

# LEACH OUT GOLD AND SILVER FROM SULFIDE CONCENTRATE CONTAINING COPPER WITH CYANIDE AND AMMONIA SOLUTIONS<sup>①</sup>

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## ABSTRACT

A cyanidation leaching process for a sulfide concentrate containing gold and silver with ammonia and other complexes was investigated, and its potential in decrease of cyanide consumption was examined. The equilibria behaviors of copper and other metal ions in the  $\text{CN-NH}_3\text{-H}_2\text{O}$  system and the  $\text{CN-NH}_3\text{-EDTA-H}_2\text{O}$  system were analyzed by a microcomputer program. Experiments revealed that the leaching yield of gold in ammonia-cyanide solutions was raised from 86% to 99% from addition of EDTA in a certain concentration and its cooperative action with ammonia on the cyanidation of gold. Meanwhile, the leaching yield of silver was significantly increased from about 20% to 55% and the consumption of cyanide was decreased.

**Key words:** gold, silver, sulfide, cyanidation leaching

## 1 INTRODUCTION

Satisfactory recovery of gold through direct cyanidation is not attainable with the majority of sulfide concentrates containing copper. The copper and sulfide sulfur have been recognized as the ore components which prevent efficient gold extraction<sup>[1]</sup>. The harmful effects of the copper sulfides in ores are two-fold. Firstly, many copper sulfides, such as chalcocite, chalcociclite or guagacanite, have great solubility in the cyanide solution and would be dissolved in a high percentage, e.g. more than 65% at the room temperature,

and even chalcopyrite, the most refractory mineral of copper, has 5.6% dissolved in the same conditions<sup>[1]</sup>. Secondly, cupric ions in solutions react as an oxidant and cause the unnecessary consumption of cyanide due to the degradation of following reactions<sup>[2]</sup>.

$$\text{Cu}^{2+} + 4\text{CN}^- + 2\text{OH}^- = \text{Cu}(\text{CN})_2^{2-} + \text{OCN}^- + \text{H}_2\text{O}$$
$$2\text{Cu}(\text{CN})_4^{2-} = 2\text{Cu}(\text{CN})_3^{2-} + (\text{CN})_2(\text{g})$$

The fundamental research on the kinetics of cyanidation extraction of gold from a sulfide concentrate shows that the extracted yield of gold would be retarded by the presence of cupric ions. It can be concluded that copper minerals in ores exhaust cyanide and lime, and

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diminish both leaching rate and extracted yield of gold and silver. An attempt to address refractoriness has therefore focused on the roles of complex agents amenable to replace cyanide for copper and other base metal ions.

The technology dealt with the leaching of an oxidized ore containing gold and copper by using ammonia and cyanide solutions was early proposed and applied in heap leaching of tailings<sup>[3]</sup>. It was shown by a further study of Putnam<sup>[4]</sup> that the maximum dissolution rate would be achieved in the ammonia solution with 1 g/l sodium cyanide, the technology was used also in heap leaching of an oxide tailing with a high content of copper (Cu 1.2%, Au 6 g/t) at Paris of Australia. It was indicated by Ruane that the consumption of sodium cyanide was decreased from 20 to 1.55 kg/t and 70% gold and 35% copper were extracted respectively with the addition of 5 kg/t ammonia in the cyanide solution. Moreover, the copper complex with ammonia could be as an oxidant for gold leaching as follows

$$\text{Cu}(\text{NH}_3)_2(\text{CN})_2 + \text{Au} = \text{Cu}(\text{NH}_3)_2^+ + \text{Au}(\text{CN})_2^-$$

However, up to date it has not been found the reports concerning with leaching of sulfide gold-copper concentrates by ammonia-cyanide solutions. This paper will discuss the investigation in the respect.

## 2 THERMODYNAMIC EQUILIBRIA

In Cu-CN-NH<sub>3</sub>-H<sub>2</sub>O system there is a quite complicated chemistry as cupric ions form the mineral react with cyanide to form the cuprous-cyanide complexes alone by degradation reactions and take place in competitive complexing reactions between ammonia and cyanide. In an elementary consideration, the thermodynamic equilibria were calculated on the basis of a simple solution consisted of

10 mM Cu<sup>2+</sup>, 10 mM Fe<sup>3+</sup>, 1 mM Au<sup>+</sup> and 1 mM Ag<sup>+</sup>, which near the metal concentrations of the pregnant solutions from direct cyanidation of gold-copper sulfide concentrate. The total concentration of sodium cyanide is taken as 25 mM, near 1 g/l, and the value of *pe*, a characteristic of redox potential in solutions is 10 which is suitable to the condition of oxidation leaching in air.

All constants used for equilibrium calculations come from the ref.[7] and [8]. The calculation is carried out by a micro-computer program.

Fig.1 is the diagram of dominative zones of copper in the Cu-CN-NH<sub>3</sub>-H<sub>2</sub>O system and shows the effects of concentrations of both ammonia and hydrogen ions on the equilibria. As shown as in Fig.1, the cuprous-cyanide complexes will be subsequently replaced by cupric-ammonia complexes, Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> in majority and Cu(NH<sub>3</sub>)<sub>3</sub><sup>2+</sup> in minority, when the concentration of ammonia is higher than 0.1 M. The oxygen atmosphere therefore forward the reaction to the left.

The equilibrium behaviours of copper ions in the EDTA-ammonia systems are given in Fig.2. It is clear that EDTA is a more strong ligand than ammonia for copper ions, and all the copper ions in the concentration level like that in the pregnant solutions of simple cyanide leaching process become Cu-EDTA complexes in the mixture solutions containing 0.01 M EDTA.

## 3 EXPERIMENT

The sulfide concentrate used in the study was selected and supplied by Boliden Mineral AB, Sweden. The result of elemental analysis is shown as table 1.

In mineralogy major minerals are pyrite,

chalcopyrite, pyrrhotite and silicate, a minor mineral included sulfides of zinc and lead in the concentrate.

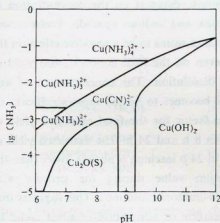


Fig.1 Dominative zones of copper in Cu-CN-NH<sub>3</sub>-H<sub>2</sub>O system

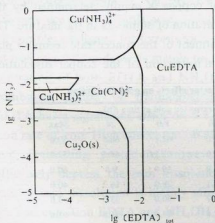


Fig.2 Dominative zones of copper in Cu-CN-NH<sub>3</sub>-EDTA-H<sub>2</sub>O system

All chemicals used in this investigation were reagent grade. Deionized water was used

for preparation of all solutions. The leaching experiments of Cu-Au concentrate with cyanide and ammonia mixture were carried out in a stirred baffled glass reactor with a capacity of 2 l. The concentrate used was all pass 120 mesh sieve, and the stirring speed is 700 rpm in all experiments. The ratio of liquid and solid was kept in 10:1. All experiments were performed at ambient temperature.

Determination of metal concentrations (Au, Ag, Fe, Cu, Pb etc) in leaching solutions were carried out by using ICP-AES (inductively coupled plasma-atomic emission spectroscopy ARL 3520). Solid samples were digested with a nitric-hydrochloride mixing acid (aqua regia), and the elements were measured in 5 N hydrochloride solutions. The concentration of free cyanide in leachate solutions was determined by FIA (flow injection analysis) in combination with spectrophotometer as the detector. This technique was based on the principle that free cyanide ions form CNCl with chloramine-T in a phosphate buffer solution (pH = 6) and then transferred into a coloured compound in reaction with mixture solution of pyridine and barbituric acid. The maximum adsorption peak was at 576 nm.

## 4 RESULTS

### 4.1 Leaching With Cyanide-ammonia Solutions

In order to select an experimental strategy, which has a reasonable chance of correctly identifying factor effects, a fractional factorials procedure of an experimental design

Table.1 The content of element (wt.-%) of sulfide concentrate used

Element	Cu	Fe	Pb	Zn	S	As	Ni	Hg	Au	Ag
wt.-%	7.02	28.47	0.42	0.42	24.80	0.024	0.004	0.0018	59-62 *	87-90 *

\* The unit of Au and Ag is g / t.

involved 8 runs with 5 factors and 2 levels was performed. The factors being examined in the investigation are the concentration of sodium cyanide and ammonium, the presence of triethanolamine and EDTA, and the pretreatment of the concentrate by aeration in nature water for 3 h.

The factorial experimental design and estimation of factor effects are conducted by a micro-computer program of statgraphics.

Experimental results and estimates of factor effects on the dissolution rate, the final extracted and the possible maximum extracted fraction of gold and silver in the process are listed in Table 2 and 3 respectively.

From Table 2, it can be seen that the most effective factors determining the dissolution rate of gold are the concentration of both NaCN and ammonia. The presence of EDTA and the cooperative action of EDTA and ammonia are the second important factors. Addition of EDTA together with triethanolamine, however, makes the dissolution rate of gold

decline. The main factors promising to achieve a possible highest extraction of gold are the concentration of  $\text{NH}_4\text{OH}$ , EDTA and NaCN.

Similarly, from Table 3, the rate of silver dissolution, depends on the concentration of ammonia and sodium cyanide. Pretreatment of aeration seems to be a negative effect on the rate, even on the final concentration yield of silver dissolution. The concentration of ammonia becomes to be the most significant effective factor for the final extracted yield of silver in 8 h and 24 h. The extracted yield of silver in 24 h leaching is always lower than the maximum value during the process with cyanide-ammonia solutions. This suggests that precipitation or adsorption of silver could be accelerated by addition of ammonia.

Experimental data and the statistic analysis of factor effects show that the dissolution rate of copper is mainly determined by the concentration of ammonia in the mixture. The pretreatment of the concentrate seems to play a role in restriction of the copper dissolution

Table 2 The experimental results and estimates of factor effects on gold dissolution

Run	Response; the extracted gold at time t(h)					
	0.5	1.0	2.0	8.0	24	Max
1	30.2	36.6	52.0	62.1	68.5	52.0
5	30.2	36.6	52.0	62.1	68.5	52.0
8	38.5	60.0	51.0	19.0	9.5	60.0
3	21.2	26.3	27.1	28.0	16.2	40.0
2	64.7	76.1	80.7	90.0	93.0	93.0
7	40.1	54.3	62.8	84.4	91.8	91.8
4	9.8	10.8	13.0	44.3	46.6	46.6
6	75.4	89.6	94.6	99.9	98.8	99.9
Estimates of factor effects						
ave+ABD+ACE+BCDE	43.5	53.9	57.8	64.1	64.7	71.9
A+BD+CE+ABCDE	24.0	33.0	29.2	16.0	17.2	28.0
B+AD+ABCE+CDE	0.3	-5.6	-7.7	0.5	-2.1	-4.6
AB+D+BCE+ACDE	32.2	32.2	38.6	40.4	47.3	24.6
C+ABCD+AE+BDE	8.0	7.5	10.0	31.1	35.8	21.3
AC+BCDE+E+ABDE	-3.6	-4.5	2.7	8.9	8.3	-2.5

A—the concentration of NaCN, g/l; B—the concentration of triethanolamine, M;

C—the concentration of EDTA, M; D—the concentration of  $\text{NH}_4\text{OH}$ , M;

E—pretreating by aeration.

**Table 3 The experimental results and estimates of factor effects on silver dissolution**

Run	Response: the extracted yield of silver at a time t (h)					
	0.5	1.0	2.0	8.0	24	max.
1	9.7	11.8	13.6	2.4	2.3	25.6
5	16.1	17.2	16.9	6.1	1.7	17.2
8	9.0	8.4	6.1	2.5	5.5	9.0
3	32.5	34.0	35.8	41.7	4.9	41.7
2	28.4	36.4	42.7	52.3	44.3	52.3
7	21.4	25.3	26.4	35.9	13.4	35.9
4	3.6	3.8	4.7	10.8	2.1	10.8
6	36.8	40.0	42.6	54.5	12.1	54.5
Estimates of factor effects						
ave+ABD+ACE+BCDE	19.7	22.1	23.6	25.8	10.8	30.9
A+BB+CE+ABCDE	14.0	14.0	13.7	17.6	-5.5	12.9
B+AD+ABCE+CDE	1.6	-1.1	-2.6	3.2	-9.3	-3.8
AB+D+BCE+ACDE	14.3	16.9	20.2	23.9	10.2	25.3
C+ABCD+AE+BDE	5.7	8.5	11.0	25.4	14.4	15.0
AC+BCD+E+ANDE	-0.9	-1.5	-2.9	-3.9	-4.9	0.8

rate. Owing to excellent complexing ability of ammonia, naturally, the total amount of copper in final pregnant liquors for 8 h or 24 h leaching is noticeably increased with the elevation of concentration of  $\text{NH}_4\text{OH}$ . Except for the presence of triethanolamine, a characteristic complexing ligand for ferrous ions, the rate of iron dissolution depends mainly on the concentration of both EDTA and  $\text{NH}_4\text{OH}$ . The combining action of triethanolamine and EDTA has a significant effect on the dissolution rate of iron. High concentration of NaCN and pretreating procedure, however, may effectively depress the iron dissolution. The rate of lead dissolution is mainly affected by the concentration EDTA and  $\text{NH}_4\text{OH}$  in solutions. The presence of triethanolamine, high concentration of NaCN in the mixture and pretreatment of aeration may limit the lead dissolution.

In summary, the preliminary study based on the experimental design indicates that ammonia and EDTA are the most effective factors that determine the dissolution rate and yield of gold and other metals in leaching

process of Au-Cu concentrate, and both will be discussed in detail as following.

#### 4.2 Effect of Ammonia

The dissolution of gold in the solutions of various concentrations of ammonia and a fixed concentration of sodium cyanide in 1 g/l or 4 g/l are plotted in Fig.3. The results indicate that the dissolution rate and cumulative recovery of gold, at the concentration level of 1 g/l sodium cyanide, are increased in the result of addition of ammonia and its growing concentration of the leach liquors. Addition of ammonia, ranged from 0.1 M to 1 M, depresses the dissolution rate and extracted fraction of gold at the level of 4 g/l initial sodium cyanide, showing a negative effect from the predication of the thermodynamic equilibria analysis. This unusual phenomenon may be contributed to diminish of the oxygen concentration and ion diffusion speeds. The relative concentration of oxygen in blank leach liquors has been measured with oxygen selective electrode, and the results are listed in the Table 4. It can be seen from the results that a notable



reduce of the oxygen concentration owing to addition of ammonia, from 8–12%, can not be omitted in the viewpoint of gold dissolution. Moreover, high concentration of salts may cause decrease of the diffusion coefficient of reagent pieces. As known, the rate of gold dissolution is controlled by oxygen diffusion in the process<sup>[9]</sup>.

The dissolution behaviors of silver in mixture liquors become intricate due to presence of ammonia and at the concentration level of 1 g/l NaCN, the cumulative leached yields of silver in the initial period are higher than that without adding ammonia see Fig.4. It suggests that the initial rate of silver leaching be elevated with the addition of ammonia. However the concentration of leaching solution is declined after reacting for 1–1.5 h, which means that a certain precipitate reaction of silver takes place in liquors. At the level of 4 g/l

NaCN, the duration time of silver yields which keep at a higher level is more longer in solution with higher concentration of ammonia. During this period, the silver cumulative yields in a certain interval increase with the concentration of ammonia on the mixture solutions. The bubbling of compressed air, which is a necessary condition for gold dissolution in cyanidation, may cause the violent volatile of ammonia from leaching liquors, and results in the depleting of ammonia concentration. In addition, the concentration of complexing reagents, both ammonia and cyanide, are reduced with leach time, and then the precipitation reactions will be violently developed. The most possible form of the silver precipitation may refer to sulfides because of its very low solubility constant. As it can be seen from Fig.4, leach time is not a helpful factor for silver dissolution when it is longer than 6 h.

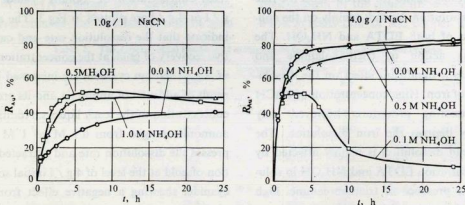


Fig.3 Effects of ammonia on gold leaching

$R_{Au}$ —leaching rate of Au;  $t$ —leaching time

Table 4 Relative concentration of oxygen in solutions

Component of solution	NaCN, g/l	0	1.0	1.0	1.0	2.0	4.0
	NH <sub>4</sub> OH, M	0	0.05	0.2	1.0	1.0	1.0
concentration of oxygen		1.00	0.96	0.94	0.93	0.92	0.88

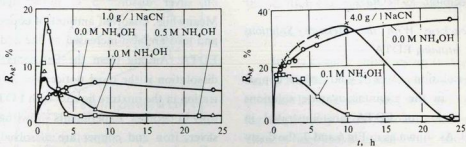


Fig.4 Effects of ammonia on silver leaching

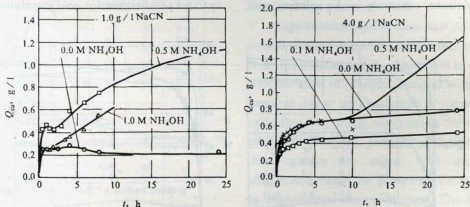
 $R_{Ag}$ —leaching rate of Ag;  $t$ —leaching time

Fig.5 Effects of ammonia on copper leaching

 $Q_{Cu}$ —Copper dissolved in liquors;  $t$ —leaching time

The experiments illustrate that the content of copper dissolved in the mixture solutions is higher than that in the single cyanide solutions and increases with growth of ammonia concentration for leaching of the concentrate at the ambient temperature. This phenomenon can be contributed to the excellent ability of ammonia to complex with copper ions. Fig.5 is the plots of copper dissolution in liquors with varied initial concentration of ammonia and a fixed initial concentration of 1 g/l or 4 g/l sodium cyanide, respectively. In contrast with, the ferric amount dissolved in the mixture solutions is much lower than that

in the single cyanide solution. The results indicate that the initial rate of dissolution of iron minerals in the mixture solutions increases with the elevation of ammonia concentration. The concentration of iron in liquors is kept at an approximate constant level in a certain period of leaching. This may be contributed to that the iron content in liquors depends on the concentration of its cyanide complexes, and that almost whole of the cyanide may be exhausted with the formation of ferrous-cyanogen complexes because of the copper ions form dominantly the copper-ammonia complexes. In fact, much ferric ions, dissolved

simultaneously with copper from chalcopyrite, may precipitate as  $\text{FeOOH}$ .

### 4.3 Leaching With the Mixture Solutions Containing EDTA

Dissolution curves of gold, silver, copper and lead in the ammonia-cyanide solutions with addition of EDTA are illustrated in Fig.6-9. As shown as in Fig.6 and 7, the dissolution rate and accumulating extracted yields of both gold and silver are increased significantly by the addition of EDTA in mixture solutions, especially in the solution with

low level of  $\text{NaCN}$ , such as  $1 \text{ g/l}$ . The effect on silver dissolution is more significant. Meanwhile, dissolved amount of copper, iron and lead are also increased by the addition of EDTA. Among them the behaviors of lead dissolution is the most noticeable, its concentration in the mixture liquors with EDTA multiply in decades. Experiments show that gold, silver, iron and copper are dissolved a tiny amount in the mixture solution of ammonia and EDTA without cyanide. This suggests that ammonia and EDTA themselves have no ability to act as a lixiviant for gold dissolution.

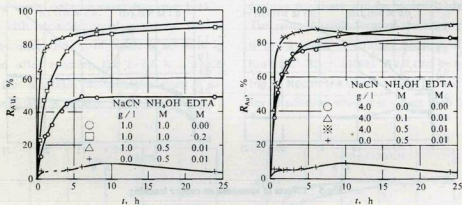


Fig.6 Effects of EDTA on gold leaching

$R_{Au}$ —leaching rate of Au;  $t$ —leaching Time

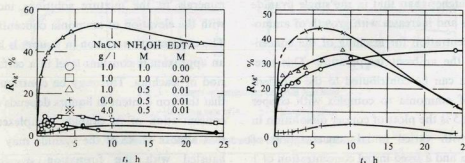


Fig.7 Effects of EDTA on silver leaching

$R_{Ag}$ —leaching rate of Ag;  $t$ —leaching time



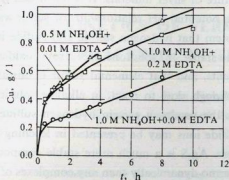


Fig. 8 Effects of EDTA on copper leaching

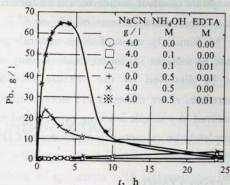


Fig. 9 Effects of EDTA on lead leaching

The concentration of free cyanide in leaching solutions containing of EDTA is enhanced with leaching time at the starting period of the leaching, and decreased after two hours later. The level of concentration of free cyanide in solutions containing EDTA is much higher than that in the solutions of solitary cyanide or mixture of cyanide and ammonia. It therefore indicates that EDTA is a very stable ligand for copper and can completely substitute the cyanide from cyano-copper complexes. On the other hand the elevating of EDTA concentration, e.g. from 0.01 M to 0.2 M, has no more favorable influence on the dissolution of precious metals. Instead, the content of copper, iron and lead in solutions are seriously increased. The concentration of free cyanide in

leaching liquors, however, are not affected by the addition of ammonia in cyanide solutions.

## 5 DISCUSSION

In the cyanide solutions up to 4 g/l (40 kg/t) NaCN, the extracted yields of gold and silver are less than 85% and 36% in 24 h leaching respectively. Conventional cyanidation is likewise ineffective in achieving satisfactory gold extractions from the concentrate in the absence of any complexing agents other than cyanide. The Au-Cu sulfide concentrate is considered as a refractory ore.

Experimental results show that one of the critical factors retarded dissolution of gold from the concentrate in cyanidation is the low concentration of cyanide in regard with its exhaustion due to the dissolution of copper, iron and other base metal minerals. In the cyanide solutions, therefore, presence of ligand other than cyanide for copper and iron will efficiently enhance the extracted yield of gold, as experimental data confirmed. The dissolution rate of precious metals is little heightened by the addition of ammonia in cyanide solutions at a lower cyanide concentration, e.g. 1 g/l NaCN, although the concentration of cyanide in solutions is not been increased. The dissolution rate and leaching yield of gold in the liquor with high concentration of cyanide are not more improved by the addition of more ammonia although equilibrium calculations predicate that a higher concentration of ammonia is favorable to release the cyanide from copper-cyanogen complexes. The measurements show that there is no increase of the level of free cyanide in leaching solutions due to the addition of ammonia. Therefore, at least in the sense of kinetics, ammonia is not a sufficient strong ligand that can compete with

cyanide in the respect of complexing with base metals. In other hand, the quantity of copper dissolved in liquors is rapidly increased with the concentration of ammonia and result in incompletely replacing cyano-copper complexes and excess consumption of cyanide.

EDTA is a more stable ligand for copper ions than ammonia and can completely replace cyanide ions in the cyano-copper complexes, as seen from equilibrium analysis. The concentration of free cyanide in the mixture solutions has a stepping increase by addition of EDTA, as seen from Fig.10. Therefore, the dissolution rate and extracted yield of gold and silver are greatly enhanced by adding EDTA in mixture solutions of cyanide and ammonia.

The cooperative action of EDTA and ammonia is another important factor favorable to dissolution of precious metals. Neither the mixture solution of cyanide and ammonia without EDTA nor the mixture solution of cyanide and EDTA containing lower concentration of ammonia (e.g. 0.1 M) has no capacity to dissolve gold and silver with the rate and extracting yield as high as that in the mixture solution of cyanide and EDTA with ammonia at a proper concentration. Although a proper concentration of ammonia, e.g. 0.5 M, is a necessary condition for the formation of copper and ammonia complexes, as described in the section of equilibrium calculations, the complexing action can be certainly developed in the presence of EDTA in the mixture.

The maximum extracted yield of silver in the cyanidation with optimum conditions is less than 55%, and much lower than the extracted yield of gold. In the experiments, it is also found that the concentration of silver in leaching solutions decreases with reaction time. This result is reasonably attributed to the

nature of silver minerals. It is illustrated from the potential pH relationship for sulfur-water system that hydrogen sulfide and sulfide ions are stable in solutions free from oxidizing agents, and that elemental sulfur is unstable, although slow to react, in alkaline solutions. As the results, a certain hydrogen sulfide or sulfide ions may be presented in leaching liquors.  $\text{Ag}_2\text{S}$  is a much more stable compound thermodynamically than any complexes of silver, either silver-cyanogen or silver-EDTA. A precipitate of silver sulfide would be formed if the concentration of ions of  $\text{HS}^-$  or  $\text{S}^{2-}$  is at  $10^{-8}\text{M}$ . Similarly, most of silver minerals presented as sulfides in the concentrate may also not be dissolved by the mixture solutions. Therefore, silver minerals are non-completely dissolved in a simple leaching process and may completely be extracted in a process of CIP or RIP.

## 6 CONCLUSION

In cyanidation of the Au-Cu sulfide concentrate the extraction of gold and silver are elevated by the addition of ammonia at a proper concentration. In the process ammonia acts as a competing ligand for copper ions. With adding of EDTA in the mixture solution of cyanide and ammonia the dissolution rate and yield of both gold and silver are efficiently enhanced. EDTA plays the role of the instinet of cyanide ligand in cyano-metal complexes and release free cyanide. Total gold and a high portion of silver in the concentrate could be extracted by the mixture solution of ammonia, EDTA and cyanide in certain conditions. Deficiency of complexing ligand for copper in the leaching liquors is therefore recognized as the refractoriness for the sulfide concentrate under

(To be continued on page 57)