Mines Branch Information Circular IC 213

APPLICATION OF SOLVENT EXTRACTION TO

COMMON BASE METALS (A REVIEW)

by

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ABSTRACT

This review describes some of the more pertinent solvent extraction systems, as found in the literature, for the extraction and separation of the common base metals from various aqueous media. The advantages and disadvantages of certain organic reagents are indicated. The economics of solvent extraction processing are discussed briefly.

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Circulaire d'information IC 213

APPLICATION DE L'EXTRACTION PAR SOLVANT AUX MÉTAUX COMMUNS COURANTS (ÉTUDE)

par

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RÉSUMÉ

Cette étude décrit quelques-uns des systèmes d'extraction par solvant les plus pertinents, relevés dans les divers ouvrages sur le sujet, pour l'extraction et la séparation des métaux communs courants de divers milieux aqueux. L'auteur indique les avantages et les désavantages de certains réactifs organiques et discute brièvement de l'économie de l'extraction par solvant.

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CONTENTS

FIGURES

TABLES

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INTRODUCTION

The purpose of this review is to explore the possibilities of recovering base metals, either separately or in bulk, by solvent extraction, particularly for plants that are at present using hydrometallurgical techniques in their operations.

Solvent extraction, although relatively new as a unit process in extractive hydrometallurgy, has been practised for many years by analytical chemists to separate and determine chemical elements. This is achieved by extraction of molecular species from aqueous media by means of immiscible specific organic solvents. The active organic, which is a co-ordination compound, is usually dissolved in a relatively inexpensive, inert diluent, such as kerosene. The compounds formed with the complexing agent must also be soluble in the diluent. In order to avoid high losses of the solvent in processing, it is advisable to employ a system in which the organic solvent is almost immiscible in water. Also, the organic reagent, which should be fairly specific for the metal in question, should be safe (as regards toxicity and fire hazard), inexpensive, stable, and compatible with stripping and regeneration procedures. Often, the terms "organic", "solvent" and "extractant" are interchangeable to describe the organic phase. The aqueous phase, after contact with the organic phase, is called the "barren" or raffinate. Recovery of the metal values from the extract is accomplished by stripping or leaching with an aqueous solution.

A schematic drawing of the process of solvent extraction is shown in Figure 1.

Various types of mixing devices are used to effect the desired contact between the aqueous and organic solutions. Brief descriptions of these devices will be given later in this review.

Base-metal plants in the future will be concerned with the treatment of low-grade, possibly complex, deposits. Present processing techniques for the recovery from such deposits could be uneconomic. Recent techniques in the industry, such as heap leaching, dictate a relatively cheap recovery method, such as the solvent-extraction step practiced in Arizona by Bagdad Copper and by the Duval Corporation[1]. Solvent extraction is used for the separation of metals from complex solution mixtures and for the recovery of an upgraded solution containing the values amenable to electrolysis, precipitation, etc.

Metal-bearing Solution

Organic
extractant in kerosene → Extraction

Raffinate
to further metal
recovery or waste

Extract

Scrubbing ← Scrub Solution

Scrub
raffinate
to waste or
recovery

Scrubbed Extract

Stripping ← Aqueous Strip Solution

Stripped organic
to extraction

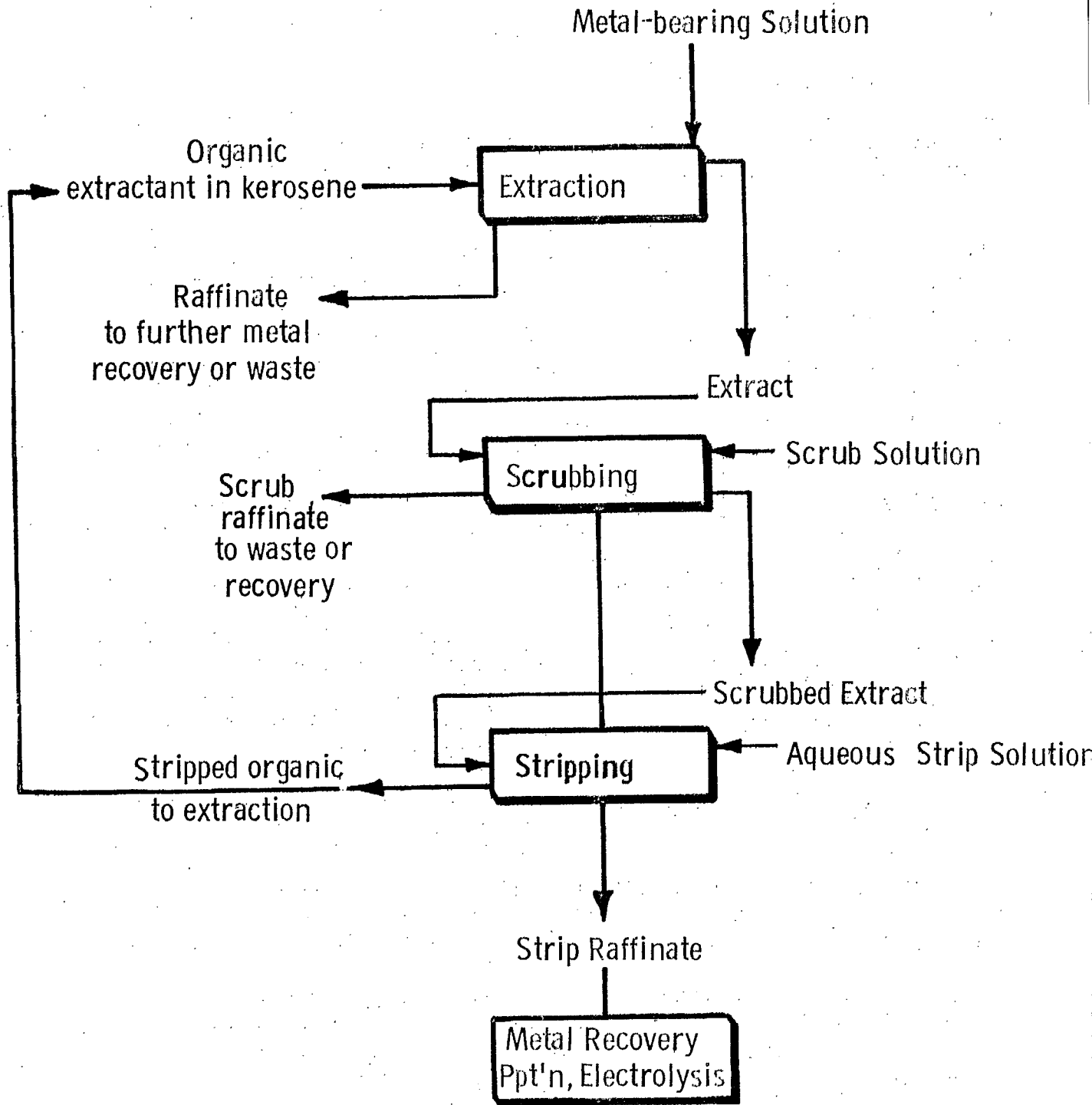Strip Raffinate

Metal Recovery
Ppt'n, Electrolysis

Figure 1 :   Processing by Solvent Extraction

At the present time commercial solvent-extraction plants are in operation, or are planning start-up, for the separation of uranium from vanadium, cobalt from nickel, niobium from tantalum, zirconium from hafnium, and for the purification of copper, uranium, thorium, and the rare earths.

SPECIFIC EXTRACTION SYSTEMS

Nitrogen-containing Extractants

Amines have been the most common of the nitrogen compounds used in the extraction or separation of base metals. The use of amines as extractants dictates the use of an aqueous chloride medium. Quaternary amines have been found to be the most powerful extractants, followed in order by tertiary, secondary, and primary. From sulphate media[2], only ferric iron was found to extract with long-chain amines. The use of long-chain primary amines (C 14, C 15) was successful in the extraction and separation of iron, copper and nickel[3] in a chloride system.

Cobalt, nickel and zinc have been extracted from a chloride medium by using a tertiary or quaternary amine[4,5,6,7]. An 8% solution of tertiary amine, methyl-di-n-octylamine (MDOA), in xylene[8] has been found to separate and extract zinc, in the pH range 2-3 M HCl, from other metals such as Mn, Co, Ni, Cu, Cr. Ferric iron requires reduction to the ferrous state to prevent co-extraction. At a lower pH of 1.8 M HCl, lead may be extracted with a quaternary amine[9].

The separation of cobalt from nickel at concentrations of 6-10 M HCl has been achieved with a 0.1 M solution of a tertiary amine, triisooctylamine (TIOA), in a hydrocarbon diluent[10]. The U.S. Bureau of Mines has demonstrated a successful process[11] for separating cobalt and nickel in the HCl-TIOA-xylene system.

In general, the extraction of cobalt from HCl solution by amines was of the order tertiary > secondary > primary. Nickel extraction was very low in all cases.

In Figure 2 are shown typical extraction curves for the separation of certain base metals from HCl solution, using a tertiary amine, as obtained by Mahlman et al.[8] and Ishimori and Nakamura[12].
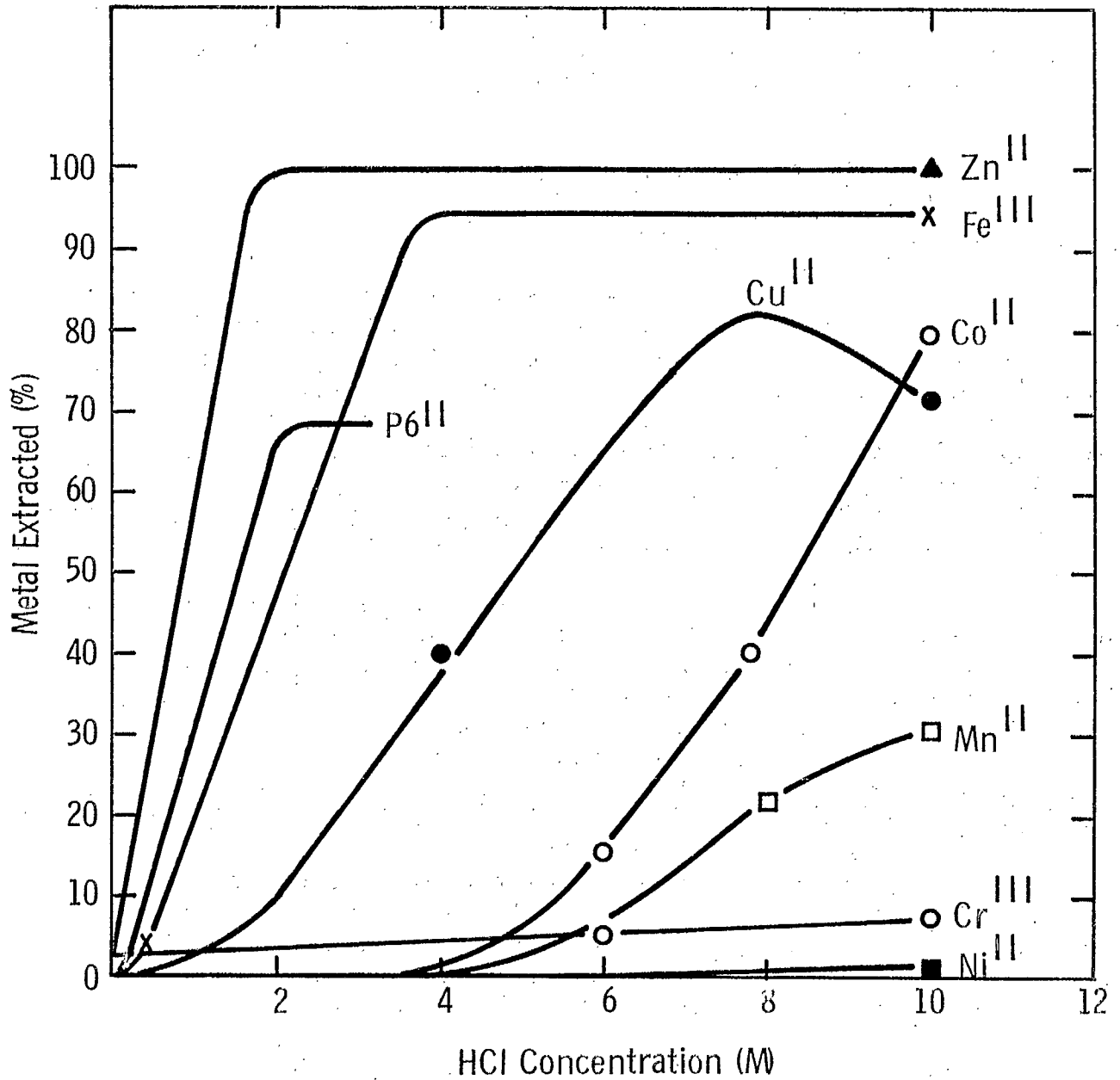
Figure 2: Extraction of Base Metals with a Tertiary Amine in HCl Media
(from Mahlman, Leddicott and Moore[8] and Ishimori and Nakamura[12])

Various nitrogen-containing organic chelating compounds have been used for the extraction of copper from leach liquors. Hydroxyoximes, such as LIX-63 and LIX-64 by General Mills Inc., have been used for the extraction of copper from ammoniacal[13] or sulphuric acid leach solutions[14]. Eldorado Nuclear made use of a mixed solvent of LIX-63 and di-(2-ethylhexyl)phosphoric acid to achieve a synergestic effect for the separation of copper, nickel, and cobalt[15]. Oximes have also been shown to extract small amounts of tin and antimony from cadmium obtained from flue dust and other residues from non-ferrous smelting[16].

Neutral Organophosphorous Compounds

From hydrochloric acid medium, the use of tributyl phosphate (TBP) as an extractant of the base metals appears feasible[12,17,18]. Nickel is not extracted, and ferric iron requires reduction to the ferrous state to prevent co-extraction. Typical results of this system are shown in Figure 3.

Tributyl phosphate, in kerosene or by itself, has been shown to be quite effective for the separation of zinc from cadmium in a hydrochloric acid medium[19], at pH values above 2, as shown in Figure 4. Zinc was recovered from the extract by stripping with water.

Alkylphosphoric Acids

The use of alkylphosphoric acids, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA), for the extraction of the base metals from HNO_3 or HCl solution was reported by Kimura and Lamb[20,21]. The results showed extraction occurring at pH > 2 for Co and Ni, pH > 1.2 for Cd, 0.01 M HCl for Pb, and pH > 0.9 HNO_3 or < 0.01 M HCl for Zn.

A process has been described by Hazen[22] whereby copper and zinc are separated from a H_2SO_4 solution by the use of D2EHPA. The range for extraction of Zn is given as pH 1.5 to 4.0, and that of Cu as pH 2.5 to 3.5.

More recent work has been published by Eldorado on the satisfactory extraction and separation of cobalt and nickel from acid[23] or alkaline[24] solutions, using D2EHPA. In the presence of copper, in an acid system such as H_2SO_4 or HNO_3, it has been found advantageous to mix two organics which individually extract copper and when mixed together cause a shifting in the extraction pH[15]. This synergistic effect is shown in Figure 5. A brief description of the history of the development of the Eldorado
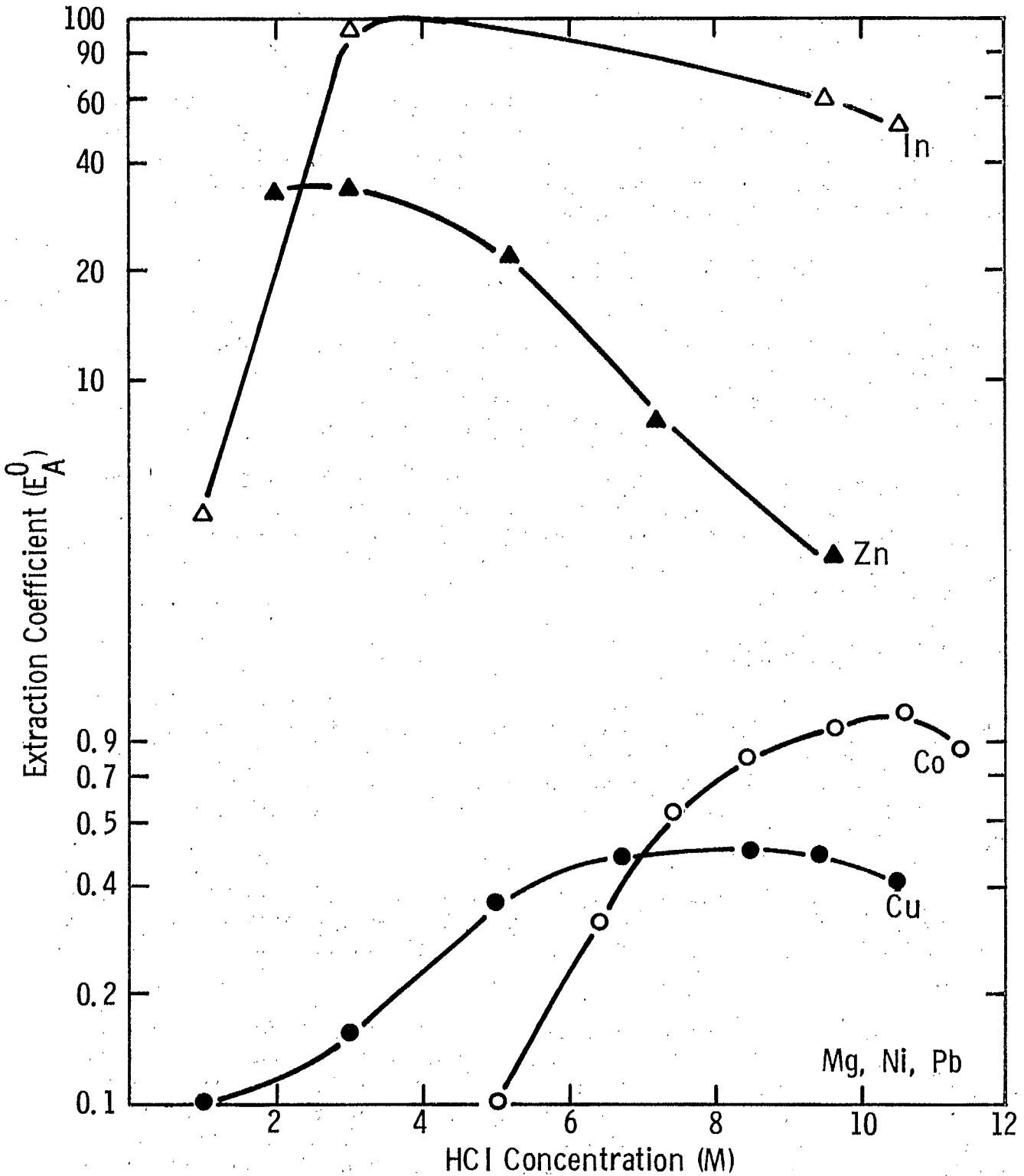
Figure 3. Extraction of base metals with TBP from HCl. (From Irving and Edginton [18])
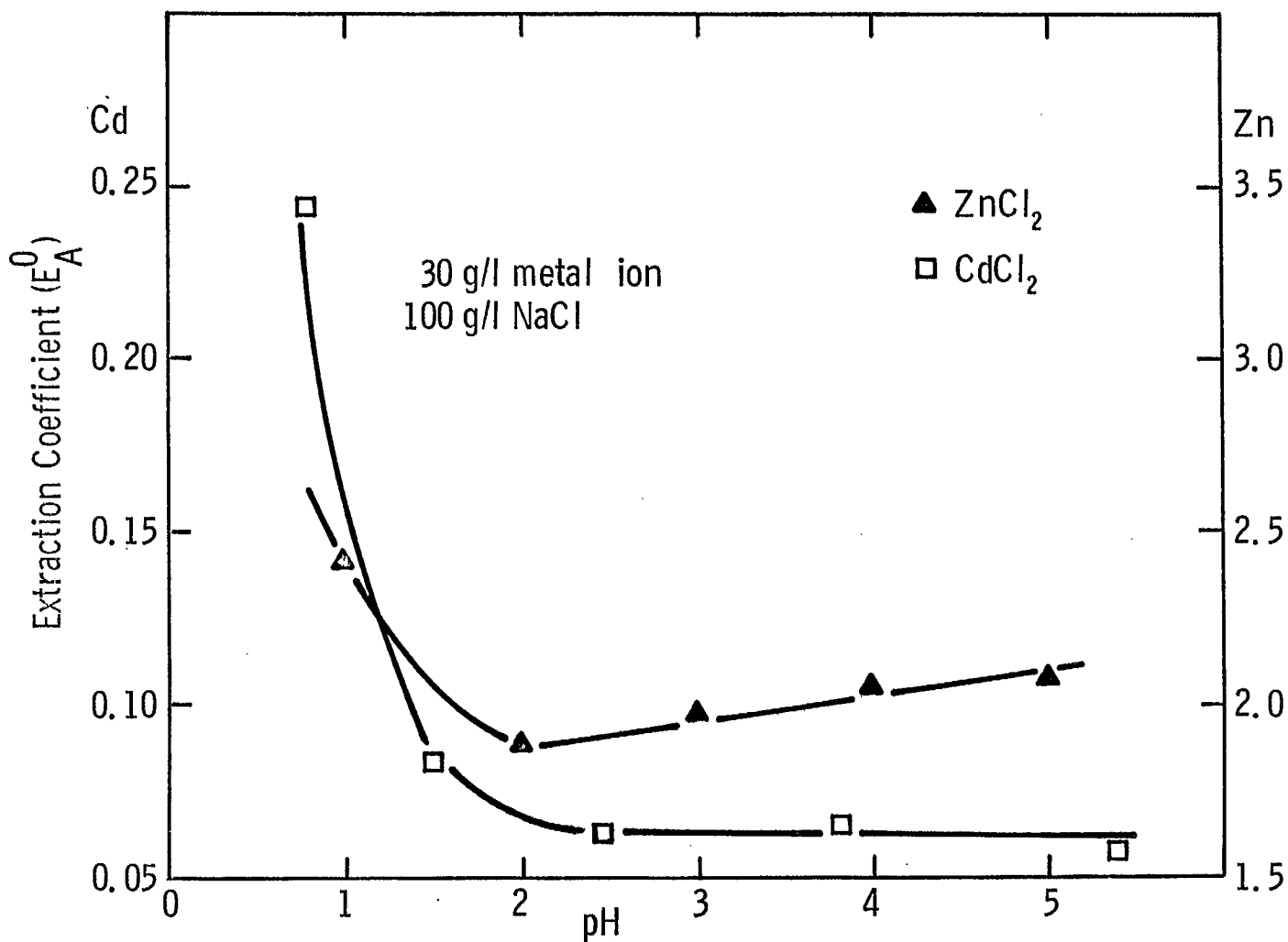
Figure 4.   Separation of Zn and Cd with TBP in HCl media.
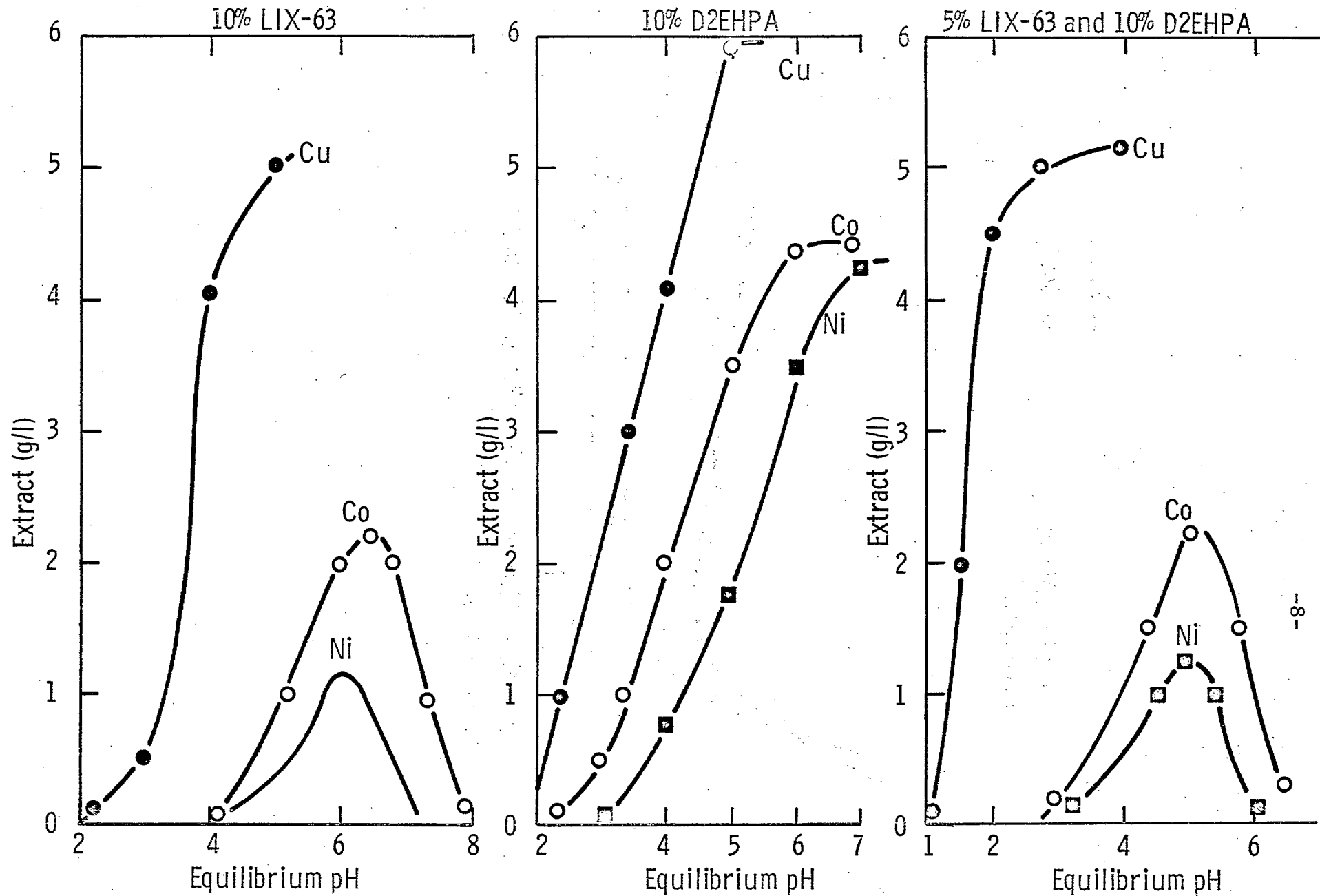(From Fletcher, Flett et al. [19])

Figure 5. Use of mixed extractant for Cu, Ni, Co. (From Joe, Ritcey and Ashbrook [15])

-8-

process has been published, showing the high purity that can be achieved by the use of sieve-plate pulse columns[25] for the extraction and separation of cobalt and nickel.

Figure 6 shows what we might expect for the extraction of the base metals from HNO_3 or H_2SO_4 solutions, using D2EHPA.

Carboxylic Acids

The naphthenic acids are high-molecular-weight carboxylic acids (mol. wt., 165-300). They are perhaps not as specific as the organophosphorous compounds, but they can be used to separate copper, nickel, zinc, iron, cadmium and cobalt from sulphuric acid leach liquors. Maximum extraction of any particular metal occurs at a pH approximately 0.5 below that of the hydroxide precipitation point. The extraction is therefore highly pH-dependent.

Alpha-halo-substituted aliphatic carboxylic acids, e.g. α-bromo lauric acid, extract the required metal at a lower pH, from either sulphate or chloride, which minimizes the risk of hydroxide precipitation prior to extraction[26]. Typical extraction curves are shown in Figure 7.

Naphthenic acid has been shown to be quite effective for the separation of zinc from cadmium in a hydrochloric acid system[27], producing a final raffinate containing a Cd:Zn ratio of better than 10,000:1, at a cadmium recovery of around 99 per cent. Co-extraction of iron and lead may prove to be a problem. Stripping of the extract is accomplished by use of dilute mineral acids. A typical separation curve is shown in Figure 8.

Versatic 911, a tertiary monocarboxylic acid, is a very selective extractant. It has been used successfully in a sulphuric acid leach solution containing iron, copper, nickel, and zinc[28,29,30,31].

A kerosene solution of the highly branched carboxylic acid, Versatic 9, a Shell product, is very suitable for the selective extraction of iron, copper, zinc, cadmium, nickel and cobalt from the aqueous solution of their sulphuric acid salts[32]. By use of a gradual neutralization technique with NaOH, Na_2CO_3, or NH_4OH, iron can be separated between pH 2 and 2.6, copper between pH 3.6 and 4.7, and zinc between pH 4.7 and 5.6. Nickel and cobalt are co-extracted between pH 5.5 and 6.5. The typical results are shown in Figure 9.

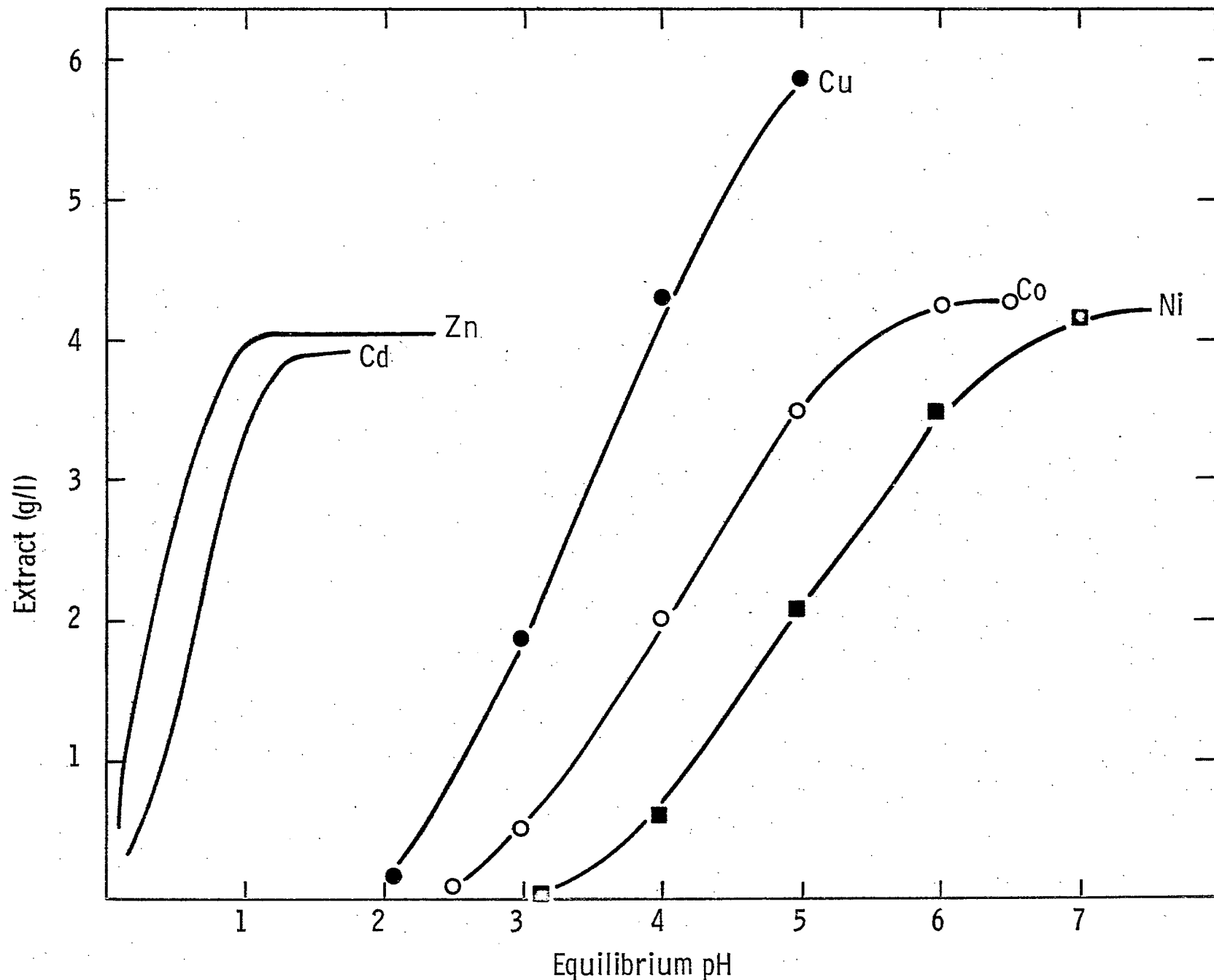Figure 6. Extraction with D2EHPA. (From Kimura [20], Hazen and Hendrickson [22], and Ritcey and Ashbrook [23])
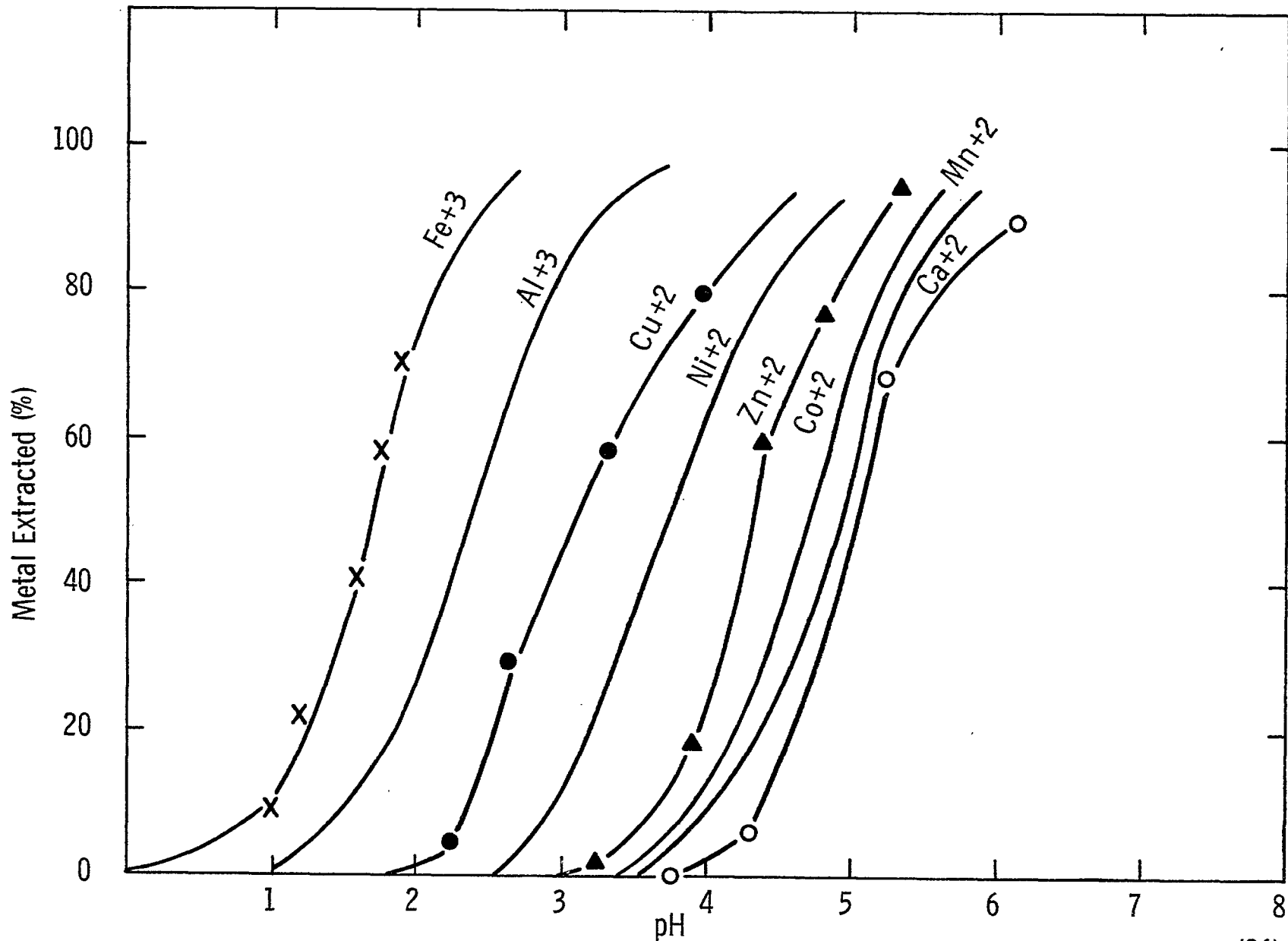
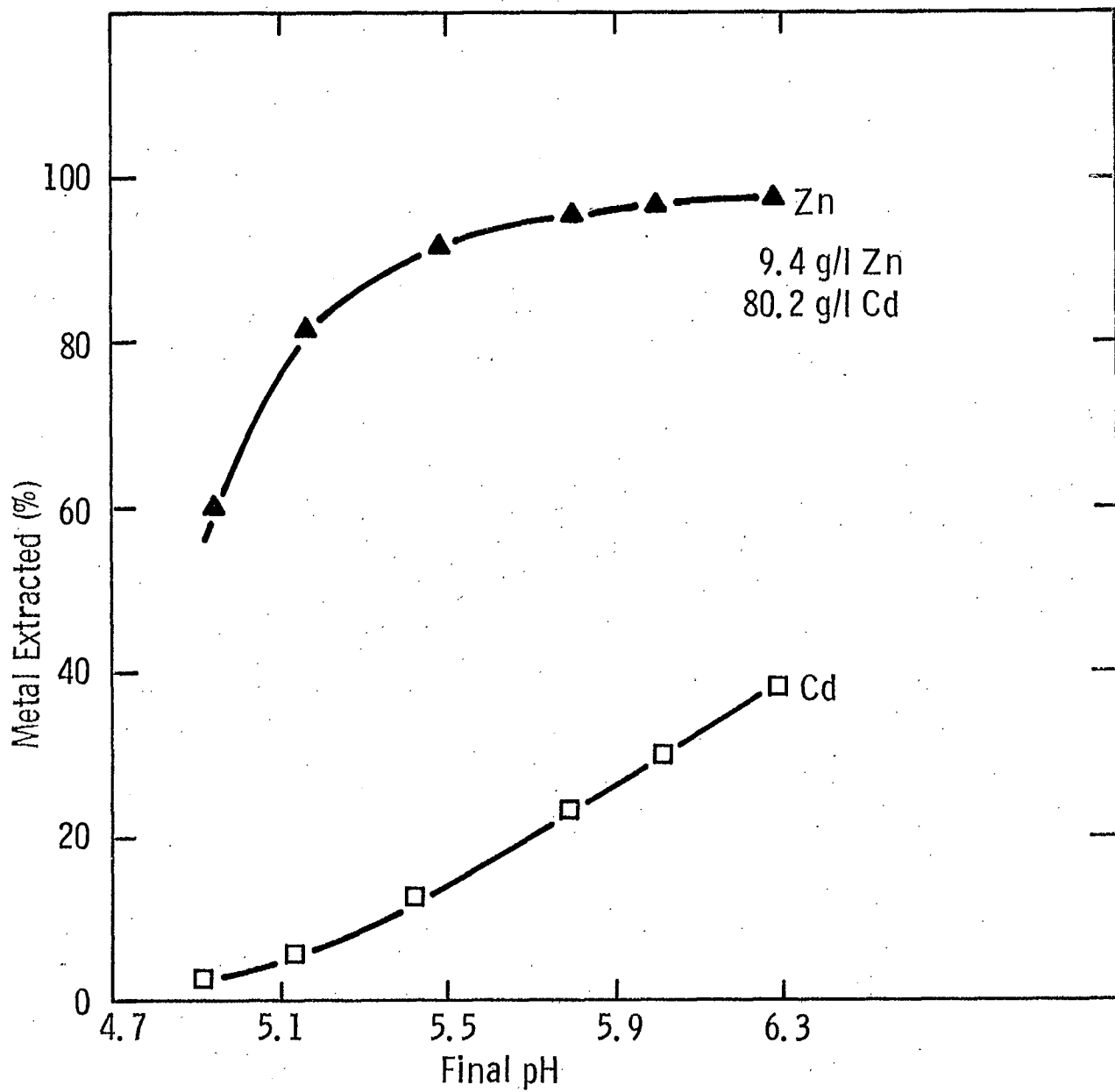Figure 7. Extraction of metals using -bromo lauric acid. (From Blumberg and Melzer [26])

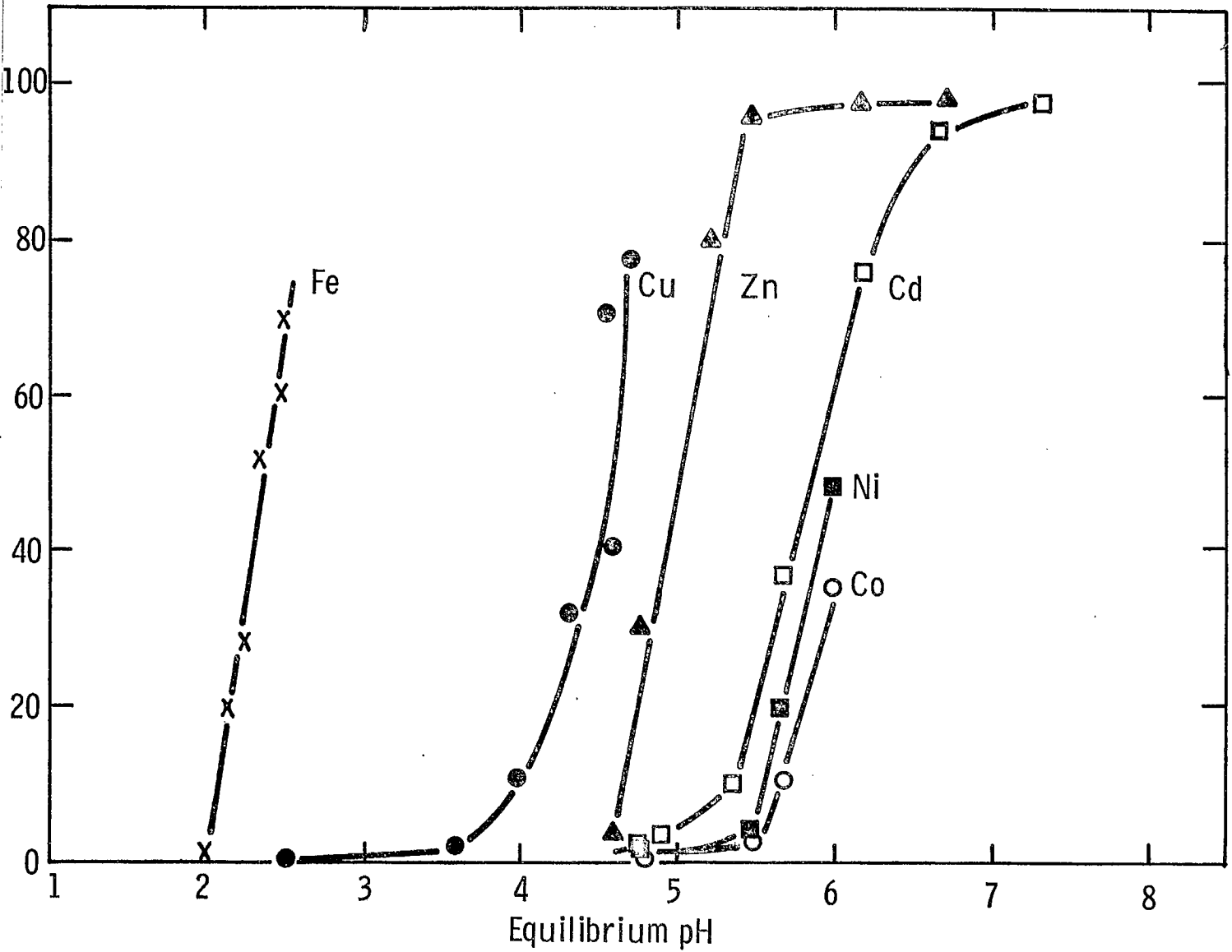Figure 8. Separation of Zn from Cd, using naphthenic acid. (From Fletcher, Flett et al. [27])

Figure 9.   Extraction of Fe, Cu, Zn, Ni and Co with Versatic 9.
(From Spitzer, Radder and Muys [32])

Metallic Soaps and Surface-active Agents

Metallic soaps of fatty acids (C_7-C_{13}) diluted in kerosene have been used to extract the heavy metals. The extraction is by displacement whereby the metal in the aqueous solution displaces the metal in the fatty-acid soap. The more basic metals concentrate in the aqueous phase, and the less basic metals in the organic phase. About 99% pure cobalt can be obtained by soap extraction of cobalt from solutions of anode slimes containing nickel and cobalt[33,34,35]. The order in which the metals extract is shown in Table 1, and some separation factors for selected metal pairs are shown in Table 2. In Figure 10 is shown the relationship between the equilibrium pH of the aqueous solution and the extraction coefficients (E_A^O) of Pb, Cu, Cd, Zn, Ni and Co in H_2SO_4, HCl or HNO_3 solutions.

Surface-active agents are potential extractants of the base metals[36]. A variety of these agents have been studied, including polypropylene glycols and high-molecular-weight sulphonic acids. For example, dinonylnaphthalene sulphonic acid co-extracts cobalt and nickel selectively from sulphate-leach liquors containing other metals[37,38].

Miscellaneous Reagents

Alcohols and ketones, such as 2-octanol, capryl alcohol, or methyl iso-butyl ketone (MIBK), can be used to separate chemically similar metals. The octanols exhibit selectivity in the separation of cadmium from zinc[39], and also of cobalt and nickel from chloride[40] and sulphate[41] systems. Separation factors were very low in the sulphate system, of the order of 1.5 between Co and Ni. The extraction coefficients of Co, Ni and Fe sulphates with n-butyl alcohol were similar and small; the results shown in Figure 11 indicate that the separation of the metal sulphates with alcohols is difficult and that the aid of other factors, such as complexing agents, would be required. The methyl iso-butyl ketone (MIBK) shows selectivity for the extraction of some metals. For example, the separation factor between cobalt and nickel thiocyanates with MIBK is as high as 390,000[42]; and the separation of zinc and cadmium has also been reported[43].

The main disadvantage of both the alcohol and the ketone systems for use in the extraction of metals from dilute solutions is their high water solubility.

TABLE 1

Order of Extraction of Metals into Metallic Soaps*
(From Bobikov and Gindin[34])

IV		III		III		II		III		II		II		II		II		II		II		II>		II		I
Sn	>	Bi	>	Fe	>	Pb	>	Al	>	Cu	>	Cd	>	Zn	>	Ni	>	Co	>	Mn	>	Ca	>	Mg	>	Na

In this series the most alkaline metal is sodium and the most acid is tin.

*Metallic soap is a salt of a fatty acid.

TABLE 2

Separation Factors for Some Metal Pairs
Using Metallic Soaps

(From Bobikov and Ginden[34])

Pairs of Metals	Separation Factor	Comments
$Ni^{II} - Co^{II}$	1.8	The separation factor is
$Zn^{II} - Co^{II}$	5.0	practically a constant value
$Cd^{II} - Co^{II}$	35.0	for the entire range of
$Co^{II} - Mn^{II}$	1.4	concentrations.
$Cu^{II} - Co^{II}$	100-500	The separation factor is a
$Fe^{III} - Co^{II}$	> 10,000	variable and a function of the
$Co^{II} - Na^{I}$	100-200	concentrations.

Separation Factor = the ratio of the relative extraction
coefficients (E_A^O)

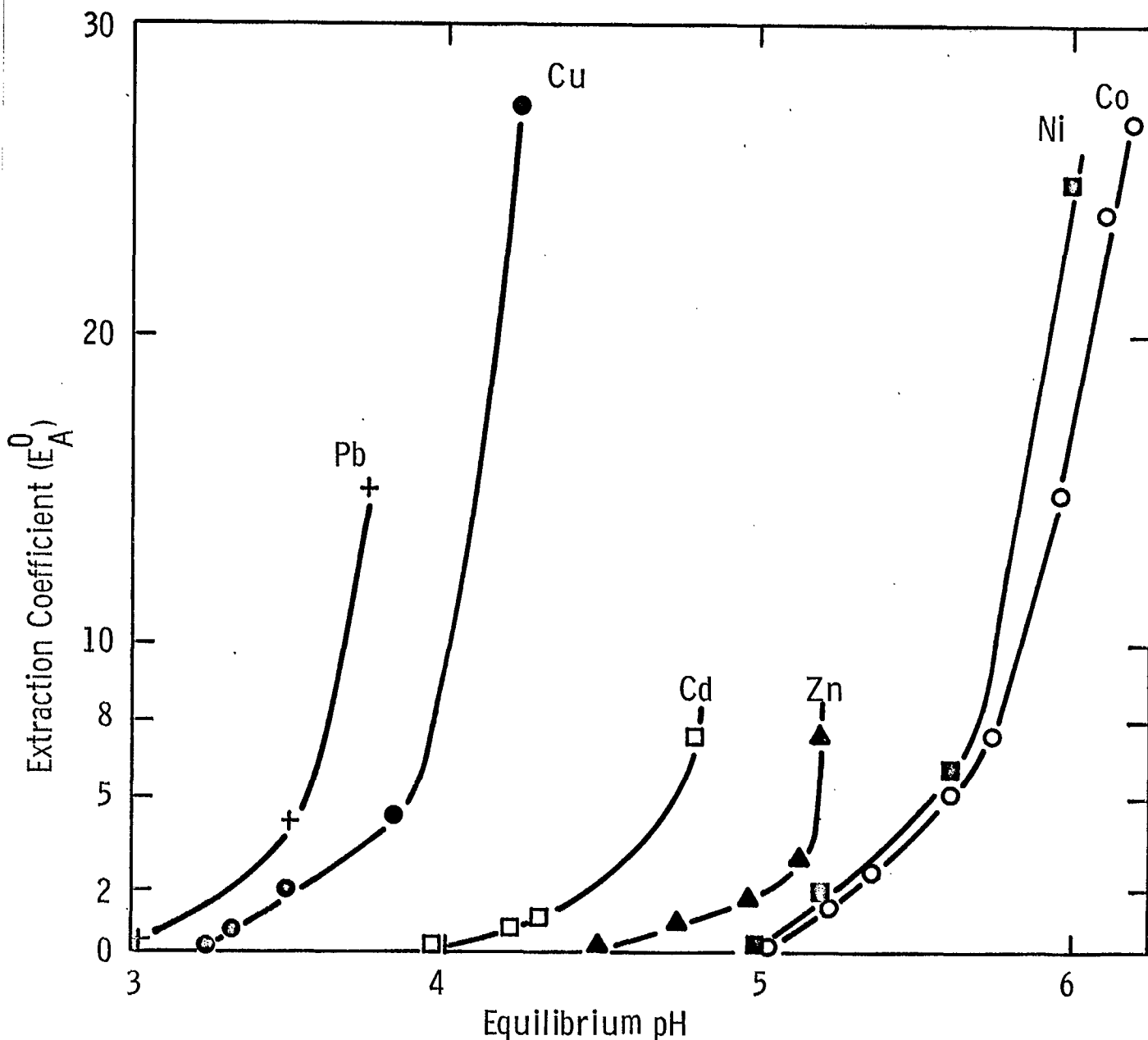$$E_A^O = \frac{conc.\ organic}{conc.\ aqueous}$$

Figure 10. Extraction of base metals with metallic soaps from chloride, sulphate or nitrate solutions. (From Gindin, Bobikov, Kouba, Bugaeva [33])
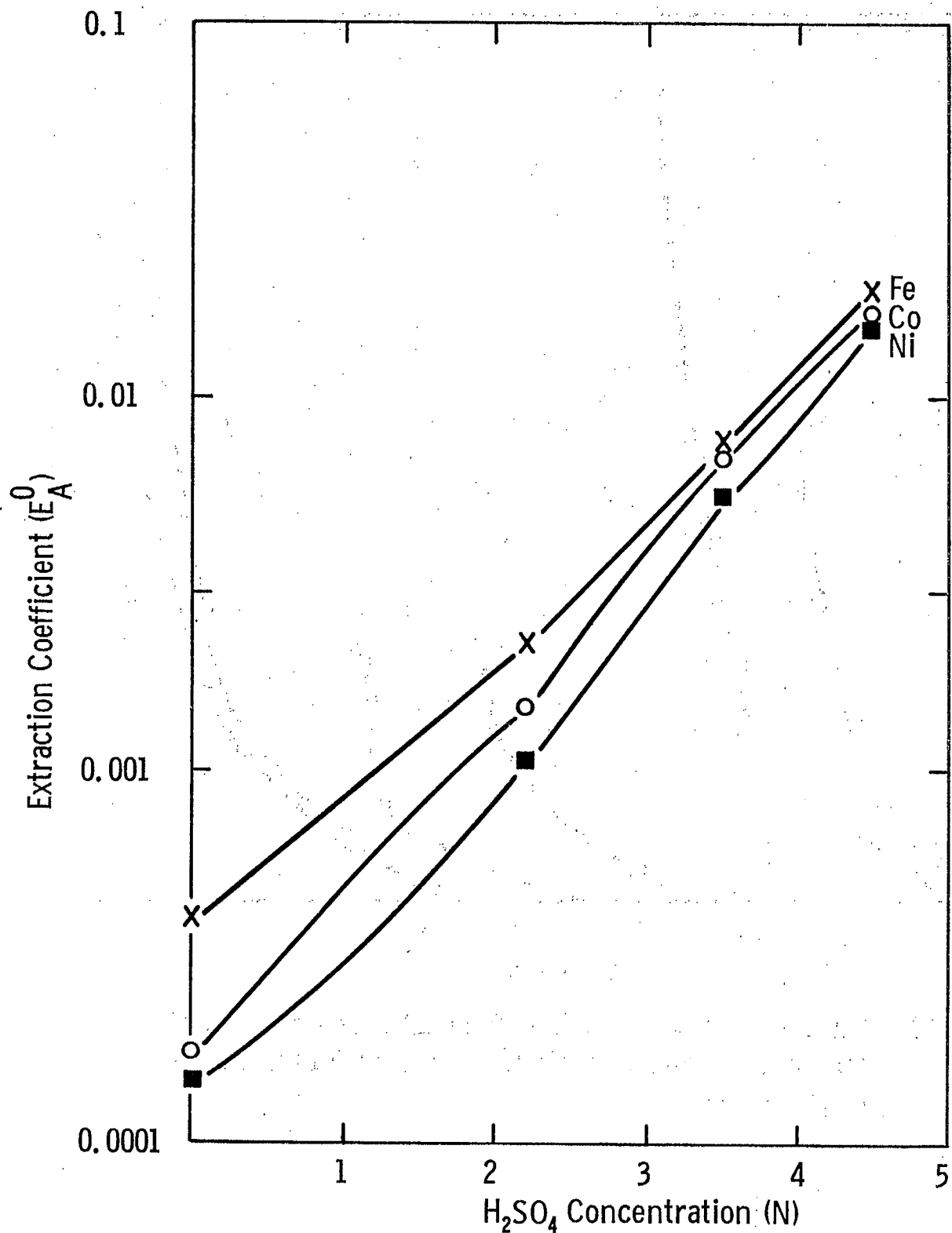
Figure 11.   Use of butyl alcohol from H_2SO_4 media.   (From Schlea and Geankoplis [41])

Sulphonium compounds based on dialkyl sulphides are useful extracting agents for selective separation of cobalt from nickel[44]. The best results were obtained with 0.4 M solution of di-n-octylmethylsulphonium chloride in 1.2-dichloroethane. This mixture extracted 99% of the cobalt from a 6 N HCl medium. About 0.5% of the nickel was co-extracted. Removal of the cobalt from the extract is accomplished by water-stripping the sulphonium chloride complex. Typical extraction curves for this system are shown in Figure 12. The sulphonium chlorides are insoluble, however, in the commoner diluents, and require chlorinated solvents.

EQUIPMENT

The mass transfer of the desired metal from one phase to the other phase is accomplished by the use of various types of equipment in which the aqueous phase is flowing countercurrent to the organic stream. This equipment can be classified as either stagewise or differential contactors. In the stagewise contactor, such as a mixer-settler, the two immiscible phases are mixed and then are allowed to separate or disengage, because of their difference in density, in a separate settling chamber. These settlers are often very large, making the over-all units bulky and occupying a large plant area. However, they are relatively inexpensive, and ideal where a small number of stages (1-2) are required.

Differential contactors, such as columns or centrifuges, are more compact for a given throughput and therefore require less floor area in the plant. These columns, whether packed, pulsed or rotating-disc units, provide continuous contacting and therefore many mixing, settling or coalescing stages. To achieve a shorter contact time, the centrifugal force applied in a centrifugal contactor produces countercurrent flow and accelerates the phase separation.

The choice of the proper contactor for any particular solvent-extraction system will be dictated by the following: First, the special physical-chemical requirements must be satisfied, such as contact time, settling characteristics, floor area, or head room. Next, the number of contact stages and the desired throughput must be considered, as well as the increasing cost of maintenance as the contactor becomes more complex. Finally, the contactor having the lowest cost and highest suitability for the specific extraction operation must be ascertained.
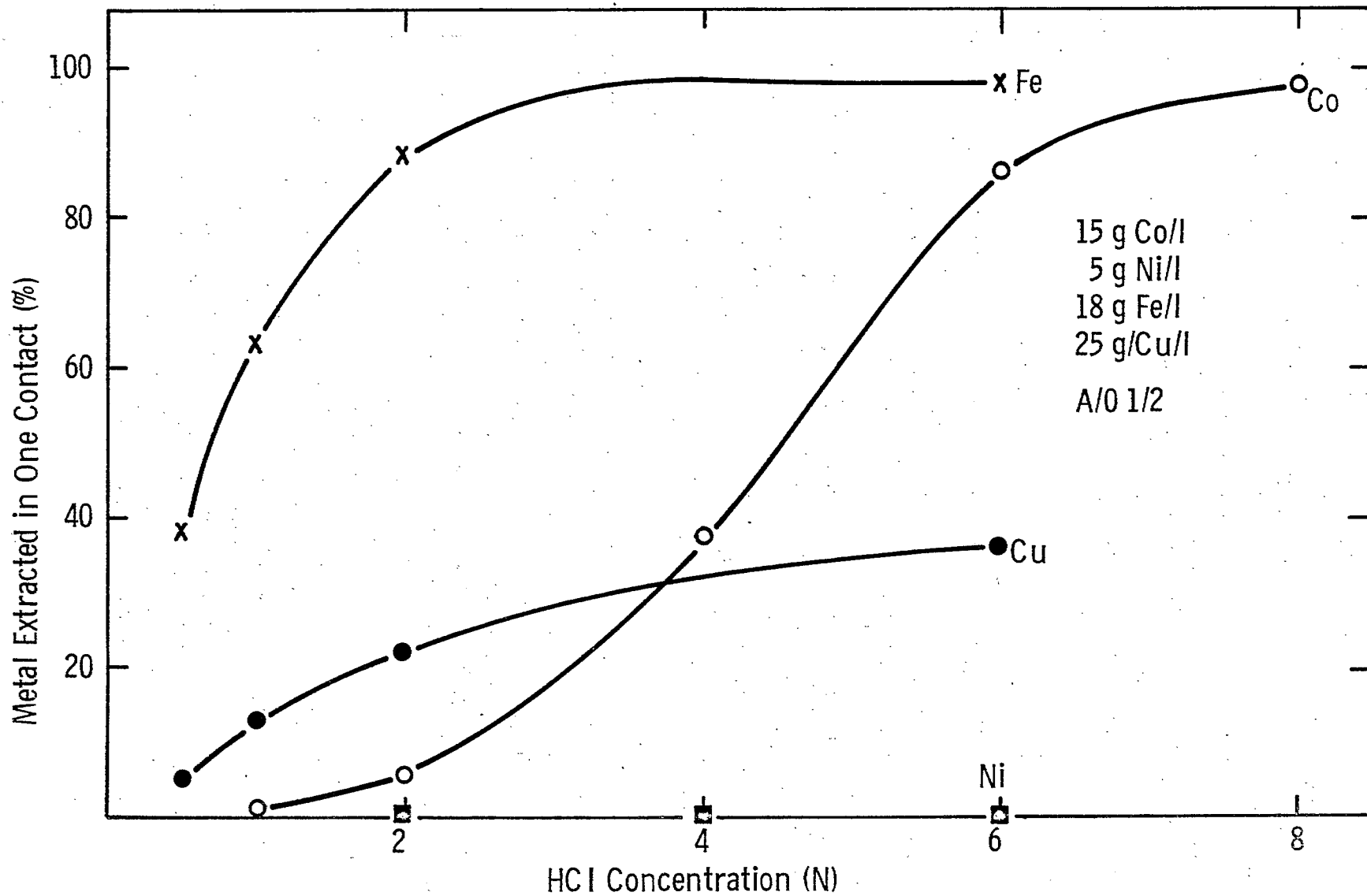
Figure 12.   Extraction of metals, using trialkylsulphonium chlorides, 0.4 M di-n-octyl methyl sulphonium chloride.   (From Spitzer and Radder [44])

ECONOMIC CONSIDERATIONS

Two fields of metals recovery in which solvent extraction will likely find increased applicability are: (1) the recovery of metals from process effluents, from dump (or heap) leaching, and from mine waters, in those cases where ore-processing costs have not been significant; (2) the treatment of complex ores containing a variety of the base metals, some of which are lost or only partly recovered in the conventional flotation-pyrometallurgical processing.

In solvent extraction, as in other hydrometallurgical operations, the economic factor is important. The values of the metals considered for recovery must be compared against the cost of extraction. At the present, one criterion is that if a metal is of less value than copper, recovery by solvent extraction will not be economic. However, for the purification of aqueous electrolytes in the base-metal operations, which is a by-product process, not involving the primary recovery circuit, other metals of less value than copper may be considered economic.

Any successful solvent-extraction process depends upon the selection of inexpensive extractants which can operate at the natural condition of the solution, with minimum loss of the organic phase to the aqueous solution. Also, a cheap means of recovery of the metal from the organic extract is necessary. In some cases, the cost of neutralization of the feed solution prior to solvent-extraction processing, and/or the cost of maintaining a buffered pH during extraction, may prove to be excessive when coupled with solvent losses.

In a general review of the costs of industrial solvent-extraction processes in the United Kingdom, Warner[45] has suggested the following as ranges of magnitude, per ton of metal processed. (The precise figures obviously depend on the scale of the operation, the concentration of the metal in the feed solution being treated, the metal recovered and organic system used, and the type of extraction equipment employed.)

(a) Capital cost of equipment .... $ 6 - 140

(b) Solvent losses .... $ 3 - 30

(c) Solution preparation for solvent
extraction; e.g., pH adjustment,
use of complexing agents, etc. ..... $85 - 335

Although these ranges are wide, they emphasize the importance of the feed-solution preparation for solvent extraction. If the extraction can be carried out at the natural leach acidity, obviously this cost will be minimal.

An estimate of the operating cost, including solvent loss, electricity, and chemicals, for the solvent extraction of copper from dump-leach solutions, using LIX-64, is given as $70 per ton of metal produced[46]. In a plant that is producing 60,000 pounds of copper per day, the operating costs for solvent extraction and electrowinning have been calculated to be about 7 cents per pound of copper produced[47].

SUMMARY

The extraction systems discussed in this review all offer possibilities for the separation of base metals. Certain systems have possible disadvantages, however, which may be noted here.

The use of amines or tributyl phosphate dictates the use of chloride aqueous media and the prior conversion of the ferric iron to the ferrous state.

Alkylphosphoric acids are probably the most versatile organic extractants with respect to the acid systems that can be tolerated. Here again, iron requires conversion to the ferrous state, or prior removal.

One possible drawback to the use of some of the carboxylic acids is the relatively high solubility of some of these reagents in the aqueous solution.

With respect to the use of the soaps of the fatty acids, the literature is rather vague on the solubility in the aqueous medium but the impression gained is that the reagent solubility is low.

When the alcohol extraction system is used, the separation factors for metal pairs are comparatively low, whereas in the ketone system the separation factor is high. Both systems have high organic solubility in the aqueous medium. The use of sulphonium chloride compounds necessitates the use of chlorinated diluents, such as 1.2-dichloroethane.

CONCLUSIONS

The successful introduction of solvent extraction to any base-metal operation will depend on a number of considerations. In all cases, the advantages of a solvent-extraction process lie in the possibilities of concentrating initially dilute values, of purification, and of separation of metals.

Metals such as copper can be concentrated from dilute process streams and heap-leaching solutions. Purification and concentration of a metal from leach liquors for electroprocessing may lead to the direct production of the metal in a high state of purity. The recovery and purification of metals from the leaching of complex ores is made feasible by the use of solvent extraction.

In general, processing is simple, so that operating costs of solvent extraction will be low in comparison with the total processing cost per unit of metal produced. If the extraction is carried out near the natural acidity of the leach-feed solution, the main potential contributor to costs is the loss of organic reagent. With a properly chosen extraction system, the solubility of the organic phase in the aqueous phase is usually very low. Naturally, mechanical losses must be kept to a minimum by proper selection of equipment and operating conditions. The economics of applying solvent extraction cannot be generalized, and particular circumstances must be considered in every potential application.

This review has shown that there are several organic reagents available for the solvent-extraction separation of the base metals. The producers of these chemical reagents have the ability and willingness to design a specific reagent for a particular recovery application when sufficient interest is shown in a system.

GLOSSARY OF SOME TERMS

Contactor - Device for dispersing and disengaging immiscible
solutions; extractor. May be single stage, as in a mixer-
settler, or multiple stage, as in columns and certain centrifuges.

Countercurrent extraction - Multistage extraction in which the
aqueous and organic solutions flow in opposite directions.

Diluent - Inert organic solvent in which an active organic
extractant is dissolved.

Extraction or distribution coefficient - Extraction coefficient,
E_A^O, or stripping coefficient, S_O^A, representing the ratio of
metal solute concentrations after contacting (equilibrating) an
aqueous and organic solution under defined conditions.

Extraction or distribution isotherm - Graphical representation of
isothermal equilibrium concentrations of a metal solute, in
aqueous and organic solutions, over an ordered range of conditions
in extraction (extraction isotherm) or stripping (stripping
isotherm)..

Extract - Organic phase after extraction (loaded solvent), or
aqueous phase after stripping (loaded strip liquor); the
solution into which transfer of a metal solute is effected;
used as a verb to describe transfer of a metal solute between
two immiscible liquids.

Extractant - Organic solution or the active organic solute.

Loaded organic - Organic solvent containing metal solute after
contacting the aqueous feed liquor; the extract.

Loading capacity - Saturation limit of metal solute in organic or
strip liquor.

Mixed solvent - Solution of more than one organic extractant in
an organic solvent or in miscible organic solvents.

Mixer-settler - Device for liquid-liquid extraction, comprising
separate mixing and settling compartments.

Modifying agent - Substance added to an organic solution to
increase the solubility of the extractant, or of salts of the
extractant that form during extraction or stripping.

Pulse column - Multistage contactor comprised of a column usually
   containing parallel, horizontal, perforated plates (disks)
   through which the aqueous and organic feed streams are advanced
   countercurrently by a pulsing motion.

Raffinate - The liquid phase from which solute has been removed
   by single- or multiple-stage contacting with an immiscible
   solvent.

Reextraction - Same as stripping; back extraction.

Scrub - Selective removal of a contaminating metal or other
   solute before or after stripping the loaded organic extractant;
   also, removal of solvent-degradation products, usually after
   stripping.

Separation factor - Ratio of the extraction coefficients of two
   metals being compared.

Settling - Separation of dispersed immiscible liquids by coalescence
   and sedimentation.

Solvent - In liquid-liquid extraction, the liquid phase that
   preferentially dissolves the extractable solute from the feed.
   The term is often used to describe the organic phase.

Solvent extraction - Separation of one or more metallic solutes,
   from a mixture, by mass transfer between immiscible phases in
   which at least one phase is an organic liquid.

Stage - Single contact (dispersion and disengagement); sometimes
   refers to a theoretical stage which is a contact that attains
   equilibrium conditions.

Stripping - Removal of extracted metal solute from loaded organic
   extract; re-extraction; back extraction. Selective stripping
   refers to separate removal of specific metal solutes from an
   extract containing more than one metal solute.

Synergism - Co-operative effect of two or more extractants that
   exceeds the sum of the individual effects.

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