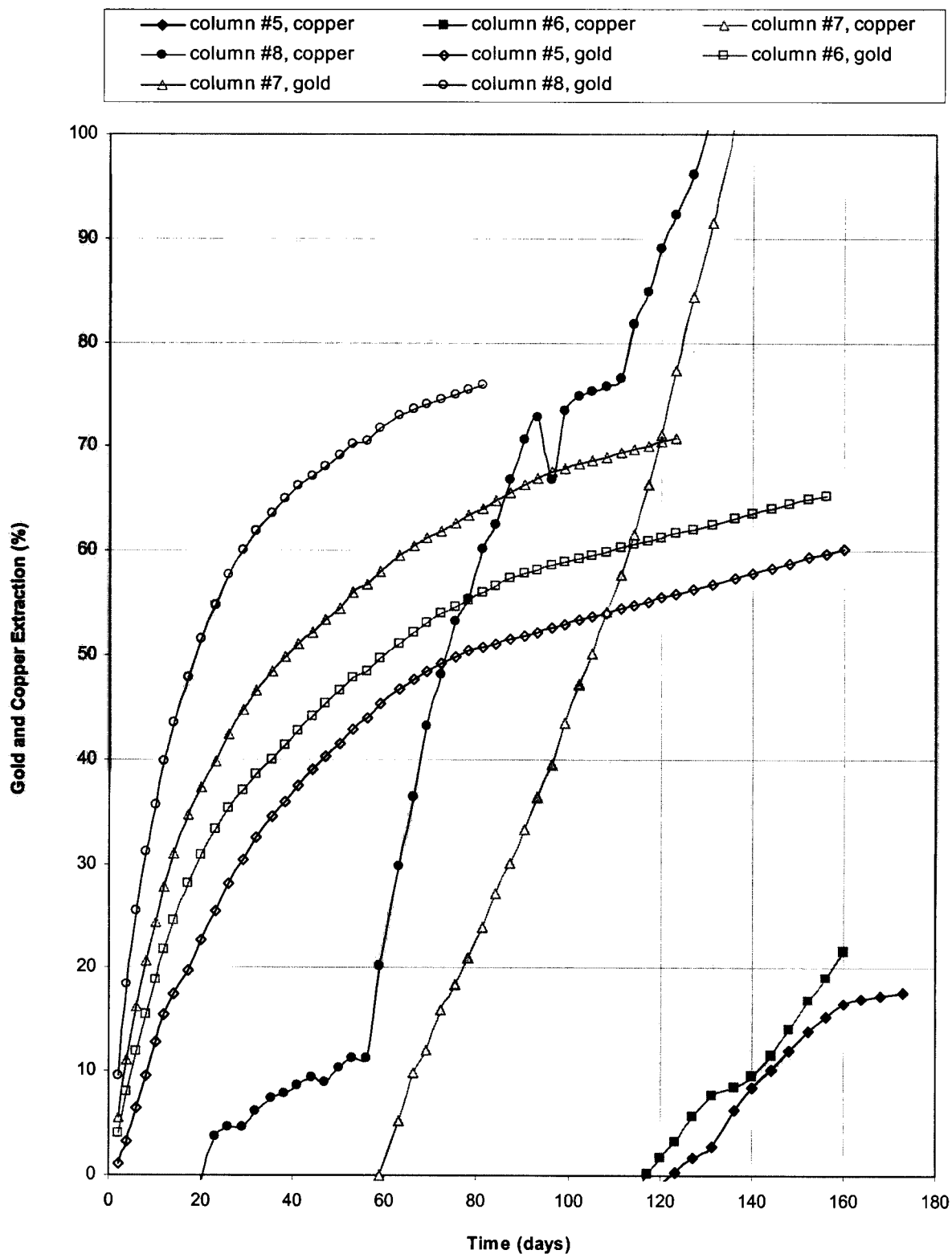
Figure 5-16 Presentation of gold and copper extraction curves, phase III [*].

[*] The extracted copper during the pre-rinsing period has been cut off in this figure.
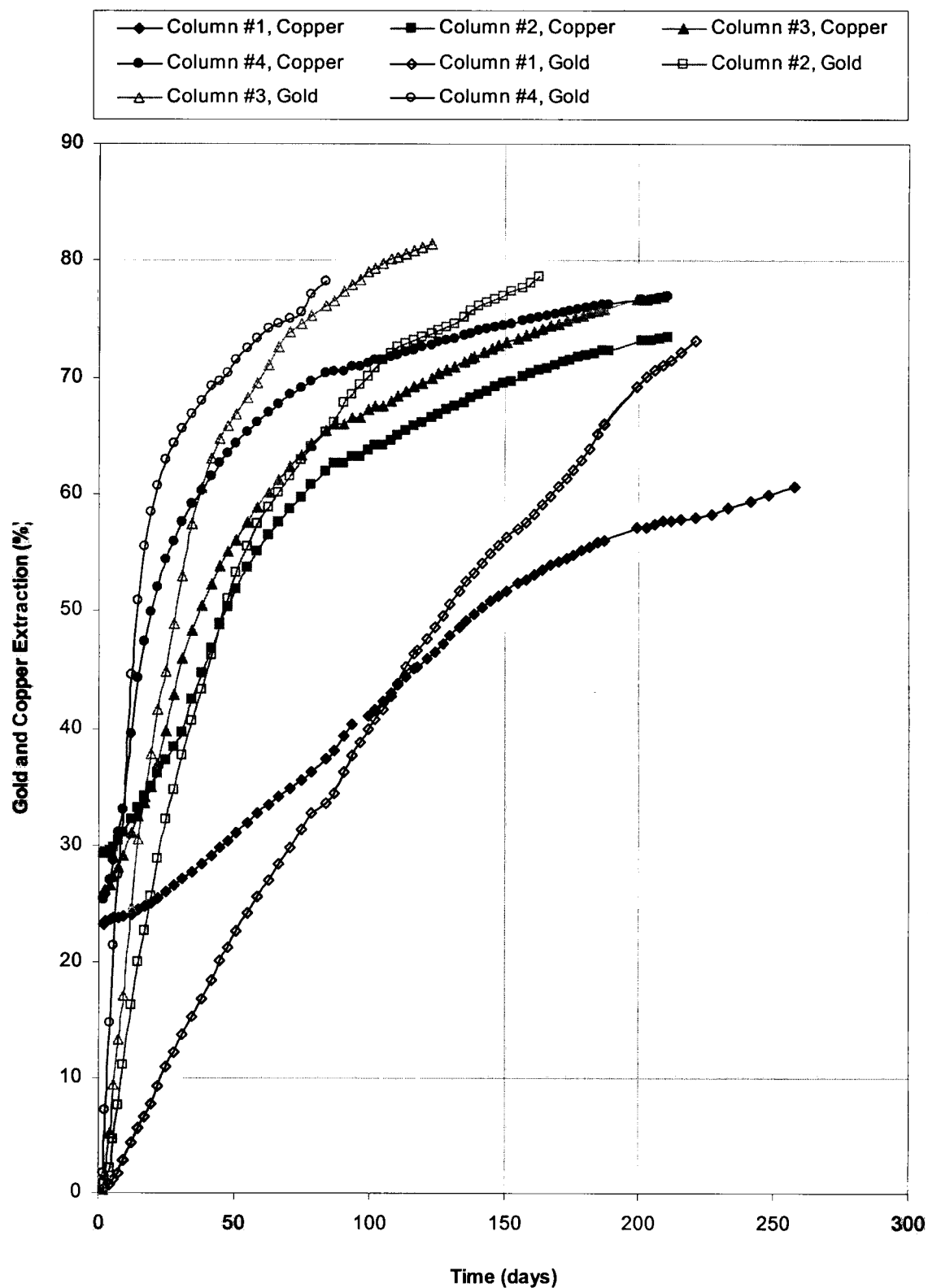
Figure 5-17 Presentation of gold and copper extraction curves, phase II

The gold extraction plots of phase II and phase III show similar behavior of this metal in cyanide solutions or in cyanocuprate solutions. Such comparisons are provided in Figure 5-18 and Figure 5-19 between columns with equivalent sodium cyanide concentrations. Except for the columns with equivalent 200 ppm NaCN, the others show very similar behavior in their extraction curves. The two curves in each of these figures perform very similarly until 40% extraction, and which point the columns with free cyanide as the leachant gradually show improved recoveries, on the order of 10%.

Figure 5-18 Comparisons of gold recoveries.
a-Columns 1 & 5, EQ 200 ppm [NaCN]. b-Columns2 & 6, EQ 500 ppm [NaCN]
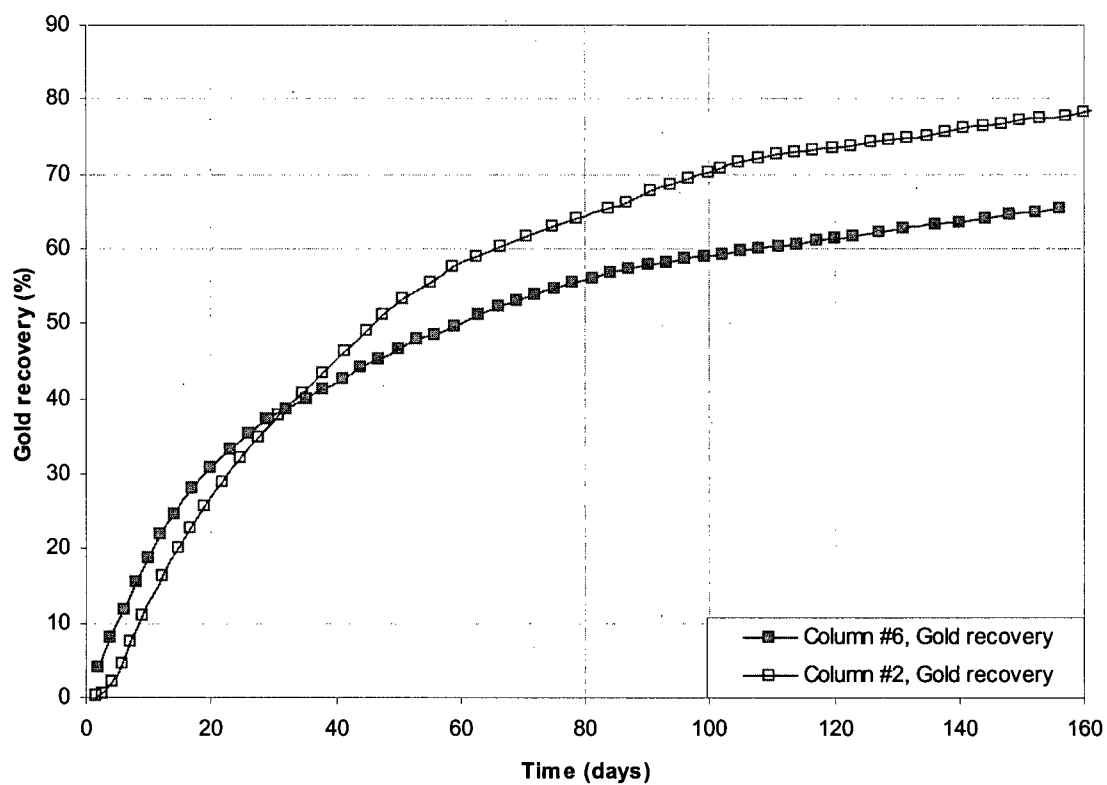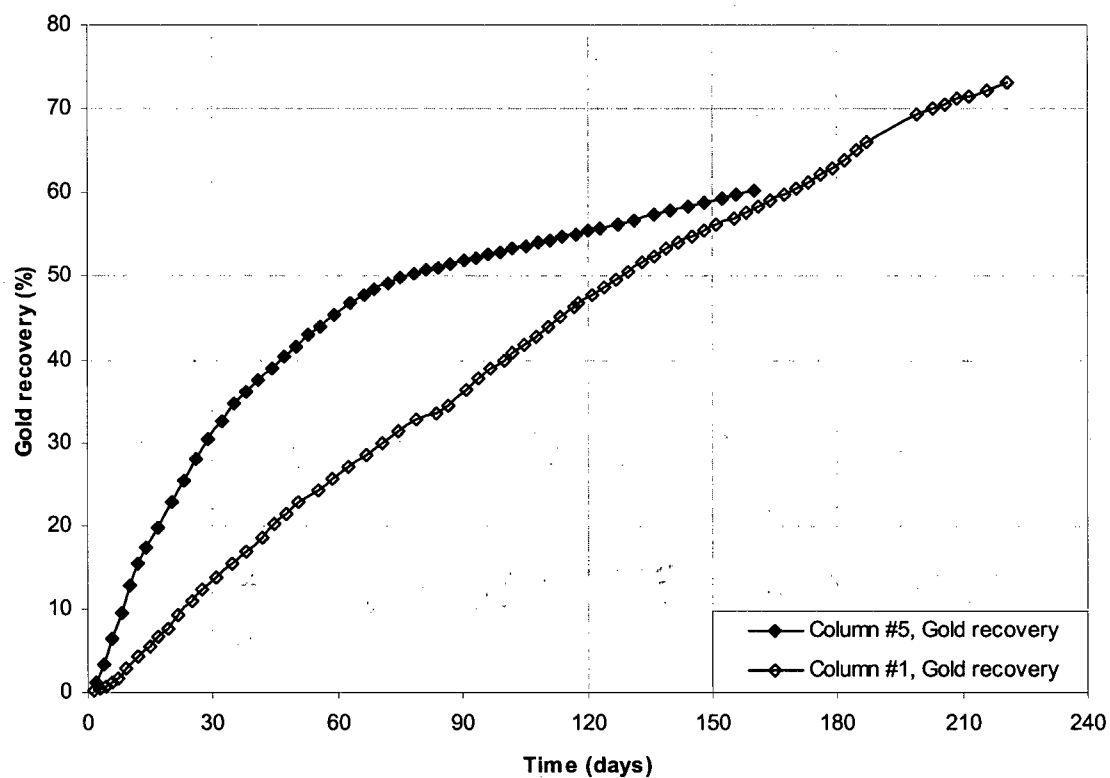
Figure 5-19 Comparisons of gold recoveries.
a-Columns 3 & 7, EQ 500 ppm [NaCN]. b-Columns 4 & 8, EQ 2000 ppm [NaCN]
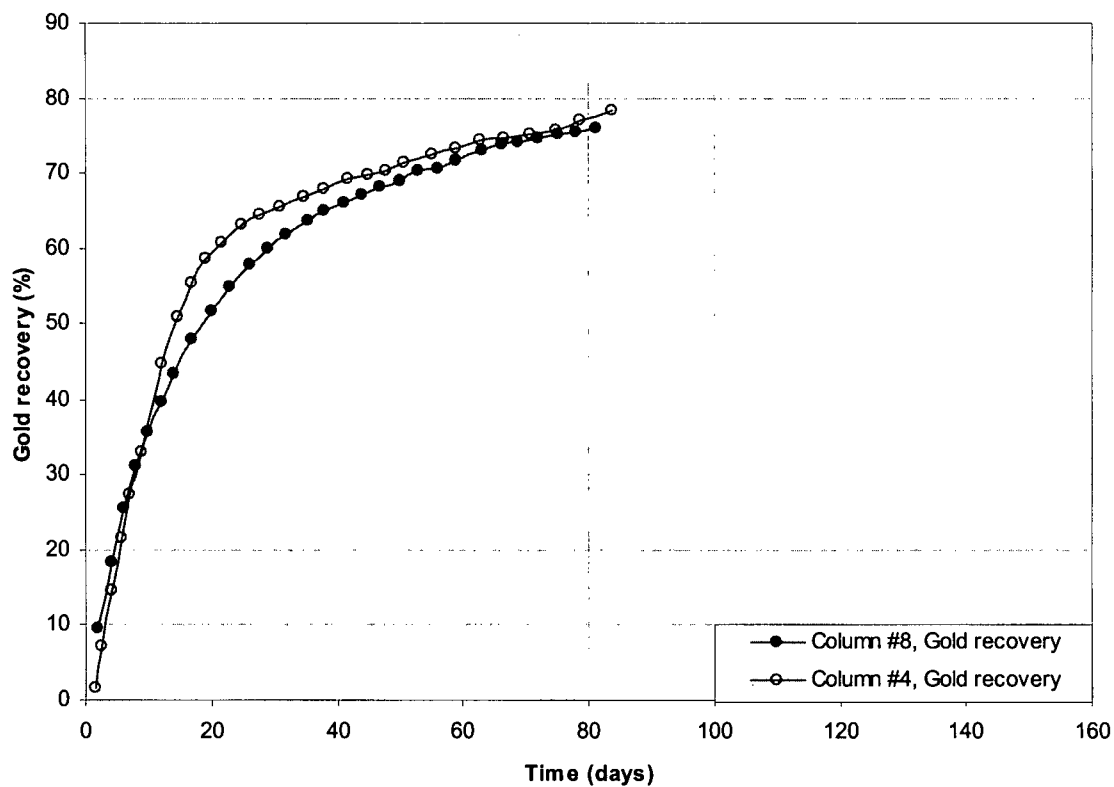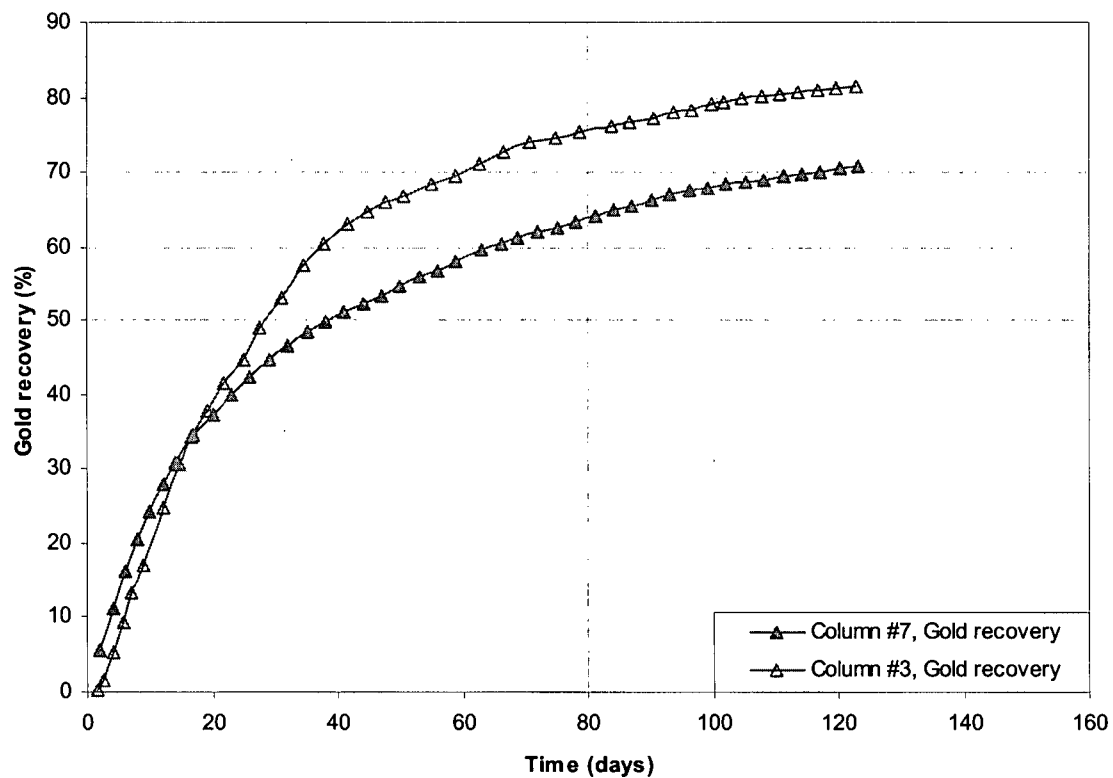
6 Recommendations and the future works

- Speciation Calculations

Practicing some speciation calculations, using the effluent concentrations of elements such as CN, SCN, Cu(I), S^{2-} (which would have to be calculated based on copper minus SCN), particularly around the time of cyanide breakthrough might help us on understanding what the precipitate is that causes the sharp peak in copper concentration .

- Cyanide balance

A full cyanide balance is highly recommended, as it can be helpful on the estimating of the cyanide consumption under different influent leaching solutions and gaining a better understanding of different precipitates in these leaching systems.

- Future modeling work

While the modeling practice in phase I of this project failed to model the effluent pH, it seems the inclusion of the reactions of copper sulfates with sodium hydroxide and considering the concentration of these minerals in the ore can be helpful in this matter.

- Experimental work

Also using an extra column will be helpful on determining the reproducibility of these experiments.

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Appendix A.   Supplementary chemical analyses

Chemical analysis of the Telfer 'E' composite ore has been done several times in different phases of this project. The provided data are acceptably close, however the analyses have been done by different analyzers.

Table A-1 ICP chemical assays by Chemex labs Ltd, done in phase I

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 (%)**
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

Table A-2 Results of analysis done by Chem Met Consultants Inc., done in phase I

Au (g/t)	S_{total} (%)	S^{2-} (%)
0.58	2.58	2.48

Table A-3 Results of analysis done by International plasma laboratory Ltd., done in phase II

Size	Au (g/t)	Ag (g/t)	Cu (%)	Fe (%)	Pb (%)	Zn (%)
-50 mesh	0.59	3.3	0.230	7.287	0.044	0.011
-100 mesh	0.42	1.4	0.216	6.334	0.030	0.006
-270 mesh	0.90	3.2	0.327	6.405	0.029	0.010

Appendix B. Safety issues for working with cyanide:

Human contact with cyanide compounds, whether external or internal, can be harmful in several ways. If cyanide enters the body, it will make strong complexes with iron and interfere with the transport of oxygen by hemoglobin.

The basic safety precautions are outlined as the following:

1. Sodium cyanide in contact with acids or weak alkalis liberates HCN gas which is highly toxic. Therefore cyanide compounds and solutions never have to be stored near acids. Also for preparing cyanide solutions, the pH always have to be adjusted to pH > 10.5.

2. It is a must to avoid skin contact with cyanides. Wearing protective gloves (chlorinated polyvinyl, viton or butyl) is suggested when handling solid cyanides or working with cyanide solutions. Washing hands and gloves thoroughly with running water is highly recommended after handling cyanides.

3. Wearing chemical splash goggles for eyes protection is necessary.

4. Any spilled cyanide has to be swept up immediately; the dilute hypochlorite solution can be used to treat contaminated area.

5. Every precaution has to be taken to not to breathe the cyanide dust or gas. Eating, drinking or smoking has to be prohibited in the cyanide lab or any place, which cyanide is present.

6. Cyanide solutions cannot be poured down the drains, and the cyanide content has to be completely destroyed before doing so.

Appendix C.   Copper head grade calculations phase II

Table C-1

Column 1				
	Total weight (g)	**concentration [Cu] %**	**concentration [Cu] ppm**	**Total Cu (g)**
Section 1	2704.090	0.064	640	1.731
Section 2	2787.230	0.112	1120	3.122
Section 3	2746.930	0.104	1040	2.857
Section 4	2751.690	0.087	870	2.394
Section 5	3131.770	0.164	1640	5.136
	14121.710			15.239

Table C-2

Column 2				
	Total weight (g)	**concentration [Cu] %**	**concentration [Cu] ppm**	**Total Cu (g)**
Section 1	3096.080	0.049	490	1.517
Section 2	2610.340	0.052	520	1.357
Section 3	2553.330	0.087	870	2.221
Section 4	2818.660	0.045	450	1.268
Section 5	2772.840	0.057	570	1.581
	13851.250			7.945

Table C-3

	Total weight (g)	concentration [Cu] %	concentration [Cu] ppm	Total Cu (g)
	Column 3			
Section 1	2881.300	0.083	830	2.391
Section 2	2800.480	0.047	470	1.316
Section 3	2744.370	0.043	430	1.180
Section 4	3287.310	0.075	750	2.465
Section 5	2802.080	0.030	300	0.841
	14515.540			8.194

Table C-4

	Total weight (g)	concentration [Cu] %	concentration [Cu] ppm	Total Cu (g)
	Column 4			
Section 1	2966.590	0.024	240	0.712
Section 2	2967.490	0.029	290	0.861
Section 3	2876.380	0.043	430	1.237
Section 4	2977.770	0.129	1290	3.841
Section 5	3057.690	0.048	480	1.468
	14845.920			8.118

Table C-5

The Correction Factor for calculating the Net Copper in residual ore				
	Column 1	Column 2	Column 3	Column 4
Total Weigh of the residual ore	14121.7	13851.3	14515.5	14845.9
Total Weigh of the initial ore in the Column	15000.0	15000.0	15000.0	15000.0
The Correction Factor	1.062	1.083	1.033	1.010
Net Copper in residual ore (not Corrected) (g)	15.239	7.945	8.194	8.118
Net Copper in residual ore (Corrected) (g)	16.187	8.604	8.467	8.203

Table C-6

Column Number	1	2	3	4
Nominal [NaCN] ppm	200	500	1000	2000
Column Leach test period (day)	258	210	210	210
Net Copper Leached in Prewash (g)	9.479	9.337	9.479	8.903
Net Copper Leached in Cyanide column leach (g)	15.537	14.450	18.867	18.449
Net Copper in residual ore (g)	16.187	8.604	8.467	8.203
Total net Copper (g)	41.203	32.391	36.813	35.554
Weight of ore in column (g)	15000	15000	15000	15000
Calculated Head Copper grade (ppm)	2747	2159	2454	2370

Appendix D.   Gold head grade calculations phase II

Table D-1

Column 1			
	Total weight (g)	**Concentration [Au] ppm**	**Total Au (mg)**
Section 1	2704.090	0.41	1.109
Section 2	2787.230	0.22	0.613
Section 3	2746.930	0.22	0.604
Section 4	2751.690	0.2	0.550
Section 5	3131.770	0.27	0.846
	14121.71		3.722

Table D-2

Column 2			
	Total weight (g)	**Concentration [Au] ppm**	**Total Au (mg)**
Section 1	3096.080	0.12	0.372
Section 2	2610.340	0.24	0.626
Section 3	2553.330	0.22	0.562
Section 4	2818.660	0.2	0.564
Section 5	2772.840	0.12	0.333
	13851.25		2.456

Table D-3

	Column 3		
	Total weight (g)	Concentration [Au] ppm	Total Au (mg)
Section 1	2881.300	0.15	0.432
Section 2	2800.480	0.13	0.364
Section 3	2744.370	0.13	0.357
Section 4	3287.310	0.31	1.019
Section 5	2802.080	0.12	0.336
	14515.54		2.508

Table D-4

	Column 4		
	Total weight (g)	Concentration [Au] ppm	Total Au (mg)
Section 1	2966.590	0.1	0.297
Section 2	2967.490	0.12	0.356
Section 3	2876.380	0.1	0.288
Section 4	2977.770	0.27	0.804
Section 5	3057.690	0.12	0.367
	14845.92		2.111

Table D-5

The Correction Factor for calculating the Net Gold in residual ore				
	Column 5	Column 6	Column 7	Column 8
Total Weigh of the residual ore	14121.7	13851.3	14515.5	14845.9
Total Weigh of the initial ore in the Column	15000	15000	15000	15000
The Correction Factor	1.062	1.083	1.033	1.010
Net Gold in residual ore (not Corrected) (mg)	3.722	2.456	2.508	2.111
Net Gold in residual ore (Corrected) (mg)	3.954	2.660	2.592	2.133

Table D-6

Column Number	1	2	3	4
Nominal [NaCN] ppm	200	500	1000	2000
Column Leach test period (day)	258	210	210	210
Net Gold Leached in Cyanide column leach (mg)	10.291	9.838	11.380	7.681
Net Gold in residual ore (mg)	3.954	2.660	2.592	2.133
Total net Gold (mg)	14.244	12.498	13.972	9.814
Weight of ore in column (mg)	15000	15000	15000	15000
Calculated Head Gold grade (ppm)	0.95	0.83	0.93	0.65

Appendix E. Experimental results of phase II

Table E-1

Pre-Rinsing period Column #1			
Day	**Solution Weight (g)**	**[Cu] (ppm)**	**% Extraction of Cu**
0.0	First Drop		
3.1	2620.24	2613.00	16.62
4.6	1908.84	366.00	18.31
6.1	2018.23	215.41	19.37
7.4	1576.97	167.00	20.01
8.6	1577.12	129.20	20.50
10.1	1891.75	109.00	21.00
11.6	1846.33	95.54	21.43
13.1	1884.00	82.47	21.81
14.6	1871.20	29.53	21.94
16.1	1861.11	66.42	22.24
17.6	1901.66	67.63	22.55
19.2	1844.75	64.09	22.84
21.5	1632.27	41.68	23.01

Table E-2

Pre-Rinsing period Column #2			
Day	**Solution Weight (g)**	**[Cu] (ppm)**	**% Extraction of Cu**
0.0	First Drop		0.00
3.1	2724.96	2614.00	21.99
4.6	1860.32	305.80	23.75
6.1	1921.51	158.10	24.69
7.6	2027.02	118.80	25.43
8.9	1590.10	98.29	25.91
10.1	1590.16	75.59	26.28
11.6	1912.93	78.55	26.75
13.1	1863.58	69.60	27.15
14.6	1903.43	67.13	27.54
16.1	1887.30	62.87	27.91
17.6	1878.48	59.11	28.25
19.1	1926.96	55.37	28.58
20.7	1210.60	58.55	28.80
23.0	123.70	76.18	28.83

Table E-3

Pre-Rinsing period Column #3			
Day	**Solution Weight (g)**	**[Cu] (ppm)**	**% Extraction of Cu**
0.0	First Drop		0.00
3.0	2563.46	2659.00	18.52
4.5	1940.74	437.00	20.82
6.0	2009.85	169.90	21.75
7.5	2133.80	121.70	22.45
8.8	1668.97	102.90	22.92
10.0	1672.19	90.68	23.33
11.5	2012.69	80.27	23.77
13.0	1962.41	72.84	24.16
14.5	2003.26	70.50	24.54
16.0	1987.19	66.54	24.90
17.5	1971.52	59.96	25.22
19.0	1961.29	58.22	25.53
20.6	1204.53	57.99	25.72
22.9	116.69	82.43	25.75

Table E-4

Pre-Rinsing period Column #4			
Day	**Solution Weight (gr)**	**[Cu] (ppm)**	**% Extraction of Cu**
0.0	First drop		0.00
3.1	2829.32	2508.00	19.96
4.6	1925.02	228.00	21.19
6.1	1974.40	105.17	21.78
7.7	2104.11	92.60	22.32
8.9	1612.92	75.93	22.67
10.1	1568.72	75.90	23.00
11.6	1974.96	68.35	23.38
13.1	1923.30	61.62	23.72
14.6	1963.94	57.47	24.03
16.1	1950.69	54.16	24.33
17.6	1943.24	41.65	24.56
19.1	1992.82	48.64	24.83
20.7	1182.47	46.67	24.99
23.1	283.08	66.51	25.04

Table E-5

General results of Column #1 (200 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
1.7	1758.40	73.05	0.40	0.02	0.24	4.68	0.00	0.00	2.89
2.7	1209.18	57.42	0.62	0.02	0.40	4.88			
4.2	1764.99	41.84	0.86	0.02	0.64	5.10			6.51
5.7	1774.17	25.37	1.00	0.04	1.13	6.16			
7.2	1825.86	17.02	1.10	0.05	1.75	6.34			
9.0	2140.30	17.15	1.21	0.07	2.77	7.38	0.00	0.00	34.42
12.1	3315.32	28.87	1.51	0.07	4.34	7.88			
14.7	3027.17	43.01	1.92	0.06	5.58	8.14			
16.8	2464.18	48.92	2.30	0.06	6.58	8.29			
19.1	2717.83	52.52	2.75	0.06	7.69	8.28			
21.8	3326.77	54.95	3.33	0.07	9.28	8.27	0.00	0.01	33.26
24.9	3440.03	63.06	4.01	0.07	10.91	8.32			
27.6	3229.43	67.69	4.70	0.06	12.23	8.64			
30.9	3632.72	62.67	5.42	0.06	13.71	8.65			
34.6	4004.64	62.77	6.21	0.06	15.35	8.76			
37.8	3562.63	69.87	7.00	0.06	16.80	8.72	0.00	0.02	30.37
41.6	4053.91	75.08	7.96	0.06	18.45	8.75			
44.9	3735.95	76.01	8.85	0.07	20.23	8.71	1.00		
47.7	3161.71	85.35	9.70	0.05	21.31	8.73			
50.7	3346.02	81.78	10.57	0.06	22.67	8.86			
55.2	4826.00	73.63	11.69	0.05	24.31	8.80	2.00	0.11	36.15

General results of Column #1 (200 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
58.8	3961.60	83.92	12.73	0.05	25.66	8.93			
62.7	4092.21	70.66	13.64	0.05	27.05	9.46	5.00	0.01	
66.6	4147.91	65.32	14.50	0.05	28.46	9.72			
70.8	4309.15	64.70	15.38	0.05	29.93	9.77			
74.8	4253.08	70.73	16.33	0.05	31.37	9.69	5.00	0.00	28.92
78.7	4273.01	67.25	17.23	0.05	32.82	9.81			
83.8	5572.23	85.52	18.73	0.02	33.58		3.00	0.00	
86.8	3496.35	79.70	19.61	0.04	34.53	9.93			
90.7	6425.13	81.74	21.27	0.04	36.28				
93.8	4243.48	91.90	22.50	0.05	37.72	9.62	6.00	0.00	
96.8	3397.87		22.50	0.05	38.88				
99.8	4038.99	80.33	23.52	0.04	39.98		4.00	0.00	
101.9	2892.13	77.54	24.23	0.04	40.76	9.43			
104.7	3413.03	77.92	25.07		41.69	9.78			23.14
107.9	4020.46	77.28	26.04	0.04	42.78	9.99	8.00	0.00	
110.7	3693.91	76.86	26.94		43.91	10.14			
113.7	3846.38	76.03	27.86	0.05	45.22	10.22	9.00	0.00	
116.7	3733.44	72.25	28.71		46.36	10.31	17.00	0.87	
118.0	1271.11	76.79	29.02	0.04	46.71	9.78			
121.1	3749.23	69.90	29.85		47.73	10.16	21.00	0.84	
124.1	3556.16	70.56	30.64	0.04	48.70	10.28			
127.1	3608.24	70.64	31.44		49.68	10.26	28.00	0.86	13.02

General results of Column #1 (200 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN] (ppm)	[Fe] (ppm)	[SCN] (ppm)
130.1	3600.85	79.77	32.34	0.04	50.66	10.31			
133.2	3813.43	76.43	33.26	0.04	51.69	10.40			
136.1	3553.08	71.22	34.06		52.54	10.38	33.00	0.71	
138.9	3459.53	65.88	34.78		53.30	9.90	37.00	0.31	
142.1	3904.01	59.57	35.51	0.03	54.10	10.28	44.00	0.43	
145.1	3919.94	54.86	36.19		54.90	10.33			
148.1	3724.59	51.29	36.79	0.03	55.66	10.20			
151.0	3800.20	47.57	37.36		56.31	10.39	50.00	0.35	
155.3	5098.50	48.57	38.14	0.02	57.00	10.40			
158.2	3658.18	45.41	38.67		57.62	10.40	54.00		17.35
161.0	3557.99	44.00	39.16	0.03	58.35	10.39			
164.2	3913.87	41.21	39.67		59.15	10.41			
167.2	3706.50	39.78	40.13	0.03	59.90	9.87	56.00	0.24	
170.3	3620.74	38.68	40.58		60.64	10.20			
173.0	3447.59	36.07	40.97	0.03	61.34	10.35	61.00	0.31	
175.9	3827.87	35.95	41.40		62.12	10.35			
178.9	4090.02	34.60	41.85	0.03	62.96	10.34			
181.9	4263.01	32.17	42.28		63.97	10.43	65.00	0.27	
184.9	4233.13	30.01	42.68	0.04	65.12	10.62			
187.3	3416.07	29.73	43.00	0.04	66.05	10.75	67.00	0.41	
199.0	15684.2	28.18	44.39		69.25	10.21	69.00	0.35	
202.7	4737.39		44.39		70.06	10.39		1.01	

General results of Column #1 (200 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
205.7	4002.26	28.02	44.75	0.02	70.60	10.50	71.00	0.35	
208.7	3965.68	25.74	45.07		71.14	10.55	70.00	0.28	
211.7	3025.71		45.07	0.02	71.55	10.33	65.00	0.54	
215.7	5164.07	33.68	45.24		72.25	10.34	69.00	0.43	
220.7	6351.56	26.92	45.45	0.02	73.12	10.06	71.00	0.21	
226.7	4679.73	31.66	45.92			10.02	67.00	0.63	
232.8	7288.44	26.64	46.53			10.09	70.00	0.33	
241.7	10941.5	25.05	47.39			10.18		0.26	
247.9	7477.36	24.14	47.96			10.46		0.27	
257.9	12128.9	26.53	48.98					0.34	

Table E-6

General results of Column #2 (500 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
1.7	1755.3	90.41	0.69	0.01	0.14	4.65	0.00	0.00	3.62
2.7	1246.3	43.84	0.93	0.05	0.64	5.49			
4.2	1822.1	19.84	1.08	0.10	2.10	6.38			
5.7	1836.7	45.36	1.44	0.17	4.60	8.06			
7.2	1888.5	93.20	2.21	0.20	7.63	8.51			
9.0	2230.5	106.18	3.23	0.19	11.02	8.92	3.00	0.00	
12.1	3608.1	104.03	4.86	0.18	16.22	8.74			57.85
14.7	3149.7	102.86	6.27	0.15	20.01	8.77			
16.8	2559.8	108.31	7.47	0.13	22.67	8.81			
19.1	2809.7	101.75	8.71	0.13	25.60	8.85			
21.8	3211.1	110.59	10.25	0.13	28.94	8.88	3.00	0.00	60.74
24.9	3667.0	101.20	11.86	0.11	32.18	8.89			
27.6	3269.8	113.58	13.47	0.10	34.79	8.72	1.00	0.00	
30.9	3701.4	115.87	15.33	0.10	37.76	8.88			
34.6	4111.0	215.09	19.17	0.09	40.72	8.94			
37.8	3593.2	197.81	22.25	0.09	43.31	9.29	1.00	0.00	
41.6	4150.4	171.21	25.33	0.09	46.31	9.72	59.00	0.72	22.56
44.9	3727.9	165.75	28.01	0.09	48.99	9.92	75.00	0.68	
47.7	3206.9	161.79	30.26	0.08	51.05	9.88			
50.7	3397.8	144.81	32.40	0.08	53.23	10.12	96.00	0.65	
55.2	4875.7	123.80	35.02	0.06	55.57	10.05	108.00	0.42	21.69

General results of Column #2 (500 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
131.8	3441.3	32.08	54.45	0.01	74.63	10.59	174.00	0.21	
134.9	3725.2	28.07	54.91		75.08	10.55	175.00	0.22	
137.8	3643.9	33.57	55.44	0.02	75.66	10.79			
140.7	3508.5	27.47	55.86		76.08	10.34	189.00	0.19	14.61
143.9	3948.6	26.04	56.30	0.01	76.40	10.61			
146.9	3963.6	23.60	56.71		76.72	10.67	203.00	0.18	
149.9	3762.8	23.90	57.10	0.01	77.02	10.69	205.00	0.19	
152.8	3836.5	22.17	57.47		77.33	10.77	202.00	0.19	13.02
157.0	4959.8	23.13	57.96	0.01	77.72	10.80			
159.9	3270.6	26.53	58.34		78.12	10.73	202.00	0.40	
162.8	3587.3	21.68	58.68	0.02	78.69	10.68			
165.9	3943.2	21.53	59.05			10.75			
169.0	3734.0	20.41	59.38			10.56	207.00	0.18	
172.0	3648.3	19.77	59.69			10.48			
174.7	3473.6	18.59	59.97			10.61	208.00	0.12	
177.7	3857.7	16.85	60.25			10.48	211.00	0.15	
180.7	4111.6	16.42	60.54			10.64			
183.7	3995.5	16.18	60.82			10.37	202.00	0.27	
186.7	4275.7	15.38	61.11			10.67			
189.1	1763.2	15.11	61.23			10.04	199.00	0.22	
200.7	14984.5	15.39	62.23			10.58	212.00	0.30	
204.5	4804.3		62.23			10.67			

General results of Column #2 (500 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
207.5	4029.8	13.24	62.46			10.76	217.00	0.23	
210.5	3994.7	12.82	62.68			10.77	218.00	0.22	
213.5	1999.4		62.68			10.74	217.00	0.19	

Table E-7

General results of Column #3 (1000 ppm NaCN)									
Day	**Weight (g)**	**[Cu] (ppm)**	**% Rec of Cu**	**[Au] (ppm)**	**% Rec of Au**	**pH**	**[CN⁻] (ppm)**	**[Fe] (ppm)**	**[SCN⁻] (ppm)**
1.7	1832.3	77.27	0.52	0.02	0.26	5.32	0.00	0.00	
2.7	1304.3	18.67	0.61	0.15	1.66	7.35			69.71
4.2	1905.6	91.56	1.25	0.26	5.19	8.77			
5.7	1925.1	135.71	2.20	0.31	9.45	9.23			
7.2	1977.6	144.58	3.25	0.27	13.26	9.36			142.88
9.0	1994.1	186.62	4.61	0.27	17.10	9.59	4.70	0.00	
12.1	3799.0	195.11	7.32	0.28	24.69	9.49			130.16
14.7	3296.0	146.99	9.09	0.25	30.57	9.32			
16.8	2695.6	151.02	10.58	0.19	34.23	9.30			
19.1	2945.8	181.69	12.54	0.17	37.80	9.12			132.76
21.8	3313.9	210.47	15.09	0.16	41.58	9.12	6.00	0.00	
24.9	2858.2	374.79	19.01	0.16	44.85	9.13			
27.6	3135.3	354.25	23.07	0.18	48.88	9.36	10.10		
30.9	3836.2	295.95	27.23	0.15	52.98	9.55	123.60	6.38	57.12
34.6	4224.5	212.35	30.51	0.15	57.50	10.00	161.30	4.59	
37.8	3864.4	201.58	33.36	0.11	60.54	10.08	219.10	3.13	
41.6	3228.5	203.33	35.76	0.11	63.07	10.10		2.62	
44.9	3835.9	148.58	37.85	0.06	64.71	10.10	242.00	2.56	
47.7	3351.1	133.86	39.49	0.05	65.91	10.37		2.89	61.46
50.7	2210.7	156.57	40.75	0.06	66.85	10.21	249.50	2.88	

General results of Column #3 (1000 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
55.2	5167.4	117.76	42.98	0.04	68.33	10.29	296.10	1.92	58.14
58.8	4179.2	111.02	44.68	0.04	69.52	10.36			
62.7	4263.7	100.66	46.25	0.05	71.04	10.46			
66.6	4443.2	94.80	47.79	0.05	72.63	10.41			
70.8	4607.6	89.75	49.30	0.04	73.94	10.37			
74.8	4548.7	83.59	50.69	0.02	74.59	10.38	338.50	1.20	36.01
78.7	4571.5	77.41	51.99	0.02	75.25	10.51			
83.8	5995.6	68.94	53.50	0.02	76.10				
86.8	3281.5	65.60	54.29	0.02	76.57	10.58			
90.7	5226.7		54.29	0.02	77.32	10.29			
93.8	4021.2	54.47	55.09	0.02	77.89	10.55	369.20		
96.8	3574.8		55.09		78.40	10.14		0.57	
99.8	4216.2	51.28	55.88		79.00	10.18			27.48
101.9	2139.9	46.42	56.24	0.02	79.31	10.34			
104.7	3611.5		56.24	0.02	79.82	10.29			
107.9	4198.6	41.60	56.88	0.01	80.12	10.71	398.50		
110.7	3841.8	37.93	57.41	0.01	80.40	10.63			
113.7	3948.3	38.51	57.97	0.01	80.68	10.59			
116.7	3889.3	37.94	58.51	0.01	80.95	10.82			
119.7	3813.8	36.91	59.03	0.01	81.23	10.82			
122.8	3882.7	35.74	59.53	0.01	81.50	10.81	406.90		
125.8	3670.4	35.70	60.01			10.80		0.56	

General results of Column #3 (1000 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
128.8	3706.1	34.90	60.49			10.57		0.65	
131.8	3645.5	34.63	60.95			10.84			
134.9	3809.0	32.02	61.39			10.74			
137.8	3588.0	27.27	61.75			10.71	417.00		
139.1	1492.3	31.36	61.92			10.33			
142.2	3713.8	40.41	62.47			10.70	406.30		
145.2	4011.6	27.11	62.87			10.76			
148.2	3807.2	26.85	63.24			10.78			
151.1	3878.9	25.44	63.61			10.85	423.20		
155.3	5339.9	27.02	64.13			10.85			
158.3	3747.1	25.63	64.48			10.83			
161.1	3644.1	24.33	64.81			10.82			
164.2	4009.1	24.62	65.17			10.82			
167.3	3796.7	23.99	65.50			10.81	425.40		
170.4	3704.9	24.56	65.84			10.81			
173.1	3536.6	23.28	66.14			10.80	427.30		
176.0	3798.3	22.17	66.45			10.79			
179.0	4089.4	18.60	66.72			10.85	433.70		
182.0	4023.2	20.16	67.02			10.78			
185.0	4357.3	18.50	67.32			11.12	436.70		
187.4	1697.8	17.70	67.43			11.11			
199.1	14883.7	20.00	68.51			10.81	433.70		

General results of Column #3 (1000 ppm NaCN)									
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
202.8	4889.6		68.51			10.68			
205.8	4081.3	17.35	68.77			10.89	441.10		
208.8	4023.9	16.93	69.02			10.82	440.40		
211.8	1708.1		69.02			10.87			

Table E-8

General results of Column #4 (2000 ppm NaCN)								
Day	Weight (gr)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
1.7	1838.9	63.14	0.44	0.09	1.69	5.89	0.00	0.00	
2.7	1287.5	106.63	0.95	0.42	7.20	9.08	0.00		228.5
4.2	1882.9	253.40	2.74	0.39	14.68	9.61	.		301.1
5.7	1910.4	300.46	4.89	0.35	21.49	9.80	9.20	0.00	
7.2	1963.6	442.79	8.16	0.30	27.49	9.94			296.61
9.0	2040.2	338.47	10.75	0.27	33.11	9.69	11.10		
12.1	3764.2	608.05	19.34	0.30	44.61	9.69	12.40		
14.7	3271.5	518.61	25.70	0.19	50.95	9.98	281.00	13.50	193.5
16.8	2637.4	406.38	29.72	0.17	55.51	10.25	406.70	10.00	
19.1	2925.0	305.99	33.08	0.10	58.49	10.32	515.50	7.33	
21.8	3003.6	265.11	36.07	0.07	60.64	10.37	534.80	6.14	
24.9	3823.6	209.73	39.08	0.06	62.97	10.28			102.68
27.6	3424.9	173.23	41.30	0.04	64.37	10.18	593.50	4.78	
30.9	3854.5	143.96	43.39	0.03	65.55	10.45			
34.6	4198.5	132.99	45.48	0.03	66.83	10.26			
37.8	3668.8	117.32	47.10	0.03	67.95	10.41	687.30	3.41	
41.6	4458.8	100.56	48.78	0.03	69.32	10.54			60.45
44.9	3803.2	96.17	50.15	0.01	69.70	10.50			
47.7	3443.4	85.56	51.26	0.02	70.40	10.56			
50.7	3459.6	83.97	52.35	0.03	71.46	10.56			
55.2	5098.4	74.25	53.77	0.02	72.50	10.63	742.60	2.59	

General results of Column #4 (2000 ppm NaCN)									
Day	Weight (gr)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
58.8	3892.4	73.08	54.83	0.02	73.29	10.63			43.1
62.7	4277.2	68.04	55.93	0.02	74.17	10.26			
66.6	4397.7	61.73	56.95	0.01	74.61	10.56			
70.8	4189.0	64.56	57.96	0.01	75.04	10.64			40.78
74.8	4484.4	50.23	58.81	0.01	75.50	10.57	777.20	2.13	
78.7	3831.7	50.98	59.54	0.04	77.06	10.68			
83.8	5912.6	43.30	60.50	0.02	78.26	10.76	757.90		
86.8	1383.2	39.87	60.71			10.75		2.08	
90.7	4334.0		60.71						
93.8	3608.0	41.24	61.26			10.71	793.80	1.89	
96.8	3574.4		61.26			10.37			
99.8	4001.0	28.16	61.69			10.53	802.70	1.51	
101.9	2204.4	27.06	61.91			10.67			29.07
104.7	3561.4		61.91			10.76			
107.9	4164.5	22.70	62.27			10.78	839.60		
110.7	3805.8	20.98	62.56			10.86			
113.7	3910.4	21.12	62.87			10.58			
116.7	3845.0	19.60	63.16			10.85			
119.7	3770.8	19.16	63.43			10.85			
122.8	3844.3	19.66	63.71			10.79	855.70		
125.8	3633.1	18.46	63.96			10.86			
128.8	3666.8	19.13	64.23			10.81			

General results of Column #4 (2000 ppm NaCN)									
Day	Weight (gr)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
131.8	3660.8	19.73	64.50			10.90	852.90		
134.9	3866.9	18.75	64.77			10.89	. . .		
137.8	3597.5	18.44	65.02			10.87	837.30		
140.7	3510.6	17.94	65.26			10.72			
143.9	3956.4	16.48	65.50			10.84	868.00		
146.9	3972.1	15.08	65.72			10.87			
149.9	3771.9	14.95	65.94			10.87			
152.8	3847.6	14.85	66.15			10.90	881.50		
157.0	4668.2	15.29	66.42			10.90			
159.9	3252.3	17.97	66.64			10.84			
162.8	3606.2	13.74	66.82			10.85			
165.9	3963.5	13.96	67.03			10.92			
169.0	3753.8	13.35	67.22			10.88	870.00		
172.0	3667.4	13.35	67.40			10.92			
174.7	3491.5	12.91	67.57			10.92	883.10		
177.7	3877.5	12.10	67.75			10.90			
180.7	4020.7	10.76	67.91			10.93			
183.7	3946.0	11.40	68.08			10.83	846.60		
186.7	4312.1	10.19	68.24			11.23	901.50		
189.1	1720.6	10.88	68.31			11.17	902.80		
200.7	14884.4	11.21	68.94			10.93	888.80		
204.5	4819.0		68.94			10.88			

General results of Column #4 (2000 ppm NaCN)									
Day	Weight (gr)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[CN⁻] (ppm)	[Fe] (ppm)	[SCN⁻] (ppm)
207.5	4059.9	9.38	69.08			11.01	908.50		
210.5	4019.6	9.24	69.22			11.03	905.40		
213.5	1925.7		69.22			10.88			

Appendix F. Experimental results of phase III

Table F-1

Pre-Rinsing period Column #5			
Day	**Solution Weight (g)**	**[Cu] (ppm)**	**% Extraction of Cu**
0.0			0.00
3.7	6319.65	1521.12	24.84
7.5	5706.49	120.97	26.62
12.5	6388.06	81.39	27.97
16.9	6289.39	67.66	29.07
19.3	3455.90	60.15	29.60
29.4	14961.48	45.46	31.36

Table F-2

Pre-Rinsing period Column #6			
Day	**Solution Weight (g)**	**[Cu] (ppm)**	**% Extraction of Cu**
0.0			0.00
3.7	6151.35	1572.95	25.00
7.5	5651.73	111.36	26.63
12.5	6555.89	76.17	27.92
16.9	6261.82	61.44	28.91
19.3	3992.97	54.61	29.48
29.4	14864.92	46.99	31.28

Table F-3

Pre-Rinsing period Column #7			
Day	Solution Weight (g)	[Cu] (ppm)	% Extraction of Cu
0.0			0.00
3.7	6268.30	1480.48	23.98
7.5	5600.88	123.68	25.77
12.5	5634.02	78.44	26.91
16.9	6158.85	69.99	28.03
19.3	3956.93	75.88	28.80
29.4	14866.36	43.46	30.47

Table F-4

Pre-Rinsing period Column #8			
Day	Solution Weight (g)	[Cu] (ppm)	% Extraction of Cu
0.0			0.00
3.7	6033.72	1459.48	22.75
7.5	5955.90	119.18	24.59
12.5	3652.31	92.34	25.46
16.9	6662.52	70.01	26.67
19.3	5313.00	55.49	27.43
29.4	14925.89	53.25	29.48

Table F-5

General results of Column #5 (Eq 200 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
2.0	2674.29	45.71	-2.15	0.05	1.08	5.04	0.13	11.57
4.0	2988.94	52.11	-4.48		3.26	5.55		
6.0	3006.39	115.75	-6.10	0.13	6.42	6.27		
8.0	3022.36	146.89	-7.37		9.59	6.56	0.20	30.23
10.0	3105.16	152.37	-8.62	0.13	12.86	6.82		
12.0	3092.00	153.28	-9.85		15.48	7.17		
14.0	3006.84	159.83	-10.97	0.08	17.43	7.29		
17.0	3535.38	162.51	-12.26		19.71	7.26		
20.0	4578.82	173.31	-13.73	0.08	22.67	7.21	0.21	36.59
23.0	4560.28	169.60	-15.27		25.44	7.16		
26.0	4583.82	177.13	-16.68		28.03	7.32		
29.0	4481.02	172.35	-18.14	0.07	30.39	7.36		
32.0	4593.48	193.53	-19.27	0.06	32.62	7.47		
35.3	4998.89	189.56	-20.58		34.64	7.59	0.40	20.83
38.0	4241.74	203.66	-21.46	0.04	36.01	7.45		
41.0	4596.98	194.27	-22.59		37.50	7.68		
44.0	4709.66	188.93	-23.83	0.04	39.02	7.79		
47.0	4613.74	228.66	-24.35		40.32	7.90	0.36	
50.0	5120.00	237.26	-24.77	0.03	41.57	7.95		10.41
53.0	5724.71	246.25	-25.05		42.95	8.05		
56.0	4199.65	319.12	-24.10	0.03	43.97	8.05		

General results of Column #5 (Eq 200 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
59.0	5505.47	267.29	-23.93		45.31	8.45		
63.1	6165.11	353.57	-21.73	0.03	46.80	8.83		
66.2	4742.89	345.17	-20.19		47.76	9.44	1.06	5.78
69.0	4239.92	342.59	-18.86	0.02	48.45	9.57		
72.0	4597.94	333.28	-17.57		49.19	9.75		
75.2	4304.14	332.78	-16.38	0.02	49.89	9.67	1.01	
78.2	4309.71	336.05	-15.13		50.41	9.84		
81.1	4361.16	334.26	-13.89	0.01	50.76	9.95	1.03	2.89
84.2	4748.03	329.53	-12.63		51.15	9.95	0.93	
87.2	4475.91	331.19	-11.41	0.01	51.51	9.98		
90.2	4537.30	329.50	-10.21		51.88	9.89		
93.1	4428.95	318.92	-9.21	0.01	52.23	9.93		
96.2	4644.00	324.44	-8.07		52.61	9.95	0.84	14.16
99.2	4521.76	299.04	-7.39	0.01	52.97	9.96		
102.1	4483.83	317.91	-6.39		53.34	10.02		
105.2	4554.47	316.78	-5.40	0.01	53.71	10.05		
108.1	4415.87	312.43	-4.51		54.06	10.04		
111.3	4824.37	317.17	-3.46	0.01	54.45	9.98	0.48	11.28
114.2	4298.57	316.49	-2.53		54.80	9.99		
117.2	4424.55	311.13	-1.66	0.01	55.16	9.97		
120.2	4481.06	313.57	-0.74		55.52	9.89		
123.2	4473.19	322.69	0.34	0.01	55.88	9.93		

General results of Column #5 (Eq 200 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
127.2	5641.64	323.34	1.70		56.34	9.89		14.46
131.2	5913.64	309.26	2.82	0.01	56.82	9.92		
136.1	7350.00	386.55	6.35		57.41	9.85		
140.1	6107.96	353.62	8.53	0.01	57.90	9.75		
144.2	5547.16	339.87	10.22		58.35	9.87		
148.1	6071.17	340.00	12.07	0.01	58.84	10.01	0.15	
152.2	6107.98	338.13	13.89		59.34	10.00		
156.0	5142.89	328.79	15.24	0.01	59.75	9.99		
160.0	5942.62	318.73	16.57		60.23	9.94	0.00	
164.1	5780.17	275.00	16.92	0.01		9.92		
168.3	4782.48	275.00	17.21			9.86		
172.9	5326.87	275.00	17.53	0.01		9.84		

Table F-6

General results of Column #6 (Eq 500 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
2.0	2730.7	26.04	-6.39	0.19	3.95	5.13	0.26	24.15
4.0	2982.3	269.24	-10.63		8.03	6.16		
6.0	3004.0	392.75	-13.52	0.17	11.92	6.79		
8.0	3026.5	404.69	-16.29		15.49	7.19	0.23	36.59
10.0	3086.5	263.59	-20.75	0.14	18.78	7.10		
12.0	3089.3	471.77	-22.79		21.83	7.31		
14.0	3003.6	531.17	-24.11	0.12	24.58	7.55		
17.0	4589.6	477.33	-27.06		28.07	7.47		
20.0	4572.5	469.56	-30.13	0.08	30.85	7.62		18.51
23.0	4556.8	484.83	-32.92		33.28	7.64	0.16	
26.0	4583.8	522.35	-35.09	0.06	35.37	7.72		
29.0	4560.8	520.39	-37.28		37.11	7.90		
32.0	4589.9	652.46	-37.20	0.04	38.51	7.85	0.35	33.55
35.3	5002.2	469.41	-40.56		40.03	8.02		
38.0	4233.4	690.40	-39.88	0.04	41.32	8.11		
41.0	4593.9	619.76	-40.37		42.71	8.22		
44.0	4700.1	732.70	-38.88	0.04	44.15	8.33		
47.0	4608.7	734.52	-37.38		45.37	8.35		
50.0	5095.0	710.29	-36.18	0.03	46.54	8.52	0.41	2.89
53.0	5694.7	685.23	-35.39		47.84	8.65		
56.0	2461.2	741.16	-34.52	0.03	48.40	8.94	0.21	

General results of Column #6 (Eq 500 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
59.0	5416.0	684.05	-33.79		49.63	9.01		
63.1	6118.8	781.33	-30.72	0.03	51.03	9.50		
66.2	4715.9	762.88	-28.68		52.11	9.75		19.96
69.0	4219.9	732.07	-27.35	0.03	53.07	9.77	0.20	
72.0	4585.9	752.50	-25.55		53.94	9.82		
75.2	4687.3	755.12	-23.66	0.02	54.66	9.74		
78.2	4319.5	735.03	-22.25		55.31	9.95	0.57	
81.1	4354.1	721.97	-21.04	0.02	55.98	9.96		2.89
84.2	4738.5	722.37	-19.71		56.70	10.00		
87.2	4466.7	704.06	-18.77	0.02	57.38	10.01		
90.2	4527.2	717.86	-17.58		57.90	9.99	0.47	
93.1	4415.2	747.89	-15.92	0.01	58.23	10.08		
96.2	4628.7	729.31	-14.51		58.58	10.05		2.89
99.2	4511.4	763.78	-12.54	0.01	58.93	10.04	0.34	
102.1	4477.0	787.19	-10.20		59.27	10.08		
105.2	4543.4	803.82	-7.54	0.01	59.61	10.08		
108.1	4411.6	763.62	-5.62		59.95	10.08		
111.3	4825.7	754.07	-3.69	0.01	60.32	10.01		6.65
114.2	4345.5	752.94	-1.98		60.65	10.00	0.22	
117.2	4436.4	772.23	0.09	0.01	60.98	9.98		
120.2	4482.7	741.38	1.67		61.33	9.95		
123.2	4466.4	745.93	3.31	0.01	61.67	9.95		

General results of Column #6 (Eq 500 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
127.2	5742.9	760.89	5.75		62.10	9.94	0.49	8.68
131.2	5933.6	738.73	7.77	0.01	62.55	9.92		
136.1	7400.0	675.57	8.54		63.12	9.86		
140.1	6082.3	694.07	9.59	0.01	63.58	10.10		
144.2	5533.5	745.62	11.63		64.00	10.07		
148.1	6076.3	753.00	14.02	0.01	64.46	9.88		
152.2	6124.5	766.88	16.76		64.93	9.71		
156.0	5472.8	756.34	18.99	0.01	65.35	9.73		
160.0	5949.4	766.87	21.65			9.77		
164.1	5789.9					9.84		
168.3	4888.1					9.76		
172.9	5325.2					9.80		

Table F-7

| General results of Column #7 (Eq 1000 ppm NaCN) |
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
2.0	2721.5	170.84	-11.39	0.25	5.56	6.01	0.17	34.85
4.0	2952.4	482.40	-20.33		11.12	6.88	0.22	
6.0	2965.6	795.94	-25.85	0.21	16.21	7.36		
8.0	2991.1	1310.83	-25.70		20.62	7.49	0.40	40.49
10.0	3046.3	1262.44	-26.09	0.15	24.35	7.51		
12.0	3044.5	1282.58	-26.25		27.84	7.69		
14.0	2962.4	1424.32	-24.85	0.13	30.99	7.98		
17.0	4528.1	1108.72	-28.02		34.69	7.90	0.28	
20.0	4516.1	1581.20	-23.25	0.07	37.28	8.01		33.26
23.0	4495.0	1538.37	-19.22		39.85	8.06		
26.0	4523.0	1335.66	-18.57	0.07	42.44	8.12		
29.0	4700.7	1323.24	-18.11		44.75	8.26		
32.0	4521.4	1376.46	-16.77	0.05	46.60	8.32	0.56	39.05
35.3	4922.4	1398.17	-14.92		48.41	8.50		
38.0	4173.7	1400.25	-13.32	0.04	49.77	8.76		
41.0	4525.9	1395.82	-11.66		51.07	9.18		
44.0	4632.3	1368.75	-10.42	0.03	52.21	9.44	0.46	
47.0	4535.7	1373.00	-9.14		53.32	9.20		
50.0	5015.5	1363.52	-7.90	0.03	54.55	9.40		15.62
53.0	5685.6	1394.48	-5.84		55.94	9.59		
56.0	3332.1	1344.12	-5.26	0.03	56.76	9.42	0.46	

General results of Column #7 (Eq 1000 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
59.0	5350.0	1561.39	0.00		58.07	9.43		
63.1	6047.3	1532.73	5.30	0.03	59.56	9.71		
66.2	4666.8	1562.34	9.90		60.51	9.82	0.46	17.79
69.0	4168.7	1434.83	12.03	0.02	61.19	9.81		
72.0	4534.5	1524.85	15.87		61.94	9.87	0.29	
75.2	4669.5	1443.44	18.41	0.02	62.70	9.76		
78.2	4297.0	1462.15	21.05		63.40	9.91		
81.1	4213.1	1477.34	23.88	0.02	64.09	9.95		2.89
84.2	4677.3	1489.76	27.23		64.86	10.00	0.39	
87.2	4409.5	1471.27	30.08	0.02	65.58	10.02		
90.2	4471.4	1493.19	33.34		66.31	9.91		
93.1	4361.9	1486.49	36.41	0.02	67.02	9.95		
96.2	4576.5	1477.97	39.49		67.58	9.96		5.78
99.2	4455.8	1537.24	43.47	0.01	67.95	9.98	0.10	
102.1	4420.7	1526.42	47.24		68.31	10.01		
105.2	4489.1	1467.51	50.08	0.01	68.68	10.01		
108.1	4353.4	1554.08	54.24		69.03	10.01		
111.3	4764.8	1495.59	57.76	0.01	69.42	9.95	0.08	5.93
114.2	4291.2	1532.41	61.51		69.77	9.95		
117.2	4383.0	1597.02	66.40	0.01	70.13	9.90		
120.2	4431.0	1581.12	71.08		70.49	9.84		
123.2	4413.2	1679.73	77.36	0.01	70.86	9.83		

General results of Column #7 (Eq 1000 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
127.2	6022.4	1612.17	84.41			9.84	0.00	5.78
131.2	5862.8	1623.61	91.53			9.82		
136.1	7300.0	1647.20	101.03			9.74		
140.1	6021.0	1595.10	107.70			9.78		
144.2	5462.2	1513.86	112.10			9.82		
148.1	6003.2	1530.08	117.30			9.80		
152.2	6053.1	1451.86	120.78			9.74		
156.0	5657.2	1506.24	125.18			9.76		
160.0	5884.3	1374.74	126.88			9.76		
164.1	5725.1					9.75		
168.3	5563.9					9.76		
172.9	5269.3					9.73		

Table F-8

General results of Column #8 (Eq 2000 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
2.0	2715.3	499.56	-20.82	0.35	9.59	6.33	0.34	47.44
4.0	2991.7	2025.16	-27.03		18.34	7.22	0.55	
6.0	3064.0	2890.36	-23.68	0.23	25.46	7.51	0.60	
8.0	3087.6	2602.65	-23.56		31.22	7.83		37.6
10.0	3144.5	2969.68	-19.21	0.14	35.66	7.83		
12.0	3147.7	2922.75	-15.40		39.79	8.03		
14.0	3060.9	2879.75	-12.17	0.12	43.50	8.20		
17.0	4282.0	2934.17	-6.80		47.82	8.23	0.70	
20.0	4660.8	2946.90	-0.74	0.08	51.58	8.32		46.28
23.0	4640.1	2855.34	3.74		54.86	8.32		
26.0	4662.5	2642.92	4.61	0.06	57.68	8.43	0.86	
29.0	4555.3	2594.29	4.65		59.98	8.57		
32.0	4664.0	2682.39	6.19	0.04	61.86	8.63		
35.3	5074.4	2655.00	7.36		63.66	8.87		46.28
38.0	4307.1	2627.93	7.93	0.03	64.96	9.33	0.67	
41.0	4666.7	2635.73	8.68		66.14	9.65		
44.0	4776.8	2633.27	9.40	0.02	67.10	9.83		
47.0	4680.4	2563.89	8.92		68.04	9.85	0.77	
50.0	5176.9	2666.23	10.33	0.02	69.09	9.80		29.94
53.0	5898.4	2637.76	11.32		70.28	9.59		
56.0	1488.4	2593.65	11.32	0.02	70.58	9.62	0.83	

General results of Column #8 (Eq 2000 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
59.0	5506.6	3032.23	20.21		71.69	9.62		
63.1	6210.5	3015.07	29.83	0.02	72.95	9.81		
66.2	4800.4	2967.04	36.43		73.67	9.90		15.91
69.0	4287.9	3021.19	43.18	0.01	74.10	9.86		
72.0	4664.9	2879.81	48.09		74.58	9.94	0.47	
75.2	4281.6	2918.58	53.22	0.01	75.01	9.81		
78.2	4361.5	2728.73	55.40		75.45	9.99		
81.1	4427.3	2889.70	60.23	0.01	75.89	10.01		8.97
84.2	4809.9	2721.38	62.51			10.09	0.34	
87.2	4537.6	2847.14	66.76			10.16		
90.2	4598.3	2820.56	70.61			10.09		
93.1	4484.7	2729.62	72.87			10.20		
96.2	4706.4	2245.27	66.89			10.12	0.50	9.83
99.2	4581.9	2980.01	73.40			10.16		
102.1	4544.2	2681.94	74.90			10.20		
105.2	4615.1	2613.99	75.27			10.21		
108.1	4469.3	2621.42	75.75			10.22		
111.3	4896.6	2632.91	76.49			10.13	0.40	2.89
114.2	4406.8	2916.62	81.73			10.10		
117.2	4420.5	2787.97	84.90			10.00		
120.2	4553.0	2842.51	89.08			9.88		
123.2	4534.1	2785.64	92.30			9.93		

General results of Column #8 (Eq 2000 ppm NaCN)								
Day	Weight (g)	[Cu] (ppm)	% Rec of Cu	[Au] (ppm)	% Rec of Au	pH	[Fe] (ppm)	[SCN⁻] (ppm)
127.2	4722.3	2813.24	96.13			9.97	0.28	2.89
131.2	6023.9	2885.00	102.60			9.96		
136.1	7500.0	2915.63	111.49			9.85		
140.1	6169.6	2691.89	113.75			9.98		
144.2	5613.5	2688.53	115.73			10.05		
148.1	5773.1	2720.00	118.44			10.05		
152.2	6207.4	2648.48	119.73			9.93		
156.0	5396.4	2509.22	118.09			10.02		
160.0	6042.1	2734.93	121.25			10.01		
164.1	5873.8					9.99		
168.3	4639.7					10.02		
172.9	5411.9					9.94		

Appendix G.   Procedure for sampling/ reducing samples to testing Size

Because of the importance of these procedures, the details of sampling procedures are described in this section.

Fine materials

A sample splitter, Three catch pans and a Wide, flat-edged scoop were the apparatus which have been used for sampling from fine materials using splitting method.

First the sample was dried enough to allow free flow of the material through the chutes.

The sample was placed on a hard, clean surface. Then it was thoroughly mixed until it appeared homogenous. A catch pan was placed under the chutes on each side of the splitter, then increments of the sample were placed on the wide, flat-edged scoop and uniformly distributed from edge to edge, so when it was introduced into the chutes, approximately equal amounts were flow through each chute.

The above step was repeated until the entire sample was introduced into the chutes. Sometimes it was necessary to use a brush to collect the fine material of the sample for splitting.

It was tried to introduce the sample in a rate at which a free flow of material from the scoop and through the chutes into the catch pans below was allowed.

The material contained in one of the catch pans was used and the previous steps were repeated until the sample was reduced to the desired size. Entire increments were splited during this procedure.

Coarse material

The apparatus, which were used in the quartering method for sampling and/or size reduction of coarse materials, have been:

1- A suitable surface

2- Straightedge, scoop, shovel or trowel

3- Broom or brush

The sample was placed on a hard, clean, level surface where there was neither loss of material nor the addition of foreign material. The material then was mixed thoroughly by turning the entire sample over three times. With the last turning, the entire sample was shoveled into a conical pile by depositing each shovelful on top of the preceding one. Then the conical pile was flattened to a uniform thickness and circled by pressing down the apex with a shovel so that each quarter sector of the resulting pile contained the material originally in it. After that the flattened mass was divided into 4 equal quarters with a shovel and 2 diagonally opposite quarters were removed, including all fine material, and the cleared spaces were cleanly brushed. Then the remaining material successively was mixed and quartered until the sample reduced to the desired size.