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A Review of New Developments in Amine Solvent Extraction Systems for Hydrometallurgy

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Abstract

Amine extractants, regardless of structure, have been of limited utility for the extraction of complex metallic anions from alkaline solution due to an inability to increase the amine's basicity. This situation is contrasted to acid extractants in which case such control of extractant strength is possible. Recent studies with amine extractants have shown that the use of specific modifiers allows for the control of amine basicity over an appreciable pH range for certain anions. Particularly significant is the potential for the extraction of gold from alkaline cyanide solutions.

INTRODUCTION

Amines are one of the more commonly known class of extractants in solvent extraction technology, having been used industrially for the recovery of uranium since the 1950s. Extensive study of these extractants is reported in the literature (1-4) and it is known that the selectivity to be achieved with these extractants is modest at best. Quaternary ammonium compounds behave as strong bases with extraction of anions possible at essentially all pH values. In some cases stripping of such compounds may be difficult (5). On the other hand, the simple amines capable of protonation (weak base amines) only extract anions from acidic or neutral solutions, and thus their utility is limited (6). Tremendous progress has been made in the control of the strength of acid extractants such as hydroxyoximes, phosphoric acids, and carboxylic acids, but little attention has been given to the control of amine strength or its basicity.

Recent research has found that the basicity of these simple amines can be controlled by the addition of modifiers so that the selective extraction of cyanoanions can be accomplished in alkaline solution (7-9). It is expected that such behavior will be found for the extraction of other anions from alkaline solution. Stripping of such loaded organics is quite easy with more alkaline strip solutions.

Of particular significance is the extraction of gold from dilute, alkaline cyanide solutions and the possible use of solvent extraction for gold recovery in cyanidation processes. Engineering considerations of such a process strategy are discussed.

STATUS OF ANION EXTRACTION BY AMINES

The amines capable of protonation which have been tested on an industrial scale as metallic and nonmetallic anion extractants are primary, secondary, and tertiary amines, especially alkyl amines. Instances of the industrial use of secondary and tertiary amines are presented in Table 1.

It is important to note that industrial use of these amine extractants has been limited to acid solutions. This is because amines capable of protonation in organic diluents are weaker bases (10) than water-soluble amines and only act effectively as extractants in acidic and neutral solutions.

Amine Type

In the laboratory, primary, secondary, and tertiary alkyl amines have been used for the extraction of many other metallic anions. However, extraction of such metallic anionic complexes by amines, again, is generally limited to pH values less than 7. This can be seen from the compilation presented in Table 2 based upon the pH_{50} for extraction with a 0.05 *M* amine/xylene solution.

TABLE 1
Industrial Solvent Extraction Systems Which Use Simple Amine Extractants

Metal	Aqueous feed solution	Amine extractant
Molybdenum	Acid sulfate	Tertiary
Tungsten	Acid sulfate	Secondary
Uranium	Acid sulfate	Tertiary
Vanadium	Acid chloride	Tertiary

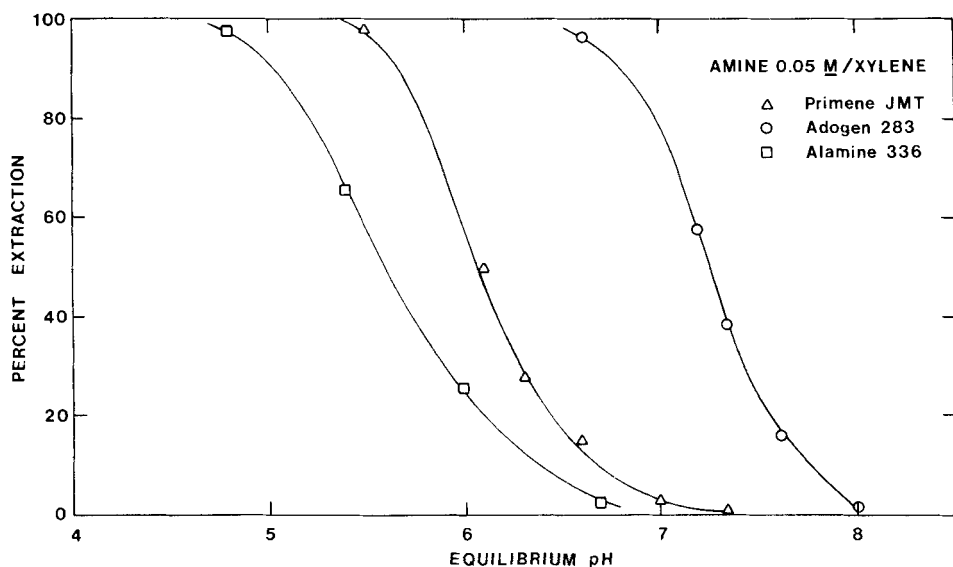


FIG. 1. Percent extraction of $\text{Au}(\text{CN})_2^-$ (1.0 g/L Au) versus pH for primary, secondary, and tertiary amines (0.05 M in xylene) (δ).

As is well known, the pH_{50} of a given extraction is that pH at which 50% of the desired metal has been extracted from the aqueous solution. The pH_{50} value can be considered to be a measure of the amine's strength, i.e., ability to extract, or an indication of its basicity. A higher value of pH_{50} is indicative of an increase in base strength or basicity. Further, note from Table 2 that there is very little discrimination with respect to anion type. Selective extractions by pH control are difficult.

Extensive study of gold extraction from alkaline cyanide solution has shown that the amine basicity is only slightly influenced by amine structure.

TABLE 2
Amine Basicity for Selected Anions as Revealed by pH_{50} Values for 0.05 M Amine in Xylene

Amine extractant	Amine basicity pH_{50} values				
	$\text{Au}(\text{CN})_2^-$	$\text{Fe}(\text{CN})_6^{3-}$	MoO_4^{2-}	CrO_4^{2-}	VO_4^{3-}
Primary (Primene JM-T)	6.55	5.50	5.85	5.90	6.96
Secondary (Adogen 283)	7.15	5.70	5.80	6.35	6.90
Tertiary (Alamine 336)	5.66	—	5.08	4.80	5.18

TABLE 3
 pH_{50} Values for Gold Extraction from Aurocyanide Solutions (1.0 g/L Au) by Various Amine Extractants (0.05 M in xylene)

Amine	Supplier	Structure	pH_{50}
Primary:		RNH_2 :	
Primene 81-R	Rohn & Haas	$\text{R} = \text{C}_{12-14}$	6.55
Primene JM-T	" "	$\text{R} = \text{C}_{18-22}$	6.05
Secondary:		R_2NH :	
Andogen 283	Sherex	$\text{R} = \text{C}_{13}$	7.15
LA-2	Rohm & Haas	$\text{R} = \text{C}_{10-12}$	7.15
Alamine 204	Henkel	$\text{R} = \text{C}_{12}$	7.15
Alamine 226	"	$\text{R} = \text{C}_{16-18}$	7.06
Tertiary:		R_3N :	
Adogen 364	Sherex	$\text{R} = \text{C}_{8-10}$	5.55
Adogen 363	"	$\text{R} = \text{C}_{13}$	5.35
Alamine 308	Henkel	$\text{R} = \text{iso-C}_8$	5.45
Alamine 310	"	$\text{R} = \text{iso-C}_{10}$	5.35
Alamine 336	"	$\text{R} = \text{C}_{8-10}$	5.66

Percent gold extraction from aurocyanide solution is shown in Fig. 1 as a function of pH for typical primary, secondary, and tertiary amines.

The order of increasing pH_{50} (tertiary, primary, secondary) follows the order of increasing basicity of alkyl amines in water (11). However, in aprotic organic diluents the order of increasing basicity is primary, secondary, tertiary (10). For a particular anion, the order is thought to be related to the extent of solvation of both the extractant and the extracted complex. In any event, extraction from alkaline solution is not possible with any of the simple amine extractants. See Tables 2 and 3. Variations in the nature of the amine alkyl chains, in terms of branching and/or length, do not have a marked effect on the relative position of the curves for a particular amine type. This is demonstrated by the pH_{50} values for the different amines presented in Table 3.

Diluent Type

The effect of diluent type 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, reduced the pH_{50} values for secondary and tertiary amines by 0.5 pH unit compared to the aromatic diluent, xylene. See Table 4. Similarly, only slight variations in amine basicity with respect to diluent type can be expected for other anions.

TABLE 4
Effect of Diluent Type on the Extraction of Gold (1.0 g/L) from Alkaline Cyanide Solution. All Extractants 0.05 *M*

Amine	Diluent	pH ₅₀
Primary:		
Primene 81-R	Xylene	6.05
"	Hexane	6.05
Primene JM-T	Xylene	6.55
"	Hexane	6.55
Secondary:		
Adogen 283	Xylene	7.15
"	Hexane	6.55
"	Chevron IX ^a	6.50
"	Chloroform	6.40
Tertiary:		
Alamine 336	Xylene	5.65
"	Hexane	5.01

^aChevron ion-exchange solvent: Paraffin 54%, napthenes 35%, xylenes and C₈ aromatics, 11%.

Amine Concentration

For both aliphatic and aromatic diluents, the pH₅₀ value for gold extraction with 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. See Table 5. This, as expected, is due to the mass action effect, shifting the extraction equilibrium to the right:

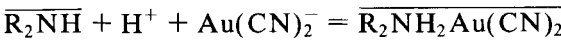


TABLE 5
Effect of Amine (Adogen 283) Concentration on the Extraction of Gold (1.0 g/L) from Alkaline Cyanide Solution

Concentration (<i>M</i>)	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

Note for both diluents that an increase in amine concentration by one order of magnitude causes an increase in pH_{50} by about one pH unit. Again, this increase in apparent base strength can be expected for simple amine extraction of most anions.

Finally it has been found that there is little or no effect of indifferent electrolyte concentration on amine extraction. Ionic strength was not a significant parameter in determining the extent of gold extraction by cyanide solution by simple amines.

From these results, simple, weak base amine extraction of anions clearly is limited to acidic or neutral solutions, even with regard to amine type, alkyl group, diluent, and ionic strength. At high amine concentrations, slight extraction from alkaline solution is possible as presented in Table 5. These results confirm our general understanding of amine solvent extraction which was recognized over two decades ago (6), "The simple alkyl amines are effective extractants only at low pH's and with acidic leach liquors."

CONTROL OF AMINE BASICITY WITH TRIBUTYL PHOSPHATE

Although some reports in the literature indicate that control of amine strength by the addition of modifiers is not particularly effective (12-14), it has been found that the amine basicity can be controlled for the extraction of certain anions with appropriate modifiers (7-9). From these findings it seems that in certain cases the modifier increases the apparent basicity of the amine by rather specific solvation effects which stabilize the extracted adduct at higher pH values. This effect seems to be quite different and more specific than that described for the interaction of alcohol modifiers with amines and amine salts (15).

The general effect of increasing the amine basicity by the addition of modifier is shown in Fig. 2. The shift of the extraction curve to the right to a higher pH_{50} value is in essence an increase in the basicity of the amine for a particular anion, and to do this selectively with respect to different anions is an exciting new area of research currently being pursued. Strong Lewis base compounds such as organic phosphorus oxides are especially effective as modifiers. Such interesting behavior has been found in a number of anion systems, and selected examples are given in the following sections for TBP as modifier.

Cyanoanions

Increased amine basicity and selectivity can be achieved for certain cyanoanions, particularly gold, as shown in Fig. 3 and Table 6. Figure 3 shows percent extraction versus pH curves for the extraction of $\text{Cu}(\text{CN})_4^{3-}$

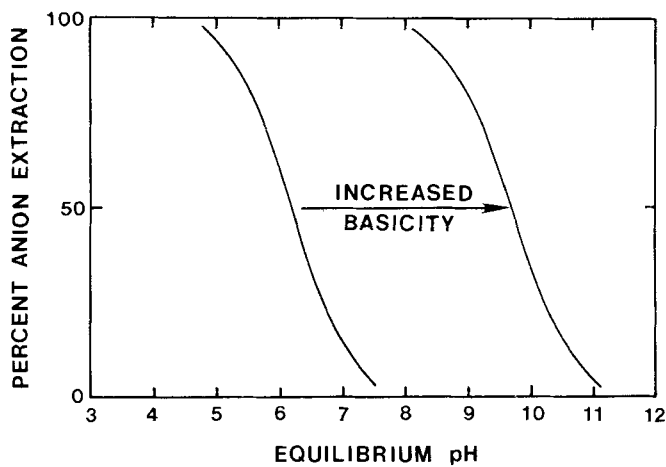


FIG. 2. Representation of increased amine basicity.

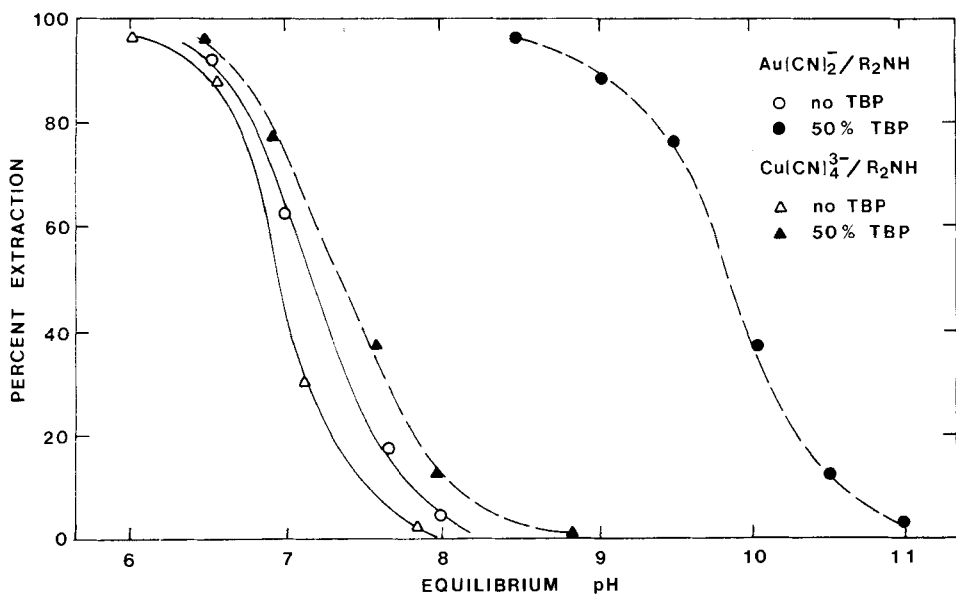
FIG. 3. Effect of TBP on the extraction of $\text{Au}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_4^{3-}$ ($5 \times 10^{-3} M$) by a secondary amine, Adogen 283 ($0.05 M$ in xylene) (8).

TABLE 6
The Effect of Modifier (TBP) on Amine Basicity (pH_{50}) for Selected Cyanoanions ($5 \times 10^{-3} M$) at 0.05 M Extractant in Xylene

Element	Anion	Adogen 283		Primene JM-T	
		No TBP	50% TBP	No TBP	50% TBP
Cu	$\text{Cu}(\text{CN})_3^{2-}$	6.78	7.60	—	—
Cu	$\text{Cu}(\text{CN})_4^{3-}$	6.90	7.20	6.10	—
Fe	$\text{Fe}(\text{CN})_6^{3-}$	5.66	6.80	5.68	6.72
Ag	$\text{Ag}(\text{CN})_2^-$	6.30	8.50	5.10	8.60
Zn	$\text{Zn}(\text{CN})_4^{2-}$	7.10	8.45	7.20	8.20
Au	$\text{Au}(\text{CN})_2^-$	7.05	9.78	6.05	9.78

and $\text{Au}(\text{CN})_2^-$ 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 almost three orders of magnitude. This selectivity for gold seems to be true with respect to most cyanoanions for both primary and secondary amines, as shown in Table 6.

The data presented in Table 6 are for tributyl phosphate (TBP) as modifier, but similar results are found for other organic phosphorus oxides.

Oxyanions

The extraction of oxyanions is of considerable interest in the hydrometallurgy of tungsten, molybdenum, rhenium, chromium, vanadium, and other metals. Selective extractions between certain combinations of these oxyanions may be possible depending on the modifier selected and its concentration. For example, in the case of tributyl phosphate it has been found that the modifier has only a small effect on molybdenum extraction, whereas, in the case of chromium extraction, the amine's basicity is

TABLE 7

The Effect of Modifier (TBP) on Amine Basicity (pH_{50}) for Selected Oxyanions (1.0 g/L) at 0.05 *M* Extractant in Xylene

Element	Anion	Adogen 283		Primene JM-T	
		No TBP	50% TBP	No TBP	50% TBP
Cr	CrO_4^{2-}	6.35	7.05	5.90	7.10
Mo	MoO_4^{2-}	5.72	5.92	5.70	6.20
V	VO_4^{3-}	6.76	7.60	7.05	7.42
W	WO_4^{3-}	5.95	6.70	—	—
Re	ReO_4^-	~6	8.80	~6	9.15

increased by about one order of magnitude from pH 5.90 to pH 7.10 for the primary amine as shown in Table 7.

Even more significant is the increased effectiveness of extraction of rhenium which shows an increase of about 3 orders of magnitude from a pH_{50} of about 6 with no modifier to a pH_{50} of 9.15 for 50% TBP for the primary amine. It is recognized that in some cases a mixture of anions might be present, e.g., polyvanadates, but this does not affect the significance of these results.

Carbonatoanions

The most common carbonate complexes are the uranyl carbonate anions. Again, as indicated in Table 8, tributyl phosphate is found to increase the amine's basicity with respect to $\text{UO}_2(\text{CO}_3)_3^{4-}$. A pH_{50} shift of almost one pH unit was found for the secondary amine, Adogen 283.

MODIFIER TYPE AND CONCENTRATION

As mentioned in the previous section, only those modifiers which have a strong Lewis base functionality, such as TBP, are effective in the control of amine basicity. The effect of modifier type is vividly revealed in experiments

TABLE 8

The Effect of Modifier (TBP) on Amine Basicity (pH_{50}) for the Uranyl Carbonate Anion (5×10^{-3} *M*) at 0.05 *M* Extractant in Xylene

Element	Anion	Adogen	
		No TBP	50% TBP
U	$\text{UO}_2(\text{CO}_3)_3^{4-}$	6.50	7.30

TABLE 9

The Effect of Modifier Type on the pH_{50} for Gold Extraction (1.0 g/L Au) by a Secondary Amine. 0.05 M Adogen 283 in Xylene/10% Modifier

Modifier	pH_{50}	ΔpH_{50}
None	7.15	0
TBP	7.83	0.68
Isodecanol	6.64	-0.51
MIBK	7.00	-0.15

on gold extraction from cyanide solutions with different modifiers. Table 9 presents the pH_{50} and ΔpH_{50} for some well-known solvating modifiers, viz., TBP, MIBK, and isodecanol.

Modifiers such as isodecanol and MIBK actually reduce the amine basicity.

The increase in amine basicity is even more pronounced with organic phosphorus oxides other than TBP, as shown in Table 10. In addition to the results in Table 10, Fig. 4 shows the complete percent extraction vs pH curves for the extraction of gold by a secondary amine, Adogen 283, in the presence of equal amounts of various organic phosphorus oxide modifiers.

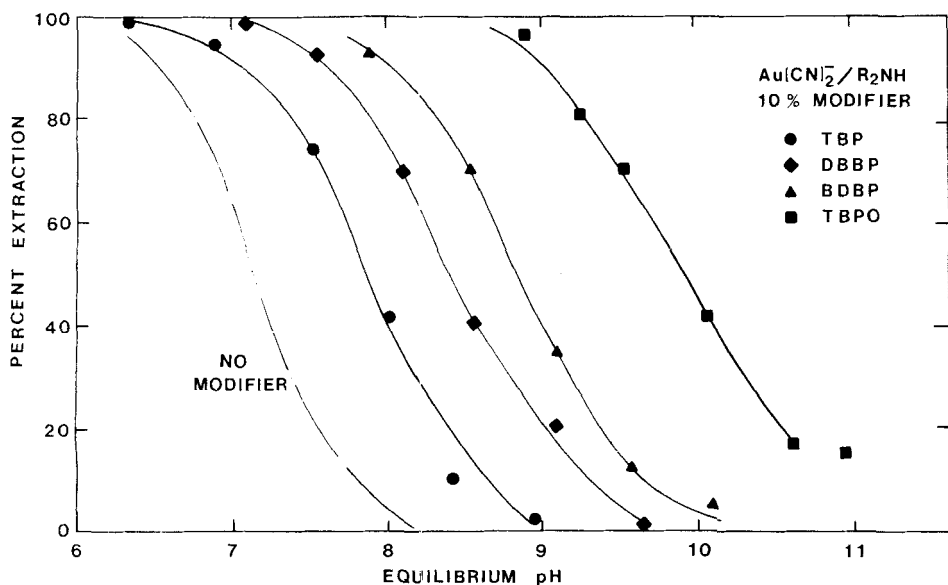


FIG. 4. Effect of modifier type on the extraction of $\text{Au}(\text{CN})_2^-$ (1.0 g/L Au) by a secondary amine, Adogen 283 (0.05 M in xylene).

TABLE 10

The Effect of Organic Phosphorus Oxide Modifier Type on the Extraction of Gold (1.0 g/L) from Cyanide Solution. 0.05 *M* Adogen in Xylene/10% Modifier

Modifier	Structure ^a	pH ₅₀	ΔpH ₅₀
No modifier		7.15	0
Tributyl phosphate, TBP	(RO) ₃ P=O	7.83	0.68
Dibutyl butyl phosphonate, DBBP	(RO) ₂ RP=O	8.30	1.15
Butyl dibutyl phosphinate, BDBP	(RO)R ₂ P=O	8.72	1.57
Tributyl phosphine oxide, TBPO	R ₃ P=O	10.10	2.95
Trioctyl phosphine oxide, TOPO	R ₃ P=O	9.45	2.30

^aR = C₄H₉ except for TOPO where R = C₈H₁₇.

The modifiers increase the pH₅₀, i.e., the amine basicity, in the order phosphate < phosphonate < phosphinate < phosphine oxide. 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.

The increase in amine basicity could be related to solvation of the amine or amine/anion adduct by the modifier. 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. It appears that the *n*-alkyl chain length and degree of branching has little effect on the amine's basicity.

As expected, increasing the concentration of modifier in the organic phase increases the amine basicity. Figure 5 shows the increase in basicity, ΔpH₅₀, as a function of the amount of TBP in a xylene diluent for the three types of amine at 0.05 *M*. It is interesting to observe that the TBP has an increasing effect in the order tertiary < secondary < primary amine. This appears to be in accord with the water-solvation/amine-basicity concept. It is thought that the primary amines have three waters of solvation, secondary two, and tertiary one (16). Thus the solvating effect and the increase in basicity should be greater for primary amines than for secondary than for tertiary. This is exactly what is observed in our experiments. However, as mentioned previously, it could, in fact, be the modifier which is solvating the amine.

It is conceivable that other strong Lewis bases, such as sulfoxides, R₂S=O, would function as modifiers. In this regard, experiments are presently in progress at our laboratories.

As a result of these findings, new solvent extraction systems may be devised for the processing of alkaline leach solutions containing tungsten,

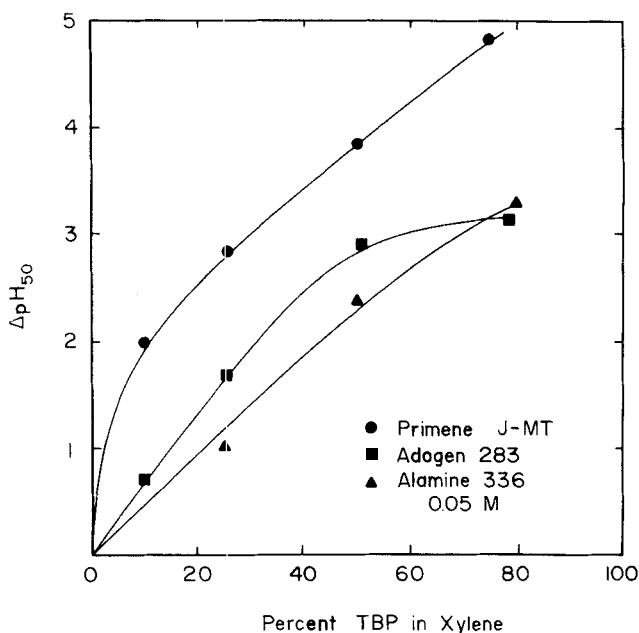


FIG. 5. Effect of TBP concentration on the pH_{50} for $\text{Au}(\text{CN})_2^-$ (1.0 g/L Au) extraction by primary, secondary, and tertiary amines (0.05 M in xylene).

molybdate, and/or rhenate. One possibility of particular interest is the extraction of gold from alkaline cyanide solutions as discussed in the following section.

ENGINEERING CONSIDERATIONS IN GOLD EXTRACTION FROM ALKALINE CYANIDE SOLUTIONS BY MODIFIED AMINES

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

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

The composition of these solutions will differ significantly both with regard to gold concentration and contaminant level. Gold concentration might vary

from 1 ppm in the case of heap leach solutions to an estimated concentration of 30,000 ppm for a solution prepared from precious metal scrap.

Stripping can be accomplished at pH values where the amine deprotonates, i.e., pH 12–13 or a caustic solution of about 0.1–0.5%. The loading and stripping reaction rates are relatively fast, and therefore long contact times are not necessary. Excellent selectivity for gold over other cyanoanions present in alkaline cyanide leach solutions, e.g., $\text{Fe}(\text{CN})_6^{3-}$, $\text{Cu}(\text{CN})_2^{2-}$, etc., has been demonstrated (8) which should allow for the production of a relatively pure gold product.

The modified amine extractant system has great flexibility with a large number of variables such as amine type and concentration, modifier type and concentration, extraction pH, diluent type, etc. However, 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, organic entrainment, etc. are important.

Consider, by way of an example, the use of solvent extraction for gold recovery from heap or dump leach liquors (15). The modified amines will extract gold from these alkaline cyanide solutions containing low-gold tenors. The modified amines will extract gold over a wide range of concentrations. The results in Table 11 demonstrate that decreasing the gold concentration does not affect the percentage of gold extracted.

If a conventional solvent extraction scheme were to be used, the pregnant leach liquor from the heap might have to be filtered to reduce the suspended solids content and prevent excessive organic losses (adsorption by suspended particles). Further, such filtration may also be necessary to minimize the formation of interfacial crud and to prevent phase disengagement problems. With conventional mixer-settlers, the raffinate will have to be passed through a coalescer to scavenge entrained organic. If the entrained organic were not minimized, the solvent and associated gold losses would be excessive. The

TABLE 11
The Effect of Gold Concentration for Extraction by 0.05 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

organic entrainment problem could possibly be solved by the use of other contactors such as centrifugal, raining drop, or reciprocating column contactors.

Another interesting approach would be to impregnate the solvent into a substrate. For example, solvent impregnated resins could be used with a conventional resin in column flow sheet (17). Alternately, solvent impregnated membranes could be used by allowing extraction and stripping to occur simultaneously.

The possibility of generating a concentrated, purified gold cyanide solution for the recovery of high-purity electrolytic gold sheet is an exciting concept. Such a concept requires an extractant with high selectivity. Progress in the development of such extractants, modified amines, has been discussed in previous sections. Research on this topic continues both with regard to a detailed explanation of the chemistry of extraction and with regard to the application of this technology to industrial operations.

SUMMARY AND CONCLUSIONS

Recent research indicates that control of amine basicity for the selective extractive of certain complex metallic anions from alkaline solution is possible by the addition of modifiers. These modifiers are found to be Lewis bases; in particular, organic phosphorous oxides such as tributyl phosphate (TBP), although other modifiers are even more effective. Selectivity seems to be related to anion size/charge and the extent of solvation by the modifier. Possible applications for this new development include alkaline separation of oxyanions and cyanoanions. The potential for selective extraction of gold from complex cyanide solutions is of considerable interest.

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