Commercial Application of Extracting Reagents for Metal Recovery

Part - II. Basic and Neutral Extractants

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Abstract

The developments in reagents' availability and their application in commercially successful metal recovery operations have been described in this review. Basic and neutral or solvating extractants are presented in this part of the paper.

Introduction

In part–I of this paper1, the developments in reagents' availability and extraction of acid and chelating extractants in commercially successfully metal recovery operations were described. The present paper deals with the developments and application of basic and neutral or solvating extractants.

Basic Extractants

For metals existing in solution in anionic form, an anion exchange process is more effective, so basic extractants are used. The only basic extractants studied for the extraction kinetics are high molecular weight amines. The extraction takes place through the formation of an ion-pair and for this reason these extractants have also been called liquid anion exchanger. Metal ions can be extracted both as negatively charged complexes and natural complexes. The neutral or negatively charged metal species are formed in the aqueous phase with water soluble anions. This type of extractants is based on the principle of ion association; whereby a large positively charged organic moiety causes the extraction of a large, anionic metal complex into the organic phase, with concomitant expulsion of a small common anion to the aqueous phase. Henkel Corporation markets two classes or compounds which fall into the general classification. Alamine and Aliquat are the registered trade names of Henkel Corporation for them.

Alamine Series

The Alamine Series of reagents contain a basic nitrogen capable of forming amine salts with a variety of inorganic and organic acids. The amines which find the widest use in metals recovery processing by solvent extraction are the tertiary amines of the general formula R3N where R can represent a verity of hydrocarbon chains. The equations below represent the extraction chemistry of the Alamine series reagents:

 $[R_3 N]_{org} + [HA]_{aq} [R_3 H^+A^-]_{org}$ (1)

$$[R_3 H^+A^{\cdot}]_{\text{org}} + [B^{\cdot}]_{aq} [R_3 H^+B^{\cdot}]_{\text{org}} \longleftarrow$$
$$+ [A^{\cdot}]_{aq}$$
(2)

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Equation (1) is simply amine salt formation while equation(2) represent true ion exchange. The extent to which [B-] will exchange for [A-] is a function of the relative affinity of the two anions for the organic cation and the relative stability of the anions in the aqueous medium. Since tertiary amines can form salt with a wide variety of acids, the choice of reagents for a liquid ion exchange process is not strictly limited, i.e. bisulphate, chloride, etc. of any of the Alamine reagents can be used. Amine type extractants can be stripped with a wide variety of inorganic salt solution such as NaCl, Na2CO3 and (NH4)2SO4. The choice of stripping agent depends on the overall recovery process but in general basic stripping agents which deprotonate the amines give the best stripping in the fewest stages. The equation below shows the stripping action of Na2CO3 on an amine salt.

 $2 [R_{3} N H^{+} B^{\cdot}]_{org} + [2 Na^{+} + CO_{3}^{2 \cdot}]_{aq}$ $2 [R_{3} N]_{org} + [H_{2}O^{\cdot}]_{aq} + CO_{2} + 2 [Na^{+}]_{aq}$ $+ 2 [B^{\cdot}]_{aq} \qquad (3)$

The greatest commercial acceptance for Alamine type reagents has been in uranium recovery process however, any metal capable of forming anionic complexes in aqueous solutions is a candidate for extraction by an amine type extractant.

Some of the known uses of Alamine extractants commercially available from Henkel Corporation are given below:-

(i) Alamine 300 (tri-n-octylamine)

This is used in cobalt extraction from chloride leach solutions^{2,3}, extraction of zirconium – hafnium from sulphate solution4, separation of zirconium – hafnium from sulphate solutions5,6, extraction of iron from chloride solution⁷ and copper extraction from chloride solution⁸.

(ii) Alamine 308 (tri-iso-octylamine)

This finds application from cobalt / nickel separation from hydrochloric acid liquors9,10 and copper/nickel extraction from hydrochloric acid solutions10. In Falconbridge Matte Leach process practiced Falconbridge Nikkelwerk atat Kristiansand, Norway9,10, finally divided coppernickel converter matte is treated with strong HCl and nickel is selectively dissolved, leaving copper and platinum metals in the insoluble sulphide residue. The oxidized iron is extracted with 4% TBP (tri-n-butyl phosphate) in aromatic hydrocarbon diluent. From the loaded TBP, iron is stripped with water and solvent is recycled. From the iron free solution, both copper and cobalt are extracted as anionic chloro-complexes, with 11 vol. % solution of tri-iso-octvl amine in an aromatic diluent. The metals from the extract can be stripped with water and from the raffinate nickel is recovered as NiCl2.4H2O by passing HCl gas through it. The extraction of element 104 Rutherfordium (Rf) and its group 4 homologs11 into tri-iso-octylamine in xylene from various concentrations of HF has been studied.

(iii) Alamine 336 (tri-(C8-C10) amine)

This finds application in:

- (i) Vanadium extraction¹²
- (ii) Cobalt-nickel separations from HCl¹³
- (iii) Chromium extraction^{14,15}
- (iv) Iron extraction from aluminium chloride solution^{16,17}
- (v) Uranium recovery from sulphuric acid leach liquors¹⁸ or sulphuric acid resin eluate solutions^{19,20}
- (vi) Platinum group metals separations²¹
- (vii) Tungsten recovery and separation of zirconium and hafnium from sulphate solution^{22,23}. Extraction isotherms²⁴ for various metals from chloride solutions by Alamine 336 is shown in Figure 1.
- (viii) Extraction of copper and cadmium from acidic chloride solutions²⁵
- (ix) Separation of molybdenum, vanadium and nickel²⁶

Fig. 1 Alamine® 336 extraction isotherms from chloride solution at 40°C and pH=2 (24).

(v) Alamine 310 (tri-isodecylamine)

This is used in uranium and vanadium extraction from acidic sulphate leach liquors and platinum group metals separations²¹.

(vi) Alamine 304 (trilaurylamine)

This is used for uranium and molybdenum extraction from acidic leach liquors, the advantage being that the molybdenum amine complex is highly soluble.

Aliquat Series

The Aliquat series of reagents is based on methyl chloride quarternization of a respective Alamine reagent. Because a quarternized amine is always positively charged, anion extraction with Aliquat reagents is not pH dependent as it is with the tertiary amines. As a result, some basic metals leach solutions may be successfully treated by Aliquat type reagents without pH adjustment. The biggest disadvantage of using an Aliquat reagent is that these reagents will not deprotonate, therefore, stripping is usually more difficult than with the parent amine type reagents.

Aliquat 336 (tri-(C₈-C₁₀) methyl ammonium Chloride)

extraction¹², Vanadium of separation metals^{21,27}. platinum group rare earth arsenic extractions²⁸. rhenium recovery²⁹, extraction from refinery electrolytes³⁰, extraction of chromium³¹, tungsten and copper are carried out with this reagent. Mixtures of Aliguat 336 and TOPO (tri-n-octyl phosphine oxide) result in synergistic extraction of zirconium and hafnium³² from acidic thiocyanate media. Extraction of cadmium from copper and acidic chloride solutions²⁵. zinc and cobalt recoverv and separation³³, purification of nickel sulphate solutions from micro quantities of Co(II), Zn(II) and Cu(II)³⁴ and gold extraction³⁵ have been achieved by solvent extraction using this reagent.

Aliquat 336 Nitrate

The nitrated salt of Aliquat 336 is a specific product for rare earth separations. Extraction mechanism of bismuth (III)³⁶ from nitrate aqueous solution with trioctyl methyl ammonium nitrate in xylene has been studied.

Further possible uses of these types of reagents (Alamine and Aliquat series) may lie in the areas of :-

- (a) Inorganic acid purification³⁷
- (b) Niobium, titanium, tantalum and zirconium separations³⁸
- (c) Separation of cobalt, copper and zinc from nickel³⁹
- (d) Reclaiming metals from spent catalysts⁴⁰

In addition to these two classes of extractant (Alamine and Aliquat series), the other important extractants of this type are :-

Primene JM-T (Primary amines, R-NH₂)

This can be obtained from Rohm and Haas and is used for the extraction of iron from sulphate solution and separation of hafnium and zirconium from sulphate solutions⁴¹.

Amberlite LA-1 and Amberlite LA-2

[Secondary amine. R₂NH (n-laurylalkyl methylamine)]

These are the products developed by Rohm and Haas and are used for the extraction of uranium from sulphate solutions and extraction of iron and cobalt from chloride solutions⁴².

Hostarex-A327 (Tertiary amine, N_3N , $R=C_8 - C_{10}$)

This is the product developed by Farbwerke Hoechst AG., Germany and is used for the extraction of uranium, vanadium, molybdenum and tungsten from sulphate solution. It is also used for the extraction of cobalt and copper from chloride solution and separation of zirconium from hafnium. The purification of nickel sulphate solutions from micro-quantities of Co(II), Zn(II) and Cu(II)³⁴ by Hostarex-F3541 has been studied for optimal conditions.

Adogens

Sherex Chemicals Co. introduced the following reagents:

 i) Adogen 283: (Secondary amine, di,tridecyl amine)

This is proposed for the extraction of vanadium and tungsten.

ii) Adogen 364 (Tertiary amine, tri-iso-octyl amine)

This may be used for the extraction of platinum group metals from chloride solution. Commercial mixtures of tri-octyl to tri-decyl amines (e.g.Adegen 364 or Alamine 336) are used to recover uranium from H2SO4 leach liquors in the Amex process. The Amex process is widely used than the Depex process because of the greater selectivity of tri-alkyl amine for uranium in H2SO4 solution than that of DEHPA (di (2ethylhexyl phosphoric acid).

iii) Adogen 381 (Tertiary amine)

This has various uses, e.g. extraction of uranium and cobalt42.

iv) Adogen 464 (Quaternary amine)

It is proposed for the extraction of uranium, vanadium, chromium and tungsten.

TOA (Tri-cctylamine)

Sumitomo Metal Mining Company of Japan utilized a different approach for the recovery of cobalt and nickel from a sulphide concentrate at their Niihama refinery³. The concentrate, assaying 25% Ni and 15% Co, with iron, manganese, copper and silica as impurities, is pressure leached autogenously with air. After removing impurities, cobalt and nickel are extracted together from the resultant solution, using Versatic-10 and stripped out from the loaded solvent using HCl. From the chloride solution, cobalt is selectively extracted with tri-octylamine. Both nickel and cobalt are finally recovered as metals electrolytically from the chloride solutions.

Baroncelli et al⁴³ have used TOA to extract gold from chloroanions of, for example copper, iron, tin and zinc, in aqua regia solution. The selectivity is attributed to the presence of TOA. Coextracted metals are scrubbed with dilute HNO₃ and gold is recovered by an HCL-thiourea solution.

Figure 2 illustrates the effect of HCl concentration on cobalt extraction, with a maximum cobalt extraction observed at approximately 9 M. Above this concentration, the HCl_{2^-} ion competes with $CoCl_{4^{2-}}$ for the extractant, replacement of HCl by a metal chloride solution,

such as LiCl, eliminates this maximum. The figure also shows that extraction depends on the concentration and type of extractant⁴⁴, thus, extraction is greater for tertiary > secondary > primary amines. This anion exchange process⁴⁵ is used commercially in Norway (Falconbridge Nikkelwerk) and Japan (Sumitomo) for cobaltnickel separation.

In general, the use of organic phase modifiers, normally polar organics such as long chain alcohols, is required with amines in order to keep the amine metal complexes soluble, to prevent third phase formation and/or to have acceptable phase separation.

Fig. 2 Extraction of metal chlorocomplexes as a function of chloride concentration (44).

Neutral or Solvating Extractants

A fourth category of extractants is known as netural or solvating type extractants. Extractants of this type are basic in nature and facilitate extraction by coordinating with the metal complexes and simultaneously replacing waters of hydration and formation of a neutral complex through ion association, thereby causing the resulting organo-metal complex which is insoluble in the aqueous phase and soluble in the organic phase. Solvating extractants have an atom capable of donating electron density to a metal in the formation of an adduct and are classified according to that ability:-

$$R_3PO > (RO)_3PO > R_2CO > ROH > R_2O$$

Trialkylphosphine oxides > trialkylphosphonates > ketones > alcohols > ethers.

Extractions with solvating extractants are limited due to:

- a) The metal's ability to form neutral complexes with anions.
- b) The co-extraction of acid at high acid concentrations.
- c) The solubility of the organo-metal complex in the organic diluent.

Important extractants of this type are tri-nbutyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO), di-butyl butylphosphonate (DBBP), di-noctylsulphide (DOS), Methyl isobutyl ketone (MIBK).

TBP (tri-n-butyl phosphate)

This has been marketed by Union Carbide, U.S., Albright & Wilson, U.K. and Daihachi Chemicals Co., Japan. TBP is one of the first phosphorous-based extractants and today has many commercial applications. It is used in uranium refineries at various locations in the USA, Canada, UK and France, A mining company in South Africa uses TBP to recover uranium from tailings from a copper operation⁴⁶. TBP has also been used in nuclear fuel reprocessing plants in the USA, UK, France and Germany⁴⁷. The solvent extraction process that uses TBP solutions to recover plutonium and uranium from irradiated nuclear fuels is called Purex (Plutonium and uranium extraction). The Purex process provides recovery of more than 99% of both U and Pu and also provides excellent decontamination of both elements from fission products. Many variations of the Purex process have been extensively developed and demonstrated on a plant scale. This process is now used world wide to reprocess spent reactor fuel.

TBP is used in the separation of rate earth elements in plants in USA and France. TBP was also used in plants in USA and Canada to recover purity zirconium from mixtures with high hafnium, for use in nuclear applications. Neither plant is currently operating. However, it is used in a nickel refinery in Norway to remove iron, prior to the separation of copper and cobalt and precipitation of nickel^{48,49}. At one time nucleargrade thorium was produced with TBP in the USA and France, now neither facility is operating⁴⁶. TBP is used as a synergist or phase modifier in various solvent extraction processes including those for uranium, yttrium and indium. TBP is also used for the extraction of zirconium and for separating it from hafnium in the Port Hope refinery of Eldorade Nuclear Limited, Ottawa^{44,50} and in India⁵¹.

TBP is used commercially in the recovery of molybdenum and tungsten⁵², extraction of arsenic from electrolyte copper refinery in Australia⁵³, recovery of nitric acid and hydrogen fluoride from waste acid from steel pickling in Sweden and Japan⁵⁴, recovery of platinum in Canada. separation of iridium from rhodium in West Germany, recovery of iridium in South Africa⁴⁶ and removal of chromium from chrome plating wastes in France⁵⁵. From the mixture of high temperature chlorination of fly ash by Hichlor process, titanium can be recovered from the aqueous phase using the TBP in kerosene¹⁷. Recently, there has been interest in the use of solvating extractants such as TBP and DBBP, for the extraction of gold⁵⁶ from alkaline cyanide solution. Extraction of trivalent ions of La, Pr, Nd and Sm (Lanthanum, Praesodymium, Neodymium and Samarium) from aqueous nitrate solution by either one component (TBP or DEHPA) or a mixed organic phase (TBP-DEHPA) has been carried out⁵⁷. The synergistic effect was discovered only in

the case when the aqueous phase contained NH_4NO_3 . Extraction of Cd and Zn halo-complexes has been carried out by TBP⁵⁸ to determine separation factor.

The Belgian firm of Metallurgie Hoboken Overpelt⁵⁹ (MHO) holds a patent for leaching the ocean nodules with hydrochloric acid. The leach solution is amenable from metal recovery only by a solvent extraction technology. In the proposed scheme, iron, zinc, molybdenum and vanadium are separated by extraction using TBP and LIX 63 while copper, cobalt and manganese are recovered by chemical precipitation. However, there appears to be no reason why the latter, particularly copper, nickel and cobalt, cannot also be recovered by solvent extraction. This process has the advantage of a closed loop operation resulting in the elimination of pollution problems.

Solvent extraction of Mn(II) and Co(II) from thiocyanate solutions⁶⁰ by TBP, Rutherfordium (Rf) and its group 4 homologs and other tetravalent cations from various concentrations of HBr and HCI⁶¹ by TBP, Europium, Eu(III), from aqueous nitrate, perchlorate and thiocyanate solutions⁶² by TBP, TOPO and dioctylsulfoxide, and silver⁶³ by the commercial extractants TBP and Cyanex 471X has been studied

The use of the TBP, Cyanex 923 and many other extractants are reviewed for the recovery of arsenic, antimony and bismuth from copper electrolytes⁶⁴. The chemistry and processes are presented and discussed. The mechanisms involved in the extraction of rare earths using different types of extractants like TBP, DEHPA, 2ethylhexyl 2-ethylhexyl phosphoric acid and quaternary ammonium salts are discussed in a review⁶⁵ with 69 references. The flowsheets designed for the separation of various rare earths are also given.

Extraction of zinc (II) from spent pickling HCl solutions⁶⁶ obtained in zinc hot dip galvanizing plants has been studied. TBP and its mixtures with DEHPA, HOEF 2562, Aliquat 336, Alamine 336 and many other Alamine 304, Alamine 308,

Alamine 310, and Cvanex 301 were used as extractants. The acidic extractants (DEHPA and Cyanex 301) did not extract both zinc (II) and iron (III) from 10% HCl. A precipitation occurred or stable emulsions were formed when Alamines 304. and 310 were used. Each of other reagents coextracted both zinc (II) and iron (III). The latter had to be reduced to iron (II) prior to extraction. TBP and HOEF 2562 showed the best extraction performance. TBP was used for separation carried out in laboratory mixer settlers. The dynamics of extraction and stripping was studied and successfully modelled.

Cyanex 921 (tri-n-octylposphine oxide)

This has been developed by American Cyanamid Company and is known as TOPO. The extraction characteristics of TOPO with a wide variety of metals have been investigated⁶⁷. The most important commercial application of TOPO in solvent extraction is its synergistic combination with di (2-ethylhexyl) phosphoric acid (DEHPA) for the extraction of uranium from wet process phosphoric acid⁶⁸⁻⁷⁶.

TOPO-DEHPA The process, originally developed at the Oak Ridge National Laboratory⁶⁸, is the most widely accepted one for industrial scale exploitation. The solvent consists of a mixture of di (2-ethylhexyl) phosphoric acid (DEHPA) and dissolved in kerosene. TOPO This solvent combination is effective for extracting hexavalent uranium from phosphoric acid. The extraction coefficient with the mixture is higher than with either reagent alone. Commercialization of the process developed at Oak Ridge has been done by Wyoming Minerals, Fla., by the Freeport Uranium Recovery Co. La., and by the International Minerals & Chemical Corp. (IMC), Fla. The process for the recovery of uranium using a synergistic mixture of Cyanex 921 extractant and DEHPA is operating successfully in a number of commercial plants in the U.S.A. Canada and Belgium. TOPO is a solid which must be melted prior to blending the solvent and is being used for

many years. Albright and Wilson supplies DEHPA/TOPO blends to customers who prefer to avoid this step. TOPO has good performance in other solvent extraction applications for many other metals but its high price has limited its wide spread use.

A pilot plant process using Cyanex 921 extractant to recover and separate niobium and tantalum has been demonstrated^{77,78}. Both metals wee extracted from a hydrofluoric sulphuric acid leach liquor and then selectively stripped from the loaded organic. The advantages of Cyanex 921 extractant in comparison to the commercially used MIBK extractant were shown to be higher stability, lower aqueous solubility, rapid phase disengagement and particularly the production of high purity niobium oxide which meets the stringent specifications required for nuclear, optical and electronic applications.

Rhenium has been recovered using Cyanex 921 from petroleum reforming catalysts source materials⁷⁹. The process involves leaching the spent catalyst with sulphuric acid extracting rhenium and then stripping with ammonium sulphate. Excellent selectivity against typical impurity metals such as aluminium, calcium, magnesium and iron is achieved.

The removal of arsenic impurities from copper electrolytes⁸⁰ by solvent extraction with Cyanex 921 has been carried out. The process describes the selective extraction of arsenic followed by stripping with an acidic sodium sulphate solution and recovery of arsenic from the strip liquor by precipitation with H₂S. Cyanex 921 is shown to be stronger extractant for arsenic than tributyl phosphate which is now used in two commercial arsenic solvent extraction plants.

A novel solvent extraction process using Cyanex 921 extractant to recover lithium from one of its sources (neutral brines) has been described⁸¹. Extraction of lanthanum (III) and Yttrium (III)⁸² from aqueous HCl containing KSCN by TBP or TOPO in benzene has been studied. It is found that extraction efficiency of TOPO is higher than that of TBP. The partition of Eu(III) between benzene containing solvating extractants (TBP, TOPO, dioctyl sulphoxide) and aqueous nitrate, perchlorate and thiocyanate solution⁶² has been investigated.

Cyanex 923

This extractant is a mixture of four trialkyl phosphine oxides where alkyl groups are hexyl and octyl groups. It exhibits extraction properties similar to those of TOPO. The major advantage of Cyanex 923 extractant over similar extraction reagents, e.g. TOPO (trioctylphosphine oxide), is that it is a liquid and is completely miscible with all commonly used hydrocarbon diluents. It is particularly useful for the removal of arsenic from copper electrolytes and the recovery of carboxylic acids, phenols and ethanol from effluent streams. Cyanex 923 extractant is a potential substitute for TOPO in the process for the recovery of uranium from wet process phosphoric acid. The advantage of using Cyanex 923 extractant in place of TOPO in niobium-tantalum separation is due to its liquid state and higher solubility in organic solvents. Recently Cyanex 923 extractant has been used for the extraction of hafnium⁸³ from acidic chloride solution. The solvent used for the extractant is kerosene. The use of TBP, Cyanex 923 and many other extractants⁶⁴ are reviewed for the recovery of arsenic, antimony and bismuth from copper Recovery of cobalt⁸⁴ using solvent electrolytes. extraction has been carried out with Cyanex 923.

Cyanex 925 (Bis (2,4,4-trimethylpentyl) octylphosphine oxide)

Cyanex 925 is a highly hindered phosphine oxide which exhibits a greater degree of selectivity than conventional straight chain phosphine oxides. Potential applications of this extractant include the recovery of tin from chloride solutions, removal of arsenic from copper electrolytes and the separation of niobium and tantalum⁸⁵.

DBBP (di butyl butylphosphonate)

DBBP is an under-used extractant with properties lying somewhere between TBP and TOPO. Recently, interest in DBBP has increased due to new commercial and developmental applications. DBBP has been used with DEHPA in the recovery of uranium from wet process phosphoric acid. It was used in the USA to recover americium-241 from plutonium in waste streams recovery system, but is no longer used in this application⁸⁶.

Recently, there has been interest in the use of DBBP in new processes in the recovery of titanium, gold and silver but these have not yet been commercilized⁸⁷. This has been marketed by Albright and Wilson as Albrite DBBP.

DOS (di-n-octylsulphide)

It is used for the extraction of palladium from chloride solutions⁸⁸. Two commercial flowsheets been developed using either di-nhave octylsulphide or a hydroxyoxime as selective extractants to remove the palladium, followed by TBP and an amine to recover platinum. The extraction of palladium by the sulphide is slow with 2-3 hours to achieve the equilibrium, which inhibits flowsheet design. However, it has been shown that tertiary amines can act as a kinetic reducing equilibrium accelerator, times to minutes. High loading of the sulphides is possible and stripping is easy with aqueous ammonia.

MIBK (Methyl iso-butyl ketone)

It is used for the separation of zirconium and hafnium from a chloride solution^{89,90} by American Metal Climax, Teledyne, Wah Chang and Ugine, who are the major zirconium producers in the World. It is also used for the separation of niobium/tantalum. Selective extraction of gold from chloride solutions⁹¹ is being carried out by Matthey Rustenberg Refiners, United Kingdom for their Royston refinery. **Figure 3** shows the extraction of elements from a chloride medium by MIBK⁹². Kinetics of extraction of copper and cadmium¹⁵ from an acidic aqueous chloride medium into a coexisting organic phase containing MIBK and high molecular amines have been studied for stirred and unstirred systems.

Fig. 3 Extraction of elements from a chloride medium by MIBK ((2).

DHSO (di-n-heptyl sulphoxide)

A suggested flow sheet for the extraction of platinum group metals (Pd, Pt, Ir, Rh) using DHSO as extractant in trichloroethylene has been described by Lewis et al⁹³. Solvent extraction study of Nd (III), Eu(III) and Tn(III) has been carried out by dimethyl sulphoxide (DMSO)⁹⁴.

Dibutylcarbitol (diethyleneglycol dibutyl ether)

Gold exists in the leach solution as AuCl₄⁻ and all the processes rely on the extraction of this ion or the parent acid by ion pair or solvating extractants respectively. The early studies by Morris and Khan⁹⁵ led to the adoption of dibutylcarbitol (Butex) by INCO in a gold refinery several years before the complete solvent extraction refining flowsheet was produced. The extractant has a high selectivity for gold and coextracted elements can be easily scrubbed with dilute HCl. Because of the high distribution coefficient recovery of gold is best achieved by chemical reduction. Thus, oxalic acid at 90°C produces easily filtered gold grain. However, the slow kinetics necessitates a batch process.

INCO has utilized solvent extraction methods for recovering gold from solutions. The process is based on the extraction of gold in oxidized form with dibutylcarbitol from 3 to 4 M HCI solution. Barnes and Edwards⁸⁸ have described in detail the flow sheet developed by INCO for their Acton Precious Metals Refinery. Extraction of elements from chloride medium by dibutylcarbitol⁹⁶ is shown in **Figure 4**.

Fig. 4 Extraction of elements from a chloride medium by dibutylcarbitol (96).

Cyanex 471X (tri-isobutyl phosphine sulphide, TIBPS)

Cyanex 471X is particularly useful extractant for the selective recovery of sliver using a DEHPA phase modifier and separation of palladium and platinum using a nonylphenol phase modifier. It will also extract mercury and gold. Solvent extraction of silver⁶³ by commercial extractants TBP, Cyanex 471X, Cyanex 301 and Cyanex 302 has been carried out.

It is of interest to note that virtually all the equilibrium and phase modifiers commonly used come from this class of extractants. This is no surprise since both equilibrium and phase modifiers require a group having the ability to donate electron density and in some cases hydrogen bond.

Conclusions

The potential of solvent extraction is well documented by the wide variety of metal containing solutions which are amenable to recovery, purification and concentration by liquid ion exchange. Although the above-mentioned list of extracting reagents is very impressive but still it should not be considered as limiting. The development and successful marketing of the existing reagents has resulted in the commercially successfully metal recovery operations around the World. The researchers are constantly working on the development of new reagents and new applications for the existing extractants. A day will come when the hydrometallurgist could have an unlimited selection of commercially available chemical reagents at his disposal in order to make efficient and economic extraction and separation of virtually all metals in solution.

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