

SOLVENT EXTRACTION REAGENTS FOR GOLD RECOVERY

FROM ALKALINE CYANIDE SOLUTIONS

J. D. Miller and C. A. Garcia
Department of Metallurgical Engineering
University of Utah
Salt Lake City UT 84112, USA

Abstract

Three different solvent extraction systems for the recovery of gold from alkaline cyanide solutions are reviewed. These include the modified amine extractants in which the basicity of simple alkyl amines, with respect to the aurocyanide anion, is controlled by the addition of alkyl phosphorous esters. The selectivity of such modified amines for gold extraction from alkaline cyanide solutions is excellent

Next, solvating extractants, undiluted alkyl phosphorous esters and phosphine oxides, are discussed. The significance of ion pair extraction by a solvation mechanism is evident from data reported in the literature for these extractants. The industrial application of these solvating extractants is demonstrated for the treatment of waste electroplating solutions and for the selective extraction of gold from mercury in a carbon eluate strip solution.

Finally, research on the use of substituted guanidines for gold extraction from alkaline cyanide solutions is reviewed. These guanidines have a greater basicity than amines, and extraction can be accomplished at higher pH values without the use of modifiers. In addition to the di- through pentasubstituted guanidines discussed by Henkel researchers, recent research at the University of Utah shows that monosubstituted guanidines are quite effective extractants as well. The substituted guanidines is the most recent gold solvent extraction system studied, and the experimental results indicate that excellent extractions can be achieved at pH 11 and stripping above pH 13 provided that an appropriate alcohol is used in the diluent (carrier). The suitability of the substituted guanidine solvent extraction system for treating dilute leach solutions has been demonstrated in pilot-plant testing.

Introduction

The recovery of gold from alkaline cyanide solutions is generally accomplished by zinc dust cementation and/or carbon adsorption. Both methods are well established and proven industrial processes. Nevertheless, each process has its own disadvantages and other alternatives for solution concentration and purification have been considered (1).

During the past decade, solvent extraction for gold recovery from alkaline cyanide solution has been examined in some detail and reviewed in 1987 (2). These past research and development efforts and more recent efforts (3,4) have resulted in the identification of three different extractant types for the selective extraction of gold from alkaline cyanide solution; modified amines, alkyl phosphorous esters, and guanidines. The characteristic features of these extractants are reviewed together with experimental results for each of these systems.

Modified Amines

Ideally, the selective solvent extraction of the aurocyanide anion from alkaline cyanide solution should be accomplished at pH 11 with stripping achieved at a higher pH (pH \cong 13). This condition requires that the extractant exhibit the appropriate basicity and have the desired specificity for the aurocyanide anion. Simple amines in themselves are ineffective due to their weak basicity and their lack of specificity. These characteristic features of the simple amines have been established for primary, secondary, and tertiary amines both with respect to the structure/length of the hydrocarbon chain and with respect to the solvent type used as a diluent. The extraction reaction can be represented as indicated by the following reaction for a primary amine:



where overscoring denotes a species in the organic phase. Of course the extraction reaction is favored at low pH, and such an extraction can be characterized by the pH at which 50% extraction is possible, i.e., pH₅₀. In this regard, it is clear from Tables 1 and 2 that the simple amines are rather weak bases with respect to gold extraction with pH₅₀ values from about pH 5 to pH 7 and that the pH₅₀ value for gold extraction from cyanide solution is largely insensitive to amine type (primary, secondary, and tertiary), hydrocarbon chain length, structure of the hydrocarbon chain, etc. More detailed discussion of amine basicity is given elsewhere (5,6).

The important discovery in the early '80s was that the addition of a Lewis base modifier such as an alkyl phosphorous ester or other compounds, had a significant effect on the amine basicity with respect to the aurocyanide anion. For example, the effect of tributyl phosphate, TBP, on gold extraction by a secondary amine is presented in Figure 1. The same effect was found for all amines types, and it was established that the pH₅₀ is increased substantially in the presence of such modifiers. As might be expected, the increase in amine basicity is determined by the amount of modifier added, as shown in Figure 2, for various TBP additions to the secondary amine, Adogen 283.

Modifier Type

By the addition of modifiers, the increase in amine basicity could be related to solvation of the amine or the amine/anion adduct by the modifier. As generally known, modifiers such

Table 1. The Effect of Amine Type on the Extraction of Gold (1000 ppm in 0.5 Na₂SO₄) from Aurocyanide Solution, all Amine Extractants, 0.05 M in Xylene (5)

Amine	Supplier	Structure	pH ₅₀
<u>Primary</u>		<u>RNH₂</u>	
Primene 81-R	Rohm & Haas	R = iso C ₁₂ -C ₁₄	6.55
Primene JM-T	Rohm & Haas	R = iso C ₁₈ -C ₂₂	6.05
<u>Secondary</u>		<u>R₂NH</u>	
Adogen 283	Sherex	R = iso C ₁₃	7.15
LA-2	Rohm & Haas	R = iso C ₁₀ -C ₁₂	7.15
Alamine 204	Henkel	R = nC ₁₂	7.15
Alamine 226	Henkel	R = iso C ₁₆ -C ₁₈	7.06
<u>Tertiary</u>		<u>R₃N</u>	
Adogen 364	Sherex	R = nC ₈ -C ₁₀	5.55
Adogen 383	Sherex	R = nC ₁₃	5.35
Alamine 308	Henkel	R = iso C ₈	5.45
Alamine 310	Henkel	R = iso C ₁₀	5.35
Alamine 336	Henkel	R = nC ₈ -C ₁₀	5.66

Table 2. The Effect of Diluent Type on the Extraction of Gold (1000 ppm in 0.5 M Na₂SO₄) from Aurocyanide Solution, all Extractants 0.05 M (5)

Amine	Diluent	pH ₅₀
<u>Primary</u>		
Primene 81-R	Xylene	6.55
Primene 81-R	Hexane	6.55
Primene JM-T	Xylene	6.05
Primene JM-T	Hexane	6.05
<u>Secondary</u>		
Adogen 283	Xylene	7.15
Adogen 283	Hexane	6.55
Adogen 283	Chevron IX*	6.50
Adogen 283	Chloroform	6.40
<u>Tertiary</u>		
Alamine 336	Xylene	5.65
Alamine 336	Hexane	5.01

*Chevron Ion Exchange Solvent: 54% paraffins, 35% naphthenes, 11% xylenes and C₈ as aromatics.

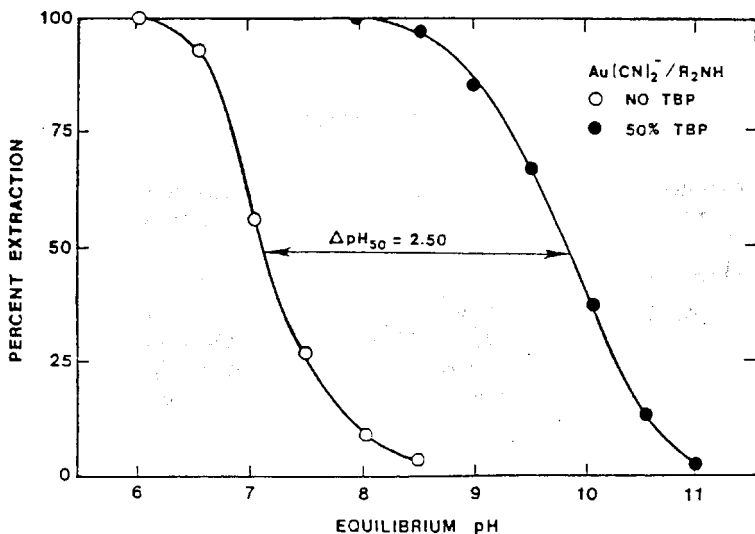


Figure 1. The effect of TBP on the extraction of gold (1000 ppm) from aurocyanide solution by a secondary amine, Adogen 283, 0.05 M in xylene (2).

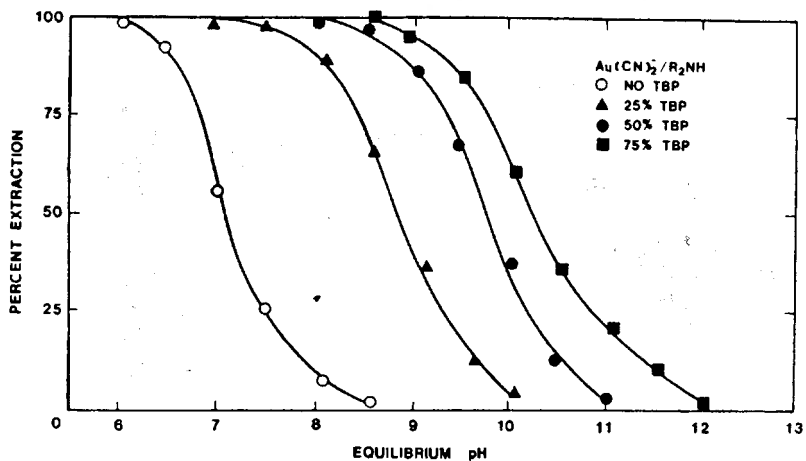
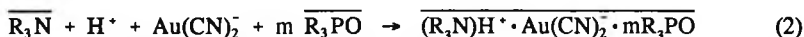


Figure 2. The effect of TBP concentration on the extraction of gold (1000 ppm) from aurocyanide solution by a secondary amine, Adogen 283, 0.05 M in xylene (7).

as alkyl phosphorous esters are solvation extractants.

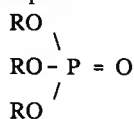
The overall extraction for the aurocyanide anion would be



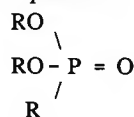
where overscoring denotes a species in the organic phase, and R = H, an alkyl, or alkoxy group.

As mentioned previously, it was found that alkyl phosphorous esters and phosphine oxides are particularly effective in increasing the basicity of simple amines for gold extraction. The structures of these modifiers are as follows:

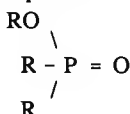
Phosphate



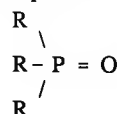
Phosphonate



Phosphinate



Phosphine Oxide



The modifiers increase the pH_{50} for gold extraction, i.e., the amine basicity, and the basicity of the extractant depends on the polarity of the modifier. The polarity of the phosphorous esters increases in the order trialkyl phosphate < dialkyl alkyl phosphonate < alkyl dialkyl phosphinate < trialkyl phosphine oxide. Thus at a fixed addition of modifier there is a systematic increase in amine basicity as the polarity of the modifier increases. This effect is evident for the butyl derivatives as shown in Figure 3. The pH_{50} values increase in the order TBP < DBBP < BDBP < TBPO at 10% modifier in xylene. This sequence follows the order of increasing Lewis basicity, i.e., electron donor power of the modifier, and indicates that solvation effects should be important in explaining the behavior of the modified-amine extraction system. So the increase in amine basicity for gold extraction could be related to solvation of the amine. On the other hand, the improved extraction may be due to an increase in water content of the organic phase. Indirect evidence for the latter effect is supplied by the fact that the order TBP < DBBP < BDBP < TBPO is also the order of increasing water solubility in the pure modifier. Solvent losses for the modified amine extraction system have been examined and were discussed at ISEC '86 (8).

Selectivity

Selectivity is another important factor in evaluating any solvent extraction (SX) system. In the cyanide leach solution, there are a host of complex cyanide anions that could be found. The modified amines are particularly selective for gold (9).

Figure 4 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 (6). 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, upon 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 increases only slightly, while the basicity of the modified amine toward gold has increased by almost three orders of magnitude.

Again, the results presented in Table 3 demonstrate that, for the solvation of various cyanoanions by an unmodified amine, the pH_{50} values are quite similar, and nonselective extraction is possible only from acid solution. With an addition of 50% TBP as a modifier, the pH_{50} for gold extraction increases significantly, whereas other cyanoanions show only a modest shift in pH_{50} , with the exception of silver and perhaps zinc. The results show that the selective extraction of gold from alkaline cyanide solution is possible.

The order of increasing pH_{50} for the modified amine is $\text{Au}(\text{CN})_2^- > \text{Ag}(\text{CN})_2^- > \text{Zn}(\text{CN})_4^{2-} > \text{Cu}(\text{CN})_4^{3-} > \text{Fe}(\text{CN})_6^{3-}$. The selectivity sequence can be explained by consideration of the charge/size effect, the compatibility of the hydrated anion with the organic phase, and the extent of solvation of the amine/anion adduct in the organic phase (6). The reason for the rather unique behavior of $\text{Au}(\text{CN})_2^-$ in extraction by modified amines is believed to be due, in part, to its lower level of hydration when compared with other cyanoanions.

As a summary of the modified-amine SX system for gold recovery from alkaline cyanide solution, the following conclusions have been reached:

- * The apparent basicity of simple weak-base amines with respect to $\text{Au}(\text{CN})_2^-$ can be increased as much as five orders of magnitude by the addition of alkyl phosphorous esters.
- * The increase in basicity of these modified amines with respect to $\text{Au}(\text{CN})_2^-$ appears to be due to improved solvation of the amine salt allowing for protonation to occur at high pH values.
- * Finally, the weak hydration of $\text{Au}(\text{CN})_2^-$ in the aqueous phase facilitates the partition of this large, singly charged anion into the organic phase as an amine/anion adduct.

Table 3. The Effect of Modifier (TBP) on Amine Basicity (pH_{50}) for Selected Cyanoanions ($5 \times 10^{-3} \text{ M}$) at $5 \times 10^{-2} \text{ M}$ Adogen 283 in Xylene (6)

Element	pH_{50}		ΔpH_{50}
	No TBP	50% TBP	
Cu	6.90	7.20	0.3
Fe	5.66	6.80	1.14
Zn	7.10	8.45	1.35
Ag	6.30	8.50	2.20
Au	7.05	9.78	2.73

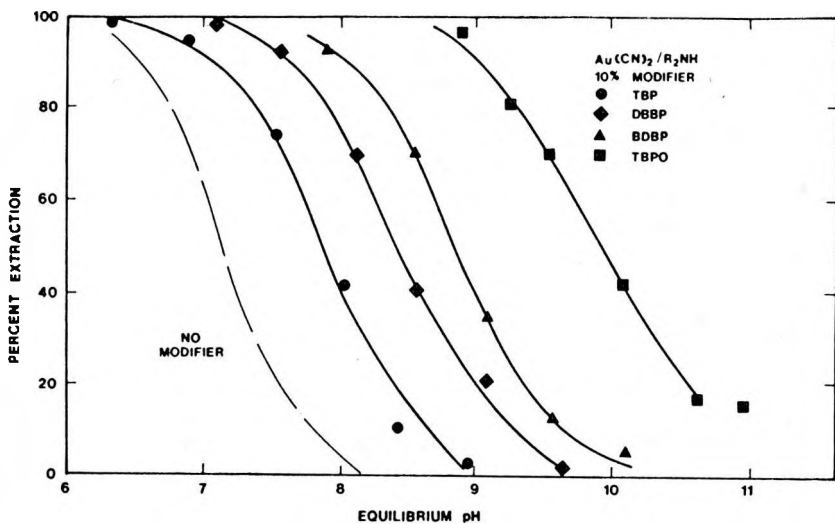


Figure 3. The effect of modifier type on the extraction of gold (1000 ppm) from aurocyanide solution by a secondary amine, Adogen 283, 0.05 M in xylene (10).

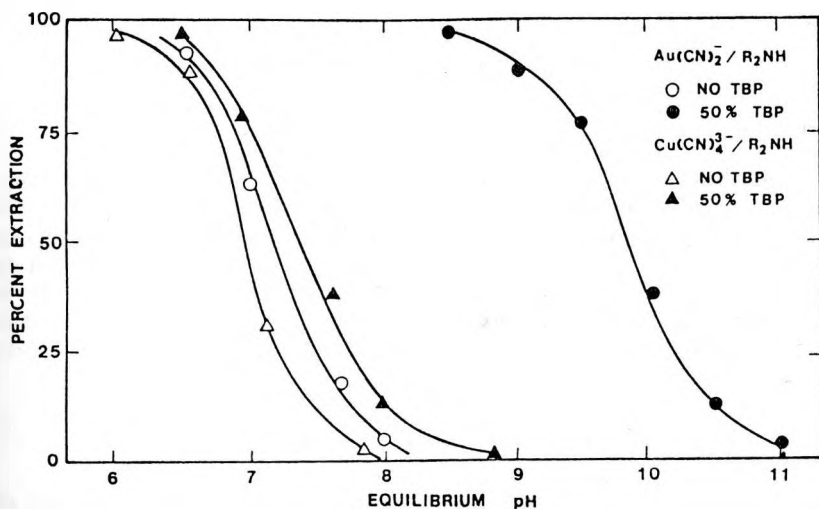


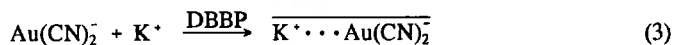
Figure 4. The effect of TBP on the extraction of gold ($5 \times 10^{-3} \text{ M} = 1000 \text{ ppm}$) and copper ($5 \times 10^{-3} \text{ M}$) from cyanide solution by a secondary amine, Adogen 283, 0.05 M in xylene (2).

Alkyl Phosphorous Esters

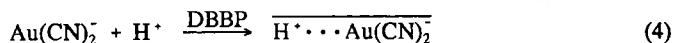
Importantly, the alkyl phosphorous esters and phosphine oxides which are used as modifiers in the modified amine extraction system are, in their undiluted state, effective for gold extraction from alkaline cyanide solution. The structure of these extractants has been discussed previously in the section entitled *Modified Amines*. These Lewis base compounds have been shown to selectively extract the aurocyanide anion as an ion pair from other metallic cyanoanions (11-14). As would be expected for such an ion pair extraction mechanism, the extraction is dependent on the solvating power of the extractant and ionic strength.

The Lewis basicity of these extractants increases in the order: phosphate < phosphonate < phosphinate < phosphine oxide; and gold extraction follows the expected sequence.

Substantiation of the ion pair solvation extraction mechanism is revealed by the dibutyl butyl phosphonate, DBBP, extraction data presented in Figure 5. In this figure, the gold and potassium concentrations in the organic phase are plotted as function of pH without ionic strength control. It is clear that at low ionic strength gold extraction is a minimum at pH 7. As the ionic strength increases by going to low or high pH values, gold extraction increases substantially. Of even greater significance is the fact that on the alkaline side potassium is extracted into DBBP at the same molar concentration as gold, thus confirming the ion pair solvation extraction reaction,

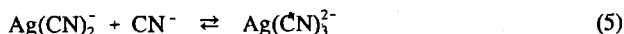


Interestingly, on the acid side, potassium is rejected from the organic phase, and it appears that the protonated aurocyanide anion is extracted by DBBP,



Selectivity

Excellent gold selectivity is achieved with alkyl phosphorous esters (9,10). The alkyl phosphorous esters and phosphine oxides seem to have a rather unique specificity for the aurocyanide ion pair as shown in Figure 6. The highly charged cyanoanions are not extracted as is evident for Cu, Zn, Ni, and Fe. Silver can be extracted as the univalent dicyano complex, but, unlike gold, the extent of silver extraction decreases with an increase in cyanide concentration. This behavior is due to the fact that silver can accommodate another cyanide ligand and form the divalent tricyanoanion which apparently is not solvated so extensively by DBBP:



In a more recent study, the selective extraction of gold from mercury in concentrated alkaline cyanide solutions has been demonstrated with DBBP (13). Not only do the results support ion pair solvation for the selective extraction of the aurocyanide ion pair, but, in addition, it was shown that mercury extraction occurred at low cyanide concentrations where the neutral aqueous species, $\text{Hg(CN)}_{2(\text{aq})}^0$, is stabilized.

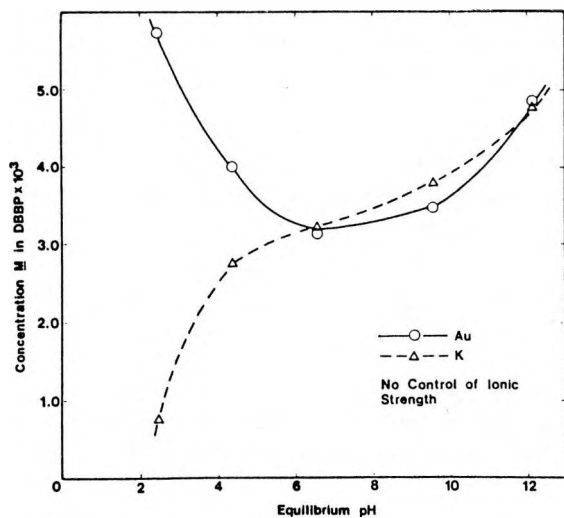


Figure 5. Extraction of gold and potassium by pure DBBP from $\text{KAu}(\text{CN})_2$ solution without ionic strength control. Initial gold concentration, 5×10^{-3} M (12).

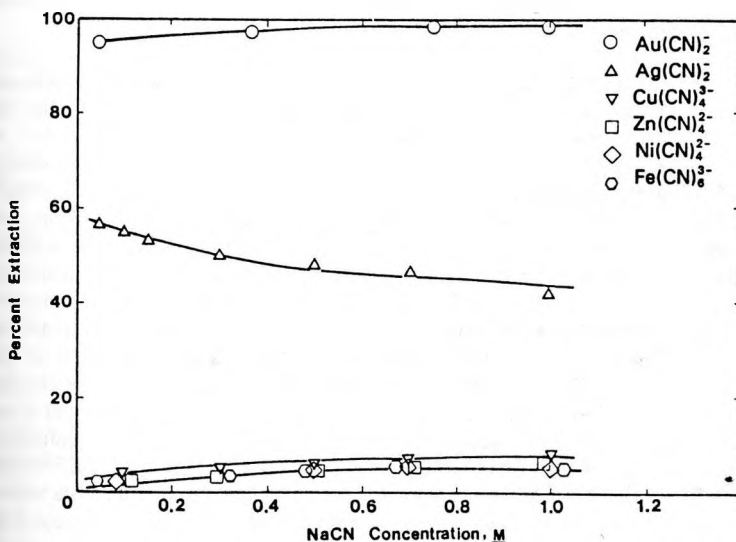


Figure 6. Percent extraction of various cyanoanions (5×10^{-3} M) by DBBP as a function of NaCN concentration at 0.1 M NaOH (12).

Table 4. The Effect of the Aqueous/Organic Phase Ratio in the Extraction of Mercury and Gold from the Carbon Eluate of a Stripping/Recovery Plant with DBBP at 60°C. Initial Conditions: 1.13 ppm Au and 20 ppm Hg (13)

A/O	% Ext.		ppm in Organic	
	Au	Hg	Au	Hg
5:1	94.7	< 0.1	5.35	ND
3:1	97.4	< 0.1	3.30	ND
2:1	98.2	< 0.1	2.22	ND
1:1	99.0	0.4	1.11	0.8

Based on these findings, carbon eluate from a stripping/recovery plant was studied, and excellent single-stage separation efficiencies were achieved, particularly at 60°C as indicated in Table 4. The separation efficiency is evident by a gold/mercury selectivity factor of greater than 50,000 from this eluate, which was 6% NaOH and contained 1.13 ppm Au and 20.0 ppm Hg.

Electrolytic Stripping

Stripping of the loaded, undiluted extractants is not easy, but is possible. One approach which has been demonstrated in the laboratory is the direct electrolysis of the organic phase (12). A schematic drawing of the electrolytic cell is shown in Figure 7 and production of metallic gold at the cathode was achieved without degradation of the extractant. Direct electrodeposition from the organic phase is possible, but the rate is facilitated by electrolysis of an organic-in-aqueous emulsion.

A previous study on the recovery of gold from waste cyanide electroplating solutions by solvation extraction with organic phosphorous esters and direct electrolysis of the loaded organic phase indicated that the proposed process strategy can be used for actual waste solutions. Three industrial waste electroplating solutions were examined. The extraction results in Table 5 demonstrate that gold can be extracted from these solutions without any pretreatment by pure DBBP. The selectivity characteristics for gold extraction from Sample No. 3 are listed in Table 6. These results confirm previous findings (12) which suggest that significant discrimination between the $\text{Au}(\text{CN})_2^-$ and other cyanoanions can be achieved. In view of the more recent results regarding the excellent gold selectivity with respect to mercury at higher temperatures (60°C), it is expected that even better selectivity can be achieved with these waste electroplating solutions if the extraction is done at higher temperatures. Electrodeposition of gold from the loaded DBBP solution (Sample No. 3) was studied in the diaphragm cell. Adherent sheet gold of high quality was produced at a current density of 10^{-3} amp/cm² and a cell voltage of about 2.4 volts. Under these conditions, the cathodic current efficiency was 56.3%. Further, it was found that the DBBP extractant exhibited excellent stability with the same level of gold extraction after five cycles of extraction and electrolysis. These results demonstrate the applicability of the process strategy to actual plant solutions.

In summary, alkyl phosphorous esters extract gold from alkaline cyanide solution through an ion pair solvation extraction mechanism. This feature allows for excellent gold selectivity with respect to other cyanoanions. Stripping of the loaded organic may be achieved by direct electrodeposition from the organic phase.

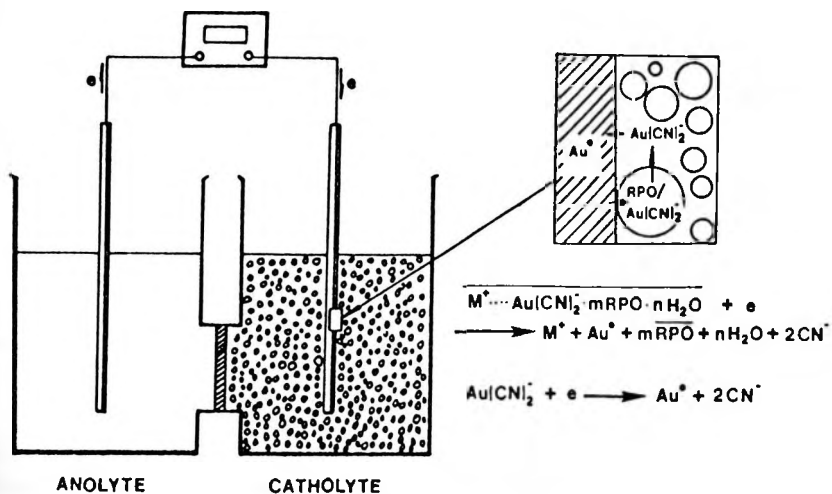


Figure 7. Schematic drawing for electrodeposition of gold from loaded alkyl phosphorous ester dispersed in an aqueous electrolyte (12).

Table 5. Single-Stage Extraction of Electroplating Waste Solutions at a Phase Ratio of 1:1 (12)

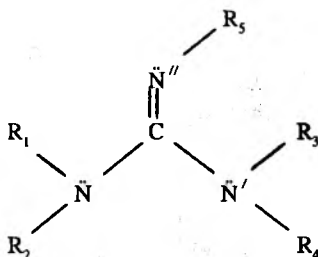
Solvation Extractant	Sample	Initial Solution Composition			Raffinate (gpl)	% Extraction
		Au (gpl)	Free CN (gpl)	pH		
DBBP	No. 1	2.68	9.05	13.3	0.126	95.3
	No. 2	5.18	3.64	13.3	0.144	97.2
	No. 3	0.93	1.04	12.6	0.021	97.7

Table 6. Selectivity Characteristics for the DBBP Extraction of Gold from Waste Electroplating Solutions (Sample No. 3) at a Phase Ratio of 1:1 (12)

Sample No. 3	Elements, ppm								
	Au	Ag	Cu	Ni	Pb	Zn	Fe	Co	Cr
Feed	932	134	979	143	119	17.6	4.7	<1.0	<1.0
Raffinate	21	37	882	132	114	14.1	3.7	<1.0	<1.0
Distribution Coefficient	43.38	2.62	0.11	0.08	0.04	0.25	0.27	—	—

Guanidines

Stimulated by gold solvent extraction research in the 1980s, Henkel researchers (3,15) began to develop substituted guanidines for gold extraction from alkaline cyanide solutions. Recently other researchers have also contributed to the study of these guanidine extractants (4). The general guanidine structure is,

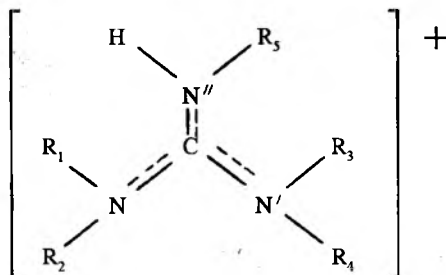


and the guanidines are classified depending on the number and location of substituents, for example,

- Monosubstituted guanidines when $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{R}_5 = \text{H}$
- Asymmetric disubstituted guanidines when $\text{R}_3 = \text{R}_4 = \text{R}_5 = \text{H}$
- Symmetric disubstituted guanidines when $\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$
- Symmetric trisubstituted guanidines when $\text{R}_2 = \text{R}_4 = \text{H}$

and other substitutions up to and including pentasubstituted guanidines.

Guanidines are much stronger bases than amines. This increased basicity is revealed by the fact that the conjugate acids of guanidines, the guanidinium ions, have pK_a values greater than 12.5 when the R groups are not electron withdrawing. Of course such a basicity should allow for the effective extraction at pH 11 and for stripping above pH 13 provided other important aspects of the solvent extraction process are satisfied, including selectivity, solubility, phase disengagement, steric factors, etc. If these conditions are satisfied, then extraction should be possible when the guanidine is protonated to form the guanidinium cation,



Symmetric Disubstituted Guanidines

It appears that Henkel researchers have examined many different guanidines (15). However, the experimental work reported in their literature is mostly limited to bis alkyl guanidines

(3,15), i.e., symmetric disubstituted guanidines where the alkyl groups are identical.

For example, extraction results are reported (15) for two different bis alkyl guanidines, N,N'-bis(tridecyl) guanidine (bis TDG) and N,N'-bis (2-ethylhexyl) guanidine (bis EHG). These compounds were evaluated as extractants for gold with organic solutions of the extractants in 10% tridecanol and 90% kerosene. The organic phases were contacted for 5 minutes with an equal volume of synthetic cyanide solution containing approximately 10 ppm gold and 500 ppm sodium cyanide. The results for bis TDG and bis EHG are presented in Table 7.

As expected, gold extraction with these guanidines is pH sensitive, and this feature allows for stripping from the loaded organic solutions at higher pH. In addition, other results show that these disubstituted guanidines selectively extract gold from solutions containing different cyanoanions. The selectivity of bis TDG for actual leach solutions follows the order Au-Zn > Ag > Cu-Fe.

In view of these interesting results, bis EHG and bis TDG were tested by Henkel with actual leach solutions in a continuous solvent extraction circuit (3). For bis EHG it was found that the gold recovery fell with time from 86% after 18 hours of operation to 50% after 46 hours of operation. The authors believe that the loss in the efficiency was due to solubility losses of the extractant in the raffinate. For bis TDG, gold extractions higher than 90% were

Table 7. Gold Extraction from Alkaline Cyanide Solution (10 ppm Gold, 500 ppm Sodium Cyanide) with Symmetric Disubstituted Guanidines, bis Tridecyl Guanidine (bis TDG) and bis 2-Ethyl Hexyl Guanidine (bis EHG), in 10% Tridecanol and 90% Kerosene as a Function of pH (15).

Extractant Concentration, 0.05 M	pH	% Extraction
bis TDG	9.85	100
	10.90	100
	12.20	90
bis EHG	9.95	100
	10.60	100
	12.20	95
Extractant Concentration, 0.01 M		
bis TDG	9.10	100
	10.05	97
	11.10	82
	12.30	19
bis EHG	8.75	100
	10.40	92
	11.80	34
	12.10	30

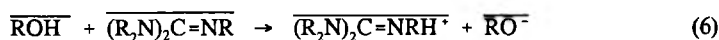
obtained when tridecanol was added to an aromatic carrier. In the absence of tridecanol gold extraction was reduced considerably. Finally, an unidentified experimental guanidine, MX 18999, has been reported to achieve gold recoveries greater than 99% when the circuit conditions were specifically chosen to obtain very high gold recovery. However, gold recovery was only 87% when the circuit conditions were the same as those used for bis DDG (3).

Monosubstituted Guanidines

Unlike the research reported by Henkel investigators, research at the University of Utah has focused on the monosubstituted guanidines for gold extraction from alkaline cyanide solution and the effect of the diluent on the extraction reaction (4). The experimental procedure for the synthesis of these substituted guanidines is described elsewhere (4).

First it should be noted that the diluent composition has a significant effect on the guanidines basicity, an effect that was recognized early-on in the research. For example, gold extraction with bis dodecyl guanidine (bis DDG) is shown as a function of pH in Figure 8 for both an aromatic diluent (toluene) and an alcoholic diluent (2-octanol) (4). It is evident that the basicity of the guanidine is increased substantially for the alcohol carrier from $\text{pH}_{50} = 10.2$ to $\text{pH}_{50} = 12.7$, over 2 orders of magnitude. The same was found to be true when an aliphatic diluent (4) was used instead of an aromatic diluent. Other substituted guanidines behave in a similar fashion, the guanidine basicity being increased by the use of alcohol as a diluent. It is clear that the alcohol plays an important role in establishing guanidine basicity and the pH_{50} for gold extraction.

Monosubstituted guanidines are no exception (4). Even with small additions of alcohol, the basicity can be increased significantly. For example, the extraction of gold from alkaline cyanide solution by monosubstituted dodecyl guanidine (mono DDG) is shown as a function of pH in Figure 9 for different levels of 2-octanol in toluene. At a mono DDG concentration of $1 \times 10^{-3} \text{ M}$, gold extraction from toluene in the absence of 2-octanol is limited to about 40% at pH 11. With the addition of 2-octanol, the extraction increases to about 65% and increases further to 80% when the diluent is 2-octanol only. Again the effect of the alcohol is evident. The presence of the hydroxyl functionality in the organic phase stabilizes the guanidinium ion



and facilitates extraction of the aurocyanide anion. Evidence of such a mechanism has been observed by spectroscopic analysis of the organic phase (4).

In addition to diluent composition, the pH_{50} for extraction should vary with guanidine concentration in the organic phase in a systematic order and preliminary results for mono DDG have been reported (4). Mono DDG appears to be a suitable extractant, and experimental results show that the basicity of mono DDG compares favorably to the bis DDG (4). Of course because of the lower molecular weight of mono DDG it would be expected to be more cost effective than the disubstituted bis DDG.

It is evident that mono DDG in 2-octanol acts as a strong base with respect to gold extraction from alkaline cyanide solution and exhibits the desired extraction/stripping characteristics. These extraction characteristics are essentially equivalent on a molar basis to the bis DDG

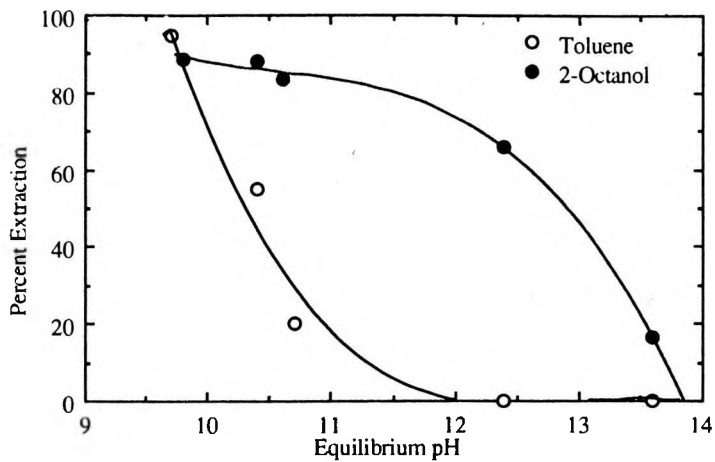


Figure 8. Effect of solvent type on gold extraction by bis DDG (1×10^{-3} M).

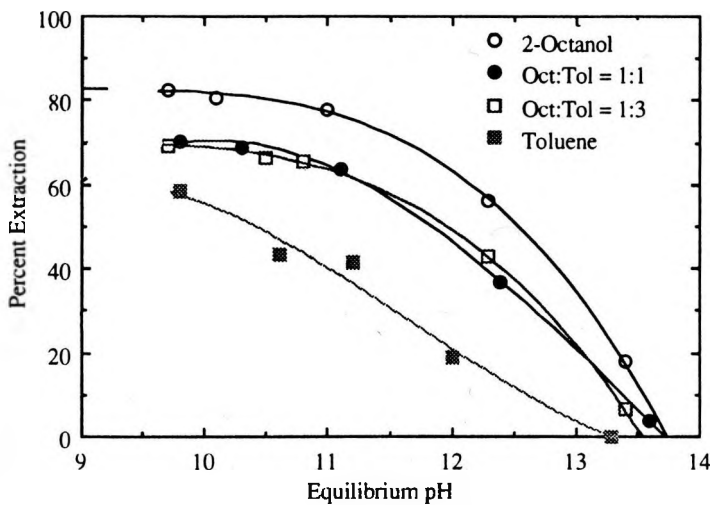


Figure 9. Effect of solvent composition on gold extraction by mono DDG (1×10^{-3} M).

in 2-octanol and indicate that monosubstituted guanidines should also be suitable extractants for gold recovery from alkaline cyanide solutions. In fact, mono DDG could be considered superior to bis DDG because its molecular weight is approximately *one-half* the molecular weight of bis DDG. This means, of course, that a significantly smaller amount of mono DDG would be required for equivalent performance.

A set of five experiments was carried out in order to determine if there was any change in the extent of gold extraction when the same organic solution (mono DDG 1×10^{-3} M in 2-octanol), after stripping with 10% NaOH, was contacted with fresh feed. It was found, after each cycle, that the extraction of gold remained constant. Furthermore, the UV spectra of the organic phase after each cycle showed the same absorbance, indicating that there was no loss of mono DDG to the aqueous phase.

In summary, it is evident that the guanidine functional group is not the only condition for effective gold extraction from alkaline cyanide solutions. It would seem that the presence of the hydroxy functional group in the solvent plays an important role in the increased basicity, either by stabilizing the guanidinium ion which reacts to form an ion pair with the aurocyanide anion or by displacing the base/conjugate acid equilibrium to favor the guanidinium ion concentration in the organic phase. The fact that the pH_{50} value is only sensitive to the alcohol content of the organic solvent for dilute ROH concentrations suggests an acid/base reaction between the guanidine and the alcohol in the organic phase which stabilizes the guanidinium ion (4).

Research done at the University of Utah has shown that it is possible to use monoalkyl guanidines as extractants for gold from alkaline cyanide solutions (4). The guanidine functionality is a necessary but not sufficient condition for gold solvent extraction at high pH values. The desired extraction characteristics are obtained when the diluent composition is adjusted (typically with alcohol) to stabilize the guanidinium ion or increase its concentration in the organic phase. Solubility losses of the monosubstituted dodecyl guanidine are minimal, and it should be a more cost-effective extractant than other more highly substituted guanidines.

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