The Effect of Ore Type, Depth, and Leach Time on Cyanide Species in Column Tests Using NaCN Leach Solutions

By J. P. SHERIDAN,[1] J. L. HENDRIX[1] and J. H. NELSON[2]

*Chemical and Metallurgical Engineering Department and **Chemistry
Department, University of Nevada, Reno, Nevada, 89557 U.S.A.

ABSTRACT

Three ores (sulfidic, oxidized and carbonaceous) were analyzed to determine the effects of leaching time, ore depth, and ore mineralogy on cyanide species concentration. NaCN solutions were percolated through opaque columns filled with milled ore. Column design made liquid sample collection possible from various depths at specific times. The concentrations of weak acid dissociable(WAD) and total cyanide, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$ were determined for each sample.

Extended percolation time led to increases in WAD cyanide concentrations and decreased SCN^- and $Cu(CN)_4^{3-}$ concentrations regardless of ore depth. WAD cyanide concentration decreased while $Fe(CN)_6^{4-}$ concentration increased with ore depth. Highest concentrations of $Fe(CN)_6^{4-}$, SCN^- and $Cu(CN)_4^{3-}$ were found in the sulfidic ore, with expected low WAD cyanide concentrations. Lowest concentrations of $Fe(CN)_6^{4-}$, SCN^- and $Cu(CN)_4^{3-}$ were found in the oxidized ore. Intermediate concentra-

tions of these cyanide species were found in the carbonaceous ore.

INTRODUCTION

Cyanide hydrometallurgy, which has been used nearly exclusively for the processing of precious metal ores, forms the basis for two primary types of precious metal processing treatments, the Merrill Crowe and the Carbon-In-Pulp(CIP) processes. Both of these processes involve the leaching of gold and/or silver with cyanide according to the following reactions.

$$2Au + 4NaCN + O_2 + 2H_2O \rightleftharpoons 2NaAu(CN)_2 + 2NaOH + H_2O_2 \qquad 1.$$

$$2Ag + 4NaCN + O_2 + 2H_2O \rightleftharpoons 2NaAg(CN)_2 + 2NaOH + H_2O_2 \qquad 2.$$

The gold and/or silver bearing solution is separated from the milled ore and the precious metal values are recovered via zinc dust precipitation (Merrill Crowe) or by adsorption onto activated carbon(CIP). The resulting "barren" solution contains free cyanide, simple cyanides, transition metal cyanide complexes(such as $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Cu(CN)_4^{3-}$), and other impurities. The reaction of cyanide with sulfide minerals in the ore body leads to the formation of SCN^-, $S_2O_3^{2-}$,CNO^-, S^{2-} and HS^- in the barren solution. Most of the barren solution is recycled to the processing mill. However, a portion must be discharged to the tailings impoundment to avoid buildup of certain impurities in the processing circuit. Two cyanide bearing streams are discharged in a slurry to the tailings impoundment: the barren solution, and the finely ground, leached ore pulp. These streams are held in the tailings impoundment where the usual practice is to allow natural degradation to cause some reduction in the concentration of cyanide.

Little information is available on the types of cyanide compounds and their probable distributions in precious metal mill tailings impoundments, due mostly to difficulties in the chemical analysis of solid and liquid mill tailings samples(1). Even less information is available concerning the mobility of cyanide compounds in precious metal mill tailings impoundments. Fuller(2) studied the mobility of KCN and $K_3Fe(CN)_6$ through columns packed with seven types of soil. He found that cyanide in the forms of $Fe(CN)_6^{3-}$ and CN^- was very mobile in soils spiked with a pulse of these ions.

CYANIDE CHEMISTRY

Simple cyanides, $A(CN)_x$, have differing solubilities and stabilities, but many ionize to release CN^- to the environment according to the following reaction:

$$A(CN)_x \dashrightarrow A^{+x} + xCN^- \qquad 3.$$

Complex metal cyanides have a general formula of $A_yM(CN)_x$, where A is often an alkali metal(but can be a transition metal), y is the number of A ions, M is a transition metal ion such as Fe^{+2}, Fe^{+3}, or Cu^{+1}, and x is the number of cyanide groups. Many of the complex metal cyanides are insoluble but some complex metal cyanides ionize to release a soluble $M(CN)_x$ group according to the following generalized reaction:

$$A_yM(CN) \rightleftharpoons yA^{+x} + M(CN)_x^{-y} \qquad 4.$$

Many of these complex metal cyanide ions undergo stepwise formation and dissociation, the extent of which depends upon pH, temperature, and free CN^- concentration. Of particular interest are the metallo-cyanide complexes of Fe and Cu present in aqueous solution.

There are a number of slightly soluble salts of formulas $A_2M^{2+}[Fe(CN)_6]$ and $AM^{3+}[Fe(CN)_6]$, where A is an alkali metal of oxidation state +1,and M^{2+} and M^{3+} are transition metals of oxidation states +2 and +3, respectively. Photochemical decomposition of the $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ ions is the most important mechanism for the release of free cyanide into the environment. Broderius and Smith(3) determined that the maximum quantities of total cyanide, released as HCN, from the decomposition of dilute $Fe(CN)6^{4-}$ and $Fe(CN)_6^{3-}$ bearing solutions are approximately 85% and 49%, respectively of the total cyanide contained in the samples.

There are a number of copper cyanide species, whose stability in aqueous solution, is dependent on free cyanide concentration and pH, as illustrated in the following equilibria.

$$Cu^{+1} + 2CN^{-} \rightleftarrows Cu(CN)_2^{-} + CN^{-} \rightleftarrows Cu(CN)_3^{2-} + CN^{-} \rightleftarrows Cu(CN)_4^{3-} \qquad 5.$$

$$Cu(CN)_4^{3-} + H^{+} \rightleftarrows Cu(CN)_3^{2-} + HCN + H^{+} \rightleftarrows Cu(CN)_2^{-} + 2HCN \qquad 6.$$

EXPERIMENTAL

Representative samples of oxidized, sulfidic, and carbonaceous gold ores were obtained from mines located in Nevada. The ores are typical of gold ores commonly processed in the western United States. Table I lists the results of chemical analysis of these ores. The sulfide ore was obtained as an ore-water slurry from the cyclone overflow stream of the processing mill. The sulfidic ore had a 55% passing size of 104 microns. The oxidized and carbonaceous ore samples, obtained from

Table I. CHEMICAL ANALYSIS OF ORES

	OXIDIZED	SULFIDIC	CARBONACEOUS
Ag	17.50	57.30	3.50
As	620.00	0.23%	0.10%
Au	2.35	8.71	8.88
Ca	0.31%	5.30%	15.00%
Cu	93.00	0.13%	61.
Fe	2.6%	10.5%	1.4%
Hg	13.0	0.12	43.
Mg	0.12%	3.6%	3.7%
Mn	84.	0.19%	260.
Ni	25.	64.	38.
Pb	*26.	800.	*24.
S^{2-}	0.0%	3.85%	0.29%
S(total)	0.18%	4.24%	0.82%
Zn	81.	0.16%	150.

Notes: - Results reported in mg/kg, "*" indicates result is near detection limit, and "%" indicates result is weight percent run-of-mine stockpiles. were ground to approximately 50% passing 147 microns prior to leaching. CaO is commonly added to ores prior to milling operations for pH adjustment. The oxidized and carbonaceous ores were blended with 0.013 and 0.005 g of CaO per kg of ore, respectively. The sulfidic ore had been treated with 0.0075 g of Portland cement(Type III) per kg of ore in the comminution circuit of the processing mill. The ores were continuously leached in columns with pH 10.5 NaCN solutions, followed by a rinse with pH 10.5 CaO solutions. The columns were rendered opaque to exclude visible light from the ore and leach solution. The concentrations of NaCN used for the leaching of the sulfidic, carbonaceous and oxidized ores were 1.59, 0.265, and 0.159 g/L CN^-, respectively. Liquid samples were drawn from levels 45, 91, 137 and 183 cm, respectively, as measured from the top of the columns. The concentration of total and WAD cyanide was determined for each sample using a methodology developed by Hendrix, Nelson and Ahmadiantehrani(4). The concentrations of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Cu(CN)_4^{3-}$, and SCN^- were determined using mobile phase ion chromatography.

RESULTS AND DISCUSSION

Samples from each ore column were analyzed regularly for total and WAD cyanide, $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$ concentrations. The concentrations of SCN^- and $Cu(CN)_4^{3-}$ were determined less frequently, usually when the presence of such compounds was indicated by ion chromatography. Material balances(Table II) were calculated for each ore from the measured concentrations of the various cyanide species exiting the ore columns. The initial cyanide, CN_0, is defined as the cumulative total of cyanide, in the form of NaCN, introduced to the column in the leach solutions.

The oxide ore was leached for a period of 180 days, during which 21 and 10 pore volumes of leach and rinse solution, respectively, passed through the column. Over 82 percent of the initial cyanide, CN_0, exited the column as so-called "free" cyanide. The conversion of initial cyanide, CN_0, to $Fe(CN)_6^{4-}$, SCN^- , and $Cu(CN)_4^{3-}$ was 7.6, 0.3, and 0.15 percent, respectively. Approximately 9.2 percent of the initial cyanide CN_0 is unaccounted for and may have exited the column as unidentified species, accumulated within the column, or reacted to form other species. Results of the material balance indicate that $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$ are produced within the oxidized ore column and move through the ore and out of the column within a period of 180 days. Solid samples of the oxide ore were analysed for total and WAD cyanide following the completion of the rinse. The total and WAD cyanide concentrations averaged 1.4 and 0.7 mg CN^- per kg of solid, respectively.

The sulfidic ore was leached and rinsed with 35 and 15 pore volumes, respectively. The overall conversions of initial cyanide, CN_0, to the individual cyanide species are much different in the sulfidic ore column than in the oxidized ore column. Only 5.9 percent of the initial cyanide exited the sulfidic column as WAD cyanide. Over 86 percent of the initial cyanide was converted to $Fe(CN)_6^{4-}$. The conversion of initial cyanide to SCN^- and $Cu(CN)_4^{3-}$ was 4.1 and 3.9 percent, respectively. The overall material balance gave no indication of unaccounted cyanide species or accumulation of cyanide within the column. The overall material balance indicated that significant quantities of $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$ are produced within the column and move through and exit the column within a leaching period of 201 days. Most of the initial cyanide is converted to $Fe(CN)_6^{4-}$ ion, with SCN^- and $Cu(CN)_4^{3-}$ being minor components. Following the H_2O rinse, the concentrations of total and WAD cyanide found in the sulfidic ore column averaged 14.4 and 1.8 mg CN^- per kg of solid, respectively.

The carbonaceous ore was leached with 24 pore volumes and rinsed with 12 pore volumes. Only 10.3 percent, by weight, of the initial cyanide entering the column exits the column as WAD cyanide. The conversion of initial cyanide to $Fe(CN)_6^{4-}$ exiting the column was 85.7 percent. The conversions of initial cyanide to SCN^- and $Cu(CN)_4^{3-}$ exiting the column were 4.0 and 0.0 percent, respectively. The $Cu(CN)_4^{3-}$ ion was detected at intermediate levels of the column but was not found in the column effluent solution. There was no evidence of cyanide accumulation within the column nor of unaccounted cyanide species. Significant quantities of $Fe(CN)_6^{4-}$, and SCN^- are produced by leaching and these ions move through the column and exit it within a period of 240 days.

The $Cu(CN)_4^{3-}$ ion is produced in the column, but is thought to be adsorbed onto carbonaceous material within the ore, which is consistent with previous reports(5). The total and WAD cyanide concentrations of solid samples of the sulfidic ore taken after rinsing averaged 4.6 and 1.2 mg CN^- per kg of solid, respectively.

Table II. OVERALL CYANIDE MATERIAL BALANCE FOR NaCN LEACHING

weight percent of initial cyanide, CN_0, present in column effluent as individual cyanide species

CN species	Oxide	Sulfidic	Carbonaceous
CN^- (WAD)	82.7%	5.9%	10.3%
CN^-(as $Fe(CN)_6^{4-}$)	7.6%	86.1%	85.7%
CN^-(as SCN^-)	0.3%	4.1%	4.0%
CN^-(as $Cu(CN)_4^{3-}$)	0.2%	3.8%	0.0%
CN^-(unaccounted)	9.2%	0.1%	0.0%

Figures 1 and 2 illustrate the differences in various cyanide species as a function of the ore types studied. Figure 1 is a plot of $Fe(CN)_6^{4-}$ concentration, in the column effluent, versus leach time. Solution concentrations of $Fe(CN)_6^{4-}$ during the NaCN leach period are much greater in the sulfidic ore than in the oxidized or carbonaceous ores. Figure 1 indicates that at the end of the leaching period, the concentration of $Fe(CN)_6^{4-}$ was decreasing in the oxidized ore but was increasing for the carbonaceous and sulfidic ores. The cyanide material balance results for the carbonaceous and sulfidic ores indicate the $Fe(CN)_6^{4-}$ ion accounts for more than 85 percent of the total cyanide. This is significant in that both the ores were leached for a period of over 200 days, with no limit in the production and mobility of the $Fe(CN)_6^{4-}$ being attained. Apparently iron was available in sufficient quantities for $Fe(CN)_6^{4-}$ formation after 200 days of leaching. The WAD cyanide concentration of the column effluent is plotted versus leach time in Figure 2, for each ore type. Although the initial cyanide concentration of the sulfidic ore was an order of magnitude larger than that of the oxidized ore, the oxidized ore had a higher WAD cyanide concentration in the column effluent than the sulfidic ore. The scatter in the sulfidic ore data suggests interfering chemical equilibria as compared to the oxidized and carbonaceous ores.

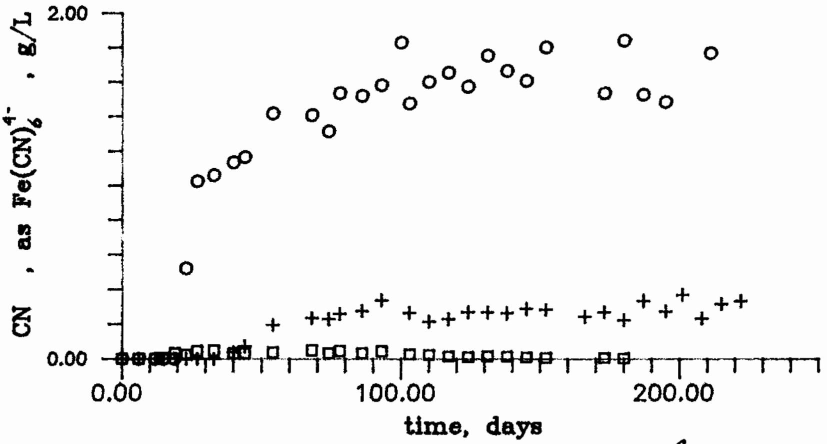

Figure 1. The effect of ore type on $Fe(CN)_6^{4-}$ concentration in solution.
(□)oxide;(○)sulfidic;(+)carbonaceous.

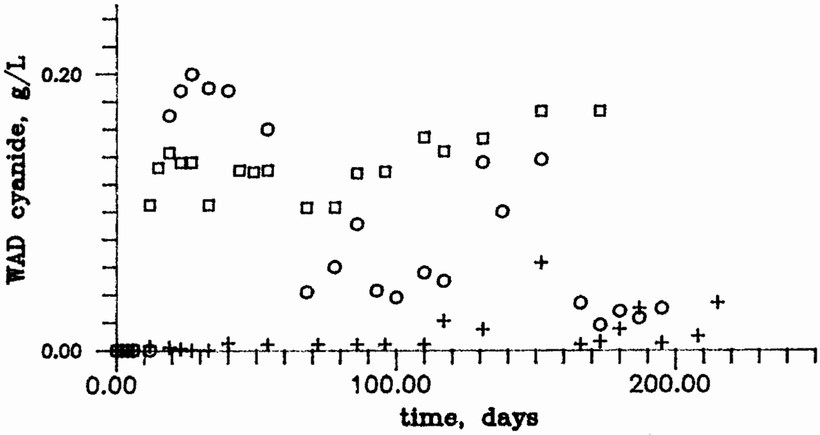

Figure 2. The effect of ore type on WAD cyanide concentration in solution.
(□)oxide;(○)sulfidic;(+)carbonaceous.

The $Fe(CN)_6^{3-}$ ion was detected in less than five percent of the samples. This was probably due to the greater stability of the $Fe(CN)_6^{4-}$ ion in aqueous solution and to the absence of any oxidizing agents in solution.

CONCLUSIONS

1. Cyanide speciation within tailings is definitely related to ore mineralogy.
2. The $Fe(CN)_6^{4-}$ ion is the most abundant cyanide species in column leaching studies when iron is present in sufficient quantities in the ore.
3. The sulfidic ore contained the highest concentrations of $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$, and consequently had the lowest WAD cyanide concentration of the three ores leached in these studies.
4. The oxidized ore contained the lowest concentrations of $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$, and consequently had the highest WAD cyanide concentration of the three ores leached in these studies.
5. The carbonaceous ore contained intermediate levels of $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$, and contained relatively low concentrations of WAD cyanide.
6. The $Fe(CN)_6^{4-}$, SCN^-, and $Cu(CN)_4^{3-}$ ions are vertically mobile in column leaching with a NaCN solution. The rate of migration of these ions is dependent on the volumetric flow rate of the lixiviant and on the ore mineralogy.

A thorough discussion of these results may be found in the M.S. thesis of Jon Sheridan(6).

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