Selectivity Considerations in the Amine Extraction of Gold From Alkaline Cyanide Solutions

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Abstract — *It has been discovered that gold can be extracted from alkaline cyanide solution with primary, secondary, and tertiary amines by adding certain Lewis base modifiers, such as organic phosphorus oxides. Under these circumstances, gold can be extracted at about pH 10, commensurate with the pH of cyanide leach liquors. The selectivity of the amines and amine/modifier combinations for* $Au(CN)_2^-$ *over other metal-cyanide complexes is discussed. Potential applications for the solvent extraction of gold from cyanide solutions are also discussed.*

Introduction

Little research has been reported for the solvent extraction of gold from cyanide solution (Das and Bhattacharyya, 1976; and Ritcey and Ashbrook, 1979). Technical literature indicates that of the amine extractants, only tertiary and quaternary amines have been studied (Ritcey and Ashbrook, 1979). It was found that gold extraction with quaternary amines was possible for all pH values, but stripping was difficult. Extraction with tertiary amines was limited to acidic solutions as has been reported for the extraction of other anions with simple, weak base amines that undergo protonation (Wilkinson, 1962).

Little attention has been given to solvent extraction of gold from alkaline cyanide solutions due to:

- Satisfaction with current processing strategies;
- Lack of a suitable extractant;
- High aqueous:organic phase ratio for production of concentrated solutions; and
- Organic loss to raffinate.

This position should be re-examined to see what advantages solvent extraction may bring to gold cyanidation processes. From a reaction rate standpoint, solvent extraction is faster than carbon adsorption processes and should offer advantages associated with fast reaction rate processes (small reactor size, low gold hold-up).

Concern for organic losses to the raffinate cannot be dismissed lightly. It would require using solvent extraction equipment that would minimize such losses. For example, using a centrifugal contactor can produce aqueous raffinates containing less than 5 ppm dispersed organic. Alternately, a carbon-column, flotation cell, or coalescer could be used to scavenge such organic dispersions in the raffinate stream.

The possibility of generating a concentrated, purified gold cyanide solution to recover high purity electrolytic gold sheet is an exciting concept. Such a process strategy requires an extractant with high selectivity.

In the cyanidation of gold ores and concentrates, there are situations where the use of solvent extraction for gold recovery from such cyanide leach solutions may be possible and used advantageously. They include:

- Heap and agitation leach solutions from low-grade ores;
- Eluate solutions from carbon strip;
- Leach solutions from complex concentrates; and
- Leach solutions from dissolving precious metal scrap.

The composition of these solutions will differ significantly both with regard to gold concentration and contaminant level. Solution compositions might vary from 1 ppm gold in the case of heap leach solutions to an estimated concentration of 30,000 ppm gold for a solution prepared from the leaching of gold scrap.

Experimental

The equilibrium distribution of a particular metal between the organic and aqueous phases was determined after contacting 50 m*l* (1.7 oz) of the two phases by rapid stirring for 10 minutes. The pH was adjusted by small additions of concentrated H_2SO_4 or NaOH and was continually monitored by a combination pH electrode. All equilibrations were at 23°C (73°F) ±2°. After phase disengagement, samples (2 m*l*, or 0.07 oz) of the aqueous solution were removed, filtered, and analyzed by atomic adsorption spectroscopy. Equal amounts of the organic phase were also removed to maintain a 1:1 phase ratio.

Solutions of the various cyanide anions were prepared at 5×10^{-3} M in the following manner:

$Au(CN)_2^-$ was prepared from reagent grade $K_2Au(CN)_2 \cdot 2H_2O$.

$Ag(CN)_2^-$ was prepared from reagent grade AgCN dissolved in 5×10^{-3} M NaCN.

$Cu(CN)_4^{3-}$ was prepared from CuCN dissolved in 1.5×10^{-2} M NaCN.

$Zn(CN)_4^{2-}$ was prepared from $Zn(CN)_2$ dissolved in 1.0×10^{-2} M NaCN.

$Fe(CN)_6^{3-}$ was prepared from reagent-grade $K_3Fe(CN)_6$.

$Fe(CN)_6^{4-}$ was prepared from reagent-grade $K_4Fe(CN)_6$.

In one series of experiments, the level of free cyanide was varied by excess NaCN additions. In another series, the gold concentration was varied by two orders of magnitude. The amine extractants used were of commercial grade.

Amine Extractants

Initial research has shown that simple amines capable of protonation can not extract gold from alkaline cyanide solutions (Mooiman and Miller, 1983). Percent gold extraction from aurocyanide solution is shown in Fig. 1 as a

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function of pH for typical primary, secondary, and tertiary amines. These amines can be characterized by the pH where 50% extraction occurs, pH_{50}. The order of increasing pH_{50}: tertiary $<$ primary $<$ secondary follows the order of increasing basicity of alkyl amines in water (Hall, 1957). Amine basicity is understood to mean the amine's strength for a particular anion with respect to the hydroxyl anion concentration — pH. Increased amine basicity is reflected by an increase in pH_{50} for a particular anion.

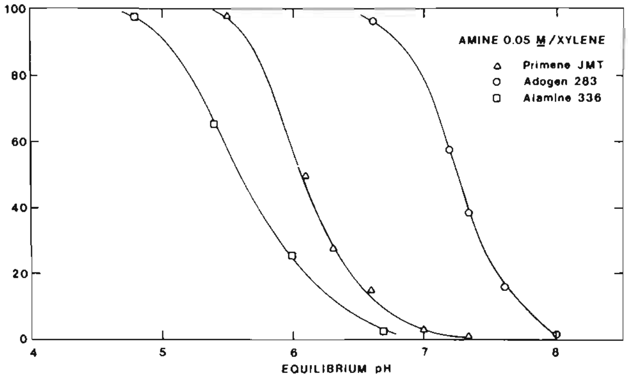

Fig. 1 — Percent extraction of $Au(CN)_2^-$ (1.0 gl^{-1} Au in 0.5 M Na_2SO_4) versus pH for primary, secondary, and tertiary amines (0.05 M in xylene)

Variations in the nature of amine alkyl chains, in terms of branching or length, does not have a marked effect on the relative position of the curves for each type of amine. This is demonstrated by the pH_{50} values for different amines presented in Table 1. The value of pH_{50} is determined primarily by the amine type — primary, secondary, or tertiary.

Table 1 — pH_{50} Values for Gold Extraction from Aurocyanide Solutions (1.0 gl^{-1} Au) by Various Amine Extractants (0.05 M in Xylene)

AMINE	SUPPLIER	STRUCTURE	pH_{50}
Primary		RNH_2	
Primene 81-R	Rohm & Haas	$R = C_{12-14}$	6.55
Primene JM-T	"	$R = C_{18-22}$	6.05
Secondary		R_2NH	
Adogen 283	Sherex	$R = C_{13}$	7.15
LA-2	Rohm & Haas	$R = C_{10-12}$	7.15
Alamine 204	Henkel	$R = C_{12}$	7.15
Alamine 226	"	$R = C_{16-18}$	7.06
Tertiary		R_3N	
Adogen 364	Sherex	$R = C_{8-10}$	5.55
Adogen 363	"	$R = C_{13}$	5.35
Alamine 308	Henkel	$R = iso\text{-}C_8$	5.45
Alamine 310	"	$R = iso\text{-}C_{10}$	5.35
Alamine 336	"	$R = C_{8-10}$	5.66

The effect of diluent on the pH_{50} values for amine extraction of gold was found to be insignificant in the case of the primary amines. The aliphatic diluent, hexane, reduces the pH_{50} values for secondary and tertiary amines by 0.5 pH unit compared to the aromatic diluent, xylene.

For both aliphatic and aromatic diluents, the pH_{50} value of the secondary amine, Adogen 283, increases as the amine concentration increases, i.e., better loading at higher pH values is obtained as the extractant concentration increases (Table 2). This, as expected, is due to the mass action effect, shifting the extraction equilibrium to the right:

$$\overline{R_2NH} + H^+ + Au(CN)_2^- = \overline{R_2NH_2Au(CN)_2} \qquad (1)$$

Note that a ten-fold increase in concentration increases the pH_{50} by about one pH unit, as suggested by Equation 1.

Table 2 — Effect of the Extractant (Adogen 283) Concentration on the pH_{50} for Gold Extraction (1.0 gl^{-1} Au) from Cyanide Solution

Concentration	pH_{50} in Xylene	pH_{50} in Chevron IX
0.025	7.15	6.15
0.05	7.15	6.50
0.20	7.75	7.75
0.50	8.30	7.90

The effect of the background electrolyte, Na_2SO_4, was investigated by performing percent extraction versus pH experiments with and without 0.5 M Na_2SO_4. There was little or no effect due to the inert electrolyte. It was concluded that ionic strength was not significant in determining the extent of gold extraction by simple alkyl amines.

These findings show that even the strongest extractant, the secondary amine, is not suitable for gold extraction from alkaline cyanide solution. However, the addition of organic phosphorus oxide modifiers increases the strength of these weak base amines to such an extent, in the case of the aurocyanide anion, that extraction from alkaline solution is possible (Mooiman and Miller, 1983; Miller and Mooiman, 1984).

Modified Amine Extractants

Adding organic phosphorus oxide modifiers to weak base amines can increase their effective pH range to extract certain anions (Mooiman and Miller, 1983; Miller and Mooiman, 1984; Irving and Damodaran, 1971). Such an effect is particularly prevalent in extracting the aurocyanide anion, $Au(CN)_2^-$. In essence, this effect can be considered to be an increase in base strength with respect to the extraction of a particular anion.

For example, there is a marked improvement in the extracting ability of the amines on addition of tributyl phosphate (TBP) as indicated by the dramatic shift of the extraction curves to the high pH range (Fig. 2). The ability to extract $Au(CN)_2^-$ at higher pH values is observed for all amines (Table 3) and the increase in base strength as revealed by the ΔpH_{50} value. The effect is greatest for the primary and secondary amines. Further research has been limited to these two extractants.

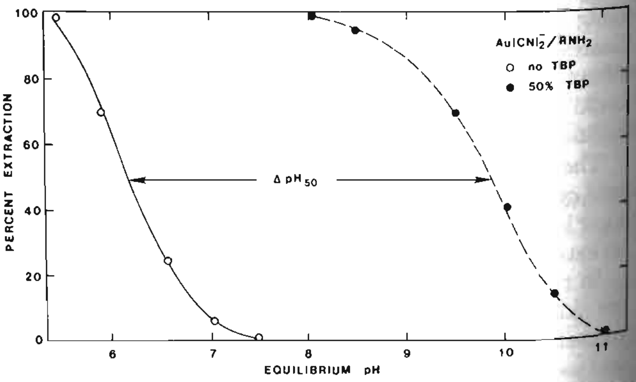

Fig. 2 — Effect of TBP on percent extraction of $Au(CN)_2^-$ (1.0 g l^{-1} Au) by a primary amine, Primene JM-T (0.05 M)

Table 3—Effect of TBP on the Extraction of Gold (1.0 gl^{-1}) from Cyanide Solution by Amines (0.05 M in Xylene)

Amine	pH_{50} no TBP addition	pH_{50} 50% TBP in xylene
Primene JM-T	6.05	9.85
Adogen 283	7.15	9.85
Alamine 336	5.66	8.05

Organic phosphorus oxides are particularly effective in this respect. Other well-established modifiers such as isodecanol and MIBK actually reduce the amine basicity (Mooiman and Miller, 1983). The increase in amine basicity is even more pronounced with other organic phosphorus oxides (Table 4).

Table 4—Effect of Organic Phosphorus Oxide Modifier Type on the Extraction of Gold (1.0 gl^{-1}) from Cyanide Solution. Extractant: 0.05 M Adogen in Xylene/10% Modifier

Modifier	Structure	pH_{50}	ΔpH_{50}
No Modifier		7.35	0
TBP	$(RO)_3P = 0$	7.83	0.48
DBBP	$(RO)_2RP = 0$	8.30	0.97
BDBP	$(RO)R_2P = 0$	8.72	1.37
TBPO	$R_3P = 0$	10.10	2.75
TOPO	$R_3P = 0$	9.45	2.10

$R = C_4H_9$ except for TOPO where $R = C_8H_{17}$

Modifiers increase the amine basicity (the pH_{50}) in the following order: phosphate $(RO)_3P = 0 \langle$ phosphonate $(RO)_2RP = 0 \langle$ phosphinate $(RO)R_2P = 0 \langle$ phosphine oxide $R_3P = 0$. This sequence follows the order of increasing Lewis basicity (electron donor power) of the modifier and indicates that solvation effects are of concern in the modified amine extraction system. The amine basicity, in terms of ΔpH_{50}, increases as the concentration of modifier increases (Mooiman and Miller, 1983).

Decreasing the gold concentration does not affect the percentage of gold extracted. This is demonstrated in Table 5 for gold concentrations of 10 and 1000 ppm. Also, excess cyanide ion in solution does not affect the extent of gold extraction, as shown in Table 6 by the extent of gold extraction with a modified amine for 100-, 1000-, and 10,000-fold excess of cyanide.

Table 5—Effect of Gold Concentration 0.25 M Adogen in Xylene/50% TBP

Equilibrium pH	Percent Extraction from 10 ppm Gold Solution	Percent Extraction from 1000 ppm Gold Solution
9.5	100	99.0
10.0	87.3	85.5
10.5	73.2	55.0
11.0	27.1	36.5
11.5	11.8	9.8

Table 6—Effect of Excess Cyanide on Gold Extraction from a 10 ppm Gold Solution at pH 9. Extractant: 0.05 M Adogen 283 in Xylene/50% TBP

Free Cyanide Conc. M	Percent Extraction from 1000 ppm Gold Solution
0	72.8
5×10^{-3}	75.0
5×10^{-2}	76.1
5×10^{-1}	77.2

These results indicate that it is possible to extract gold from alkaline cyanide solutions at pH values from 8 to 10 by modified amines. This can be accomplished at all gold concentrations and in the presence of free cyanide. Stripping can be accomplished using alkaline solutions, e.g., NaOH, with pH values greater than 12.

Progress has been made in developing extractants for gold extraction from alkaline cyanide solution using modified amines. The significance of the modifier effect is of even greater consequence when the extraction of other cyanoanions commonly found in cyanide leach solutions is considered.

Selectivity Considerations

Selectivity is important in developing any extractant. These modified amines are particularly selective for gold. There are a host of complex cyanide anions that could be found in cyanide leach solutions. The following have been studied: $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Zn(CN)_4^{2-}$, $Ag(CN)_2^{-}$, and $Cu(CN)_4^{3-}$. Percent extraction versus pH curves were determined for all these metal anions at metal concentrations of 5×10^{-3} M — equimolar with 1000 ppm gold. It is recognized, in some cases, that a portion of the metal will be present as lower-order cyanide complexes. For example, in the case of copper, $Cu(CN)_3^{2-}$ and $Cu(CN)_2^{-}$ will be present, but this should not affect the interpretation of the results.

Figure 3 shows percent extraction versus pH curves for the extraction of $Cu(CN)_4^{3-}$ and $Au(CN)_2^{-}$ by the unmodified and the modified secondary amine, Adogen 283. For the unmodified amine, the percent extraction/pH curves (represented by the solid lines) for copper and gold are almost coincident. In fact, the difference in their pH_{50} values is only 0.20 pH units, indicating that selective extraction of gold, even in acid solution, would be difficult. However, on addition of 50% TBP as an amine modifier, the gold curve moves significantly to the right with a ΔpH_{50} of 2.7. Furthermore, and most importantly, the curve for copper only shifts slightly to the right with a ΔpH_{50} of 0.45. Thus, in the presence of 50% TBP, significant discrimination is achieved, and selective separation is possible in alkaline solution. The basicity of the modified amine toward copper (I) is only increased slightly, while the basicity of the modified amine toward gold has increased by three orders of magnitude. This selectivity for gold seems to be true with respect to most cyanoanions for both primary and secondary amines (Tables 7 and 8).

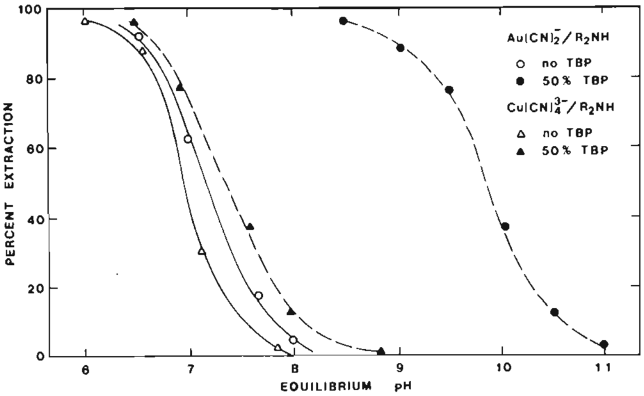

Fig. 3—Effect of TBP on percent extraction of $Au(CN)_2^-$ and $Cu(CN)_4^{3-}$ by a secondary amine, Adogen 283 (0.05 M)

In addition to the results presented in Tables 7 and 8, Fig. 4 shows the complete percent extraction versus pH curves for the extraction of selected cyanoanions by a TBP-modified secondary amine, Adogen 283.

Table 7—pH_{50} Values for the Extraction of Cyanoanions by Primene JM-T, a Primary Amine

Anion	pH_{50} Unmodified Amine 0.05 M in Xylene	pH_{50} Modified Amine 0.05 M in Xylene/50% TBP	ΔpH_{50}
$Au(CN)_2^-$	6.05	9.85	3.80
$Ag(CN)_2^-$	5.20	8.50	3.30
$Zn(CN)_4^{2-}$	7.10	8.14	1.04
$Cu(CN)_4^{3-}$	6.00	7.40	1.40
$Fe(CN)_6^{3-}$	5.50	6.75	1.25
$Fe(CN)_6^{4-}$	5.55	6.30	0.75

Table 8—pH_{50} Values for the Extraction of Cyanoanions by Adogen 283, a Secondary Amine

Anion	pH_{50} Unmodified Amine 0.05 M in Xylene	pH_{50} Modified Amine 0.05 M in Xylene/50% TBP	ΔpH_{50}
$Au(CN)_2^-$	7.35	9.85	2.50
$Ag(CN)_2^-$	6.30	8.50	2.20
$Zn(CN)_4^{2-}$	7.10	8.50	1.40
$Cu(CN)_4^{3-}$	6.98	7.40	0.42
$Fe(CN)_6^{3-}$	5.70	6.73	1.03
$Fe(CN)_6^{4-}$	5.15	6.40	1.25

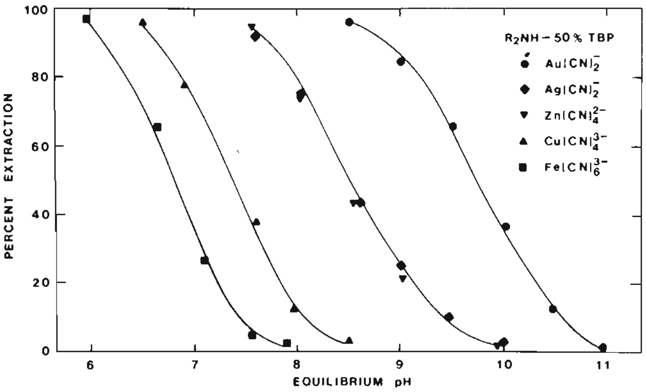

Fig. 4—Percent extraction versus pH for the extraction of various cyanoanions by Adogen 283 (0.05 M in xylene/50% TBP)

The most important result is that for both modified amines the highest pH_{50} value is obtained for the $Au(CN)_2^-$ anion. All other cyanoanions have pH_{50} values at least one pH unit lower. The increase in amine basicity on addition of a TBP modifier is the greatest for gold. This will allow the selective extraction of gold from cyanide leach liquors.

From the results in Tables 7 and 8 and in Fig. 4, the order of increasing pH_{50} in the presence of modifier is $Fe(CN)_6^{4-} < Fe(CN)_6^{3-} < Cu(CN)_4^{3-} < Zn(CN)_4^{2-} < Ag(CN)_2^- < Au(CN)_2^-$.

The selectivity sequence can be explained by considering these interrelated factors:

- charge/size ratio,
- compatibility of the hydrated anion with the organic phase, and
- extent of solvation of the amine/anion adduct in the organic phase.

The charge/size effect was demonstrated in the order of selectivity for the cyanoanions. The multi-charged anions were extracted at lower pH values than the singly charged anions $Ag(CN)_2^-$ and $Au(CN)_2^-$. For amines of like charge and geometry, there is an increase in extractability with overall molecular volume. For example, $Au(CN)_2^-$ has a greater pH_{50} than $Ag(CN)_2^-$. Irving and Damodaran (1971) found that for a given anion charge, increasing the size of an anion/quaternary ammonium cation combination will favor partition into an organic phase. On this basis, $Au(CN)_2^-$ should be extracted over $Ag(CN)_2^-$. Similar to our results, Irving and Damodaran found selective extraction of $Au(CN)_2^-$ over $Ag(CN)_2^-$ by quaternary amines. However, such a significant discrimination in either case is not expected solely on the basis of charge/size considerations. The extent of hydration of the anion is also important.

Irving and Damodaran proposed that the selective extraction of $Au(CN)_2^-$ over $Ag(CN)_2^-$ by quaternary amines is aided by the fact that Au (I) tends to form complexes of lower coordination number than Ag (I). Therefore Au (I) will not interact strongly with water and the $Au(CN)_2^-$ will be hydrated to a lesser extent that $Ag(CN)_2^-$. This lower hydration will aid the partition of $Au(CN)_2^-$ into an organic phase. These same considerations appear to hold for the modified amines explaining why $Au(CN)_2^-$ is extracted at higher pH values than $Ag(CN)_2^-$.

On the other hand, the proposed mechanism for the increased amine basicity is based on the proposition that the addition of a modifier increases the extent of solvation of the amine adduct. The modifiers, TBP and derivatives, are all Lewis bases that seem to specifically solvate the free amine and/or the amine/anion adduct, particularly the amine/$Au(CN)_2^-$ adduct. The complete explanation for the selectivity observed will involve considering charge/size ratio, anion hydration, and solvation of the amine adduct.

Summary and Conclusions

Adding organophosphorus oxide modifiers, such as TBP, to alkyl amines can increase the basicity of the amine by several orders of magnitude and allows the extraction of $Au(CN)_2^-$ from alkaline cyanide solution. Stripping is easily performed with caustic solution of pH 12 or 13. The most attractive feature of this extractant system is its excellent selectivity for the aurocyanide anion. The extraction of other anions such as $Fe(CN)_6^{3-}$, $Cu(CN)_4^{3-}$, etc., occurs at lower pH values.

The modified amine extractant system described has great flexibility with a large number of variables, such as amine type and concentration, modifier type and concentration, extraction pH, and diluent. At present, it would be difficult to suggest the best extraction system for a particular application. In this respect, engineering considerations such as phase disengagement and organic entrainment are important. Research is directed towards investigating the engineering aspects of a gold solvent extraction process. An economic evaluation of a gold solvent extraction process for heap leach liquors was presented at the Heap Leach Symposium during the 1983 SME Fall Meeting in a paper entitled "Process Alternatives in the Recovery of Gold From Heap Leach Liquors" (Mooiman et al., 1983). The economic analysis from this study suggests that solvent extraction in mixers/settlers may be an interesting process alternative for recovery from alkaline cyanide solutions at gold tenors exceeding 5 ppm. Using other solvent extraction equipment, such as centrifugal contactors, or the use of solvent-impregnated substrates may make solvent extraction even more interesting from an economic perspective. ■

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