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Solvent Extraction, Membranes, and Ion Exchange in Hydrometallurgical Dilute Metals Separation

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Solvent Extraction, Membranes, and Ion Exchange in Hydrometallurgical Dilute Metals Separation

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ABSTRACT

The separation methods which are used in the hydrometallurgical field are reviewed and compared. Some processes in solvent extraction in use for recovery of crucial metals which are important to the U.S. defense and economy are presented. Various commercial extractants are reviewed and categorized. Other methods such as liquid membranes and ion exchange resins used for dilute metal ions separation are summarized. These methods are compared with solvent extraction. Problems to overcome in the further development of these separation methods are also identified and discussed in this paper.

STATUS OF SOLVENT EXTRACTION IN DILUTE METALS RECOVERY IN HYDROMETALLURGICAL PROCESSES

Both pyrometallurgy and hydrometallurgy have been used for extracting metals from ores. Pyrometallurgy consists of processes with elevated temperatures, such as roasting, smelting, converting and refining. This method deals with process streams that are concentrated with respect to metal content. However, hydrometallurgy consists of a combination of chemical unit processes such as leaching, solvent extraction, precipitation and electrowinning. This method usually deals with far less concentrated process streams. Some metals, such as aluminum, uranium, gold, cobalt and cadmium can be produced only through the application of hydrometallurgy. Recently, due to depletion of high grade ore reserves, environmental legislation and

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political factors, increasingly significant proportions of metals production are obtained through hydrometallurgy. Examples include copper, zinc, nickel, tungsten, molybdenum, vanadium, rare earths and platinum group metals (1).

In hydrometallurgy, the leaching process is always followed by a separation process to selectively remove components from the mixture. Precipitation has been used extensively to refine multicomponent solutions. One well-known process is the Sherrit-Gordon process which produces nickel and cobalt from mixed sulfide ores. This method is carried out in a series of batch reactions. Another separation (or purification) method commonly used for copper, nickel, zinc, cobalt, uranium and rare earth elements is solvent extraction. This process is continuous. The theory behind the process is well-known. Simply, the transfer of metals depends on extraction with simultaneous chemical reaction. The reaction is reversible, and therefore solvent recovery can be accomplished by changing the chemical conditions. The development of solvent extraction processes along with novel extractants has aroused significant attention both from academy and industry in the past four decades and has resulted in processing of nuclear fuel, transition metals, and conventional non-ferrous metals. The most successful and commercially available processes are copper and uranium extraction. Table 1 shows a list of some of the many plants using this solvent extraction technique to recover such metals as uranium, thorium, lanthanides, copper, nickel, cobalt, zirconium, hafnium, platinum group metals, molybdenium, tungsten, niobium, tantalum, beryllium, boron, and possibly some of the rare metals not shown here.

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APPLICATION OF SOLVENT EXTRACTION TO CRUCIAL METALS

Crucial Metals for the US Defense and Economy

The military and economic strength of the US is dependent to a large degree upon importation of metals not only from one of the most unstable regions, Southern Africa, but also from communist bloc countries. Table 2 shows the key minerals being imported from foreign countries. Congress's office of Technology Assessment (5) underscores four minerals - chromium, cobalt, manganese, and the platinum-group metals - as being critical to America's defense program. All four come primarily from South Africa, Zaire, and the Soviet Union. Chromium, manganese and cobalt are used in high strength alloys vital to the manufacture of engines and parts of aircraft and missiles. Platinum is needed in a wide range of chemical processes. The Bureau of Mines identifies the other imported metals used in making technologically advanced equipment that America sells around the world.

Thus it becomes imperative that the United States develop the technology, regardless of cost, to produce these crucial metals with nationally based ores or resources in politically aligned nations.

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Table 1

Some Plants Using Solvent Extraction (2-4)

Metal(s) Recovered	Plant	Type of Feed	Extractant	Comments
Au	Inco, U.K.	Chloride-Nitrate	dibutyl carbitol	Batch process. Operation since 1971. Oxalic reduction to recover Au
B	American Potash and Chemical	Low grade brines	polyol	
Be	Brush Beryllium; Vitro Minerals and Chem. Co.		organo-phosphate	10 tpd pilot plant
Co, Ni	Gullspang Electrochemical Co., Sweden	chloride	tertiary amine	Control of chloride conc. for separation
	Inco, Canada	sulfate	D2EHPA	Separation from Ni in new refinery at Sudbury (1974), Mixco Columns
Co	Matthew Rustenburg Refiners, Ltd. South Africa	sulfate	D2EHPA	0.5 tpd
Co, Ni	Nippon Mining Co., Japan	chloride	alkyl phosphoric acid monoalkyl ester	Ni - 10 tpd Co - 3 tpd
	Sumitomo Mining Co., Japan	sulfate	versatic 10	Ni - 7 tpd Co - 4 tpd
Cu	Ranchers Bluebird, Arizona	sulfate	LIX 64N	First copper plant, 20 tpd
	Bagdad Copper, Arizona	sulfate	LIX 64N	20 tpd
	Nchanga Consolidated, Zambia	sulfate	LIX 64N	200 tpd
	Anamax, Arizona	sulfate	LIX 64N	100 tpd
	Anaconda, Montana	ammonia leach liquor	LIX 64N	100 tpd
	Cerro Verde, Peru	sulfate	LIX 64N	90 tpd
	Kennecott Corp., Arizona	sulfate	Alcorga P5100	110 tpd
Cu, Ni	SEC Corp., Texas	sulfate	LIX 64N	Ext'n of Cu at low pH Ext'n of Ni at pH 8

(CONTINUED)

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Table 1 (Continued)

Metal(s) Recovered	Plant	Type of Feed	Extractant	Comments
Cu, Co, Fe	Falconbridge Nickel, Kristiansand, Norway	chloride	TBP, tertiary amine	Fe ext'd with TBP. Cu + Co separated from Ni with amine
Nb	Wah Chang, U.S.		MIBK	Use pulsed columns, MIBK
	Mallinckrodt, U.S.	H_2SO_4-HF	MIBK	
	Murex, U.K.		MIBK	Mixer settlers
	Mitsui Mining and Smelting, Japan		MIBK	Pulsed columns
	Metallugie Hoboken, Belgium		MIBK	
	Herman Starek, Germany		MIBK	
Rare Earths	Thorium Ltd., U.K.	nitrate	versatic 911	Separation of individual rare earths
	Rare Earth Products Ltd., U.K.			Thorium Ltd. - Johnson Matthey joint venture
	Denison Mines, Canada	sulfate waste effluent from U process	D2EHPA	Podbielniak contactor for extraction and stripping
	Molybcorp, U.S.	HCl leach of bastnasite	D2EHPA	Mixer settlers, several individual rare earths
	Japan Yttrium Co., Japan			Use process licensed from Thorium Ltd.
V	Total of 11 plants in U.S. reported	Some U-V Carnotite leach	Tertiary amine, quat. amines, or alkyl phosphates	Equipment - mixer settlers and *Podbielniak* contactor
W	At least 3 plants reported in U.S.		Tertiary amines	

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Zr, Hf	Amax Corp., U.S.	H_2SO_4 - SCN	MIBK	Zr remains in the raffinate
	Wah Chang Corp., U.S.	H_2SO_4 - SCN	MIBK	Zr remains in the raffinate
	Eldorado Nuclear, Canada	nitrate	TBP	Hafnium remains in raffinate. Mixco columns
U	Refineries in Canada, U.S., U.K., Sweden, France, Japan,	nitrate	TBP	Essentially the same process with slight modifications.
	Numerous plants in U.S., South Africa, France, Sweden Australia	sulfate	Amines, D2EHPA	Amex, Dapex, Bufflex, Purlex, and Eluex used
	Numerous Reprocessing plants in U.S., U.K., France, Belgium, Japan, Italy, Germany, India, Spain, Norway, Sweden		TBP, Tertiary amine	Mixer settlers, or pulsed columns in use
	Freeport Uranium Recovery Co., Louisiana, U.S.	phosphate rock	D2EHPA - TOPO	1.5 tpd
	IMC Corp., Florida U.S.	phosphate rock	D2EHPA - TOPO	0.8 tpd
Zn	Bilbao Plant, Spain	chloride	D2EHPA	22 tpd

Table 2

Key Minerals for America's Defense and Military (5)

Key Metals	Export Countries [a]	Net imports as a % of consumption		Application
		1974	1984 [b]	
Chromium	South Africa Zimbabwe Soviet Union	90%	82%	alloys for springs, bearings, tools, engines
Manganese	South Africa Gabon France	98%	99%	alloys for impact-resistant steel, dry-cell batteries, chemicals
Cobalt	Zaire Zambia Canada	99%	95%	alloys for tool bits, high strength steel, aircraft engine
Platinum	South Africa Britain Soviet Union	87%	91%	oil refining, telecommunication, chemical processing and dental equipment
Vanadium	South Africa Canada Finland	36%	41%	iron and steel alloys, titanium alloys
Tin	Thailand Malasia Indonesia	84%	79%	cans and containers, electrical products, construction, transportation
Tantalum	Thailand Malasia Brazil	87%	94%	nuclear reactors, aircraft parts, surgical instruments
Columbium (Niobium)	Brazil Canada Thailand	100%	100%	used in high-strength alloys for construction, jet engines, machine tools

[a] Major foreign supplies are listed in descending order of the amount they exported to the U.S. from 1980 to 1983.

[b] 1984 figures are estimated.

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Solvent Extraction Processes for Crucial Metals

Cobalt/Nickel. Numerous solvent extractants for nickel and cobalt extraction are available such as amines, oximes, ketones, aldehydes, carboxylic acids or derivatives, cyanic acids or derivatives, organic agents containing sulphur, alcohols, phenols, naphthols, quinoline derivatives, other heterocyclic derivatives, and organophosphorous or organoboron compounds as recently reported by Jacobs *et al*. (6). It has been discovered that aqueous solutions of nickel and/or cobalts can be successfully concentrated up to their solubility by a solvent extraction process involving the use of an alkyl phosphoric acid followed by stripping with acid to form a highly concentrated solution of the salts of these metals. This process has been particularly advantageous in that iron present in the ferric state in dilute aqueous solution can first be removed with the same solvent extraction (6). Variations of the phosphorus-type extractants have shown an increasing selectivity for Co/Ni separation with change from phosphoric-phosphonic-phosphinic. However, with the increase in separation factor (by rejecting nickel), the kinetics also decreases (7). Tertiary amines, versatic 10, di-2-ethylhexyl phosphoric acid (D2EHPA), and alkylphosphonic acid monoalkyl ester have been used in commercial plants for cobalt/nickel separation. The processes and extractants for cobalat/nickel separation are well explained by Ritcey *et al*. (2), Flett (3), and Jacobs *et al*. (6).

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Chromium/Vanadium. The quaternary amines, Aliquat 336 or Adogen 464 and primary amine, N-1923 have been used for chromium(VI)/vanadium(V) separation. Pilot plants for recovering vanadium and chromium from titaniferous magnetic iron ores have been operated using the amine extractants in Canada, China, and South Africa. There are two possible types of extractants, (a) tributylphosphoric acid (TBP) and (b) amines for chromium (VI)-sulfuric acid separation system. Amines are used for dilute acid feed systems. The selectivity of TBP for chromium(VI) over sulfate and other metal ions is excellent. A commercial process is in operation for this system in France (8). It is known that the extraction of chromium (III) is more difficult. The order of chromium(III) extraction sulphate solutions using amines have been reported as primary > secondary > tertiary > quarternary (2).

Much of vanadium produced is obtained as byproducts from processing of uranium-vanadium ores, phosphate rock, vanadiferous iron ores, and titaniferous magnetites. Vanadium is also recovered from chromite, bauxite, lead vanadate ore, and oil fly ash (2). There are two main solvent extraction methods for the uranium/vanadium separation from acid leach liquors where uranium is present as UO_2^{2+}. These methods are based either on amine extractants (the AMEX and PURLEX processes) or on D2EHPA (the DAPEX process). The details of these processes are in the literature (2,8,9). Most vanadium plants in the US have used solvent extraction. Many of these are associated with uranium mills.

Niobium (Columbium)/Tantalum. The recovery of niobium from its ore is, by necessity, associated with the recovery of tantalum, since the two almost always occur together and are very similar chemically.

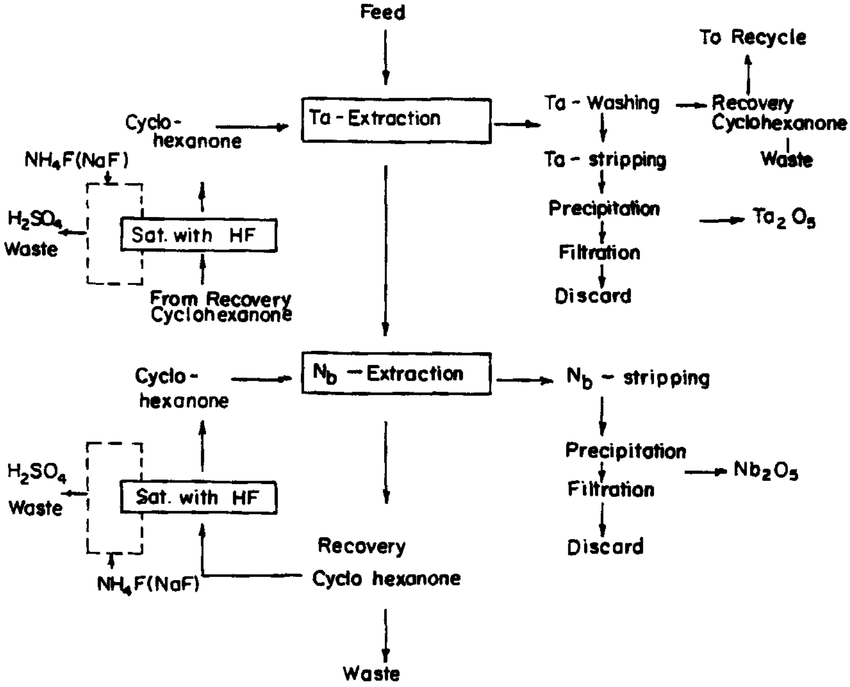

Figure 1. N_b/Ta Separation with Cyclohexanone (10)

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Often the niobium is produced as a byproduct of the tantalum operation. Solvent extraction methods have proven to be one of the better methods for separation of niobium and tantalum. Methyl isobutyl ketone (MIBK) and cyclohexanone have been the most popular of the extractants used in several existing processes (2). Tantalum and niobium are stable in solution only as tantalates, niobates, and complex ions, such as those with fluoride, thiocyanate and viscous complex ions. Most often, extraction systems with hydrofluoric acid (HF) or with mixtures of HF and H_2SO_4 or other acids are used. It is known that the use of cyclohexanone results in pure niobium, whereas the use of MIBK gives pure tantalum. Fig. 1 presents a continuous scheme of niobium and tantalum separation by extraction with cyclohexanone. This permits processing of solutions obtained in the sulfuric acid winning of titanium-niobium-tantalum raw materials with subsequent precipitation of the main bulk of the titanium by salting out of a double sulfate of titanyl and ammonium $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$. Hydrofluoric acid is introduced into the process as a solution in cyclohexanone. The losses of HF are replenished by addition of NaF, NH_4F or technical-grade HF to the sulfuric acid solution. Other extractants such as tributylphosphoric acid (TBP), petroleum sulfoxides for separation of niobium and tantalum are discussed by Yagodin *et al.* (10).

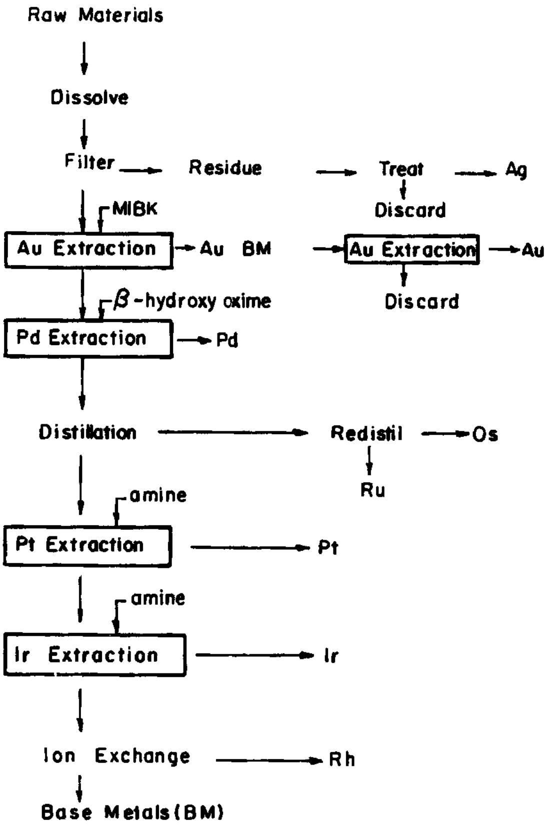

Figure 2. Separation of Platinum Groups (12)

Platinum Groups. The platinum group metals (Pt, Pd, Rh, Ir, Ru and Os) occur in minute quantities in deposits of copper-nickel sulphide ores. The separation of elements of the platinum group by conventional methods (precipitation, filtration) presents a difficuilt problem because of the similarity in properties of these elements, leading to such phenomena as coprecipitation. As a result, well-known complicated and multistage technological and analytical schemes are required (11). On the other hand, particular properties of the elements of the platinum group make possible the use of solvent extraction methods. Solvent extraction offers greater selectivity and more complete removal of metal than the precipitation methods through the use of multistage extraction. Metals are extracted selectively and sequentially from the total leach liquor. The process sequence for the separation of the platinum groups (including gold) at a pilot

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plant scale in Britain is as indicated in Fig. 2. A similar process is now being operated in South Africa at two platinum metal refineries. Solvent extraction techniques for separation of platinum groups have gained a firm foothold in the industry, and their usage is likely to increase greatly in the next few years. The various extraction systems for elements of the platinum group are reviewed by Ritcey (2), Barnes (11), Cleare (13), Gindin (14) and Edwards *et al.* (15).

Manganese. Although there are at present no known plants for producing electrolytic manganese using solvent extraction, there has been interest in treating manganese shale, and also in the treatment of deep sea nodules containing copper, nickel, cobalt, in addition to manganese. The treatment of manganese has been recently reviewed by Mohemium (16). One method of treating the maganiferous shales is by leaching with sulfuric acid. An alternative route that has proved successful is to roast a blend of the shale and the pyrite tailings, with subsequent water-leaching of the soluble metal sulphates produced. The amount of metal impurities varies depending on the type of pyrites tailings used. For example, the leach solution, in addition to Mn, could also contain Cu, Zn and other metals. Fig. 3 is one of proposed process flowsheets for separation of manganese, zinc and copper. After removal of the copper, and the extraction of the zinc at pH 3.0, any coextracted manganese is removed by scrubbing with a zinc sulphate solution.

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COMMERCIAL EXTRACTANTS FOR EXTRACTION

The Requirements of an Extractant

The general requirements of an extractant suitable for use in commercial solvent extraction operations are that it should have the following characteristics:

(i) be relatively inexpensive;

(ii) extract the metal at the required pH;

(iii) be selective for the required metal and to reject undesired metals;

(iv) have acceptable rates of extraction, scrubbing and stripping;

(v) be soluble in the organic phase and have a very restricted solubility in the aqueous phase;

(vi) be stable throughout three principal stages;

(vii) have high metal loading capacity;

(viii) be easily stripped of the loaded metal;

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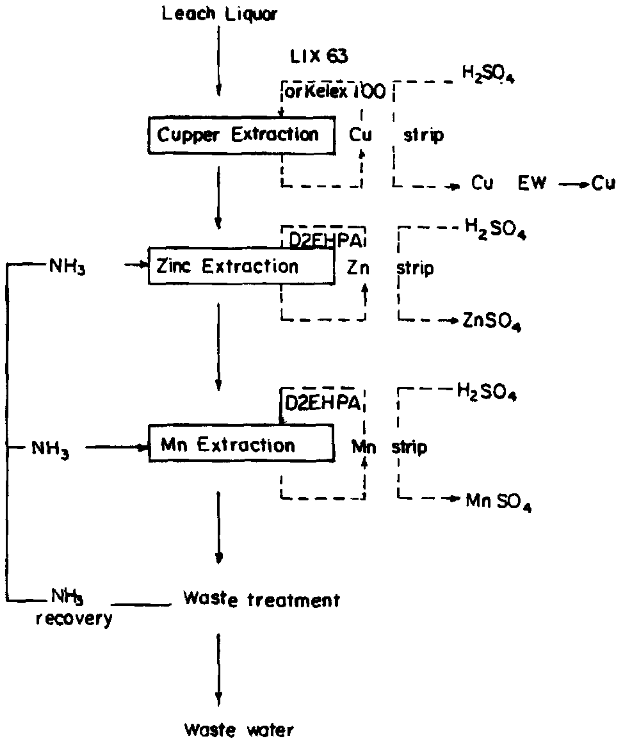

Figure 3. Proposed Process Flow Sheet for Separation of Manganese, Zinc and Copper (2)

(ix) be non-flammable, non-volatile, and non-toxic;

(x) be highly soluble in aliphatic and aromatic diluents (if necessary).

Very often these criteria, enumerated above, are incompatible so that it is important to achieve a balance between them. Modifiers are sometimes added to improve the properties of the organic phase to increase the solubility of the extractant or to change interfacial properties.

Commercial Extractants

Examples of extractants are listed in Table 3, with emphasis on those in commercial use. The classification is based on the type of extractants. There are three principal groups which can be identified

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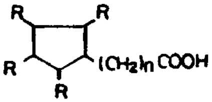
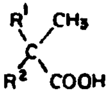
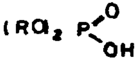
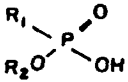
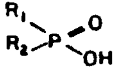
Table 3

Some Common Extractants for Use in Hydrometallurgy (17, 18)

Class	Chemical Name	Structure	Trade Name	Manufacturer	Commercial Uses
1. Acid extractants					
(a) Carboxylic acids	alkyl monocarboxylic acid		naphthenic acids	Shell	Copper and nickel separation
			versatic acids 10 911	Shell	Copper and nickel separation Cobalt/nickel/Zn separation
(b) Phosphoric acids	Di-2-ethylhexyl phosphoric acid	 R: $CH_3(CH_2)_3CH(C_2H_5)CH_2$-	DEHPA D2EHPA EHPA	Mobil	Uranium extraction, Europium extraction, Cobalt/nickel separation
(c) phosphinic acids	2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester		PC 88A	Daihachi	Nickel and cobalt separation
		$R_1 = R_2$ $CH_3(CH_2)_3CH(C_2H_5)CH$ -	SME 418 (RD 577)	Shell	
(d) Phosphinic acids	Di-2,4,4-trimethylpentyl phosphinic acid	$R_1 = R_2$ $CH_3C(CH_3)_2CH_2CH(CH_3)CH_2$—	Cynex 272	Cyanimid	Co/Ni (good rejection of Ca), rare earths, V
	Di-2-ethylhexylphosphinic acid	 $R_1 = R_2$ = $CH_3(CH_2)_3CH(C_2H_5)CH_2$ —	P-229	Chinese	

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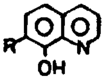
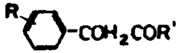
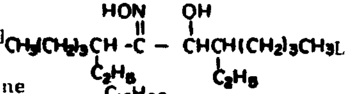
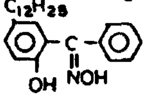
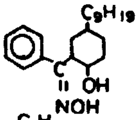
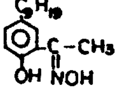
2. Acid chelating extractants					
(a) Derived from 8-hydroxyquinoline (oxine)	7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline		Kelex 100	Sherex	Proposed for copper extraction. Selective for copper over iron
(b) β-Diketones		$RCOCH_2COR'$ $R' = CH_{0-3}Cl_{0-3}F_{0-3}$	Hostarex DK 16	Farbwerke, Hoechst AG	Proposed for copper extraction from ammoniacal solution
		 $R = C_{12}$ $R' = CH_3$	LIX 54	Henkel	Copper extraction
(c) Hydroxyoximes	5,8-diethyl-7-hydroxy-6-dodecanone	 $CH_3(CH_2)_3\underset{C_2H_5}{CH}-\overset{HON}{\overset{\|}{C}}-\overset{OH}{CH}\underset{C_2H_5}{CH}(CH_2)_3CH_3$	LIX 63	Henkel	Copper extraction from ammoniacal leach liquors. Also Ni and Co
			LIX 64	Henkel	Copper extraction from acid leach liquors. Selective for Cu over Fe(III)
	2-hydroxy-5-nonyl-benzophenone oxime		LIX 65N	Henkel	Cu, Ni extraction
	2-hydroxy-5-nonylacetophenone oxime		SME 529	Shell	Cu extraction

(continued)

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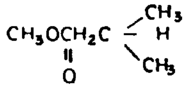
Table 3 (continued)

Class	Chemical name	Structure	Trade name	Manufacturers	Commerical use
3. <u>Basic extractants</u> (a) Secondary amines		R NH-R'	Amberite	Amberite LA-1 and LA-2	Uranium extraction
(b) Tertiary amines	Tri-(C_8-C_{10})-amine	R_3N where R: C_8-C_{10}	Alamine 336	Henkel	Widely used for U, Co, W, V extractions
(c) Quaternary amines	Tri-(C_8-C_{10})-methyl-ammonium chloride	$(R_3N^+CH_3)Cl^-$ R: C_8-C_{10}	Aliquat 336	Henkel	V and possibly Cr, W, and U
			Andogen 464	Sherex	As Aliquat 336
4. <u>Solvating extractants</u> (a) Phosphoric esters	Tri-n-butyl phosphate	$(CH_3CH_2CH_2CH_2O)_3PO$	TBP	Union Carbide, Albright and Wilson, Daihachi	U_3O_8 nuclear fuel re-processing, Fe extraction, Zr/Hf separation, rare earth separation
(b) Phosphine oxides	Tri-octyl-phosphine oxide	R_3PO R: C_8	TOPO	Cyanamid	Recovery of uranium from wet process phosphoric acid liquors with DEHPA
(c) Phosphine sulfide	Tri-isobutyl phosphine sulphide	$R_3P:S$ R: $CH_3CH(CH_3)CH_2-$	Cyanex 471	Cyanamid	Ag/Cu, Pd/Pt (SO_4, NO_3, Cl) separation
(d) Ketones	Methyl iso-butyl ketone	 $CH_3OCH_2\overset{O}{\underset{\|}{C}}-CH(CH_3)_2$	MIBK	Various	Nb/Ta separation Zf/Hf separation, H_3PO_4 extraction
(e) Ether	2,2-dibutoxy diethyl ether	$(RO(CH_2)_2)_2O$ R: $CH_3(CH_2)_3-$	Dibutyl carpitol	Various	Au extraction

in Table 3. These are the acidic extractants, the basic extractants and the solvating extractants. Although Table 3 lists most extractants, there is a great deal of effort to produce new reagents.

Acidic Extractrants. This class of extractants can be further divided into two subclasses, namely acidic extractants and chelating extractants. The former are those having reactive groups such as -COOH, $>P(O)OH$, $-SO_3H$, while the latter are those which chelate with metals. Metal cations can react with organic acids and acidic chelating agents to form neutral complexes that are preferentially dissolved by the organic phase:

$$M^{+} + n\,\overline{RH} \rightleftharpoons \overline{MR_n} + nH^{+} \qquad (1)$$

Here the overbar denotes species in the organic phase. The above equation describes a cation exchange reaction wherein hydrogen ions are exchanged for the metal cation, so the degree of extraction of metal ions depends on the pH of the aqueous phase. The degree of extraction of the metal ions will also vary with the nature of the metal.

Extractants of the acidic type which have been found useful, or promising, as metal extractants in commercial operations are organic derivatives of phosphorous acids and monocarboxylic acids. Of these, alkylphosphoric acids have proven to be the most versatile, especially di-2-ethylhexyl phosphoric acid (D2EHPA). Some particular advantages of the use of D2EHPA in solvent extraction processing are its chemical stability; generally good kinetics of extraction; good loading and stripping characteristics; low solubility in the aqueous phase; versatility in the extraction of many metals including uranium, cobalt and nickel, rare earths, and vanadium; and its availability in commercial quantities.

Chelating extractants are those which contain donor groups capable of forming bidentate complexes with metal ions. Commercially available chelating extractants are, at present, limited to two types: (a) a series of substituted 2-hydroxy benzophenone oximes produced by Henkel Corporation (General Mills Inc.) under the name LIX reagents, the Acorga reagents by Imperial Chemical, and the SME extractants of Shell Chemical; and (b) the substituted 8-hydroxyquinoline produced by Sherex (Ashland Chemical Company) and marketed under the name Kelex. Most of these extractants were developed for the specific extraction of copper from acidic leach liquors, as well as from alkaline solutions. Unfortunately, most of the chelates suffer from slow kinetics in acidic solutions, but they do possess good kinetics in alkaline systems. The general properties and extraction mechanisms of these acid extractants have been reviewed by Ashbrook (19), Flett (20,21), Danesi (22), Whewell (23), Hudson (18), Preston (24,25) and Ritcey *et al.* (17) and will not be repeated here.

Basic Extractants. Basic extractants (anion exchangers) are organic reagents which can easily form a salt while in contact with

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an aqueous acid solution. In commercial solvent extraction processing, basic extractants are limited to amines and quaternary ammonium halides. Processes have been developed which employ primary (RNH_2), secondary (R_2NR), tertiary (R_3N) amines and quaternary ammonium salts (R_4N^+). The usefulness of amines as extractants is usually considered to depend essentially on the ability of metal ions to form anionic species in the aqueous phase, which are extracted by amines in an anion-exchange process:

$$MY^{-n} + \overline{n(R_3N^+H\cdot A^-)} \rightleftharpoons \overline{(R_3N^+H)_nMY^{-n}} + nA^- \qquad (2)$$

In order to achieve this exchange, the amine is first converted to the appropriate amine salt to provide an anion to exchange with metal species:

$$R_3N + HA \rightleftharpoons \overline{R_3N^+H\cdot A^-} \qquad (3)$$

that is, amine extracts an acid to form an amine salt or polar ion-pair, $R_3N^+H\cdot A^-$, in the organic phase. On contacting this solvent with an aqueous solution containing an ionic metal species, MY^{-n}, exchanges occur like equation (2). Thus the amine salt should be considered as being the extracting agent and not the free amine. One important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which depends on the properties of the diluent and the nature of ammonium cation and anion:

$$R_3N^+H\cdot A^- \rightleftharpoons (R_3NH^+\cdot A^-)_2 \rightleftharpoons (R_3N^+H\cdot A^-)_n \qquad (4)$$

Third phase formation, that is the splitting of the organic phase into two parts, is common in these systems and occurs through solubility problems relating to aggregation. This problem can be eliminated by addition of diluent modifiers such as long-chain aliphatic alcohols.

Another factor influencing metal extraction by amines is the nature of the carbon chain, and also the number of carbon atoms in the chain. Normally aliphatic amines are the best extractants. Amines, useful for solvent extraction purposes, are generally limited to those having molecular weights in the range 250 to about 600, normally between 250 and 400. Those with molecular weights of about 250 tend to be too soluble in water, and those of about 600 are generally too insoluble in the organic phase. Extraction systems of basic extractants and their extraction mechanism have been recently reviewed by Ritcey (17), Flett (21), Cox (26), Hudson (18) Danesi (22) and Miller *et al.* (27) and will not be expounded upon here.

Solvating Extractants. Solvating extractants or neutral extractants are organic reagents that possess only donor groups that do not contain dissociating protons. Since no anionic or cationic groups are available in the reagent molecule, the metal species are extracted from the water

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phase as neutral complexes. The neutralizing ion is a water soluble negatively charged ligand. The extent of extraction by solvating extractants depends on the extent of complex formation in the aqueous phase, as in the case of the basic extractants. Extraction is by solvation of either the central metal atom of the complex or the proton in the case of formation of a complex acid species:

$$MX_n + \overline{yS} \rightleftharpoons \overline{MX_nS_y} \tag{5}$$

or

$$HMX_{n+1} + \overline{xS} \rightleftharpoons \overline{(HS_x)^+ (MX_{n+1})^-} \tag{6}$$

where S is a solvating agent. The solubility of inorganic species in the organic phase is increased by means of this solvation.

There are two main groups of extractants in this area; organic reagents containing oxygen bonded to carbon, such as ethers, esters, alcohols and ketones, and those containing oxygen or sulphur bonded to phosphorus, as in alkylphosphates or alkylthio phosphates. One major difference between these extractant types is the role played by water. The strongly polar organophosphorus components compete favorably with water, and can replace water molecules in the primary coordination sphere of metal ions. In the carbon-bonded oxygen donor systems (e.g. ethers and ketones), water usually forms an essential part of the complex, forming a hydrogen-bonded bridge between solvating agent and the solute. One marked feature of esters, ketones, etc. is the high degree of hydration of the metal in the organic phase. The fact that most of these systems show strong non-ideality in the organic phase, even at low concentrations, makes a general theoretical treatment almost impossible.

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The use of esters of organophosphorus acid has been limited to tributylphosphate (TBP) in commercial operation. Such operations have been almost entirely in the nuclear field for the refining of uranium, and in the processing of radioactive products from nuclear reactors. Tributylphosphate based processes have also been employed for the separation of zirconium from hafnium and also for the recovery of chromic acid. Although successful processes have been operated using TBP as extractant, the mechanism of extraction, degradation of TBP, and the formation of non-strippable complexes are still not properly understood (17).

The use of carbon-oxygen-bonded extractants for metal ion separation is well established, especially in the halide and nitrate systems. Dibutyl carbitol has been used commercially for extraction of gold(III). The processes involving methylisobutyl ketone (MIBK) have been limited to separation of zirconium, niobium, and tantalum because of its low flash point (26). The use of MIBK and alcohols differs from other solvents in that they are used in the undiluted form.

OTHER SEPARATION METHODS IN HYDROMETALLURGICAL PROCESS

Liquid Membranes

In a conventional solvent extraction process the degree of extraction is limited primarily by the ratio of solvent to feed and the distribution ratio of the solute between the phases. The solute may subsequently be removed from the solvent in a stripping operation, allowing the solvent to be reused, but the extent of solute stripping is again limited by the phase ratio and distribution ratio. A large amount of inventory of solvent is necessary for conventional solvent extraction. The use of liquid membranes containing a carrier material has been proposed as an alternative to solvent extraction to solve this problem for the selective separation and concentration of metals from dilute aqueous solution.

In liquid membrane extraction, the extraction and stripping operations are combined in a single process and the usage of solvent is greatly reduced. Furthermore, very high enrichment factors can be obtained in a single stage. The use of the liquid membranes significantly reduces the relative amount of the organic phase necessary for the extraction. Hence, highly selective and expensive extractants can also be used, which would not be economical in solvent extraction.

Two kinds of liquid membranes are commonly used. One is a thin layer highly microporous polymer film impregnated with carrier material (supported liquid membrane) (28,29). The other is the liquid surfactant membrane (30-32).

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Liquid Surfactant Membranes (LSM). Liquid surfactant processes have been evaluated for separation of metal ions such as Cu, Ni, Co, Zn, U and Cr. Martin *et al.* (34) have reported that solutions, ranging in concentrations from 2000 ppm copper as copper sulfate (typical of acid leach solutions) down to 100 ppm, can be treated to produce concentration solution for electrowinning in one contact stage. They have also showed that successful extraction of copper using LSM can be achieved using over two orders of magnitude less solvent than with solvent extraction. Melzner *et al.* (31) have showed that the liquid surfactant membrane (LSM) technique is especially suitable for processing Zn leach solution at low metal concentrations. They have also reported that it is easy to attain enrichment factors of 100 in a single stage for metal extraction with LSM technique and suitable extractants. Figure 4 illustrates the principle of the liquid surfactant membrane technique (31). Liquid membrane extraction is a three-phase process. It consists of forming an emulsion of two immiscible phases and then dispersing the emulsion in a third phase (continuous phase). Usually, the encapsulated (inner) phase and the continuous phase are miscible. During extraction a metal-extractant complex is formed at the interface of the continuous phase and membrane phase. The complex permeates across the membrane and decomposes at the interface of the encapsulated phase in which enrichment of the metal occurs. Although the liquid surfactant membrane process

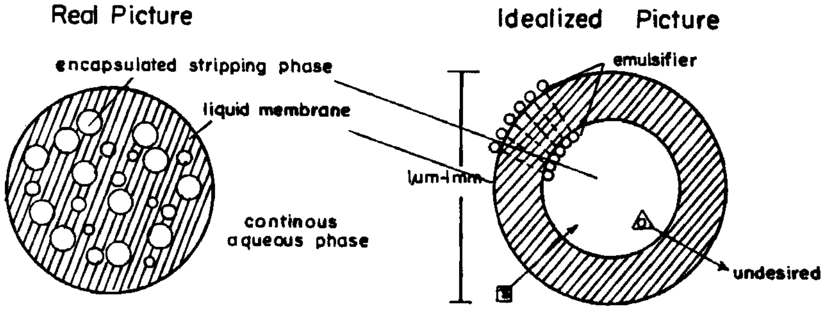

Figure 4. Schematic Diagram of Liquid Surfactant Membrane (31)

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presents a novel approach for separation of dilute metal solutions, there are problems existing in this method. In liquid surfactant membranes, metal passes from the outer surface to the surface between the carrier and inner microphase. Eventually the inner phase becomes fully loaded with metal containing species and it is then usual to break the emulsion to recover the inner phase for further treatment. The carrier is then re-emulsified with fresh stripping solution and reused for extraction. The need for intermittent breakdown and reforming of the membrane is clearly disadvantageous. Any breakdown of the emulsion will result in a reduction of extraction efficiency and a loss of strip acid solution (34,35). Supported liquid membranes (SLM) is another alternative to solvent extraction for separation of dilute metals to attempt to solve some problems existing in the liquid surfactant membranes.

Supported Liquid Membranes (SLM). These membranes offer a more convenient configuration as the carrier is immobilized and feed and stripping solutions can be continuously fed and withdrawn. Separation of metal ions by SLM have been investigated by a number of workers (33,35-42). Danesi (33) has suggested that the advantages of supported liquid membrane over other traditional separation technologies are: (a) lower capital and operating cost, (b) low energy consumption, (c) economical use of expensive, tailor-made extractants, (d) possibility of achieving high separation factor, and (e) possibility of concentrating the recovered species during the separation. Also, Danesi indicates that composite supported liquid membranes can offer a possibility of bypassing the single-stage limitation of SLM separations and that hollow-type fibers seem to be the most convenient shape of membrane support to be used for practical purposes with high throughputs.

Figure 5 illustrates the mechanism of the mass transfer process in supported liquid membranes (33). For permeation to proceed in a

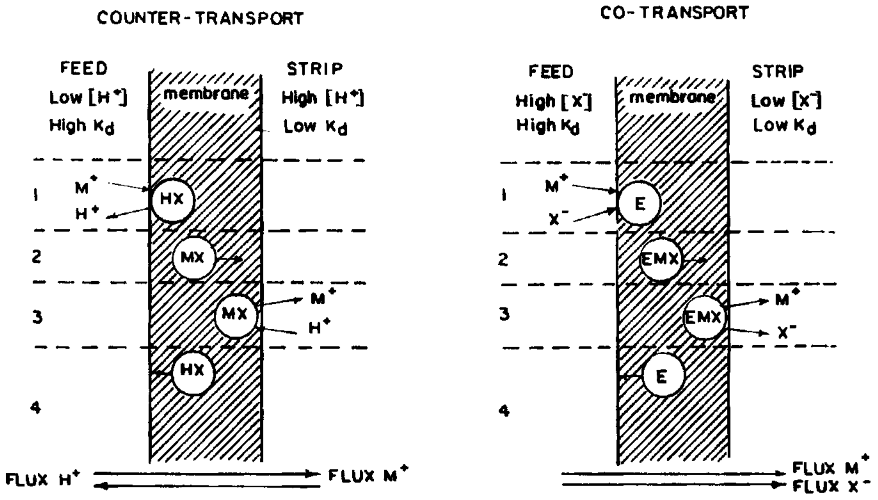

Figure 5. Schematic Description of Mass Transfer Process in Supported Liquid Membrane (33)

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liquid membrane a solute in the continuous aqueous phase must find its way to the aqueous-membrane interface where the formation of a solute-carrier complex then occurs. The resultant complex diffuses across the membrane to the other side where it then decomposes to form the solute and regenerate the carrier. The major uncertainty in the use of SLMs for industrial separation processes, resides on the limited information presently available on SLM stability. The probable causes of membrane instability observed by Danesi (33) and Pearson (35) are: (a) loss of extractant by solubility in the adjacent aqueous solutions, (b) progressive wettability of the support pores induced by the lowering of the organic-water interfacial tension which results from the surface-active nature of many carrier molecules, and (c) the differential pressure existing between the inside and the outside of the SLM caused by the pumping of the solutions when hollow-fiber SLMs are used.

Ion Exchange Resin

The solvent extraction and resin ion exchange methods involve similar chemical principles, but differ in technological principles. Solvent extraction shows advantages in mass transfer rates and offers economic superiority in size of equipment and process time. However, it is riddled with problems such as phase disengagement difficulties and reagent losses. Resin ion exchange shows lower mass transfer rates, needs large size equipment, and longer process time. However the equipment is simple, easy to operate, and there are basically no problems of phase disengagement and reagent losses.

Ion exchange resins have been used widely for the recovery of uranium from dilute leach liquors. The ion exchange techniques are well established in the uranium industry. However, conventional cation exchange resins containing sulphonic acid or carboxylic acid functional groups have limited potential for use in the recovery of transition metal ions from process solutions because of their low selectivity, particularly against alkali and alkaline earth metal cations. A number of chelating ion exchange resins have been produced by resin manufacturers to overcome this problem and encourage the application of ion exchange to a broader range of process solutions.

Impregnated ion exchange resins were developed to bridge the gap between solvent extraction and resin ion exchange (liquid-solid extraction) (43). It is anticipated that impregnated ion exchange resins should have advantage over the two individual substituent processes.

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Chelating Ion Exchange Resins. Chelating ion resins date from 1952 when Gregor *et al.* (44) published a paper on the synthesis of chelating condensation polymers. Since that time many such resins have been developed and described in the literature together with details of their chelating behavior toward metal ions and selectivity. The various methods of preparing chelating resins have been listed by Blasius *et al.* (45) and Vernon (46). Condensation or addition polymerization processes are usually employed for the introduction of the chelating function into a high polymer matrix as follows:

(i) condensation resins incorporating a chelating ligand.

(ii) condensation resins chemically converted to chelating resins.

(iii) polymerization of vinyl derivatives of chelate forming compounds.

(iv) crosslinked vinyl polymers chemically converted to chelating resins.

(v) linear polymers chemically converted (in solution) to chelating polymers followed by crosslinking reaction.

A number of researchers have recently investigated the chelating ion resins for recovery of metals in the dilute system (47-50). Table 4 illustrates some examples of chelating ion exchange resins and systems to which they can be applied.

Table 4

Some Commercial Chelating Resins (47,49)

Type of Chelating Resins	Trade	Manufacturer	Metal Ions
Imidodiacetic acid resins:	TP 207	Bayer (W. Germany)	Co/Fe
$-CH_2NCH_2(CO_2H)_2$	XE 718	Rohm and Hass (U.K.)	Ni/CO
	Dualite ES466	Dia-Prosium (France)	Cu
Picolylamine(2-aminomethyl pyridine) resins:			
$-N(CH_2C_5NH_4)_2$	XF 4195	Dow (U.S.A.)	Cu,Ni/Co
$-N(CH_2C_5NH_4)C_2H_4OH$	XF 4196	Dow	Cu,Ni/Co
Aminophosphonic acid resin:			
$-CH_2-NH-CH_2-PO(OH)_2$	Dualite ES 467	Dia-Prosium	Ca,Mg, U

The solvent extraction process becomes uneconomical in the handling of large volumes of solution containing low metal value. It is here that ion exchange has the advantage and only awaits the development of materials with high selectivity which are cheap to produce in bulk. The cost of chelating exchangers may appear high but it must be remembered that ion exchangers can be used in the metal recovery-regeneration process thousands of times with very little or no decrease in ion exchange capacity.

Impregnated Ion Exchange Resins. Although there is unquestionable evidence that the development of chelating ion exchangers is eliciting considerable interest now, there are bound to be difficulties in their preparation and cost. It is, therefore, not surprising that the idea of adsorbing an organic solvent extraction reagent onto a solid polymeric matrix has attracted growing attention in recent years. There are two kinds of impregnated ion-exchange resins made based upon the methods of preparation. The first approach which can be applied to many extractants and polymers is based on physical adsorption of an extractant into a high-surface macro-porous polymer bead. This type of ion-exchange resin is called solvent-impregnated resins (SIR). The second approach is more specific, it employs in-situ incorporation of the extractant during the resin copolymerization process. This type of resin is usually made from styrene-divinylbenzene based copolymers and is

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called Levextrel resin. Methods of preparing SIR have been discussed by Warshawasky (42) and Flett (51). Namely, the impregnation can be produced by either the dry or wet method. The Levextrel resins on the other hand are produced in a single operation by adding the extractant to the vinyl- and polyvinyl monomers and polymerizing the mixture in situ by a bead polymerization technique.

Metal recovery using impregnated ion exchange resins from dilute solutions has been reported by a number of investigators, through results in laboratory experiments, pilot plant and full scale studies (42-43,51-53). Metal ions which have been extracted through impregnated ion exchange resins include nuclear metals, strategic metals, precious metals, and base metals. Existing extractants for solvent extraction may be employed in these impregnated resin extraction systems. Di-2-ethylhexyl phosphoric acid (D2EHPA), tributylphosphate (TBP), tertiary amines (alamine 336), and hydroximes (LIX 64N, LIX 65N) are examples most of which are available commercially. Table 5 shows some impregnated resins and the associated metal ions recovery studied by Flett (51).

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PROBLEMS TO OVERCOME FOR FUTURE DEVELOPMENT

Although solvent extraction, liquid membranes and ion exchange resins have been established for the dilute metal ions separation in the hydrometallurgical field, there are still quite a few uncertainties and problems that need to be answered and resolved.

General Problems for Solvent Extraction, Liquid Membrane and Ion Exchange

Extractant. Up to now, there have been a very large number of extractants available for commercial usage as discussed in the extraction section. However, most of these extractants still suffer problems such as solvent entrainment (or loss), poor extraction selectivity, and slow extraction. The problem of solvent entrainment and selectivity may be resolved partially by properly designing the equipment or improving the process (54).

The chemistry part of the extractant will always play the most important role in the extractant development (16,17). We already have a number of excellent molecules available for most extraction situations. Development of both new reagents, and of new applications for existing reagents will doubtless continue. There have been numerous investigations on the possible use of mixed extractants to improve the extraction by synergism (7). Not only may the extractive equilibrium be affected, but also the kinetic rate may be significantly increased. Accelerators have also been added to improve the kinetics in some extraction systems. The mode of action of these substances, which are also called catalysts, is a subject needing much research. Some of

Table 5

Some Impregnated Ion Exchange Resins (51)

Extractant	Adsorbent	Metal Ions
TBP	Surface sulphonated styrene divinylbenzene (DVB) beads	Uranium
TBP	Porous polystyrene DVB resins	Uranium
TBP	Levextrel (polystyrene DVB based polymer)	Uranium
D2EHPA	Levextrel	Zinc
D2EHPA	XAD-2 (Macroporous polystyrene) (Rohm & Haas)	Zinc
Alamine 336	XAD-2 (Macroporous polystyrene) (Rohm & Haas)	Gold
Alamine 336	Silicone treated fire clay	Uranium
Alamine 336	XAD-2	Uranium
LIX 63	XAD-2	Cu,Fe,Ni,Co, etc
LIX 65N	XAD-2	Cu,Fe,Ni,Co, etc
Various hydroxyoximes	XAD-2	Copper
LIX 64N	Various clays and carbons	Copper
LIX 64N	Oleogon (expanded polyurethane)	Copper
Kelex 100	XAD-2	Cu,Fe,Ni,Co, etc
Stearo hydroxamic acid	XAD-2	Cu,Fe,Ni,Co, etc

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the possible accelerators for the extraction of copper have been reviewed by Hudson (17). The modification of existing extractants by changing side chains of the extractant has been accomplished by various investigators. This modification is to improve the selectivity of the particular metal and to decrease the solubility of extractant in the aqueous phase.

The potential of crown ethers (macrocyclic polyethers) as the next generation of specific extracting agents for metal ions, has been explored by several authors (55-61). They found that these extractants have great possibilities for use in separation of alkali and alkaline earth cations from other mono- and divalent metal ions. The Cyanex 472 extractant, which was recently developed by Cyanamid, has possible use for the selective recovery of silver and palladium (62).

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Reaction Kinetics. A significant amount of work has been done on reaction kinetics for metal extraction in hydrometallurgical processes. Extensive reviews for reaction kinetics include those of Danesi and Chiariza (22), Flett and Spink (63), Ashbrook (19), Whewell and Hanson (23), and Tavlarides and co-workers (79,87). It is well recognized that to properly describe the kinetic rate with an appropriate mechanistic description, attention should be given to a number of factors which contribute to the overall resistance to mass transfer. These include resistances of diffusion, adsorption and chemical reaction. The mass transfer resistances are strongly dependent on the nature of the hydrodynamics in the contacting device and mode of operation. The site of chemical reaction for most of the dilute metal extraction systems is still uncertain. Different reaction mechanisms have been reported (64,65) for the same metal extraction systems. This ambiguity can be attributed to different techniques and devices used for the kinetic experiment. The inability to directly observe the reaction site (or reaction zone) gives rise to various modeling techniques. All these uncertainties point out the great need for development of experimental techniques or devices which can be used for the kinetic studies.

The development of a good liquid-liquid contact device which is able to permit one to observe the reaction site of the extration is of paramount importance. Many devices have been used to study two-phase mass transfer with reaction at or near the liquid-liquid interface. The properties which a liquid-liquid contactor must have for successful kinetic studies are well defined hydrodynamics without significant end effects, and a short contact time. Some of the presently used techniques have been discussed elsewhere (22,66,67,96). These techniques include a dispersed phase contactor with centrifugal (68-70) or membrane phase separation (71), stirred mass transfer cell (Lewis cell) where two fluid layers are individually stirred (64,72,73), a diaphragm cell, single drop experiment (74-77), growing drop (65,78), and laminar liquid jet (79-81). Of these techniques the liquid jet recycle reactor appears to offer more advantages such as precise determination of interfacial surface area, the essentially absence of Maragoni type instabilities, removal of interfacial impurities without disturbing the interface, and easy adaptation to adsorption-desorption studies. The Lewis cell has been subject to redesign in order to improve bulk mixing or maintain constant interfacial surface or to achieve forced convections to the interface. The contactors which were developed by Chin and Landau (82) and Danesi and coworkers (83) are examples of the modified Lewis cell. However, these contactors still appear to have problems such as accumulation of surfactants (or impurities) at interface, or surface waves which complicate hydrodynamics. Recently Albery and Fisk (84,85) have introduced a novel technique utilizing the rotating diffusion cell (RDC) which employs a thin porous membrane filter to bring the aqueous and organic phases into contact. The filter is mounted on a rotating cylinder to provide well-defined rotating disk hydrodynamics on either side of the membrane filter. However, this technique appears to have an uncertainty of the characterization of the interfacial area.

Solvent Extraction

Equipment Design.

Any fundamental approach to the design of a two-phase liquid reactor must incorporate reactor hydrodynamics with the chemical reaction mechanism, thermodynamics and kinetics. A variety of models have been employed to predict extent of reaction and selectivity for complex reactions which occur in liquid-liquid dispersions in agitated vessels (86).

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The approach to the dispersed phase mixing problem on extractor design is shown to consist of various levels of sophistication. The nature of the model used depends upon the relative values of the rates of diffusion and chemical reaction and thus the importance of micromixing and macromixing phenomena. Noninteraction models for a tubular reactor are based on knowledge of axial dispersion coefficients for both phases. Modelling of micromixing phenomena for these models is limited to either complete mixing or completely segregated cases. These models are in general applicable to slow reactions.

Coalescence-dispersion (C-D) interaction models have been applied with success to model intermediate cases of micromixing. Population balance equations are shown to be valuable to model physically equilibrated dispersions for prediction of droplet size distributions, coalescence frequencies, and average drop size. The Monte Carlo simulation methods incorporating the interval of quiescence method have been used to model complex droplet mixing processes and their effect on the interphase mass transfer with chemical reaction (87,88). However, it must be emphasized that the interaction models have been proposed only for very restrictive hydrodynamic conditions. Furthermore most of these models pertain to single drops. Work must be done to analyze the individual drop behavior in a multidrop environment.

Hydrodynamics plays a crucial factor in determining the equipment performance. Apart from its macroscopic influence on the extent of nonidealities in the flow patterns, the affect is cascaded down to the microscopic level to influence local interphase transport processes and drop interaction rates. The overall influence is a complex function of the scale of operation and only under very fortuitous circumstances can one expect to achieve reliable scale-up based on a single criterion. More work should be done to properly model hydrodynamics of liquid-liquid stirred vessel.

One major factor which needs further research in the area of these two phase flows of liquid dispersions, especially column contactors, is the characterization of drop velocities relative to the continuous phase. The drop slip velocities determine the local holdup which in turn affects the drop size distribution and thus the extraction rate. The drop slip velocity also influences the flooding limits and thus dictates the column throughput. Investigations on the velocity of a drop relative to the continuous phase appear to be the essential key to the accurate prediction of the column performance from a fundamental standpoint.

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Knowledge of interfacial areas, drop size distributions, holdup and dispersed phase coalescence rates is also important for accurate description and prediction of mass transfer and chemical reaction rates in liquid-liquid dispersions. A review of the experimental methods and techniques developed for describing and measuring interfacial area, drop size distributions, and coalescence rate has been recently given (83). These methods have some limitations as indicated by Tavlarides and Stamatoudis (86). Development of satisfactory measurement techniques should be continued.

Process. Hydrometallurgy is an integrated process of leaching, solvent extraction, scrubbing, stripping and electrowinning. The success of the process not only depends on the solvent extraction but also on all other unit operations. Therefore proper selection and optimum operation of equipment in each unit process have to be ensured in order to obtain the maximum efficiency of the process.

In solvent extraction, the maximum mass transfer efficiency with minimum solvent losses depend on the optimum operation of the equipment. Solvent losses can be caused by solubility, entrainment, degradation, volatilization and crud (7,17). For most systems loss of solvent due to solubility in the aqueous phase is usually small, and little can be done regarding this type of loss. Entrainment losses can vary considerably, usually as a result of insufficient settling area, or time allowed for phase disengagement, poorly designed or operated mixers, too much energy input into the mixing stage, lack of additives to suppress emulsion formation, poor diluent choice, high extractant concentration in the solvent, solids in the aqueous feeds causing crud formation, and so on. Entrainment losses can be minimized by the incorporation of various devices in solvent extraction circuits. Loss of solvent by volatilization will depend on the temperature of the system and on how well the system is enclosed. Problems of volatilization do not appear to have occured to any great extent in the past, but any trend to the use of elevated temperatures would require that this form of solvent loss be thoroughly investigated. Degradation of solvent compounds can arise from various sources, such as oxidizing properties of the aqueous phase, too high a temperature of the system, aging and oxidation by atmospheric oxygen, and general instability of the various extractants, modifiers and diluents being used in solvent extraction processes (17).

Common to most solvent extraction operations in the mining industry is the problem of stable emulsions and the eventual formation of cruds (89). Some of the problems in uranium or copper hydrometallurgical plants include a) precipitation of metal hydroxides (e.g., Fe and Zr) during stripping, b) precipitation of humic acids during stripping or scrubbing because of a change in pH, c) precipitation of molybdenum complexes in uranium extraction from sulfonic acid by tertiary amines (90). The molybdenum problem is an example of third-phase phenomena, i.e., precipitation of insoluble extraction complexes as particulate solids or as viscous liquids. McDowell and Moyer have recently characterized the molybdenum problem (91).

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By definition, cruds in solvent extraction are associated with the presence of solids precipitated during liquid-liquid contacting (17,89). The cruds are either organic continuous (OC) or aqueous-continuous (AC) emulsions (90,92). These emulsions are tenacious, as hours of centrifuging fails to completely disengage the phases. Moyer has reported that among the cruds from operating uranium mills (1980-1981) and his laboratory, one crud was shown to contain a molybdenum compound, whereas another was found to contain primarily fine (<5 micron) silaceous solids. In the silaceous crud, the organic drops (AC emulsion) were coated or armored by the particulate solids. In fact, all of the drops were small, mostly 5-100 microns in diameter. McDowell and Moyer have discussed the armoring of drops by silica in relation to phase disengagement (93). Most leach solutions contain about 1000 ppm of dissolved silica after decantation and filtration. The true solubility of silicic acid lies around 100 ppm so that most of the silica precipitates gradually as colloidal matter.

Given that we know something about how the solids get into the system, it appears that an important factor in the problem is the formation of small drops (below normal drop sizes) in either phase. The source and fate of these drops are not understood. Ritcey (17,89,94) suggests that violence of agitation in mixing produces such small drops as well as enhances, in itself, the precipitation of silica. Another source of small drops is a result of coalescence of two drops wherein the result is one large drop together with several very small satellite drops. Further, it is possible that the extraction kinetics can involve a step in the organic phase that releases water and temporarily supersaturates the diluent, eventually producing haze or entrainment. Whatever the cause of the small drops, these slowly sedimenting drops are considered to have plenty of time to come into contact with particulate and become armored (90). The crud can constitute a major solvent loss to a solvent extraction circuit and therefore adversely affect the operating costs.

Obviously there are many items for consideration with respect to the chemical and physical parameters, the engineering, design and operation of solvent extraction circuits if we are to fully understand and solve the problem of crud formation. Thus, much research and basic studies are necessary in the future in order to eliminate the problems and expense caused by crud formation.

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Liquid Membranes

Both Liquid Surfactant Membranes (LSM) and Supported Liquid Membranes (SLM) have the advantage of accomplishing the extraction and stripping operation with very high enrichment factors in a single stage. However, there are several problems which need to be overcome for the future development.

Liquid Surfactant Membranes. The stability of a liquid membrane emulsion is of major importance, since breakdown of the organic films will show directly as a loss in extraction efficiency as well as a loss of strip solution. Some steps can be taken to increase the stability of the emulsion by either increasing the bulk viscosity of the organic phase by adding polymer materials or by increasing the surface viscosity (34). However, further studies are necessary to improve the stability of the emulsion. The solubility of the surfactant in the aqueous phase (raffinate and strip solutions) is important. Ideally surfactants totally insoluble in the aqueous phases should be used to prevent any overall loss from the system. In addition, the solvent losses or solubility from one phase to the other may also increase due to the surfactant added in the system. The process development problems, such as emulsion breakdown, iron poisoning and colloidal solids incorporation, have yet to be overcome (42).

Supported Liquid Membranes. As support materials and extractants are available which have higher resistance to chemical degradation, chemical stability should be easily obtainable. With membranes however the effects of chemical degradation will be magnified because of the very small inventory of extractant in the system. The production of impervious deposits of reaction products could also reduce flux by blinding the membrane, but the most probable cause of flux deterioration is the loss of carrier solution or extractant from the membrane by the processes which are mentioned earlier. Therefore, more work is necessary to understand the stability of supported liquid membranes to increase the flux. In addition to stability, the strength of the membrane and equipment scale-up present further efforts needed for future development. Another problem in SLM is that the permeation selectivity is very much dependent on the permeation rate of the metal extractant complex inside the membrane, and not on the distribution coefficient. Thus, usual data from solvent extraction studies can not easily be implemented in this process (42).

Ion Exchange Resins

Chelating Ion Exchange Resins. Chelating resins show higher effective capacity for heavy metals than conventional cation resins because of their selectivity against alkali and alkaline earth ions. However, there are few comparative performance data for the chelating resins available commercially. Therefore, fundamental studies such as the physical properties of the resins, equilibrium exchange capacities and selectivities of existing resins are necessary for evaluation of potential use. The development of chelating resins with high selectivity which are cheap to produce in bulk should be continued. The desirable properties of chelating exchangers are four fold (46):

(i) high capacity for metal of interest,

(ii) high selectivity,

(iii) fast kinetics - rapid equilibration with metal containing solutions, and

(iv) high mechanical strength and toughness of the exchanger particles.

Impregnated Ion Exchange Resin. The preparation methods of impregnated resins have shown to directly effect the availability of chelating capacity in the resin (51). Therefore, different methods (or different diluents for reagents) used for resin impregnation present interesting problems for future activity. An ideal impregnated resin should combine the properties of solvents and polymers as follows (43):

(i) high mobility of the reagent in the resin phase,

(ii) high mass transfer rates,

(iii) high selectivity factors,

(iv) low reagent losses,

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(v) good phase separation properties and

(vi) high chemical and physical stability.

One major problem with this method is solvent losses that have profound effect on the lifetime of the resin. This problem makes continuous makeup of fresh resin necessary. Little fundamental work appears to have been carried out on the actual mechanism of metal ion uptake. Undoubtedly what is needed now are design data for operation of solvent impregnated resin system which will allow scale-up calculations and capital and operating cost estimates to permit critical assessment of impregnated based resin processes against the available alternatives. The comparison among these three types of separation methods is illustrated in Table 6.

Table 6

Comparison of Separation Processes for Dilute Metals Extraction

Process	Advantages	Disadvantages
Solvent Extraction	-more established process -higher throughput -more fundamental information available -higher purification obtained	-higher solvent losses -higher capital cost -phase disengagement difficulties -large inventory of solvent
Liquid Membranes	-lower capital cost -metal ions can be pumped "uphill" -accomplishing extraction and stripping in single stage -economically using expensive extractant	-poor durability -instability of membranes -lower flux -lower purification
Ion-Exchange	-no mixing and settling requirement -simplicity in equipment and operation	-higher resin cost (chelating resin) -solvent wash-out (impregnated resin) -slow rate process -lack of fundamental information

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CONCLUSIONS

Solvent extraction is a well-established process for separation of dilute metal ions. However, some problems such as equipment design, extractant losses, lack of adequate kinetic data, etc. need more research efforts. Other separation methods such as liquid membranes which offer some advantages in the dilute metal ions separation suffer from difficulties such as instability of the membrane and low fluxes. Impregnated ion exchange resins are ideally developed to overcome some problems suffered by solvent extraction. However, this method is still immature and substantial research work is needed before it becomes a viable alternative.

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