Mines Branch Information Circular IC 237

SOLUTION PURIFICATION BY ION EXCHANGE OR SOLVENT EXTRACTION

by

G. M. Ritcey*

ABSTRACT

The subject of solution purification using ion exchange or solvent extraction as techniques in hydrometallurgical processing is described. No attempt has been made to cover the many theoretical aspects, but rather to provide an adequate background of information and references useful to those contemplating industrial processing. Among the items covered are the techniques, reagents, equipment, processing costs, and selected extraction systems.

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Direction des mines

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LA PURIFICATION DES SOLUTIONS PAR ÉCHANGE D'IONS OU PAR EXTRACTION DES SOLVANTS

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RÉSUMÉ

L'auteur traite de la purification des solutions par l'application à l'hydrométallurgie des techniques d'échange d'ions et d'extraction des solvants. Il n'est nullement question des aspects théoriques de ces méthodes, mais plutôt d'offrir les renseignements et les références nécessaires à toute entreprise désireuse d'appliquer des techniques à l'échelle industrielle. Le present texte porte sur les techniques, les réactifs, le matériel, le coût du traitement et divers procédés d'extraction.

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1. INTRODUCTION

Hydrometallurgical processing of leach solutions, both for metal recovery and for purification, has generally been accomplished by precipitation, crystallization, etc. The need for the production of rare metals in bulk quantities, especially in the case of uranium, has shown that newer separation techniques, such as ion exchange and liquid-liquid extraction, can be applied successfully on plant scale. Indeed, these two processing techniques have been used almost exclusively over the last twenty years for the recovery of uranium from leach liquors, and they have found considerable utility in the separation and recovery of other metals.

For future processing of leach solutions, the sequence followed in any metal recovery operation will be dictated by:

(a) the desired final product (oxide, sulphide, chloride, etc.);

(b) the specifications set on the product; or

(c) the contaminating effect of waste effluents from the purification circuit on the natural water resources.

In this report on Solution Purification we shall deal with ion exchange and solvent extraction as the principal processes used in the hydrometallurgical treatment of metal-bearing leach solutions. The advantage of an ion exchange or solvent extraction process lies in its capacity for the concentration of initially dilute values, for separation, and for the purification of metals. Since ion exchange resins, in particular, have the ability to concentrate metals from dilute solutions, they have a potential application in the concentration and recovery of metals from effluent wastes.

Because of the technical background of the author, the emphasis on solution purification will be in the area of solvent extraction.

2. SOLUTION PURIFICATION BY ION EXCHANGE

General

The ability of naturally occurring zeolites to exchange ions from solutions has been used for many years for the softening of water. Natural materials were later replaced with synthetic organic polymers, or "resins", having a much higher loading capacity. Apart from water softening, the prime use of solid ion exchange resins in Canada has been in the recovery of uranium from the Elliot Lake(1) and Bancroft(2) areas in Ontario, and the Beaverlodge(3) area in Saskatchewan. Following a sulphuric acid leach of the ore, the ion exchange step is carried out from the clarified solution. An anion exchange resin is normally used. The feed solutions may contain up to 2 g U_3O_8/1, at a pH of approximately 2.0.

The process involves the ability of hexavalent uranium, as the uranyl ion UO_2^{+2}, to form anionic complexes with sulphate ions. These anionic complexes are sorbed selectively and quantitatively on an anion exchange resin, such as Amberlite IRA-400, a Rohm and Haas product; Permutit's SK, or Dow Chemical's Dowex-1. These resins are strong-base anion exchange resins containing quaternary ammonium groups.

A generalized flowsheet diagram of an ion exchange circuit for uranium is shown in Figure 1, on the sorption cycle, where the metal is being recovered. The two columns are series operated with continuous solution flow. At optimum loading conditions, No. 1 column becomes loaded when about 1 to 2% of the metal being sorbed appears in the effluent stream of the No. 2 column. At this time a third column in series is connected into the circuit. The loaded No. 1 column is then desorbed or eluted with a solution of about one normal concentration. The metal in the eluate from the loaded column is concentrated from 10 to 30 times its original concentration in the sulphate leach solution. An alkali precipitant is then added to a first portion of the eluted solution to recover the saleable "yellow cake". This 50 to 80% U_3O_8 product is further refined to a nuclear-grade product.

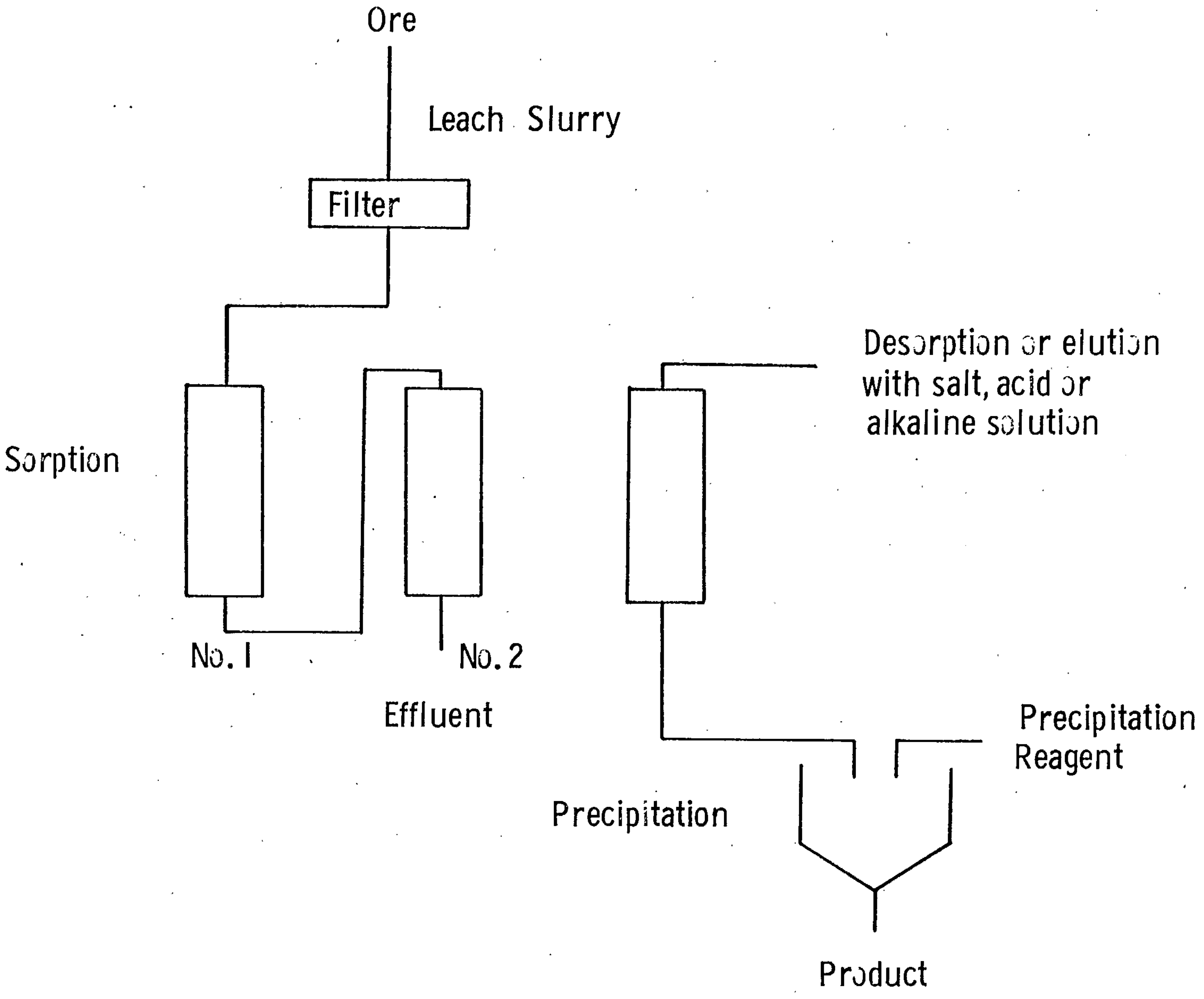


Figure 1. Ion-Exchange Processing Schematic Diagram.

Resin Poisoning and Impurities

Although an ion exchange resin may be considered as specific for one metal, e.g. uranium, impurities such as iron, thorium, silica, titanium, and vandium, which may be present in a uranyl sulphate leach solution, are sorbed to a minor degree along with the uranium. Some impurities such as molybdenum, polythionates, cobalti-cyanides, and silica act as "poisons" to the resin; that is, they are sorbed by the resin and not completely removed during the elution cycle. These poisons take up an increasing proportion of the resin capacity with each cycle, the result being that increased resin treatment or regeneration is required for their removal.

Cobalti-cyanide poisoning(4) of anion exchange resins presented the greatest problem to the South African uranium-recovery circuits. These complexes may occasionally be eliminated by ore-washing between cyanidation and sulphuric acid leaching. Polythionates, such as the tetrathionate ion $S_4O_6^{-2}$, presented a problem which was solved by eluting with a 1 M nitrate solution. This treatment destroys the polythionate by oxidizing it to sulphate. Silica poisoning is removed by a caustic + sulphuric acid wash of the resin. Cations such as molybdenum, zirconium, and titanium have been reported as resin poisons in some of the New Mexico uranium plants. Complexing agents such as EDTA are effective but expensive reagents for poison removal. The problem has been overcome by successive acid and alkaline washing of the resin(5). In the Canadian uranium industry, two areas -- Bancroft in Ontario and Beaverlodge in Saskatchewan -- had resin poisoning problems, as did a few of the early mills in the Elliot Lake area. The present mills in Elliot Lake now have no poisoning problems, due to the use of a nitrate elution. Initially they used a sulphuric acid-sodium chloride regeneration process.

Ion exchange recovery of uranium from sulphate solutions is often complicated by the presence of cations such as dissolved iron and thorium. These ions form anionic sulphate complexes and, since they are usually present in relatively large concentrations, compete for the resin in spite of the fact that they have a lower affinity for it than does the uranyl sulphate complex. This is true for the anion exchange resin Amberlite IRA-400, which is a strong-base exchanger. Initially, uranium, thorium and iron are loaded; with continued operation of the column the uranium progressively displaces the iron and thorium. The same applies to the sulphate ion. Increasing amounts of bisulphate, or low pH of the feed, results in a decrease in the saturation loading for uranium. A high pH, below that at which ferric iron will precipitate, will result in a higher uranium saturation of the resin with minimum impurity take-up.

As regards more selective anion exchangers, it has been reported recently that the Rohm and Haas Amberlite XE-270 weak-base ion-exchange resin is of interest in the purification of uranium acid-leach liquors(6). Amberlite XE-270 preferentially extracts uranium from solutions containing ferric iron and thorium, something the strong-base exchangers cannot do. Also, a slightly higher loading of uranium is achieved with this resin as compared to the conventional strong-base Amberlite IRA-400, which has been used in the Canadian mills. In addition to higher loading and greater selectivity for uranium, Amberlite XE-270 can be eluted more easily than can Amberlite IRA-400. Not only are fewer bed volumes of eluant required, but also a neutral solution such as NH_4NO_3 or NaCl can be used, thus decreasing the costs of elution considerably since acid is not necessary, as in the case with Amberlite IRA-400.

Resins and Processes

The synthetic polymers or ion exchange resins are made of stable, reactive, ionic groups which permit the exchange of the metal from the aqueous solution. These ion exchangers are divided into two types, anionic and cationic, and the following are the most common:

1. Anion Exchangers

Strong-Base

Quaternary Ammonium R_4N^+

Weak-Base

Primary amine - NH_2

Secondary amine - NHR

Tertiary amine - NR_2

In general the tertiary are the most popular because of stability.

2. Cation Exchangers

Strong-Acid

Sulphonic - SO_3H

Weak-Acid

Carboxylic acid - COOH

Phenolic - C_6H_4OH

Carboxylic resins are the commonly used weakly acidic cation exchangers.

Because of the variety of reactive groups, the resins are amenable to the recovery of metals from many solution types. Ion exchange continues to have its greatest use in the treatment of waters for purification, desalination, and for the treatment of industrial and municipal waste effluents. Also, ion exchange finds use in the recovery of metals from plating solution wastes. Although most metals have been recovered, separated and purified by some ion exchange process in the laboratory, relatively few metals have been recovered by ion exchange on a commercial scale. In hydrometallurgical processing, ion exchange methods have not developed very rapidly apart from the uranium industry. Michigan Chemicals, in the United States, separates the rare earths by ion exchange(7), using a total of 165 columns, 2.5 ft in diameter and 20 ft high. Small columns are used for separation of the less abundant rare earths(8). Chelation is used to enhance the separation of adjacent rare earths by elution with a solution containing EDTA(9); in this process, when a solution containing the complexing agent is added to a loaded resin containing the rare earths, the solution will tend to displace first those ions which form the strongest complexes in solution, that is, the smaller ions. The larger ions which form the weaker complexes in solution tend to remain on the resin. Thus, the rare earths leave the bottom of the column in reverse order of their atomic numbers.

In the presence of the large amounts of calcium and magnesium usually found in waste mine waters, the recovery of copper, nickel and cobalt using the sulfonic-acid-type cation exchange resins was not successful(10). Applicability of this system is somewhat limited, however, because the capacity of this resin for such metals decreases rapidly as the pH of the solution to be treated drops below pH 5.5. However, the use of this system could be of value either for primary recovery of these metals from the leach liquors or from the tailings following conventional precipitation procedures. Recent work has shown Amberlite IRA-120 sulphonic acid resin to be suitable for decreasing to 0.3 ppm of each metal from original values of 126 ppm Cu, 250 ppm Zn, and 60 ppm Fe. Small quantities of Ca, Mg, Al and Si salts were also present in the feed solution(197).

Amberlite IRC-50, a carboxylic acid-type cation exchanger, appeared to be highly selective for nickel, cobalt, and copper in solutions containing other metallic ions(10). The resin capacity for these metals decreases as the solution pH drops below 5.5. In some solutions, cobalt appears to show a stronger affinity for the resin than either copper or nickel. Subsequent attempts to recover copper and zinc from mine waste effluents with carboxylic ion-exchange resins proved unsuccessful(198). Using Amberlite IRC-50 and IRC-84, the tests showed both resins to be unsuitable for reducing efficiently the copper and zinc concentrations to < 1 ppm.

Table 1 shows a great many of the existing ion exchange processes, along with some process schemes not yet developed to the production scale, for the recovery of other metals. The reader is referred to the Selected Reading section for additional information.

TABLE 1

Ion Exchange Processing

Metal Adsorbed	Resin	Aqueous Phase	Comments	Ref.
Ag	Cation	Sea Water	Use of Duolite C-20 in ferric form.	11
As	"	Leach of flue dusts	Separates base metals from As.	12
Au	Anion	Cyanide	Recovery from solutions and pulps.	13,14
Au	"	"	Determination of breakthrough with radioactive gold.	15
Au	"	"	Studies on adsorption and desorption including electroelution.	16
Bi,Po,Pb	"	"	Use of Duolite A-101A to adsorb followed by selective elution.	17
Bi,Pb	"	Chloride, nitrate	Selective elution	18
Cu,Co,Ni	Cation	Mine Water pH 3.5-4.0	Carboxylic IRC-50	10,19
Cu,Zn	"	Sulphate	Amberlite IRC-120	20,197
Cd	"	Sulphate	Separation of Cd from As.	21
Cs	"	Nitrate	Separation from radioactive wastes	22
Cr	"	Various acid solutions	Recovery of chromic acid from plating wastes. Duolite C-20.	23

Table 1 (Cont'd)

Metal Adsorbed	Resin	Aqueous Phase	Comments	Ref.
Ge	Cation	Sulphate	Resin modified with tannin for selectivity of Ge	24
Li	"	Various acids	Use of Duolite C-20	25
Pd, Rh, Ir	"	Hydrochloric	Pt not adsorbed by Duolite C-20. Other metals selectively eluted with HCl	26
Ni	"	Sulphate	Recovery of ppm with Permutit Q type.	27, 28 29, 30
Nb, Ta	Anion	0.05 M HF + 9M HCl	Use of Dowex-1	31
Nb, Ta	"	Hydrochloric	Elution with 1M HCl+0.5M oxalic acid to separate Nb from Ta. Dowex-2.	32
Pa, Th	"	4-11 M HCl	Pa separated from Th and eluted with 4 M HCl Duolite A-101 D.	33
Pu	"	Nitric Acid	Both adsorbed and Th eluted with $(NH_4)_2SO_4$ and Pa with oxalate. Duolite C-20.	34
Pu	"	Sulphuric, phosphoric, oxalic	Duolite A-7 or A-101 D	35
Pu	Cation	0.3 N HNO_3	Pu^{+3} adsorbed on Duolite C-20 and eluted with 4 M HNO_3	36

Table 1 Cont'd

Metal Adsorbed	Resin	Aqueous Phase	Comments	Ref
Rare Earths (RE)	Cation	Acid solutions	Controlled pH elution with citric acid to separate the fractions. Duolite C-20.	7,8, 37
RE, Mo	Anion	Acid	Recovery from flue dusts and gases, and separation of RE from Mo. Duolite A-101 D.	38
RE, Mo	"	Alkaline	Concentrates and Separates RE from Mo.	39,40
Th, U	"	Sulphate	U removed with IRA-400 and Th with Permutit FF/530.	41
Th, rare earths	"	Sulphate	Amberlite IRA-400 for Th. Ce prevented by reduction with NaNO.	42
Th, U	Cation	Nitrate of chloride	Duolite C-3 or C-2, Th selective.	43
U	Anion	Sulphate	Amberlite IRA-400	1,6, 44,45
U, Th	"	Na_2CO_3+ $NaHCO_3$	Amberlite IRA-400. Separation U from Th. Also use of Duolite A-101, A-101D.	47,48, 49
U, V	"	Carbonate leach	Separation of U from V	50
U	"	Phosphate	Use of Duolite A-30 B, A-30 T.	51
V	Cation	Phosphate	Adsorption of V^{+4} and elution with acid or salt solution. Duolite C-20	52

Table 1 (Cont'd)

Metal Adsorbed	Resins	Aqueous Phase	Comments	Ref.
V	Anion	Solution containing Fluoride	Adsorption of V^{+5} is promoted by presence of fluoride. Duolite A-101, A-101 D.	53
Zr, Hf	Cation	Nitrate	Duolite C-20. Elution with 1 N H_2SO_4 to separate Zr. HF or oxalic to elute Hf.	54
Zn	Cation	Sulphate	Amberlite IRC-120. Elution with 25-30% H_2SO_4	55
Zr, Hf	"	0.8 M H_2SO_4	Zr eluted with 0.09 M citric + 0.45 M HNO_3, followed by Hf	56
V, U	Anion	Sulphuric	Amberlite IRA-400 for U. V oxidized and recovered with IRA-400 or XE-127	57
V, U	Anion	Carbonate	Selective elution	58

Resin-in-Pulp

An alternative to the static column ion exchange process has been developed, with varying success over the years, known as the resin-in-pulp (RIP) process. This involves the extraction of the desired metal from a leach slurry containing 10 to 50% of finely divided, undissolved ore particles. This process has been used in the uranium industry, where the resin is contained in a screen basket which is lowered into a stream of flowing pulp containing the dissolved uranium, thus eliminating the sometimes difficult and costly filtration step.

Because of higher resin losses due to attrition, the RIP circuit requires a slightly higher resin inventory than the column ion exchange. However, since processing equipment and operating costs are lowered by operating on a non-clarified system, this higher cost of resin per pound of uranium recovered may be offset by lower costs prior to the ion exchange recovery step. The RIP system has been developed to treat uranium-bearing solutions at 40% solids(45), and up to 52% solids was achieved in a gold-recovery system(14). The latter was accomplished using a pulsed column technique as shown in Figure 2.

A recent development in the treatment of leach solutions and slurries by ion exchange processing has been reported by Rosenbaum and George(46) of the U. S. Bureau of Mines They found that a countercurrent, multistage, ion exchange column, initially deveoped for recovering uranium from mine waters and clear solutions, was also effective for handling solutions containing up to 8% solids. Flow rates of 15 gallons per square foot per minute, with high recovery and efficient loading of the resin, have been reported. The column is composed of separate compartments, divided by perforated plates, so that each compartment serves as a unit in a countercurrent multistage system, as shown

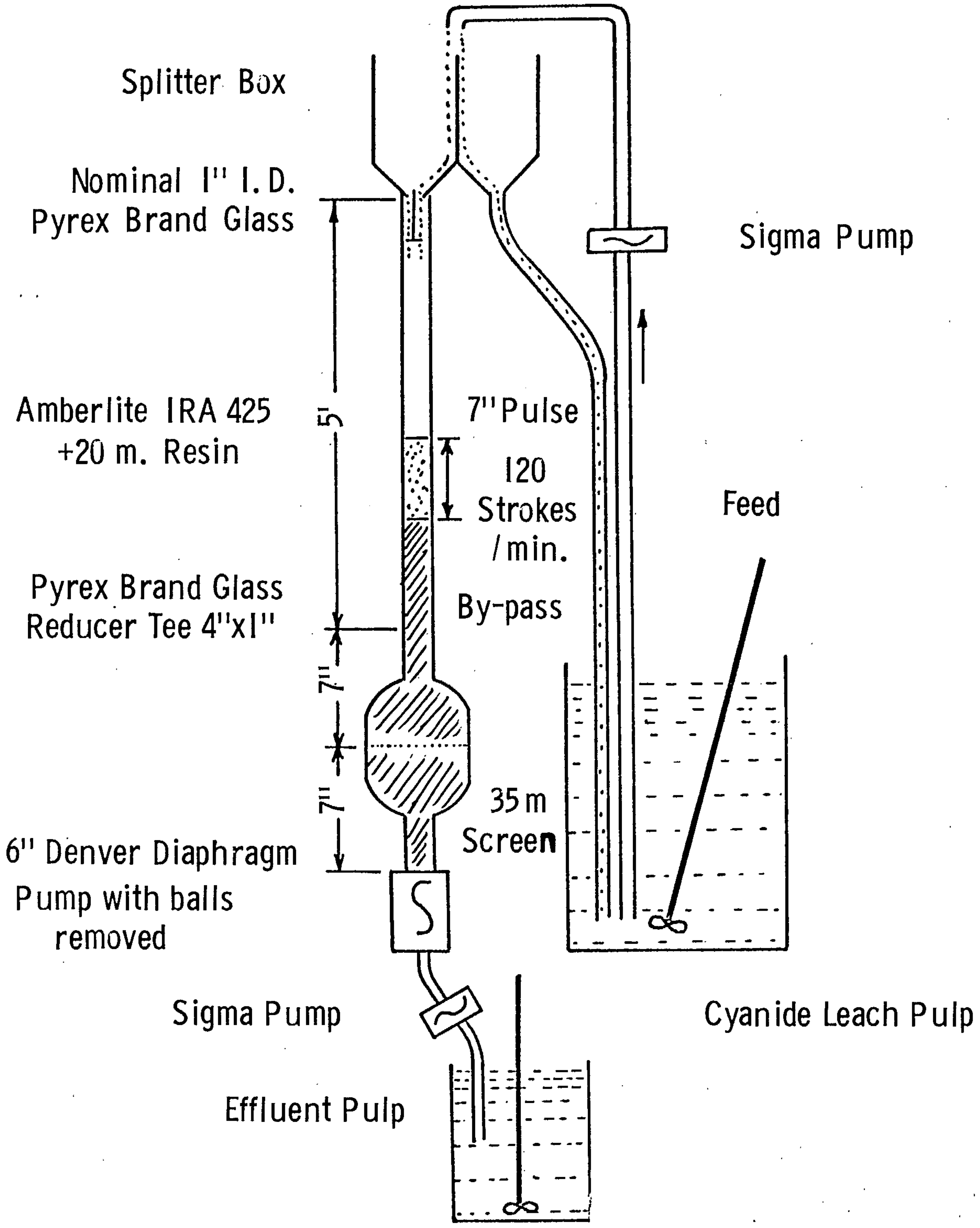


Figure 2. Pulse Column Arrangement for RIP Work. (From Gilmore$^{(14)}$)

in Figure 3. The feed solution enters the base of the column, flowing upward at a rate sufficient to fluidize the column of resin. The column operates with a continuous flow, except for scheduled interruptions when the resin is withdrawn through the resin outlet valve, and equivalent volumes of resin move downward through the perforated plates from one compartment to the next compartment below. The solution flow is stopped during resin withdrawal and resumed when the resin discharge valve is closed, and a charge of regenerated resin is conveyed to the top compartment of the column. The frequency of resin withdrawals and additions to the column are determined by the amount of metal fed to the column and the loading capacity of the resin.

Ion Exchange Equipment

Since most ion exchange systems are based upon equilibria which are reversible, complete exchange of ions cannot be achieved in a practical way unless a static column operation is employed(59). The mechanics of ion exchange is primarily the operation of beds of ion exchange resins contained in columns. Commercial metallurgical applications use static beds of resin, although other methods and apparatus for contacting ion exchange materials with liquids have been devised. One such device is the Higgins contactor(60), which is a continuous-ion-exchange apparatus where the resin and liquid containing the metal to be sorbed are pumped alternately. During the solution flow period of several minutes, the resin

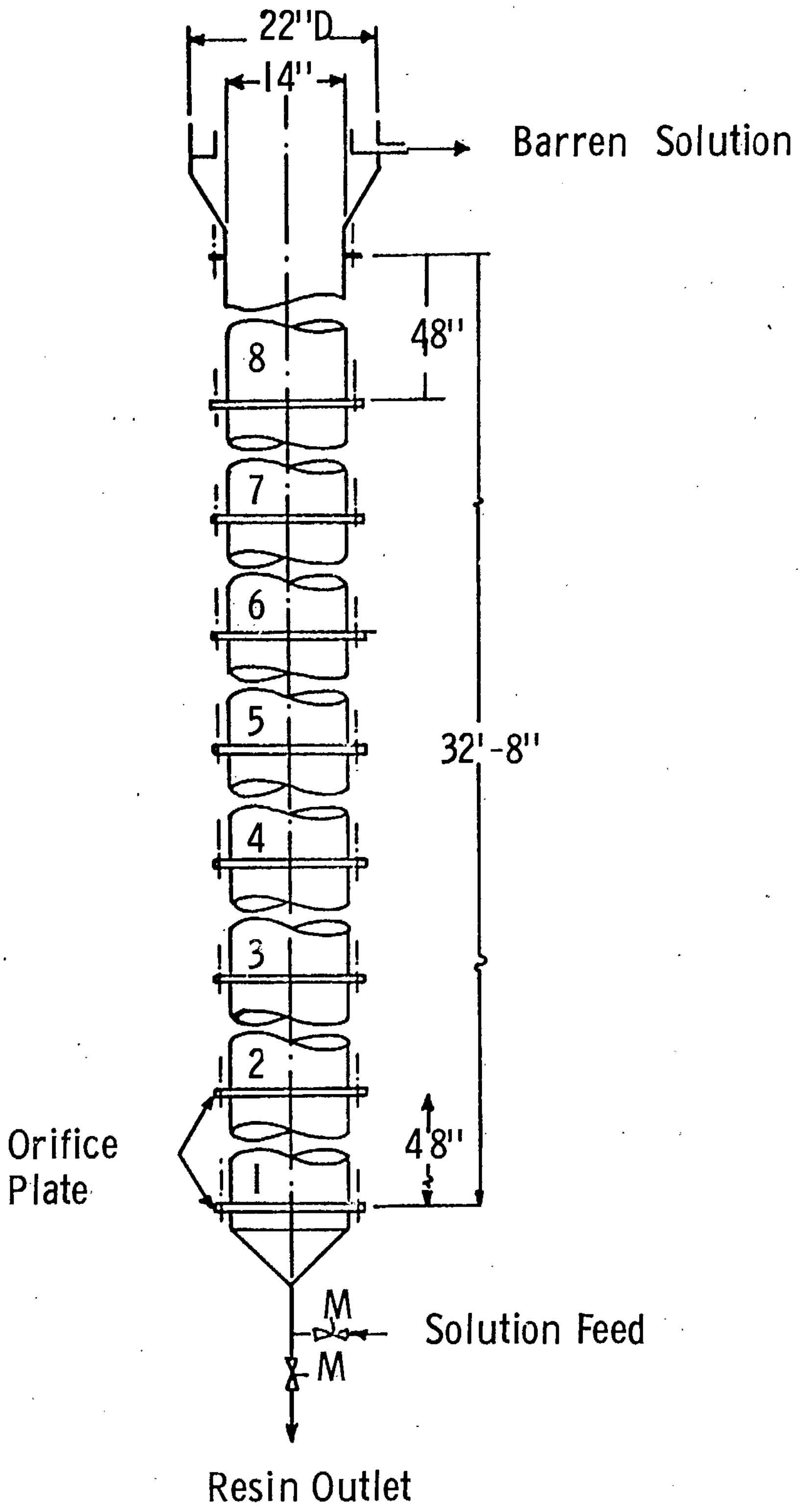


Figure 3. U.S. Bureau of Mines Multiple Compartment Ion Exchange Column. (From Rosenbaum and George(46)).

bed is in place and operates as a fixed bed. During the resin flow period of a few seconds the resin is moved in a pulsating motion by means of a suitable pump. The system is shown in Figure 4. A more recent development in continuous ion exchange processing is the Patterson Candy unit(61), based on the fluid bed contactor of Cloete and Streat. For a comprehensive review of countercurrent contactors, the reader is referred to an excellent review by Slater, No. 17 in the list of Selected Readings at the end of this report.

The basic equipment of a typical static-bed ion exchange column consists of: (1) a shell to contain the ion exchange resins; (2) a support for the resin; (3) adequate piping for distributing the flow both upwards and downwards; (4) space to accommodate about 100% expansion of the resin during backwash; and (5) inlet and outlet lines and flow control devices. A diagram of a typical unit is shown in Figure 5.

The shell for the ion exchange unit is generally of steel, up to 7 ft in diameter and up to 12 ft in height. The flow rate anticipated will determine the diameter of the column. A minimum bed depth of two feet of resin is usually required. The backwashing operation for the removal of fine slimes accumulated on the resin bed will help to dictate the height of the column. A freeboard of up to 100% of the resin bed is required to allow for the expansion of the bed.

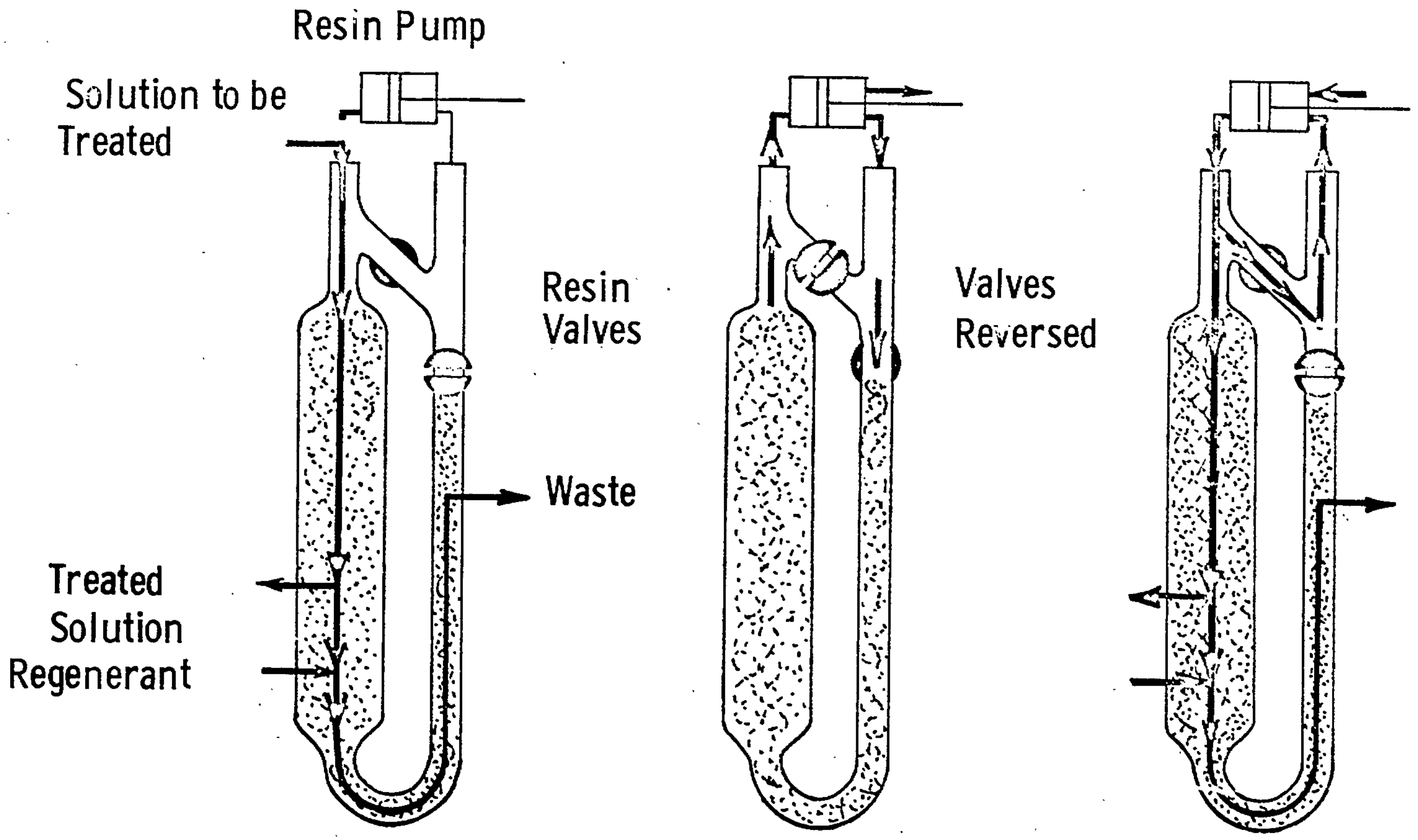


Figure 4. Operation of the Continuous Countercurrent Solid-Liquid Contactor. (From Higgins, I.R., Indust. & Engng Chem., Vol. 53 (No. 8), 635, August 1961).

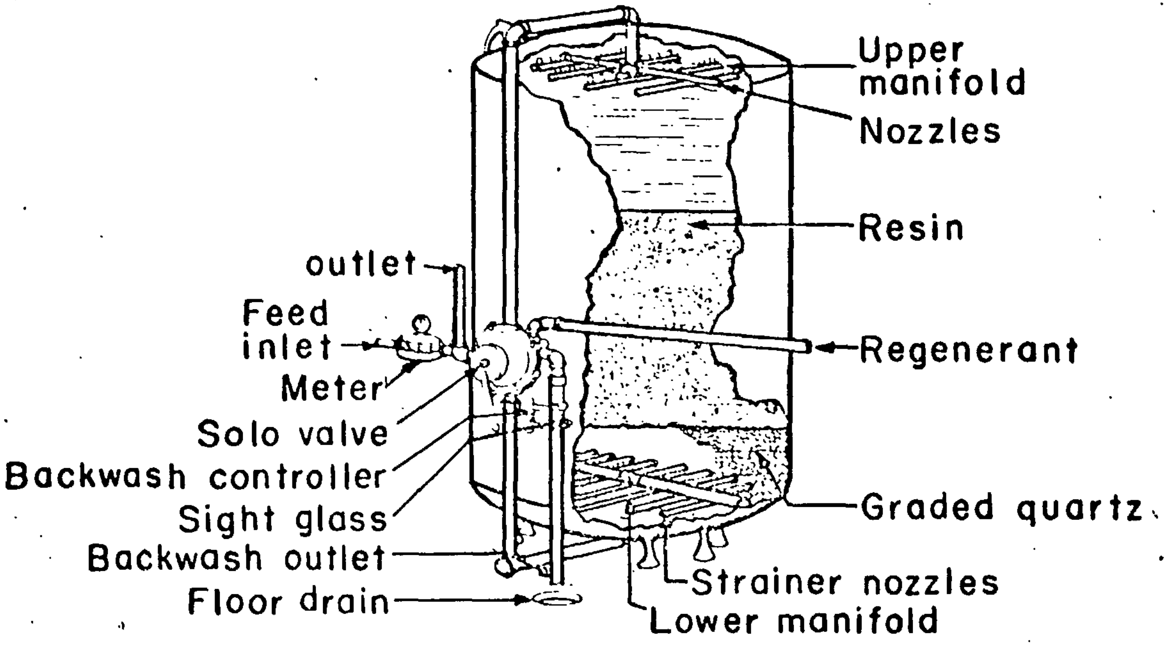


Figure 5. Typical Commercial Ion Exchange Unit. (From Kunin, R., Amber Hi-Lites, No. 70, July 1962).

Equipment Costs

Based upon fixed bed processing, it is obvious that equipment cost will be dictated by the volume of ion exchange resin and the number of columns. This variation of cost with respect to the cubic feet of volume (V) of resin for a single ion exchange column has been expressed methematically by Kunin$^{(62)}$ as:

Cost (\$) = 1208 $V^{0.55}$ (acid and alkaline resistant)

Cost (\$) = 906 $V^{0.55}$ (salt solution)

These equations are represented graphically in Table 2 and Figure 6. The estimated cost refers to the cost of the ion exchange unit, installation and automatic controls.

TABLE 2

Ion Exchange Resin Equipment Costs

Volume of Ion Exchange Resin (V) Cu ft	$V^{0.55}$	$1208V^{0.55}$[a] \$	$906V^{0.55}$[b] \$
1	1.00	1,208	906
10	3.55	4,290	3,220
50	8.60	10,400	7,790
100	12.60	15,220	11,420
750	38.10	46,000	34,500
1,000	44.70	54,000	40,500

[a] Rubber-lined, acid resistant.

[b] Steel, not acid resistant.

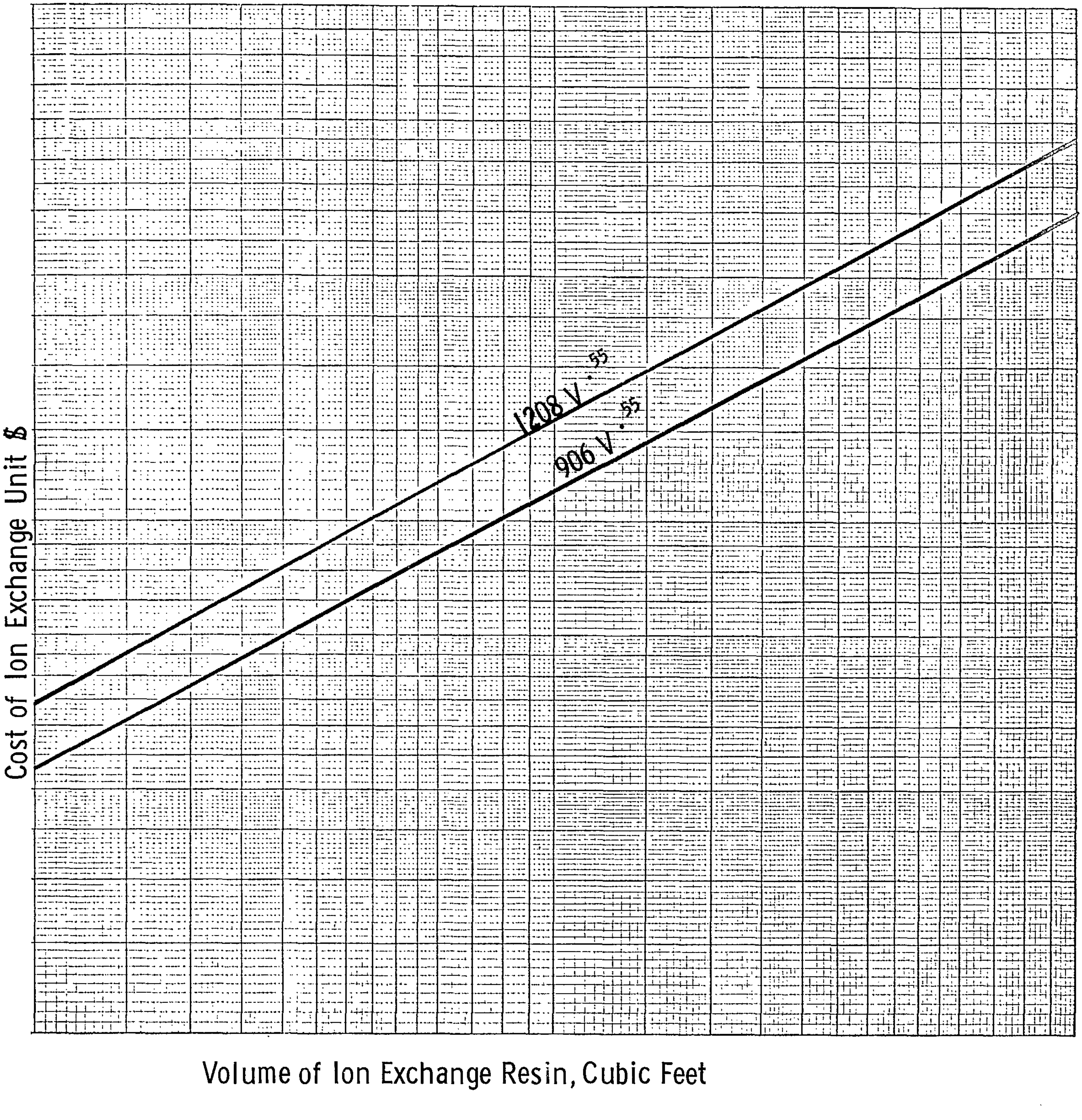


Figure 6. Cost of Ion Exchange Unit as a Function of Ion-Exchange Resin Volume.

Typical Ion-Exchange Processing Costs

Since the metallurgical applications of ion exchange processing have been primarily in the uranium industry, and therefore more information is available in this field, the following uranium recovery costs may be a guide to the recovery of other metals.

Estimates of the costs of ion exchange likely to be experienced in the three Canadian uranium-producing areas(63) are given in Table 3. For a 3,000 tons/day operation in the Elliot Lake area, a total estimated cost for the ion exchange operation is \$0.092 per pound of U_3O_8 recovered. Of this figure, \$0.057 is the cost of nitrate elution. The Elliot Lake experience has shown that nitrate elution is preferable to chloride elution because (a) it is less corrosive, (b) the volume of nitrate solution required to elute the resin is about half that of a chloride solution, and (c) nitrate solutions are more efficient in preventing resin poisoning.

Table 3 shows also that the costs of ion exchange in the Bancroft area where chloride elution was used are not much different from those incurred at Elliot Lake where nitrate elution was used. On the other hand, the estimated costs in the Uranium City area are much higher than in the other two areas, due partly to the higher cost of shipping reagents and partly to resin poisoning problems that result in high resin

TABLE 3

Ion-Exchange Processing Costs for Ore Containing 0.1% U_3O_8

	Cost Per Pound U_3O_8 Recovered		
	Elliot Lake (3,000 tpd)	Bancroft (1,000 tpd)	Uranium City (1,400 tpd)
Resin required, cu ft	3,000	1,000	1,400
Resin inventory,(1) dollars	135,000	45,000	63,000
Resin replacement,(2) \$/lb U_3O_8	0.010	0.010	0.030
Elution cost,(3) \$/lb U_3O_8			
1.6 lb HNO_3/lb U_3O_8	0.057		
(1.1 lb H_2SO_4 + 1.5 lb NaCl)/lb U_3O_8			0.098
(1 lb H_2SO_4 + 1.95 lb NaCl)/lb U_3O_8		0.032	
Resin treatment, \$/lb U_3O_8		0.006	0.015
Maintenance and labour	0.025	0.065	0.055
Total operating cost	0.092	0.113	0.198

1. Resin cost: \$45/cu ft
2. Resin replacement: 10% per year for Elliot Lake and Bancroft
   33 1/3% per year for Uranium City
3. Reagent cost: 70% HNO_3-\$70 per ton
   93% H_2SO_4-\$16 per ton
   NaCl - \$22/ton in Ontario
   Freight to Uranium City, \$100/ton

replacement cost. Whether the use of nitrate elution in the Uranium City area would be cheaper than chloride elution would depend on whether it decreased resin poisoning significantly.

Although the costs of ion exchange are modest compared with other costs experienced in ore treatment, considerable effort has been spent in searching for means whereby the solution purification step can be made more efficient. Greater efficiency could be brought about through the development of new and more efficient resins.

3. SOLUTION PURIFICATION BY SOLVENT EXTRACTION

Introduction

Solvent extraction, although relatively new as a unit process in extractive hydrometallurgy, has been practised for many years by analytical chemists. Interest in solvent extraction processes was first stimulated by work on the purification of metals in the nuclear energy field. Since then, some non-nuclear applications of solvent extraction have developed, and considerable effort is being devoted to the search for extractants and processing methods for both the less and the more common metals.

Purification by solvent extraction is achieved by separation of molecular species from aqueous media by means of immiscible specific organic solvents. The active extractant 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 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 contacting with an aqueous solution. Occasionally the extract contains undesirable impurities, and is therefore contacted or "scrubbed" with a suitable aqueous solution prior to the stripping stage. A schematic drawing of the process of solvent extraction is shown in Figure 7.

Adequate mixing of the phases is important, as is also the ready separation into discrete layers after mixing. Various types of mixing devices are used to effect the desired contact between the aqueous and organic phases. Brief descriptions of these devices will be given later.

Solvent extraction processes are not costly and their application need not be restricted to very high value metals,

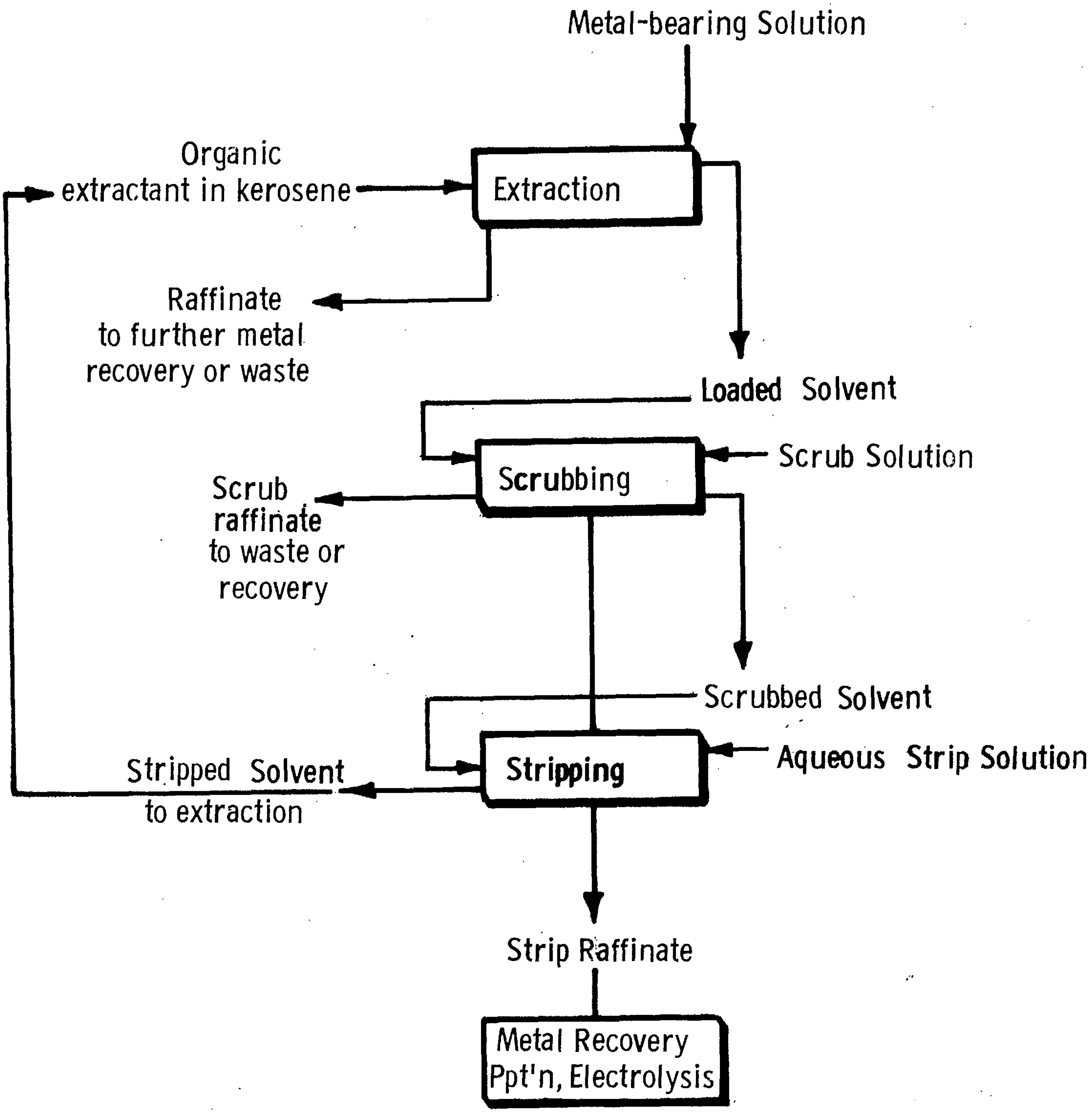


Figure 7. Solvent Extraction Processing Schematic Diagram.

as has been demonstrated in the use of this process for the recovery of copper(28,29). The chemical processing to obtain the metals in an aqueous phase suitable for solvent extraction is usually the most costly part of the overall extraction process.

Operating plants in the future will be concerned with the treatment of low-grade, possibly complex, deposits. Present-day processing techniques for the recovery from such deposits could be uneconomic. Recent techniques in the industry--e.g., 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(64). Solvent extraction is used for the separation of metals from complex solution mixtures and for the recovery of upgraded solution containing the values amenable to electrolysis, precipitation, etc.

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, and zirconium from hafnium, and for the purification of copper, uranium, thorium and the rare earths.

There are two types of processes that must be considered when we speak of solvent extraction. First, there is the liquid-ion-exchange type of extraction, which is chemically similar to extractions using ion exchange resins. There is an exchange for either an anionic or a cationic species in the aqueous phase, with an anionic or a cationic species in the extractant, depending on the particular organic system. An example of an anion exchange mechanism is the extraction of uranium from sulphate solution with a tertiary amine:

$$2[(R_3NH)_2SO_4] + [UO_2(SO_4)_3^{-4}] \rightleftharpoons [(R_3NH)_4UO_2(SO_4)_3] + [2(SO_4)^{-2}]$$

Cation exchange takes place in the extraction of cobalt with an alkylphosphate:

$$CoSO_4 + 2(RO)_2\ POOH \rightleftharpoons Co\left[(RO)_2POO\right]_2 + H_2SO_4$$

The second type of solvent extraction mechanism involves the solubility of the metal component of the aqueous phase with the organic phase. This mechanism, known as ion pairing, is demonstrated by the extraction of uranyl nitrate from nitric acid into tributyl phosphate:

$$UO_2(NO_3)_2 + 2TBP \rightleftharpoons UO_2(NO_3)_2.2TBP$$

Organic Extractants

The reagents available for the solvent extraction recovery of metals from aqueous solutions are far too numerous to deal with in length here. Since many of the extractants are still very expensive, only those reagents or reagent-groups that appear to have an immediate industrial application will be considered. These reagents fall into the following four classes: nitrogen-containing compounds, such as the amines; alkylacid phosphates; neutral organophosphorus compounds, such as tributyl phosphate; and carboxylic acids. Naturally the suppliers of these reagents can provide much additional technical information. In Table 4 are shown some of the commercially available extractants and references to their use.

Amines

The reaction between an amine, dissolved in an organic diluent, and an aqueous acid solution is essentially an acid-base reaction, and can be written in its simplest terms as:

$$R_3N \text{ (organic)} + H_3O^+ \rightleftharpoons R_3NH^+ \text{ (org)} + H_2O,$$

where the tertiary amine, R_3N, can be replaced by a secondary or primary amine.

The high-molecular-weight amines are often referred to as "liquid anion exchangers", and they have been found to behave similarly to solid anion exchange resins in extraction (65,66). The order of extraction preference in the amine organic solution is similar to that of anion exchange resins: $ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$.

The structure of the amine, and sometimes the nature of the organic diluent, will have a pronounced effect on the extraction of a metal. The classes of amines (primary, secondary, tertiary, quaternary) exert an effect, and these effects can be greatly modified by the extent of branched chains and the nature of the diluents, whether aromatic or aliphatic. The extraction of metals using amines can be modified occasionally by changing

Table 4

COMMERCIALLY AVAILABLE SOLVENT EXTRACTION REAGENTS

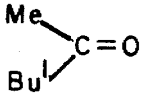
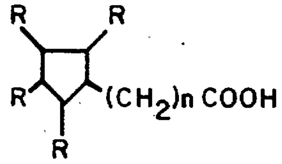
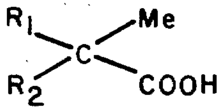
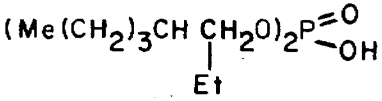
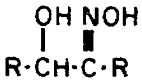
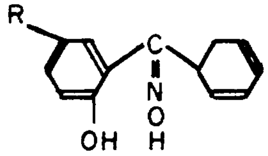
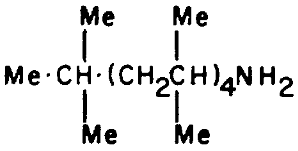
Reagent	Type	Structure	Supplier	Reference to Use
Tributyl phosphate (TBP)	Solvating extractants	$(BuO)_3P{=}O$	Canada Colors	67, 77, 90, 114, 115, 120, 122 131,144,146, 156, 158-160
Methyl isobutyl ketone (MIBK)			Chemcell	138, 141, 157
Napthenic acid	Liquid cation exchangers		Shell	173
Aliphatic carboxylic acids			Shell	72, 73, 100, 111, 125-127, 132
Di-2 (ethylhexyl) phosphoric acid (D2EHPA)		 $\mathrm{(Me(CH_2)_3CH\,\underset{\underset{Et}{|}}{C}H_2O)_2P{\genfrac{}{}{0pt}{}{=O}{-OH}}}$	Union Carbide	69-71, 98, 112-114, 117, 119, 130, 133 134, 142, 145, 149, 153-155, 161-169
LIX-63	Chelating extractant	 $\mathrm{R\cdot \overset{\overset{OH}{|}}{C}H\cdot \overset{\overset{NOH}{\|}}{C}\cdot R}$	General	71-73, 75, 76, 99, 129, 134

Table 4 (Continued)

COMMERCIALLY AVAILABLE SOLVENT EXTRACTION REAGENTS

Reagent	Type	Structure	Supplier	Reference to Use
LIX64 LIX64N	Chelating extractants		General Mills	82, 83, 128, 129, 176, 179, 180, 191, 192
LIX70			General Mills	84
Kelex 100			Ashland Chemicals	193
Primene JMT	Liquid anion exchangers	 $Me\cdot\overset{Me}{\underset{Me}{C}}H\cdot(CH_2\overset{Me}{\underset{Me}{C}}H)_4NH_2$	Rohm & Haas	118, 147, 150, 151, 170-172
LA-1, LA-2, and other Secondary amines		R_2NH N Lauryl trialkyl methyl amine	Rohm & Haas Ashland Chemicals	148, 150, 151
Tertiary amines		R_3N $R = C_8 - C_{10}$	General Mills and Ashland Chemicals	65, 66, 74, 101-105, 110, 116, 117, 121, 124, 136, 137, 143, 147, 151, 152, 182, 189, 190
Quarternary amines		$(R_3\overset{+}{N}Me)Cl^-$ $R = C_8 - C_{10}$	General Mills and Ashland Chemicals	116, 117, 135

the pH, while for some metals no effect is noted. By producing an aqueous system such that the desired metal is in anionic form, and therefore extractable with long-chain amines, the scope of liquid-liquid extraction has been greatly increased.

Useful separations can be attained between two chemically similar metals by proper selection of specific amine types. Thus, in sulphate solution, thorium can be separated from uranium by a primary amine, or uranium from thorium using a tertiary amine. In the extraction and separation of base metals, the use of amines has dictated a chloride system. The order of extractibility is quaternary > tertiary > secondary > primary. Iron, if present, requires reduction to the ferrous state to prevent co-extraction.

Tributyl phosphate -

Tributyl phosphate (TBP) is an important extractant of metals in the nuclear energy field from either chloride or nitrate solutions, and the mechanism is generally considered to involve coordination of the phosphoryl (P= O) group directly to metals, as in $UO_2(NO_3)_4 . 2TBP$. Although the extraction coefficients, E_A^O, for some metal nitrates, such as uranyl nitrate, are not affected by the nitric acid concentration, that of zirconium increases with nitric acid concentration above 7M. TBP can be used at 100% concentration, as well as at lower concentrations in an inert diluent, and in some extraction systems such as in the extraction of rare earths from nitric acid, the extraction efficiency is adversely affected by increasing the amount of diluent(67). In the refining of uranium and zirconium, 25-50% TBP is used.(90,77)

TBP has also been found to be useful in the extraction of base metals from chloride solutions. The use of a chloride system dictates the prior conversion of ferric iron to the ferrous state, to prevent co-extraction.

Alkylphosphoric acid -

The alkylphosphoric acids are possibly the most versatile groups of organic extractants with respect to the acid systems that can be tolerated. One of the most popular reagents of this group is di-(2-ethylhexyl) phosphoric acid (D2EHPA). This reagent is known to extract over a wide range of pH values, although the most satisfactory separations have been from weakly acidic solutions. The mechanism postulated for the extraction involves the displacement of hydrogen ions of the alkylphosphate to the aqueous phase, and the formation of an organometallic complex which is soluble in the organic phase:

$$M^{++}\ (aq.) + 2HR_2PO_4\ (org) \rightleftharpoons M(R_2PO_4)_2\ (org) + 2H^+\ (aq.)$$

The mechanism of extraction of a metal with the alkylphosphoric acids is usually considered as being one involving cation exchange. Alkylphosphoric acids have been used in the uranium industry, in the separation of vanadium, in the fractionation of the rare earths, and in the extraction and separation of the base metals. Usually, solutions of the reagent up to about 30% in a diluent can be used before increasing viscosity makes phase separation difficult.

Carboxylic acids -

Carboxylic acids (mol wt 200-300) are readily available in bulk from the petrochemical industry, and much research has been carried out in the last few years to develop processes utilizing these reagents. They operate by a cation exchange mechanism:

$$M^+ X^- + R\,COOH \rightleftharpoons R\,COO\,M + H^+ + X^-$$

Maximum extraction occurs just below the pH at which the metal hydroxide is precipitated, and therefore the process is highly pH-dependent. Utilization of pH permits separation to be made between copper and zinc, copper and nickel, and nickel and cobalt, to name a few. Two commercially available carboxylic acids on which research work has been reported are naphthenic(111,173) and Versatic 911(100,126,127,132).

Diluents and Modifiers

The active organic extractant is almost always dissolved in a carrier solvent, which, for most purposes, is chemically inert with respect to the aqueous phase. The primary function of the carrier is as a diluent to provide suitable viscosity in order to obtain maximum mass transfer of the metal ion from the aqueous to the organic phase. Kerosene is probably the most popular diluent, although many other hydrocarbons have been used. Within the kerosene group of diluents there is a great difference as to extractability, depending on the aliphatic or aromatic content. As is shown in Figure 8, the per cent aliphatic or aromatic component has a pronounced effect on the separation of rare earths(68). For reasons of safety, it is sometimes necessary to choose a diluent that has a flash point above 120°F.

In addition to the active organic and the diluent, occasionally it is necessary to add a third organic component to the solvent mixture. Known as a "modifier", it must also be inert to the system, soluble in the diluent, and insoluble in the aqueous phase. Its concentration generally ranges up to 10 weight % of the diluent. The main function of the additive is to ensure that intermediates in the extraction reaction will remain soluble in the diluent and not cause a third phase or emulsion formation. Modifiers that have been most commonly used include tributyl phosphate and alcohols such as capryl alcohol, 2-ethylhexanol, isodecanol, and tridecyl alcohol.

Pre-Treatment of Solvent

After the extractant, modifier, and diluent are mixed together, the solvent mixture is usually treated with an aqueous solution prior to the extraction stage. This pre-treatment stage

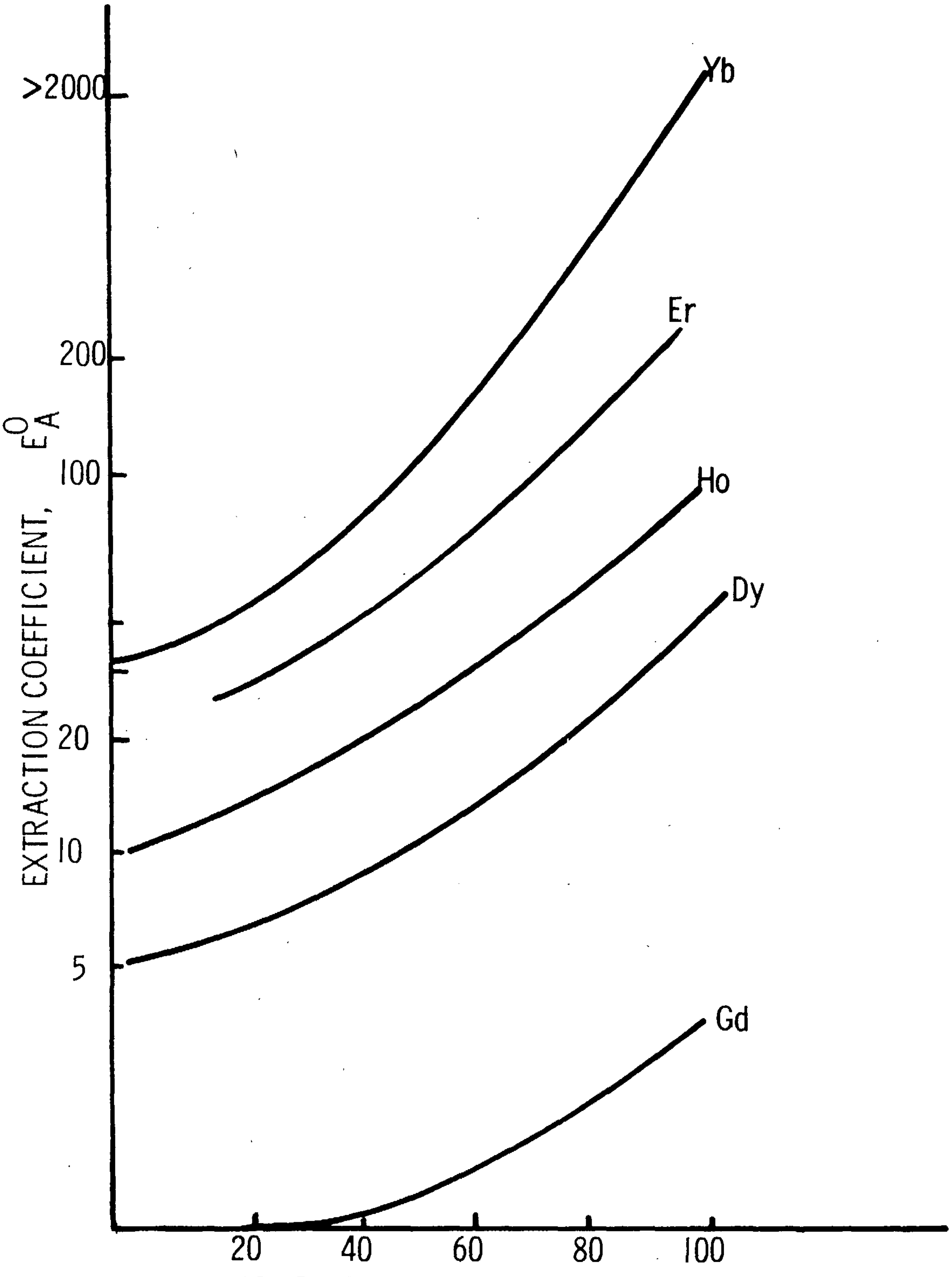


Figure 8. Effect of Diluent on Extraction Coefficients of Rare Earth Mixture. (From Ritcey and Lucas[(68)]).

is generally termed the "equilibration" of the solvent. The object is to convert the active grouping on the extracting reagent to the desired group so that optimum conditions of extraction will result on subsequent contact of the equilibrated solvent with the aqueous leach solution. For example, in the extraction of uranium from a sulphuric acid leach solution with a tertiary amine, the amine requires conversion to the H^+ form in order to extract the anionic uranyl sulphate complex. This is accomplished by contacting the amine solvent with a sulphuric acid solution.

Solvent equilibration

$$\left[2R_3N\right]_{org.} + \left[2H^+ + SO_4^{-2}\right] \longrightarrow \left[R_3(NH)_2SO_4\right]$$

Liquid ion exchange

$$2\left[R_3(NH)_2SO_4\right] + \left[UO_2(SO_4)_3^{-4}\right] \rightleftharpoons \left[(R_3NH)_4UO_2(SO_4)_3\right] + \left[2(SO_4)^{-2}\right]$$

If the uranium is recovered from the loaded solvent by stripping with an alkaline solution such as sodium carbonate, then the solvent will require equilibration with sulphuric acid prior to the next extraction cycle. If acid stripping is used, no pre-equilibration of the solvent is necessary.

Occasionally it may be necessary to maintain a buffered pH during the extraction. One means of achieving this, other than by continual additions of acid or alkali to the system, is to equilibrate the solvent. For example, in the extraction and separation of cobalt and nickel in a sulphate solution using

D2EHPA, the pH range for maximum extraction was found to be pH 5.0 - 6.5(69). However, when an aqueous feed at pH 5.5 was contacted with D2EHPA, the terminal or equilibrium pH was about 3.5. A low saturation loading resulted at pH 3.5 compared to pH 5.5. The decrease in pH was due to the release of the H^+ of the alkylphosphoric acid to the aqueous phase for the exchange of the Co^{+2} ion. It was found that the system could be maintained at the pH 5.5 range by pre-equilibrating the solvent with an alkali such as ammonium hydroxide. Thus, with the extraction of cobalt at pH 5.5, the $NH_4{}^+$ ion was released. The pH could be maintained at about 5.5 as a result of the formation of ammonium sulphate in the aqueous phase, rather than sulphuric acid as was the case when the solvent was not pre-equilibrated.

Equilibration of D2EHPA with NH_4OH

$$(RO)_2PO(OH) + NH_4OH \rightarrow (RO)_2PO(PNH_4) + H_2O$$

Extraction of cobalt into $D2EHP(NH_4)$

$$CoSO_4 + 2(RO)_2PO(ONH_4) \rightleftharpoons \left\{ \left[(RO)_2P(O)O \right]_2 Co \right\} + NH_4{}^+$$

Occasionally after a solvent has cycled several times through a circuit there will be a build-up of a "non-strippable" element. This may be either an impurity, such as iron in a rare earth circuit using di-2(ethylhexyl) phosphoric acid(68), or perhaps a build-up of the actual metal desired to be recovered. An example of the latter is the build-up of zirconium on tributyl phosphate in the nitric acid system for the separation of zirconium from hafnium(77). A separate solvent treatment stage is required, such as a sodium carbonate wash, followed then by acid equilibration prior to the extraction cycle. This clean-up sequence is generally accomplished by a "bleed" of the stripped solvent. Because it is known that amines don't extract metals well in the presence of, or from, nitric acid solutions, then in a system employing a nitric acid strip to recover a metal from an amine, an alkaline wash is also required prior to acid equilibration(150).

Synergism

Occasionally, it may be necessary to mix two extractants together to achieve a specific separation. Normally these extractants, when used separately, might be quite ineffective under the desired operating conditions. The phenonemon where extraction is enhanced by mixing extractants is known as synergism. For example, it was found that the addition of a substituted oxime, LIX-63 to D2EHPA resulted in a lowering of the equilibration pH for the maximum extraction of copper from acid solutions. In addition to an improvement in the extraction of copper, the mixing of the two reagents enabled a satisfactory separation to be made from iron, cobalt and nickel(71). The extraction curves are shown in Figure 9. Also, the addition of LIX-63 to naphthenic acid has been found to enhance the extraction of copper(72).

Scrubbing

After extraction of a desired metal from the leach

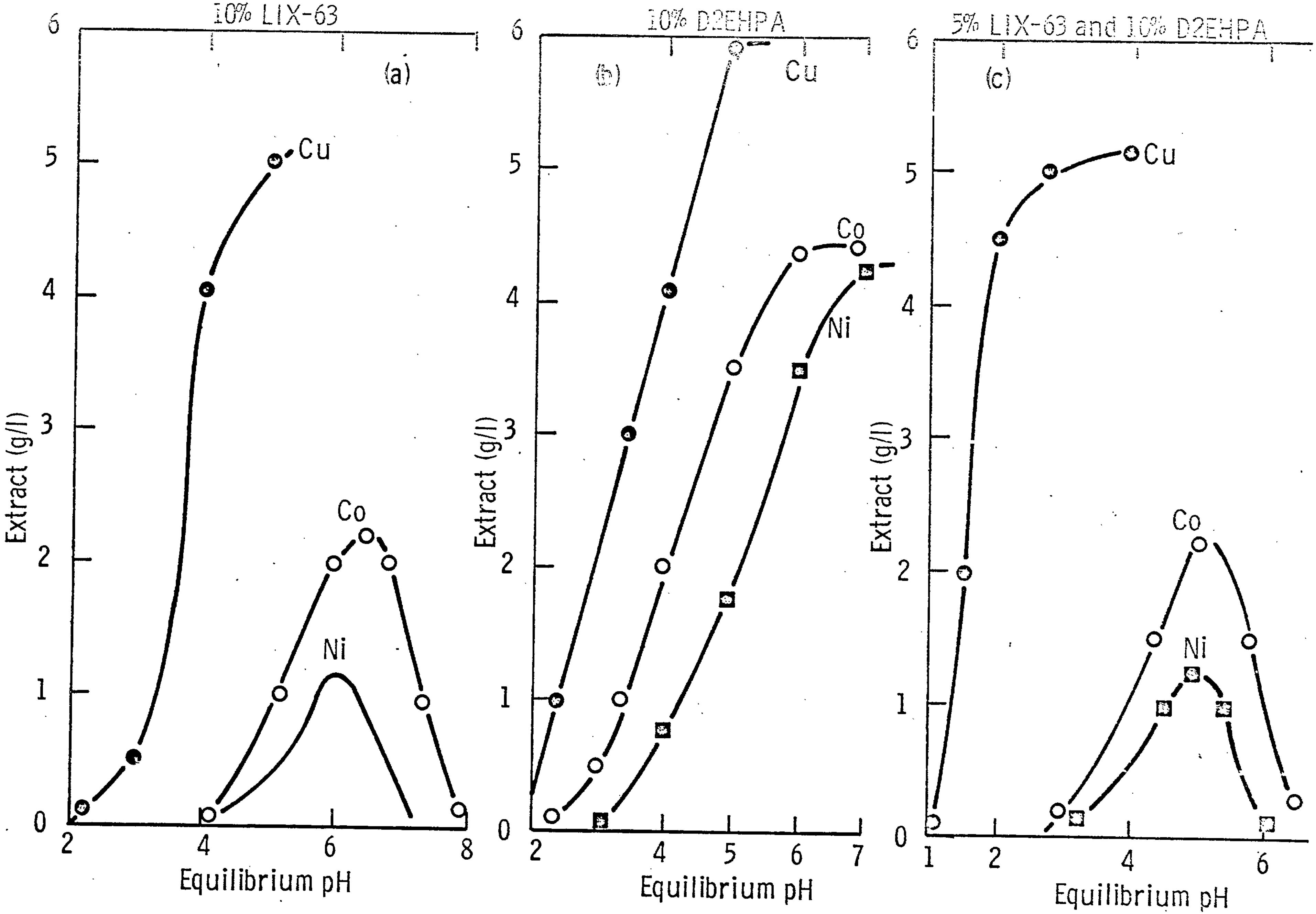


Figure 9. Use of Mixed Extractant for Cu, Ni, Co. Loading versus pH: (a) 10% LIX 63; (b) 10% D2EHPA; (c) mixture of 5% LIX 63 and 10% D2EHPA. (From Joe, Ritcey and Ashbrook$^{(71)}$).

solution, the loaded solvent will normally contain a certain amount of impurities. If the loaded solvent is stripped directly with an aqueous solution, the final product will contain these impurities. Therefore, subsequent to the extraction stage, a scrubbing stage is necessary prior to recovery of the desired metal. Scrubbing, which is essentially a controlled stripping stage, can be accomplished in any of the following four ways:

1. In the first type of scrubbing, the loaded solvent can be contacted with dilute aqueous solutions to remove readily soluble impurities. This scrubbing is effective in the recovery process for uranium from sulphuric acid leach solutions using a tertiary amine(74). During extraction, small quantities of iron are co-extracted with the uranium, and is readily removed as a water-soluble sulphate by scrubbing with water.

2. The second type of scrubbing can actually be made effective during extraction. If more stages are available than are actually required for extraction, then scrubbing will probably take place. A large number of stages during extraction can be made available if an agitated type of column, such as a pulsed sieve-plate column, is used. If two or more metals of equal concentration tend to extract under the extraction conditions used, then the one having the greatest extraction coefficient will extract first. At saturation loading of the solvent, in addition to the desired metal, there will be the other co-

extracted metal at a lower concentration. By increasing the number of stages of extraction, as in the case of additional column length, the metal having the lowest extraction coefficient ($\overset{o}{EA}$) will be replaced with the metal having the higher $\overset{o}{EA}$. ($\overset{o}{EA}$ will be explained more fully later, page 48, under Bench-Scale Testing.) This type of scrubbing has been demonstrated in the Co-Ni separation(69). Cobalt is extracted into the solvent almost immediately the solvent enters the column, and only a few feet are used for bulk extraction. The remainder of the column, with many stages, is used to scrub the co-extracted nickel out of the organic phase. As the solvent rises up the column it contacts the aqueous cobalt feed solution flowing down the column. Cobalt replaces nickel in the solvent and the extract overflowing the top of the column is essentially saturated with cobalt and contains very little nickel. With increased number of stages, the Co/Ni ratio in the extract is increased. This is shown graphically in Figure 10.

3. The third type of scrubbing is to contact the loaded solvent with an aqueous solution that will provide the most efficient exchange of metal ions. This is effected in two ways: (a) by using a salt solution of the metal desired in the loaded solvent or (b) by using a dilute acid solution. In method (a), suppose the loaded solvent contains copper with nickel as an impurity. Scrubbing the loaded solvent with a copper sulphate

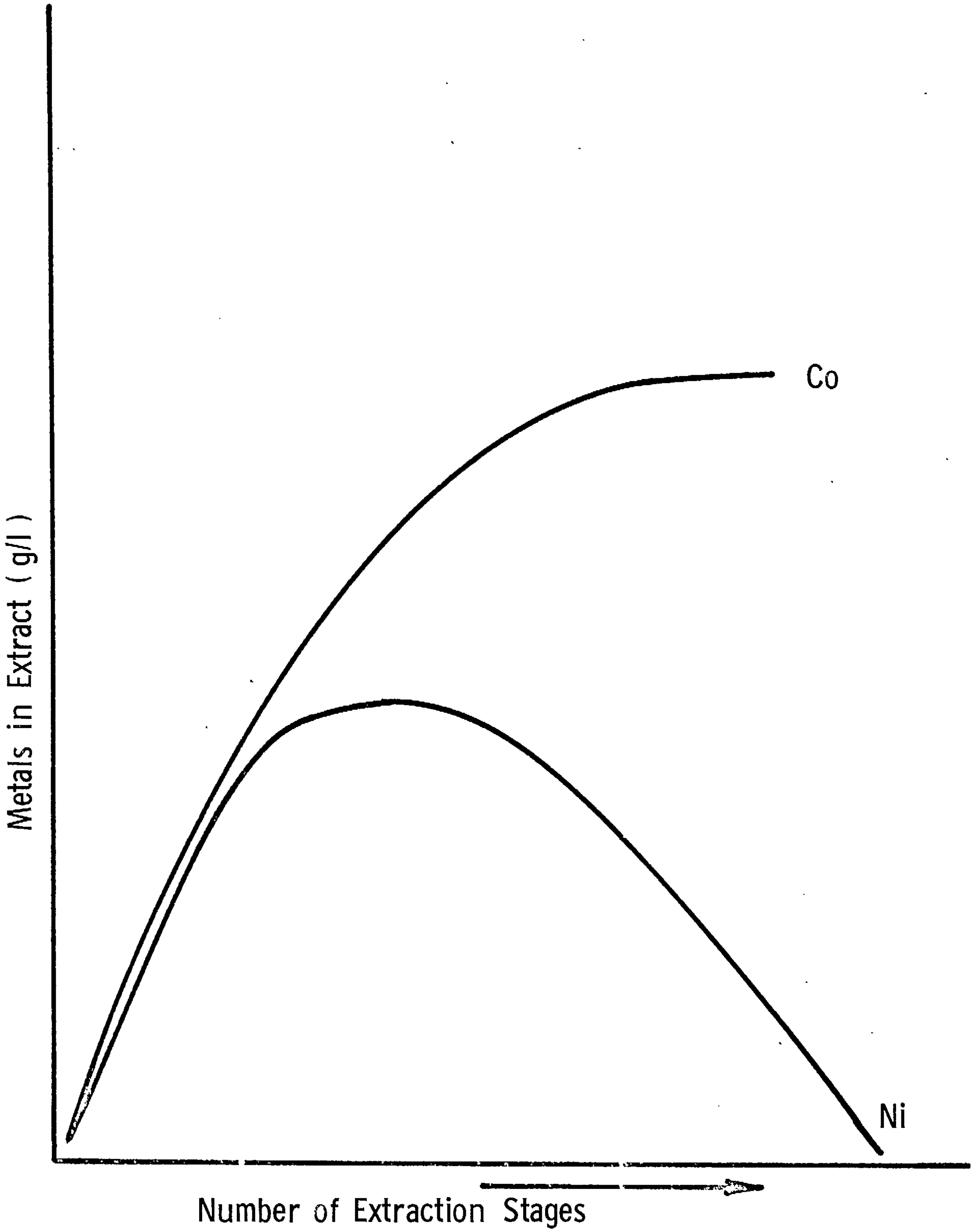


Figure 10. Stagewise Separation of Cobalt and Nickel.

solution effectively removes the nickel and results, for example, in upgrading the Cu/Ni ratio in an extract from 7 to 800 after three scrub stages(75). Method (b) utilizes pH control, using either a salt or a dilute acid. The mechanism using dilute acid has been demonstrated in plant operations(69,77). By proper choice of the acid concentration, for example 0.6N H_2SO_4 in the Co-Ni separation and by using a pulse column, the nickel is removed and replaced by cobalt(69). This is achieved when the dilute acid passing down the column actually strips some cobalt and nickel off the loaded solvent, to the point where a concentrated aqueous metal solution is present. As this concentrated cobalt solution containing nickel contacts fresh loaded solvent moving up the column, the nickel is replaced by the cobalt in the aqueous scrub solution.

4. Finally, scrubbing can be performed as a separate continuous operation in a second column; or the scrub solution may be introduced into the extraction column.

Stripping

The recovery of the metal from the scrubbed solvent is accomplished by contact with an aqueous solution. This is known as "stripping". The stripping procedure is the reverse of extraction, and thus the aqueous medium must not have the same acidity as that from which the metal was originally extracted. In the ion exchange mechanism of extraction, the metal is generally stripped with an acidic or basic solution of different pH than the original feed solution. In the ion-pair extraction system, the metal is usually recovered by stripping with water, since the metal-acid pair on the extract is solubilized in the water. The stripping medium is often dictated by the desired final product - whether a sulphate, nitrate, chloride, or oxide.

Recently, work has been described in the literature on the direct reduction, under pressure, of the loaded solvent to produce metal powders(177,178). This route has proved successful with carboxylic acids, and so might be applicable to the recovery of metals, such as copper, cobalt or nickel, from metal-carboxylates without the requirement of a stripping circuit.

Use of Complexometry in Solvent Extraction

Occasionally, in a metal recovery system using solvent extraction, the presence of other interfering metals may present a serious co-extraction problem. In some cases, change of oxidation state, or pH adjustment to precipitate the unwanted metal, may be used. Another method is the addition of a chemical reagent to the aqueous medium to form a metal ion complex which changes the extraction characteristics or extraction coefficient E_A^o of the metal ion. For example, the addition of EDTA to a solution containing cobalt and nickel sulphates will enhance the individual E_A^o for each metal ion, as well as increase the separation factor between cobalt and nickel(78). The use of the same complexing agent to inhibit the co-extraction of iron in a rare-earth separation process using D2EHPA has also been done; iron extraction is depressed, while the $\overset{o}{EA}$ of the rare earths is enhanced(68). Similar results from using chelating agents to enhance the separation characteristics of rare earths using amines, have been reported(79,80,81).

Bench-Scale Testing

In the choice of a suitable solvent for a particular system, certain preliminary screening tests can be carried out in order to narrow the range of reagents to be tested. The solvent should have a very low solubility in the aqueous medium, and no degradation on recycle; it should not form a stable emulsion when mixed with the aqueous phases, and should be relatively inexpensive. These screening tests or shake-outs are normally carried out in separatory funnels in the laboratory. When the choice of possible extractants has been narrowed, additional shake-outs are performed to determine the following: how specific the extractant is for a particular metal; the loading capacity; the pH and temperature dependency; the requirements for modifier or special diluents; and the scrubbing and stripping characteristics.

In the development of a flowsheet upon which plant design and operating cost estimates may be made, considerable information is required, but perhaps one of the most useful is the "distribution or extraction coefficient" of the metal. The extraction coefficient is a measure of the extractibility of a particular metal into a given solvent. This extraction coefficient is a constant value only for a given set of extraction conditions. Since it is a measure of the over-all chemical driving-force, it is dependent upon the chemical concentrations involved. A change in chemical composition resulting from a shift in pH can alter considerably the chemical equilibrium and therefore the extraction coefficient. The coefficient is the ratio of the concentration of the metal in the organic phase to the concentration of the metal in the aqueous phase after equilibration of the two phases.

$$E_A^o = \frac{[M]_o}{[M]_A}$$

The larger the number for E_A^o, the greater is the tendency for the metal to extract into the solvent. Extraction coefficients up to 500 are common in uranium extraction with amines. If more than one organic reagent were under consideration as the extractant for a particular system, then the reagent giving the highest E_A^o would probably be the most suitable.

If more than one metal is present in the aqueous solution, as is the general rule, than a comparison of the relative extraction coefficients of these metals is useful. The ratio of the extraction coefficients of two metals being compared is known as the "separation factor", and defines the purification level obtainable in one stage of extraction:

$$SF = \frac{(E_A^o)_a}{(E_A^o)_b} ,$$

where a and b are two metals in solution. If this ratio is greater than 1.5, one can normally expect to separate the two metals provided that a sufficient number of contacts of the organic with fresh feed solution are made.

The active organic dissolved in the inert diluent is made to a certain concentration, and therefore is capable of holding, at saturation, a limited amount of a metal. This "saturation loading" value for the system is therefore quite important, since it governs the volume of solvent flow necessary to contact a fixed tonnage of feed solution. By variation of the ratio of aqueous and organic volumes in bench-scale shake-outs, or by repeated contact of organic with fresh feed solution, the saturation loading for a particular system may be determined.

These data on saturation can also be utilized to construct an "extraction isotherm" or "distribution isotherm". If the concentration of the metal in the organic phase is plotted against the concentration of the metal in the aqueous phase at constant temperature, a curve similar to Figure 11 results.

Each process of mixing and separation of the organic

Figure 11. Extraction Isotherm.

and aqueous phases is considered a "stage". Depending upon the number of "theoretical stages", and therefore the type of equipment to be used, and knowing the E_A^o and SF, the feasibility of the process may be determined.

The extraction isotherm, however, becomes of additional value when it is used to calculate the number of theoretical stages of extraction necessary to achieve the required organic saturation with a minimum loss of metal to the raffinate. This is known as a McCabe-Thiele diagram.

In the construction of a McCabe-Thiele diagram, the extraction isotherm is first plotted. Then a second line, known as the "operating line", is drawn on the same graph. This line is straight, the slope being the ratio of the aqueous to organic flows. The operating line is based on the mass balance of the system, and therefore the concentrations of metal in the solvent entering, and in the aqueous raffinate leaving, any stage are coordinates of points on the operating line. Similarly, the concentrations of metal in the aqueous feed entering and in the extract leaving any stage are coordinates of points.

A typical diagram is shown in Figure 12. The theoretical stages are stepped off by extending a horizontal line from the upper end of the operating line to intersect the extraction isotherm; then a vertical line is drawn to intercept the operating line. This is continued until the lower end of the operating line

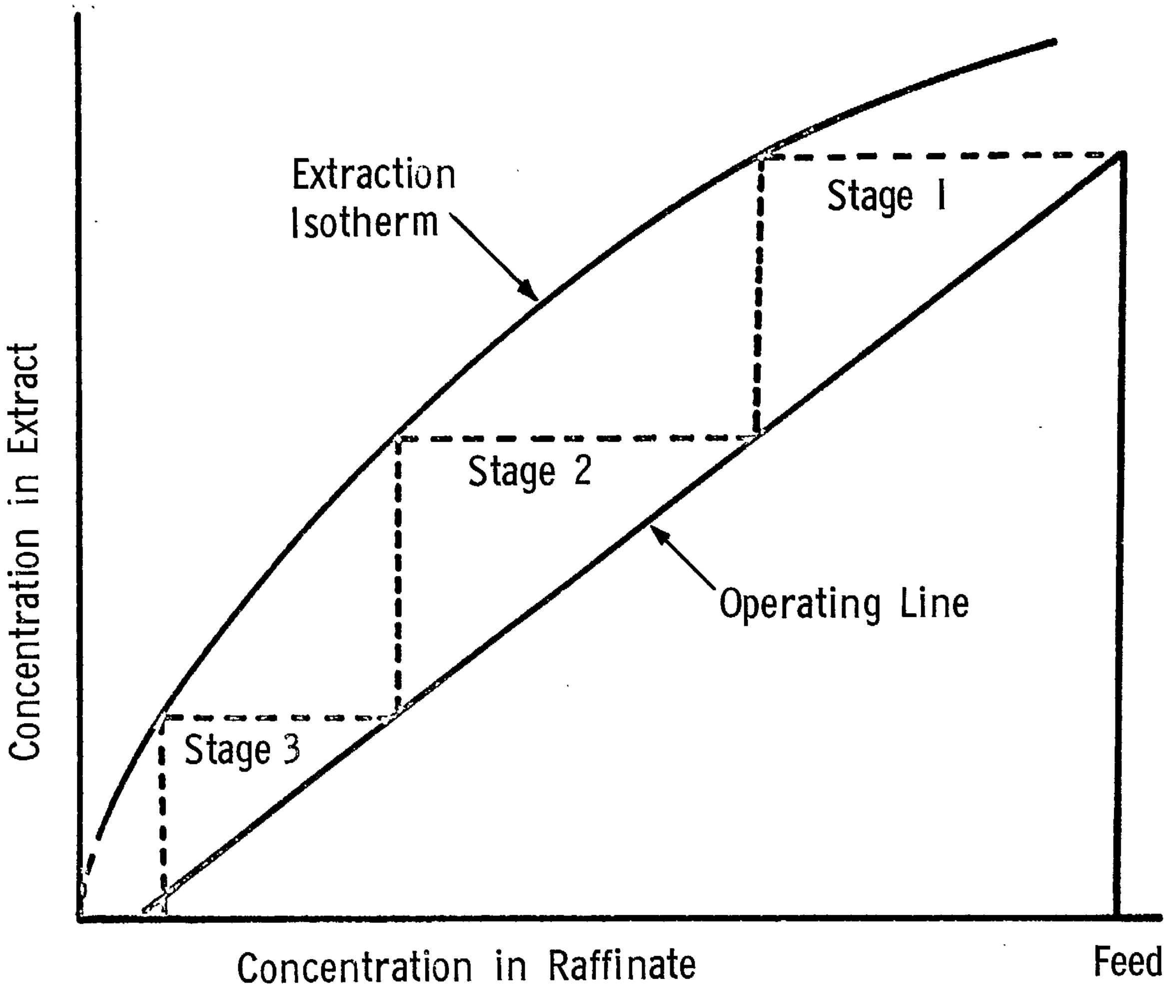


Figure 12. Hypothetical McCabe-Thiele Diagram.

is intersected. Each step is called a theoretical stage.

In the example shown, slightly over three theoretical stages would be required. In actual practice, if mixer-settlers were to be considered for extraction, a cascade of four contactors would be required. When multistage contactors such as columns or centrifuges are used, in which an extraction stage is not evident, the McCabe-Thiele diagram is used only as an approximation. Generally, the diagram permits the calculation of extraction and stripping efficiency and the correlation of this efficiency with such operating variables as flow rates, contact time, mixing, and temperature. It is usually found that the speed with which equilibrium is attained is affected by variables governing the rate of mass transfer, such as the turbulence or degree of mixing, the temperature, and the viscosity of the system.

Scale-up Plant Operation

It has been the practice, in processing by solvent extraction, to go to a small pilot-plant operation after sufficient bench-scale testing has determined the parameters of the system. Many investigators use a series of cascading mixer settlers to achieve this purpose. These are usually very small, up to 100 ml in capacity, and in some cases are ideal for testing the process in the laboratory on a continuous basis. A diagram of one of these small mixer settler systems is shown in Figure 13.

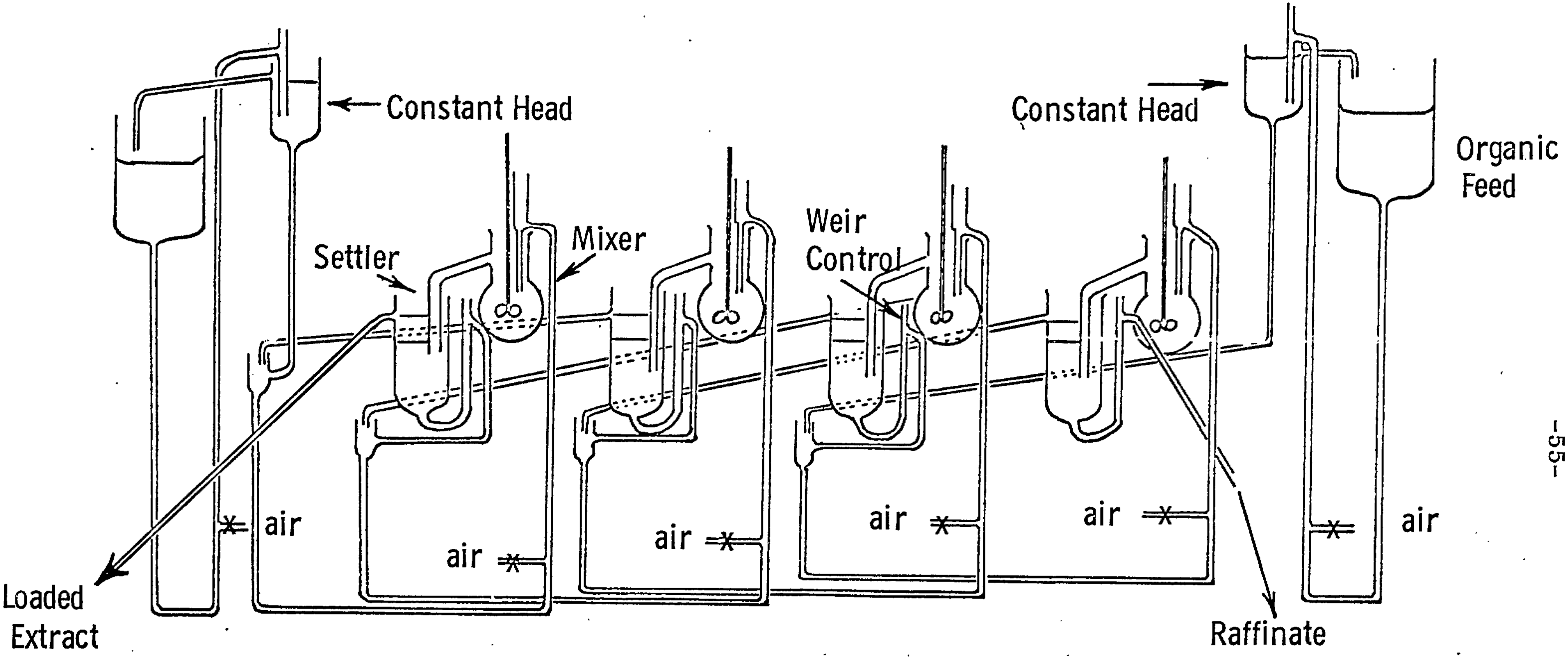


Figure 13. Diagram of Small Continuous Countercurrent Mixer-Settlers in Series.

Another approach has been a larger mixer settler unit, where 1 to 2 gallons of feed per minute would be the throughput. For a system where only a few stages of extraction are required, this type of pilot plant operation is satisfactory.

However, where many theoretical stages of extraction are necessary in order to achieve the necessary separation between two or more metals, other equipment is required. The author has found that a pulsed sieve-plate column is satisfactory. (The pulse column is described more fully in the Equipment section next following.) Initially a 1½-in.-diameter column, 7 ft high, was used, but this proved impractical due to wall effects on such a small diameter. Increasing to 2-in. diameter proved satisfactory, and numerous pilot plants have been run, and successfully scaled-up to a plant, using this size column, although 6-, 10- and 22-in. column diameters have also been used. Overall extractions and separations were slightly better with the larger columns, but did not differ significantly from those obtained by 2-in. columns. Some of the scale-up results for Co-Ni separation and Zr-Hf separation using pulsed columns(89) are shown in Table 5.

Pilot-plant studies should cover a wide range of flow rates and phase ratios, as well as changes in equipment variables. Also, in the pilot plant, provision should be made to determine solvent losses and the effect of recycling the solvent on extraction performance. Because mass transfer coefficients are very sensitive to solution impurities, pilot plant investigations for the purpose of obtaining useful scale-up data should be with actual process streams, not simulated solutions containing only the pure major components.

TABLE 5

Column Scale-Up Results

System	Col. Dia. in	Ht. ft	Cross-sectional area, in^2	Flow Rate, gal*/min		Total Throughput	
				Aqueous	Organic	Gal/min/ in^2	Gal/min/ ft^2
Co-Ni	1½	7	1.77	0.011	0.011	0.0124	1.8
	2	35	3.14	0.055	0.055	0.0354	5.1
	6	37	28.3	0.7	0.7	0.0495	7.1
	22	35	380	7.0	7.0	0.0368	5.3
Zr-Hf	2	35	3.14	0.04	0.16	0.064	9.2
	6	37	28.3	0.44	1.76	0.07	10.2

*Imperial gallons

Equipment

The mass transfer of the desired metal from one phase to another phase is accomplished by the use of various types of equipment in which the aqueous phase is usually flowing counter-current to the organic stream. Because of the simplicity and flexibility of the solvent extraction process, a wide choice of operating conditions is often available. The design of the process and proper selection of the equipment for scaling-up from the bench to the plant then becomes a most important aspect in developing more favourable economics.

The choice of a contactor suitable 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.

The design of a particular contactor to suit possible corrosion conditions is usually no problem, since a wide choice of materials of construction are available. Maintenance on solvent extraction equipment can be roughly equated with the number of moving parts or agitation speed--being greatest with centrifugal contactors and virtually non-existent with the simple unagitated columns such as the spray, packed, or plate columns.

The equipment can be classified as either stagewise or differential contactors. In a stagewise contactor, such as a mixer-settler, the two immiscible phases are mixed and then allowed to separate or disengage, because of their difference in density, in a separate settling chamber. Differential contactors, such as columns, provide continuous contacting and therefore many mixing, settling or coalescing stages.

The mixer-settler was the first solvent extraction equipment developed and is still popular. Staging is well defined since the liquids are separated after mixing. Extreme phase ratios can be used, as well as recycle of the phases to improve the efficiency of the mass transfer. The mixer-settlers are simple and have the advantage of being relatively inexpensive and easy to build. However, they require a large plant area and need large solvent inventories. Internal recycling of the solvent can be used to reduce the solvent inventory. They are very useful where only a few (2 or 3) stages of extraction, scrubbing or stripping are required.

In Canada, the Port Radium operation of Eldorado Nuclear used a mixer-settler system for the recovery of uranium(74). A diagram of a mixer-settler is shown in Figure 14. The solvent and solution are fed to the mixer, where they are dispersed and extraction occurs. From the mixer the dispersion flows to the settler, where the two phases disengage and leave the settler. The mixing and settling constitute one stage. For countercurrent operation, several mixer-settler stages are arranged in series with the flow of the liquids being countercurrent through the stages.

Over the past twenty years many designs of mixer-

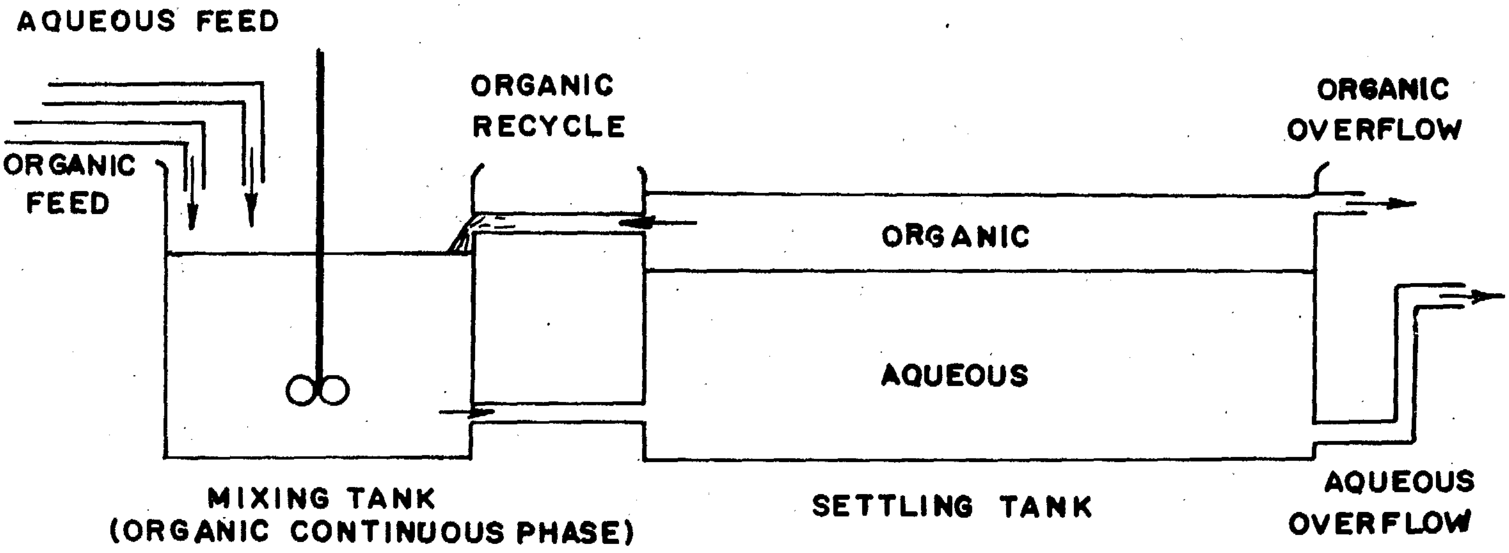


Figure 14. Mixer-Settler Diagram.

settlers have been proposed, with the general aim to decrease the necessary area while maintaining high throughput and efficiency. As an example, Power-Gas Corporation, Engineering Contractors, are installing their mixer-settler units in a copper circuit in Zambia to recover 190 tons of copper per day by solvent extraction from a solution containing 1 to 2 g Cu/l.(82,83)

Columns, in contrast to mixer-settlers, require very little plant area, and are capable of many stages of contact. Solution gravity differences are utilized for countercurrent vertical flow through a column. Generally the aqueous input is at the top of the column, while the organic input is located near the bottom.

Columns can be grouped as non-agitated and agitated. The non-agitated, such as the sieve-plate, spray and packed columns, although low in capital cost, are also low in efficiency and throughput. The packed columns are easily fouled by the process solution. Agitated columns have proved to be more successful, and the trend seems to be toward columns in which mechanical agitation of some type is provided. The rotating-disc contactor column containing 8 to 10 theoretical stages per unit has been used by Shell Oil extensively. They have scaled it up to a diameter of 3.5 metres(85). The sieve-plate column has been varied and improved in performance.

In the sieve-plate pulse column, energy is supplied by a diaphragm pump, or air, in order to move the organic droplets up the column in a pulsating motion. In an aqueous continuous operation the droplets coalesce under each sieve plate and new surfaces of contact form as the organic is pushed through the sieve-plate at the next pulse. The pulse column has proved successful in the nuclear industry, e.g. Eldorado Nuclear(89); in the separation of cobalt and nickel(69) and zirconium and hafnium(77), where many theoretical stages of extraction are required; and also in the uranium industry for the refining of mill uranium precipitates(90). Pulse columns may not be suitable for operations of 2 to 2.5 metres because of severe vibrations affecting the foundations(91), although by proper design of the engineering aspects, and provided the natural frequency of the column is not reached, large columns should be capable of operation. In actual fact, the vibrations in pulse columns operating at normal conditions for metal extraction, e.g. approximately 50 pulses per minute and of 1.5-in. amplitude, are so small as to present very few problems. A diagram of the pulse column is shown in Figure 15.

Factors which govern the control of pulsed sieve-plate columns are: flow rates and ratios; pulse amplitude and frequency--which provide the energy for dispersion of the phases; hole diameter and type of perforated plates; operation of column with aqueous or organic liquids as the dispersed phase; solvent

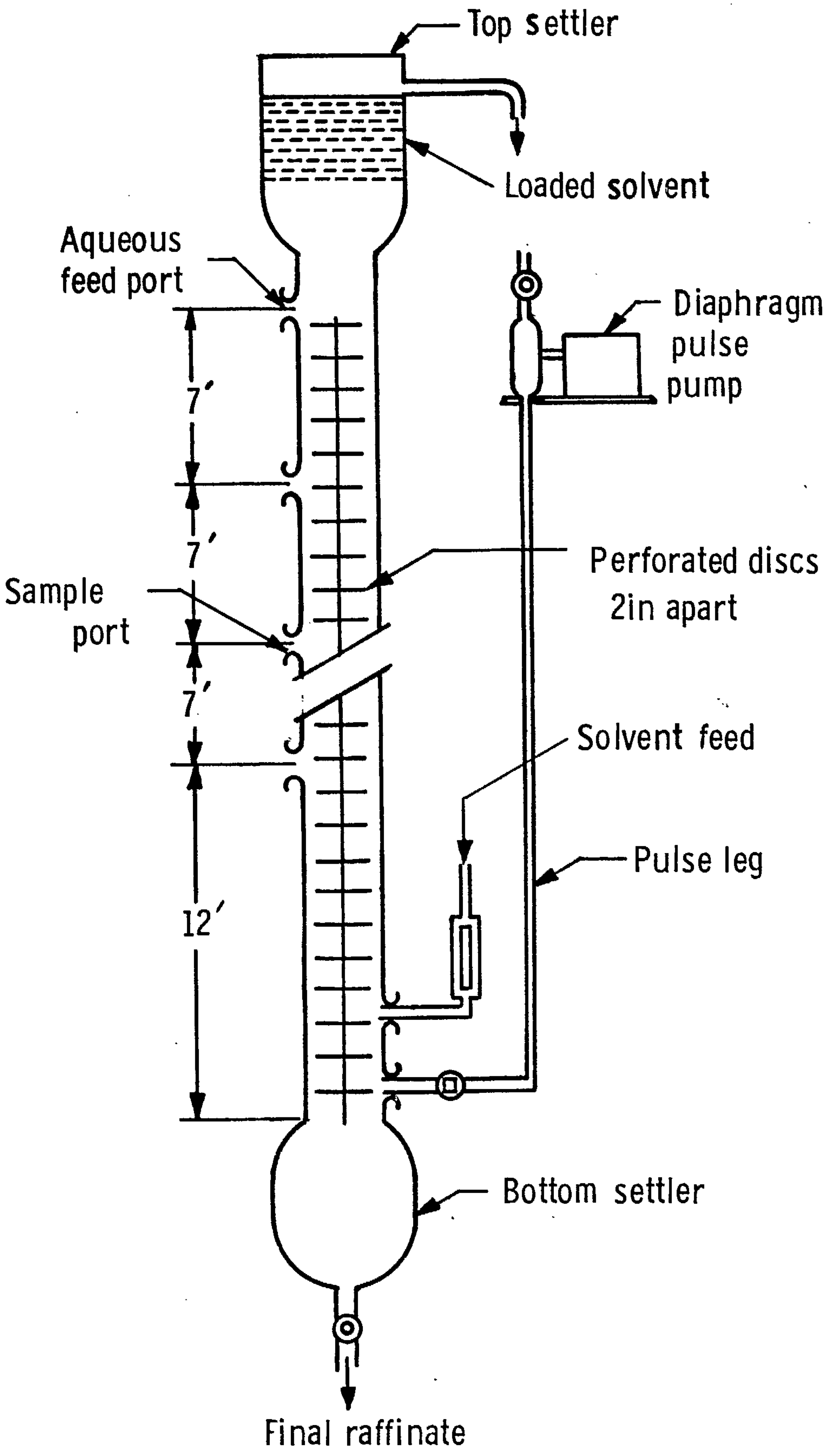


Figure 15. Sieve-Plate Pulse Column.

concentration and composition; chemical nature of the feed solution; temperature; and height of column to provide the necessary stages of contact (183). Because of the gentle action in this column, and thereby producing the necessary mixing of phases for mass transfer, extraction from leach slurries has been possible (107,108). Glass pulse columns are produced by Quickfit (QVF, Toronto), Kimax (Montreal) and EIVS (Pegasus, Toronto), while the steel columns are usually custom-built.

In the reciprocating plate column, agitation is provided by the plates moving through the solution, thus providing the necessary mass transfer. The reciprocating plate columns appear to have had the greatest popularity in the chemical and pharmaceutical industries (86). The largest reported column diameter in operation is given as 19 in., and the manufacturers hope to solve the present scale-up problems (87). Compared to the sieve-plate pulse column, where the plate hole free area is about 30%, the reciprocating plate column has a free area of 50 to 75%. Although these columns have been used to process solutions containing crystalline solids or fine precipitates, the application to processing ore leach slurries has not been investigated. Studies performed by the Czechoslovak Academy of Sciences on reciprocating plate columns showed that, under conditions usual for production units, longitudinal mixing is very small and does not excessively influence the efficiency of the extractor (88).

The reciprocating plate columns (Karr Columns) may be obtained from Pegasus, of Toronto, or Chem-Flow in the U.S.

Stirred columns operating with moving discs or impellers to cause the shearing action are produced by several manufacturers. Among these are the Mixco (Greey Mixing), Humboldt (Klockner-Humboldt-Deutz, Germany), Rotating Disc Contactor (RDC) (Pielkenrovd-Venitex of Assendelft, Netherlands), and ARDC contactor (Luwa Corp., North Carolina).

In the Mixco column, which is an improvement on the Oldshue-Rushton contactor, agitation is accomplished by a centrally driven shaft containing 6-bladed paddle mixers. The mixers are spaced equidistant down the length of the column. Equidistant from the mixer are plates with the centre portion cut out. The column is a standard baffled tank, with the baffling at approximately 1/10 the diameter. The baffles are placed around the column at 60° angles.

The power requirements are relatively small, with a 2-HP motor necessary, for example, on a 30-in.-diameter column that has a height of about 30 ft. Vibration, although minimal, may be slightly more than produced in the sieve-plate columns. The meter to drive the shaft is located at the top of the column, extending at the bottom through a teflon bearing. One of the major problems in the use of this type of column, particularly in a system that has emulsion tendencies, is the narrow range of rpm that can be used. A 5 to 10% spread in rpm can often be the difference between insufficient agitation and emulsification.

The centrifugal contactors utilize centrifugal force to increase the specific gravity difference between the two liquids and therefore enhance phase disengagement. They have the advantage of perhaps 3 to 4 stages per unit, but are rather expensive and have a high maintenance cost. They cannot tolerate any suspended solids because of the small hole-diameter within the units. However, there is a short hold-up time, of the order of a few seconds in the centrifuge, which makes it possible for use in non-equilibrium systems. For example, in the separation of two or more metals in solution, the reaction rate for one metal to attain equilibrium is considerably shorter than for the other metals. If columns or mixer-settlers were used, equilibrium may be essentially attained for all the metals in solution because of the relatively long hold-up time.

Operation of the centrifuge involves two main variables: rpm, and throughput rate. Variation of one or both these variables permits better selectivity in the separation of the desired metal from a solution mixture. Thus the centrifuge, with the short hold-up time, would permit the separation of the desired metal. With a process requiring only a few stages, and where a high throughput is desirable because of the size of the plant, or because of dilute feed solution, then the centrifugal contactor must be considered. In Canada, Denison Mines Limited are successfully using the centrifugal contactor for the recovery of rare earths from their barren solution after recovery of uranium by ion-exchange processing(93). Centrifugal contactors give the same results as a series of mixer-settler tanks, thus conserving plant space and reducing the organic solvent inventory (for example, from 75,000 gallons to 3,000 gallons).

The best known of the centrifugal extractors are the Podbielniak, the Quadronic, and the Alfa-Laval.

The design principles of centrifugal contactors have been described by Doyle, Doyle, Rauch and Lowry(92), resulting in the Quadronic Extractor manufactured by Liquid Dynamics Inc.

The rotary film contactor has been designed to permit solvent extraction of metals from leach slurries(95). This contactor consists of a number of discs mounted on a horizontal shaft rotating within a vessel. The rotation of the discs maintains the solids in suspension in the slurry occupying the lower portions of the vessel, and the discs carry a film of pulp through the upper solvent layers, thus effecting the metal transfer. However, this contactor is still in the development stage.

A relatively recent unit, available for solvent extraction processing, which has been used successfully in the chemical industry on a large scale, is the Graesser Raining

Bucket Contactor(96). The unit consists of a horizontal shaft carrying a series of discs. Buckets are fixed between the discs. Operation is by countercurrent flow, and the interface level is controlled by weir adjustment of the heavy phase. Rotation rates range from 1 to 40 rpm. When the shaft is rotated, the buckets fill with one phase and transfer this to the other phase, thus providing a dispersion of one phase in the other. The action is very gentle, and consequently there is very little tendency for emulsion formation. The unit would have application in systems having poor settling characteristics, or perhaps in the recovery of metals directly from leach slurries without prior filtration.

Of interest to the researcher in liquid-liquid extraction, and for small-scale processing, is an apparatus known as AKUFVE(97). This is the Swedish abbreviation for "apparatus for continuous measurement of distribution factors in solvent extraction". The equipment consists of a mixer and chamber with the phase separation taking place in a centrifuge separator. The centrifuge has a hold-up volume of 150 ml, a maximum throughput of approximately 3000 ml/min, and a rotative speed of up to 18,000 rpm.

Coalescence

The engineering aspects of solvent extraction are primarily concerned with dispersion of the phases in mixing, and the rate of completeness of phase desengagement.

Phase disengagement, or coalescence, can be divided into a primary break and a secondary break. In batch shake-outs, the time required for the upper and lower layers to meet at a sharply defined interface is termed the primary break or primary disengagement. Both liquids may be clear, but occasionally one is cloudy, due to a dispersion of a small quantity of the other phase that eventually settles out. This is known as the secondary break, and is more concerned with the loss of solvent in the raffinate and with entrainment of aqueous in the extract that it is with the design of a settling area. The measure of phase disengagement rate is a means to the scale-up design for extraction equipment, such as the size of a settler. In the determination of the settler area for one system, it is important not to use any data developed for other extraction systems, as there may be a considerable difference between them.

Separation of two distinct phases may be difficult if: (1) the continuous phase is viscous; (2) if solid particles are present which might cause stable emulsions; (3) or if the two phases differ only slightly in density. Occasionally an increase in the operating temperature will accelerate phase disengagement and decrease the effects of viscosity and density.

Coalescence may be accelerated in another manner, thereby increasing the capacity of a given piece of extraction equipment for higher flow rates. It is well known that by inserting solid material, that is wetted by a liquid, into the coalescing area of the settler or other extraction device, the rate of coalescence of droplets which wet the material could be greatly increased. If the system is organic continuous, with a dispersion of aqueous in the organic, then by placing, for example, stainless steel mesh which is wetted by water, in the dispersion area, the coalescence rate will increase. Also, it may be useful on occasion to provide a surface such as teflon to increase coalescence. In pulsed sieve plate columns it has been found that in the liquid-liquid separation of zirconium from hafnium, using TBP in a nitric acid system, the coalescence is accelerated by having the stainless steel plates coated on one side with teflon (77). If organic continuous, the plate would be teflon-coated on the bottom. This "sandwich" arrangement of one plate, or two plates together, has been used successfully for specific applications at the Mines Branch.

In solvent-in-pulp work at the Mines Branch, we have noticed that various types of bubbles can be produced, as well as varying degrees of coalescence. Therefore, we have performed a study on various types of sieve plates. We considered stainless steel, teflon, and "sandwich" plates of teflon and stainless. In Figure 16 are shown the results of this study. The

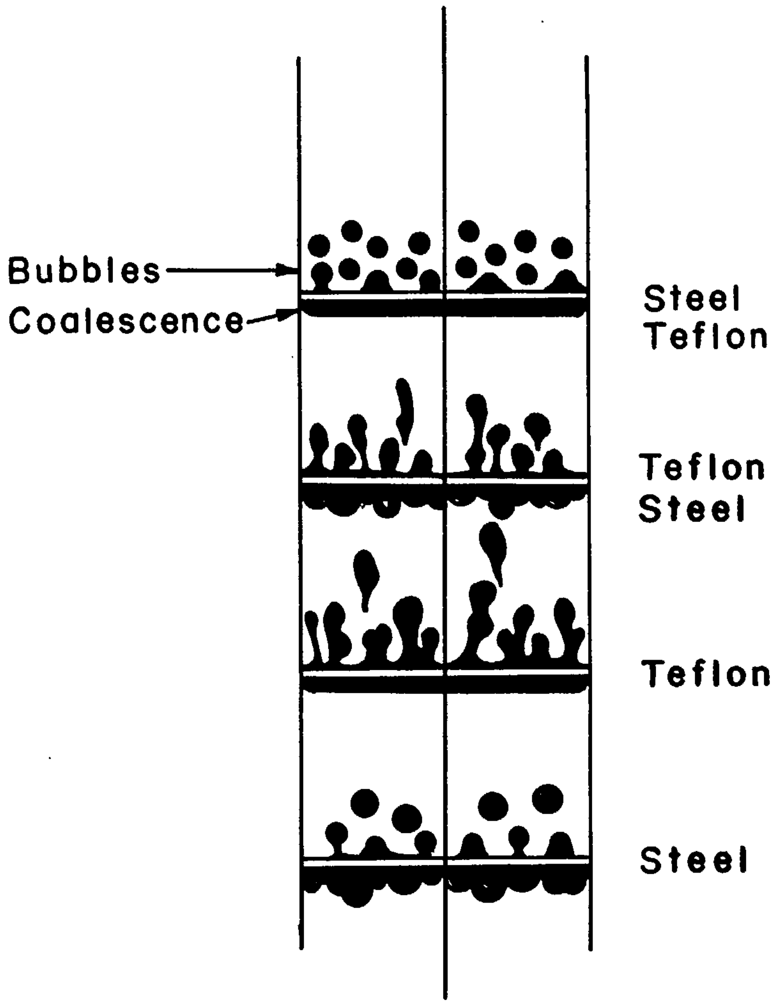


Figure 16. Effect of Plate Material on Bubbles and Coalescence.

steel plates produced slightly mishaped bubbles, while teflon produced an elongated bubble. Steel with teflon on top produced a somewhat better bubble and coalescence, while teflon on bottom and steel on top produced a round bubble the size of the perforation in the plate, together with a flat coalescence band on the teflon. The use of sandwich plates in certain situations seem to be worth consideration.

Extraction from Alkaline Solutions

No suitable extractant has been found which would be applicable to the recovery of uranium from carbonate solutions. However, the recovery of other metals has been somewhat more successful. The separation of cobalt from nickel in an ammoniacal sulphate solution has been demonstrated by Eldorado Nuclear(98). The use of D2EHPA could only tolerate 40 g $(NH_4)_2SO_4/l$ for maximum loading and separation of cobalt from nickel. Later work at the Mines Branch(100) has indicated that up to 500 g $(NH_4)_2SO_4/l$ can be tolerated in an alkaline ammonium sulphate solution for the separation of cobalt and nickel, using the oxime, LIX-64, or the tertiary carboxylic acid, Versatic 911. Also, copper has been successfully recovered from alkaline solution(99); and has been separated from nickel and cobalt, using LIX-63 reagent(75).

Processing of Ion Exchange Eluates by SX

In any of the solvent extraction operations described the recovery of the metal from the loaded solvent is by alkaline or acid stripping. In uranium processing, soda ash stripping results in a solution readily amenable to precipitation by caustic. Use of ammonium carbonate in future processing could be a possible advantage, since the strip solution can be readily converted to UO_3 and subsequently to UO_2 by reduction. Acid stripping may be the preferred route in the rare earth or thorium recovery circuit.

In the past, in mills recovering uranium by ion exchange processing, the loaded ion-exchange resin has had the uranium removed by eluting with a chloride or nitrate solution. Because of potential pollution problems the nitrate effluent would present, other types of treatment may be necessary in future processing.

An alternative to nitrate elution is elution of the uranium with approximately 1.0 M sulphuric acid, followed by a solvent-extraction separation of the uranium using a tertiary amine(101). This process, known as the Eluex process, will result in an up-grading of the final uranium precipitate. At the present time, mines with ion exchange plants in operation are considering the Eluex process as a modification to their existing process. Any economic advantage that may arise from the production of a higher-purity final product, however, will be fairly well offset by the additional costs incurred. The extra cost of the Eluex process should be the cost of conventional ion exchange plus the cost incurred by solvent extraction (7-10¢/lb U_3O_8).

The Bufflex(105) and Purlex(103,104) processes of South Africa for the treatment of sulphuric aicd eluates of uranium are essentially the same as the Eluex process. The use of a dialkyl phosphonate to extract uranium from a nitrate eluate has also been demonstrated(101,118).

Solvent-in-Pulp

The possibility of utilizing resin-in-pulp or solvent-in-pulp techniques has received much attention. Resin-in-pulp has been used in U.S. plants but has never been used in Canada. So far, neither the U.S. experience nor any other resin-in-pulp studies have indicated that resin-in-pulp has any real advantage over the ion exchange purification of clear solution as practised in Canada. However, solvent-in-pulp techniques appear more attractive because of the potential cost saving in capital and in operating of filters, as well as to decrease soluble metal losses encountered in a liquid-solids separation. Eldorado Nuclear has demonstrated that it is possible to effectively recover uranium with a tertiary amine extractant from slurry containing 35% solids in a 10-in.-diameter sieve-plate pulse column(107). Solvent losses in the solvent-in-pulp system, using the pulse column, have been remarkably low, about 0.1 lb/ton dry feed. This loss compares favourably with a liquid-liquid operation(74). It is possible that ore filtration can eventually be eliminated. This work has been substantiated with further testing at the Mines Branch on Elliot Lake ore(108), also by Eldorado Nuclear on Beaverlodge ore(109), using 2-in.-diameter pulsed sieve-plate columns.

A diagramatic flowsheet of Eldorado's solvent-in-pulp pilot plant is shown in Figure 17. Extraction took place in a 10-in.-diameter 316SS column, 12 ft in length. Located at each end were disengagement sections, 30 in. in diameter by 30 in. long. The plates, containing 3/8-in.-diameter holes, 27% open area, were spaced 2 in. apart over the 12-ft length. A diaphragm pump supplied the energy to the column. Scrubbing, stripping and acidification of the solvent took place in 30-gal tanks located in one compartment of a 4-ft x 8-ft x 2-ft-deep epoxy-coated wooden settler.

The feed slurry, containing 1-1.5 g U_3O_8/l at pH 1.5-2.0, and flow rate 5-6 gal/min., was contacted with a 0.1 M solution of Alamine 336 in Shell 140 Flash Naphtha containing $5^{v}/o$ isodecanol. The pulse rate was 50/min at an amplitude of 0.7 in. The throughput, at 96-98% uranium extraction, was 19.5 tons dry solids per day per square foot of column cross sectional area.

The leached pyrite slurry fed to the column contained

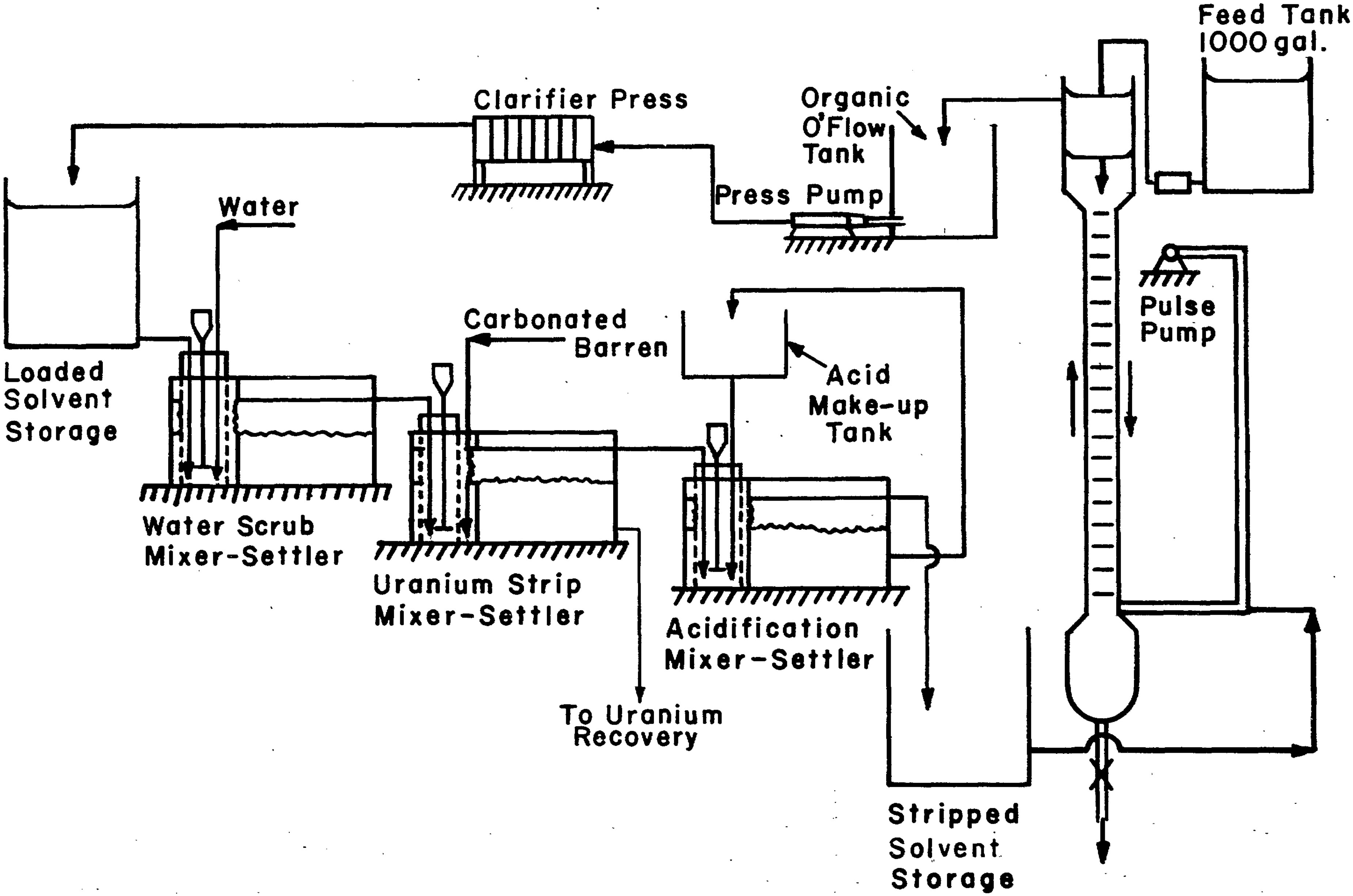


Figure 17. Diagrammatic Flowsheet of Solvent Extraction in Pulp Pilot Plant.

an appreciable amount of fine graphite. This graphite was wetted by the organic solvent and a portion overflowed with the organic phase, which necessitated filtering in a press to recover the solvent. In the treatment of this type of slurry the graphite would be removed by flotation prior to solvent-in-pulp processing.

From the results obtained, the recovery of uranium from slurries by solvent-in-pulp extraction will be cheaper than recovery from clarified solutions, particularly in a high-tonnage operation. Losses of uranium would be similar for the two systems, but plant size, capital costs and operating plus maintenance will be appreciably less for solvent-in-pulp. With additional test-work performed on two different ore-slurries, the data obtained suggest that slurries of many types can be successfully treated by a solvent-in-pulp technique, and that new plants should consider this system.

In Table 6 are noted the results of applying various types of liquid-liquid contactors to the recovery of metals from leach slurries. The mixer-settlers, mixing columns, centrifuges and the Graesser contactor have been tried and found unsuitable for processing slurries. We can conclude that, of the equipment evaluated for the recovery of metals from leach slurries, the sieve-plate pulse column or the grid-packed column of Byerlee(194), is the only equipment available. The main reasons for this are the simplicity of design, no moving parts, use of gravity to move the solids, and gentle agitation without extreme mixing as is encountered in other extraction equipment. This method of achieving mixing, and therefore mass transfer of the metals, enables extraction to take place from slurry systems as well as from clarified solutions.

TABLE 6

Comparison of Equipment for Solvent-in-Pulp Processing

Equipment Type	Results and Observations
Mixer-settlers	Formation of stable emulsions
Centrifuges (Podbielniak)	Holes plug as well as formation of stable emulsions
Horizontal Contactor (Graesser)	Ore particles not transported - no wall clearance
Agitated Columns (Mixco)	Can tolerate in the range up to 10% solids, but a tendency to form emulsions
Sieve-plate Pulse Columns	Operated satisfactorily up to 40% solids with low solvent losses

In Table 7 are shown some estimated costs for the recovery of uranium by ion exchange, or solvent extraction, from either clarified solutions or slurries. The basis for comparison is for an Elliot Lake mill with an ore grading 0.1% U_3O_8, and a tonnage of 3,000 tons per day. The values for liquid-solids separation and sand-slimes separation were reported recently by Smith and Garrett$^{(195)}$. The cost of solvent extraction from filtered and clarified solutions is estimated to be slightly cheaper than using ion exchange by approximately 2.5 cents per pound U_3O_8. However, in extraction from slurries, the solvent extraction route has a cost advantage of 8.2 cents per pound U_3O_8, with an estimated 20 cents per pound U_3O_8 compared to 28.2 cents per pound U_3O_8 for ion exchange. Also, the cost of solvent extraction from clarified solutions is approximately twice the cost of solvent extraction from slurries. With such a cost differential a mill could well afford extra processing costs of the slurry (such as flocultation, addition of depressants, surface active agents, etc.), small extra solvent losses, and the possible necessity of filtration of the extract, in order to decrease processing costs. In the example shown, we have included a possible cost incurred by filtering the solvent through a plate and frame press.

Selected Extraction Systems

In Table 8 are noted some possible extraction systems for some of the metals. This list is by no means complete, but is presented to show that there are available many laboratory studies that could, with additional tests and pilot plant studies, become a plant process. Some of the systems noted are already producing-plants, in operation or near start-up, for the recovery of uranium, molybdenum, tungsten, copper, cobalt, nickel, vanadium, chromium, rare earths, zirconium, hafnium, niobium, and tantalum. There are possibly others that have been missed in this survey.

TABLE 7

Comparison of Total Costs of Ion Exchange and Solvent Extraction from Clarified Solutions or Slurries

(Elliot Lake Ore, 0.1 per cent U_3O_8)

	Cost Per Pound U_3O_8 (¢)			
	Clarified Solutions		Slurries	
	IX	SX	IX	SX
Liquid-Solids Separation				
Operating	13.0	13.0		
Equipment	14.0	14.0		
Sand-Slimes Separation				
Operating			5.0	
Equipment			6.0	
Solvent Filtration				0.5
Resin or Solvent Loss	1.0	3.0	1.5	4.5
Elution or Stripping Reagents	5.7	1.2	5.7	1.2
Depreciation of Equipment and Instrumentation	7.0	7.0	7.0	10.8
Maintenance and Labour	2.5	2.5	3.0	3.0
	43.2	40.7	28.2	20.0

Note: 10-year straight-line depreciation of about \$630,000 for the IX or SX plants. For SX in pulp, depreciation of about \$980,000. The capital cost multiplied by 2 to give approximate installed cost. Plate and frame for solvent - 2 @ \$36,000.

TABLE 8

Selected Extraction Systems

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Actinides	Tertiary amines	HCl-LiCl	Bulk extraction and further separation with D2EHPA and Ion exchange	110
Alkali metals	Carboxylic acids	Weakly acid solutions	The extractibility increases in the order Li<Na<CS<K at pH 6.0	111
Al	Alkylphosphoric acid	Fe-free sulphate solutions at pH 2.8 to 3.2	6 N HCl for stripping	112
Be	Alkylphosphoric acids	Chloride pH 1.3 - 3.0	Iron removed with an amine	113
Be	Alkylphosphoric acids	H_2SO_4, HCl, HNO_3	Several extractants investigated. Extractibility in relation to other cations: Zr>Sc>U>Y>Be>Eu>Am>La>Ca>Sr	114
Be	TBP	2 M NHO_3	Extractibility in 100% TBP U>Pu>Th>Am>Ce>Zr>Y>Be>Zn>Co	114
Cd, Zn	TBP	2 M $CaCl_2$ or 3 M NaCl	Separation of Cd	115

Table 8 continued

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Cr	Quaternary amines	Acid Plating solutions		116
Cr	Primary amine	Sulphate solution		118
Ca, Sr	Alkylphosphoric acids	Nitrate	Dioctyl phosphoric acid as well as D2EHPA in various diluents	119
Co, Ni	Alkylphosphoric acids	pH 5-6.5	Separation of cobalt from nickel	69
Co, Ni	Alkylphosphoric acids	Sulphate solution	Separation of impurities	70
Co, Ni	Alkylphosphoric acids	pH 11	Separation of cobalt from nickel	98
Co	Carboxylic acid	pH 8.0	Separation of cobalt from nickel (Versatic 911)	100
Co, Cu	TBP	8-10 M HCl	Separation of Co from Cu	120
Co, Ni	Tertiary amine	pH 1.0	Separation of cobalt and nickel in a dissolved scrap	121
Co, Ni	Tertiary amine	Conc. HCl	Separation of cobalt	122, 123 124

Table 8 continued

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Co, Ni	Metallic soaps	pH 6	Separation from chloride, nitrate or sulphate media	125
Co, Ni	Carboxylic acid	pH 6	Nickel separated from cobalt	126, 127
Cu	LIX-64, LIX-64N	pH 2.5	Copper extracted from dump leach: oxide concentrates	82,83,128 129,176, 179,180 191,192
Cu	LIX-70	pH 2.5 or less		84
Cu	D2EHPA-LIX-63	pH	Separation from Co and Ni or Zn and Mn	71, 134
Cu	LIX-63	pH 6.5-8.0	Separation from Ni and Co in ammonium sulphate	75
Cu	LIX-64N	$(NH_4)_2CO_3$	Separation from zinc	76
Cu	Kelex-100	pH 1-2	Requires addition of long chain alcohols	193
Ga	Alkylphosphoric acids	H_2SO_4, pH 1	Scheme given for separation from various metals in various aqueous media.	130

Table 8 continued

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Ga, In, Tl	TBP	HCl	Separation of Ga, In, Tl by controlled acidity	131
Ferric iron	Carboxylic acid (Versatic 911)	Leach solution containing Fe, Cu, Ni.	Ferric iron	132
Ferric iron	TBP	Chloride solutions containing Cu, Co, Ni		122
Mn	Alkylphosphoric acid	Sulphate leach, pH 5.5	Developed for processing manganese shales of N.B.	133, 134
Mo, U	Quaternary ammonium (Aliquat 336)	Alkaline solutions	Recovery of Mo after separation of U with amines	135
Mo, W	Tertiary amine	1-4 M HCl	Co-extraction of Mo and W, and alkaline stripping	136
Mo, U	Tertiary amine	Sulphate leach	Mo as impurity in uranium processing	137
Ni, Zn	Dinonyl Naphthalene sulfonic acid	Phosphate solution	Zn separated with D2EHPA	196

Table 8 continued

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Nb, Ta	Methyl isobutyl ketone	Hydrofluoric solution of ore	Separation based on close acidity control	138
Nb	Methyl isobutyl ketone	H_2SO_4 dissolution of pyrochlore flotation concentrates	Nb stripped with NH_4F	139
Nb, Ta	Methyl isobutyl ketone	HF-KCl	Ta separated and then Nb after HCl addition	140, 141
Tl	Alkylphosphoric acid	2-3 M H_2SO_4	Results also shown for HNO_3	142
Pt, Pd, Ir Ru, Rh	Amines	Chloride-sulphate	Extraction of Pt, Pd, Ir increases with SO_4 concentration, while Ru and Rh depressed.	143
Pu	TBP	HNO_3	Use of pulsed columns	144
Sc, U	Alkylphosphoric acid	HF	After stripping U, the Sc removed from solvent with HF	145
Te	TBP	3-8 HCl		146
Th, U, RE	Amines	Sulphate solutions of monazite	Extraction of Th with primary amine; uranium with tertiary	147

Table 8 continued

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Th	Secondary amine	Sulphate leach	Recovery from Ion exchange barrens after U removed	148
Th	Alkylphosphoric acid	Sulphate leach	Recovery from Ion exchange barrens after U removed	149
Th	Primary or Secondary amines	Sulphate leach	Co-extraction and selective stripping	150
Th, Pa, U, Ru, Zr	Primary, secondary and tertiary amines	Sulphate leach		151
Sn, Pb	Amines	HCl	Sn extracted at 5-9 M while Pb depressed above 8 M HCl	152
U	Alkylphosphoric acids	Sulphate solution	Known as Dapex process	153
U	TBP	Nitric acid	Refining of uranium	90
U	Tertiary amine	Sulphate leach solutions	Either directly from leach or treatment of ion exchange eluate (the Eluex, Purlex, Bufflex processes)	74, 101 102, 103 104, 182 189, 190
U	Tertiary amine	Sulphate leach	Mo as impurity	105

Table 8 continued

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
V, U	D2EHPA	Sulphuric	Recovery and separation of vanadium from uranium	154
V, Fe	D2EHPA-TBP	Sulphuric	Recovery and separation of V^{+4} from Fe^{+2}	117
V	Tertiary amine and quaternary amines	Sulphate	Mills in U.S. using process; tertiary if acid leach, quaternary if NaCl roast	116,117
W	Amines			116
Zn, Cd	TBP	Chloride	Separation of Zn from Cd at 2 M $CaCl_2$ or 3 M NaCl	115
Zn, Ni	D2EHPA	Phosphate	Zn separated from nickel	196
Zn, Cu	D2EHPA	pH 2.5-3.5	Method of concentrating the two metals	155
Zn, Mn	D2EHPA	pH 3-5.5	Method of separation or co-extraction	134
Zr, Hf	TBP	HNO_3	Separation of Zr from Hf in a column; controlled acidity	77,156
Zr, Hf	Hexone	Chloride-thiocyanate	Separation of Hf from Zr	157

Table 8 concluded

Metal Extracted	Extractant	Aqueous Phase	Comments	Ref.
Zr, Hf	Hexone	Chloride-thiocyanate	Separation of Hf from Zr	157
Rare earths, Y	TBP	HNO_3		158, 159, 160
Rare earths, Y	D2EHPA	HNO_3		161, 162 163
Rare earths, Y	D2EHPA	HCl		164, 165
Rare earths, Y	D2EHPA	H_2SO_4		166, 167 168, 169
Rare earths, Y	Primary amine	H_2SO_4		170, 171 172
Rare earths, Y	Naphthenic acid	Sulphate	pH best at about ph 8.0. Addition of EDTA improves separation factors for adjacent pairs.	173

Recycling the Solvent - Problems

Occasionally after a solvent has cycled several times through a circuit there will be a build-up of a "non-strippable" element. This may be either an impurity, such as iron in a rare earth circuit using di-2(ethylhexyl) phosphoric acid(68), or perhaps a build-up of the actual metal desired to be recovered. An example of the latter is the build-up of zirconium on tributyl phosphate in the nitric acid system for the separation of zirconium from hafnium(77). A separate solvent treatment stage is required, such as a sodium carbonate wash, followed by acid equilibration prior to the extraction cycle. This clean-up sequence is generally accomplished by a "bleed" of the stripped solvent. Because it is known that amines don't extract metals well in the presence of, or from, nitric acid solutions, then in a system employing a nitric acid strip to recover a metal from an amine, an alkaline wash is also required prior to acid equilibration(150).

Another example of a problem encountered with recycling of a solvent is in the extraction of cobalt or nickel from a solution at pH 5 to 6 using D2EHPA. If calcium is present--and one can generally assume it is, either due to leaching, or due to the neutralization stage, with lime or limestone after leaching and filtration--calcium in such a circuit is known to co-extract with the cobalt or nickel(69). However, although some sites on the solvent are then occupied by calcium rather than cobalt or nickel, no other problems are encountered in the extraction or scrubbing stages. In stripping with sulphuric acid in a one- or two-stage mixer-settler operation, the cobalt or nickel is found to strip readily, leaving the calcium on the solvent. A third stage of stripping releases the calcium from the solvent into the sulphate, resulting in a gypsum precipitate. If this stripping operation is performed in multi-stage equipment such as a column, where more stages are available than necessary for cobalt or nickel recovery, the result will be a build-up of gypsum in the column, and eventually a shut-down is necessary. Thus, by controlling the stages of stripping we can eliminate such a problem, and take a "bleed" of the stripped solvent to a third strip stage for calcium removal(185). In this way, a level of calcium on the solvent would be maintained. Naturally, if nitric or hydrochloric acids were used for stripping, any calcium present is stripped along with the cobalt and nickel, necessitating an extra treatment stage during the production of the cobalt or nickel oxides.

A third example is degradation of the solvent with continual recycling. This can occur because of the aqueous solution composition, or temperature and concentration of the strip solution. The neutral organophosphate, TBP, in contact with strong nitric acid solution, is gradually degraded by the acid, since aqueous-soluble dibutyl phosphates are formed as the degredation products. This accounts for losses of the TBP, necessitating periodic make-up of the solvent. Amines are very susceptible to oxidation, either by the feed solution itself, or by stripping agents. Thus nitric acid at elevated temperatures and highly concentrated can't be tolerated. The feed solution may contain a highly oxidizing metal which can cause degradation. In one plant for the recovery of vanadium, the vanadium exists in a chloride-sulphate solution as vanadic acid which is a strong oxidizing agent. The tertiary amine, if allowed to remain in contact with the vanadic acid, would be quickly degraded. Because the rate of extraction of vanadium into the amine is relatively fast, centrifugal contactors were chosen in order to minimize the contact time and therefore the degradation of the amine(117).

Extreme solubility of the organic phase in the aqueous phase is a problem with recycling of some solvents. This is particularly true in the methyl isobutyl ketone system, where the aqueous solubility may be several thousand ppm(157). Carboxylic acids in certain aqueous systems also have a water solubility, in the order of 100 ppm, and higher in certain aqueous solutions(190). If the process can still be economic with such losses, and the environment can tolerate these organic materials in the streams, continual analysis of the solvent is necessary in order to provide the necessary addition of organic reagent with continual recycle.

Solvent Losses

In the past a great deal of importance has been attached to the solvent losses occurring in an extraction system, and the consequent costs to the process. In the future, concern will be directed more towards making certain that the organic losses that do occur will have no detrimental effects on the environment. Losses of the organic reagent during solvent extraction processing may result from (a) solubility of the organic phase in the aqueous phase, (b) entrainment of the solvent in the aqueous, (c) evaporation, or (d) mechanical losses due to faulty operation, such as spillage. Soluble losses of a reagent in the aqueous phase is, however, an inherent part of the process; that is, very often the solubility is due to the fixed conditions of the system. The pH of the aqueous may be such as to promote some solubility of the organic phase, since many reagent solubilities are pH-dependent. For example, both the alkylphosphoric acids and the carboxylic acids have increased aqueous solubility with increasing pH. However, often along with increasing pH, especially on the alkaline side, increased pH is accompanied by increase in the anion or salt content. For example, in Figure 18 is shown the solubility of the tertiary monocarboxylic acid, Versatic 911, in a solution of ammonium sulphate. The results show a decrease in the solubility of the

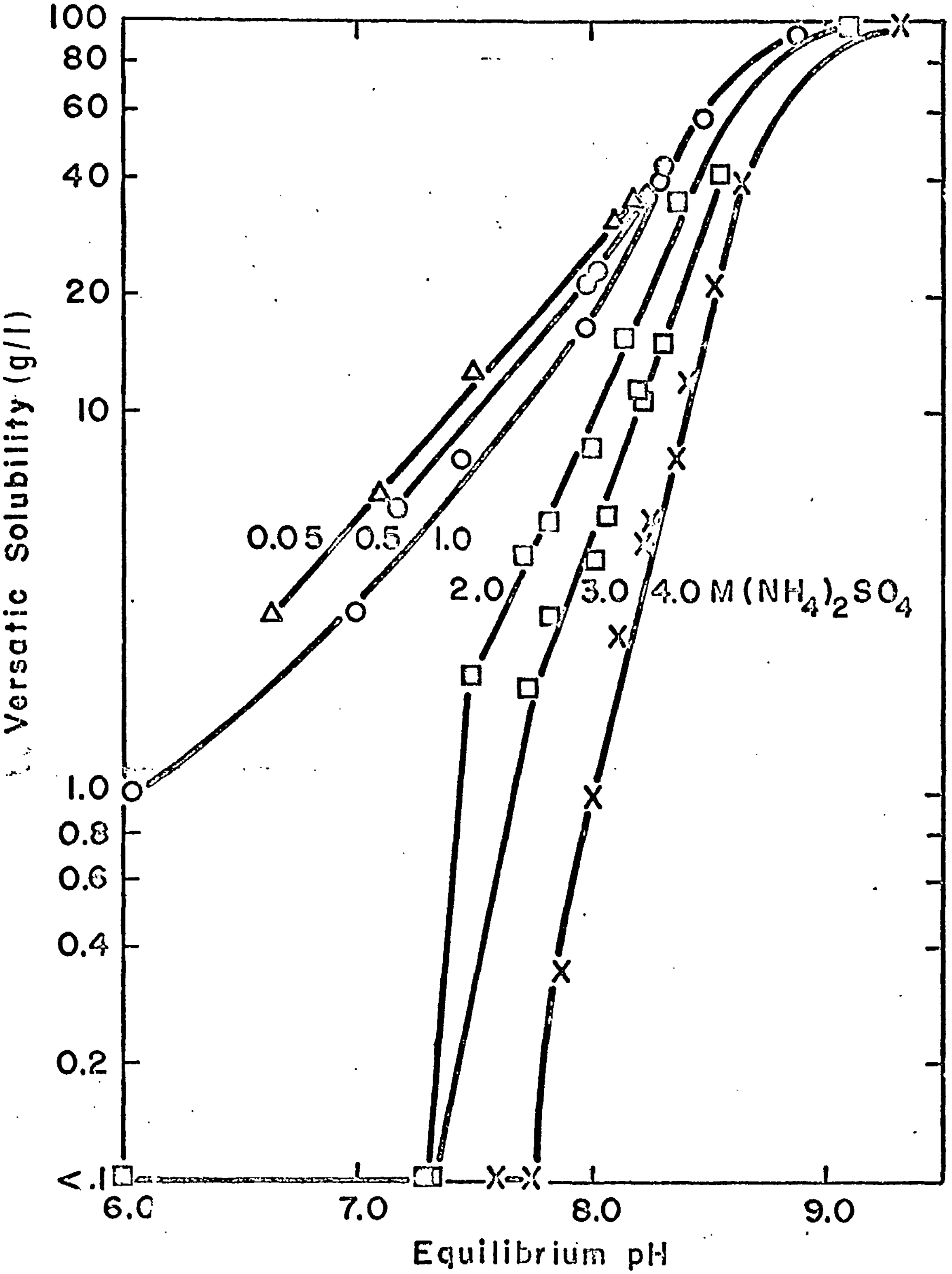


Figure 18. Effect of $(NH_4)_2SO_4$ Concentration and pH on Solubility of Versatic 911 in the Aqueous Phase.

carboxylic acid with an increase in the $(NH_4)_2SO_4$ concentration and decrease in pH(100). Up to 4 M $(NH_4)_2SO_4$ at pH 7.5 results in less than 10 ppm solubility of the Versatic 911. Thus the high concentration of ammonium sulphate acts as a "salting out" agent, preventing solubility of the solvent. In that particular system, any severe losses will be as entrainment with the aqueous raffinate.

High entrainment can be caused by insufficient settling time after the mixing stage, such as from poorly designed settlers in a mixer-settler plant. Another cause is due to insufficient or no additive to depress emulsion tendency and increase the rate of phase disengagement. Often, in spite of additions to the system, high losses still occur because of the agitation and partially stable emulsion that result. This is the case on occasion in columns, and a decrease in the rpm of the mixing device, or a decrease in the energy, such as pulse conditions, can often result in a decrease in entrainment losses. In a mixer-settler operation, it is advantageous to have the extraction occur with the solvent being the continuous phase(182). Uranium mills in South Africa have an alarm in the system which is triggered by an increase in the conductivity of the mixture, to indicate when an aqueous-continuous emulsion is formed. Often, too, the type of pump (such as centrifugal) used to pump a raffinate containing entrained solvent can produce a stable emulsion which is almost impossible to separate by settling. High entrainment losses can result due to the solvent concentration. Thus, in circuits where losses by entrainment tend to be high, the concentration is kept to a low value, such as 5 v/o amine or less in the uranium mills. By contrast, the alkylphosphoric acids can be used at concentration of 20 to 30 v/o, while maintaining solvent losses in the same order as that for dilute amine solutions.

The composition and nature of the feed aqueous solutions, such as pH, temperature, salt concentration, and solids can have an effect on solvent losses. In mixing devices, such as mixer-settlers or centrifuges, where the rpm of agitation is high, very little solids can be tolerated - probably 10 ppm. Even this amount may be sufficient to block the holes eventually in a centrifuge, because of the tendency of solids to form stable emulsions with solvent when vigorously agitated. These stable emulsions are frequently referred to as "cruds". In mixer-settlers, the presence of a small amount of solids forms cruds, which remain at the organic-aqueous interface in the settler and require periodic removal by skimming.

Formation of cruds must be kept to a minimum to decrease the cost of the solvent extraction operation. Incomplete stripping can result, as well as incomplete regeneration of the solvent, if cruds are allowed to form. In addition to undissolved solids present in the feed solution, the nature of the leach may promote cruds, such as dissolved silica which precipitates upon ageing and cooling. The pH of stripping or acidification can also be the causes of crud formation.

It has been fairly common, in both the copper(181) and uranium(182) recovery plants using the substituted oximes or tertiary amines, that a bacterial fungus develops and thrives at the interface between the organic and aqueous solutions present in the settler. The result is that substantially higher solvent losses are experienced compared to solvent losses in circuits having no fungus problem. In some of the uranium plants in South Africa, tests indicated that the presence of isodecanol, added as a third-phase inhibitor, greatly accelerated the growth of fungus in the settler, whereas aromatics inhibited fungus growth. The rate of fungus growth was reduced to an acceptable level by replacing the 2% isodecanol usually used, by 35% Solvesso 150, an aromatic solvent. In the copper plants, work is continuing on the fungus-bacteria problem. The fungus is predominant, and the bacteria probably only exist because of the fungus-bacteria problem. The fungus is predominant, and the bacteria have been identified as baccillus oxidans, while the fungus present in the kerosene has been identified as cladosporrum resinal spores.

Entrainment losses in operating plants have been minimized by installation of skimmers, centrifuges, coalescers, settlers, flotation, foam fractionation, and activated carbon. In some systems the entrainment readily separates upon standing and, therefore, is readily skimmed for recovery. Other entrainment requires extreme velocities, as with a centrifuge, to effect separation and recovery. Coalescers, having a packing of polythene granules, have been effective in some plants. The uranium plant at Buffelsfontein, South Africa, incorporates three after-settlers to aid in solvent recovery from the final raffinate(104). Emulsions may be pumped into the settlers and the solvent reclaimed after an adequate settling period. Solvent recovery in the after-settlers was equivalent to 2 ppm of amine when the amine content of the entering raffinate was of the order of 13 ppm - of amine. Also at Buffelsfontein, tests showed that about 25% of the amine in the raffinate leaving the last mixer-settler could be recovered by filtering the raffinate through a pre-coated cloth, while an additional 25% adhered to the precoat. Also by using an after-settler packed with 1½ inch raschig rings, the amine content of the final effluent was reduced to 5 ppm of amine regardless of the amount in the raffinate from the solvent extraction circuit. The volume of rings used was equivalent to one cubic foot per gallon of raffinate per minute.

In Table 9 are shown typical reported solvent losses

TABLE 9

Reported Solvent Losses in Raffinates

Extractant	Operating pH	Loss ppm	Comments	References
LIX-64	1.5-2.0	3.75-15	Cu extraction	176,179,186, 187,188,191
Tertiary Amines	1.5-2.0	10-40	U extraction	74,102,103, 105,163
Napthenic Acid	3.5	100		190
Napthenic Acid	6.5	900		190
Versatic 911	7.0	300	H_2O solubility	Shell data
Versatic 911	7.7	<10	High salt content	100
D2EHPA	2.0	7	Rare earths	Private communication
D2EHPA	5.5	35	Co extraction	185
TBP	2.0	25		184
MIBK	1-5M HCl H_2SO_4, HCNS	Up to 20,000		184
Kelex-100	1-2	4.5	Cu extraction	193

occurring in process raffinates. A range of solvent losses, as noted in some systems, is probably due to the better solvent recovery in one plant compared to another. Both the tertiary amines and the LIX-64 have low losses. The alkylphosphoric acid, D2EHPA, and the carboxylic acids are pH dependent as regards reagent solubility. However, the presence of a high salt concentration depresses the reagent solubility to <10 ppm. TBP is slightly higher than amines, and MIBK would appear impractical for process use, as regards solvent recovery costs and the potential pollution aspects.

Where solvent losses, caused either by solubility or entrainment, were usually treated as part of the necessary cost of the operation and, therefore, a problem to reduce losses in order to decrease the operating costs of solvent extraction, now the emphasis is not only on cost but also on the potential effects such solvent losses might have on the environment. It can safely be assumed that any solvent losses will have to be corrected by the mill before the effluent leaves the mill and empties into small streams and lakes. Therefore, new technology is required to identify the causes, to analyse solvents in the ppm range or lower, and to develop methods for treatment of effluents in order to remove or render the solvents bio-degradeable or non-toxic to the environment. The cost of the effluent treatment will be dictated by the following: volume of effluent stream, amount of solvent to remove, ease of separation, possibility of solvent recovery, and type and design of effluent treatment method chosen.

Costs and Economic Considerations

Uranium, because of its importance as a nuclear fuel, has recived the most attention as far as ion exchange or solvent extraction processing in Canada is concerned. In Canada, there are two aspects of solvent extraction for uranium: concentration at the mill site, and purification at a refinery. Many of the processes for other metals have resulted from uranium research. The present separation of zirconium and hafnium(73) at the Eldorado Nuclear refinery is designed to produce zircalloy-2 cladding for the UO_2-fuelled reactors. Also, the separation of cobalt and nickel(69) developed by Eldorado was a result of research carried out to provide an alternative metal to uranium to process at their refinery, using existing equipment. The cobalt-nickel process was to fill a gap in the late 1960's when there were no uranium contracts. Therefore, because of this emphasis on uranium recovery by solvent extraction processing in Canada, the processing costs shown here will be for uranium processing.

Only one Canadian plant has used a solvent extraction operation for purifying the recovering uranium from acid-leach liquors. At the Port Radium operation of Eldorado Nuclear, uranium was extracted as uranyl sulphate by an anion exchange reaction with a 0.1 M solution of a teriary amine together with 3% isodecanol in a kerosene diluent(74). As in the ion exchange process, extraction of uranium decreased as the sulphate and hydrogen ion concentration of the feed solution is increased. On the other hand, a major advantage of the amine solvent extraction process (Amex process)(147) was that loaded solvent could be effectively stripped by a wide range of reagents. The problem of poisoning as encountered in ion exchange was consquently not a problem in solvent extraction processes. The amine solvent was selective for uranium in the presence of impurities such as iron, thorium, phosphate, and rare earths.

The Port Radium operation had a total solvent loss amounting to about 3¢/lb U_3O_8 or 0.22 lb amine per 1,000 gal feed. This loss, from treatment of solutions containing 1.7 g U_3O_8/l, compares favourably with data obtained later in a solvent-in-pulp pilot plant at Eldorado's Beaverlodge operation, using a pulse-column contactor where the solvent loss was 0.13 lb amine per 1,000 gal feed(107).

Table 10 gives an estimate of the costs of processing uranium-bearing acid-leach liquors by solvent extraction. The total solvent and reagent cost for solvent extraction is about $0.05 per lb U_3O_8. The total operating costs for solvent extraction for each of the three areas are lower than the estimated costs for the ion exchange process shown in Table 3. The greatest difference shows up in the costs for the Uranium City area, because no poisoning problems arise in the solvent extraction step.

TABLE 10

Solvent-Extraction Processing Costs for Ore Containing 0.1% U_3O_8

	Cost Per Pound U_3O_8 Recovered		
	Elliot Lake, 3,000 tpd	Bancroft, 1,000 tpd	Uranium City[(3)] 1,400 tpd
Solvent required, cu ft	1,200	400	560
Solvent inventory, \$6 per cu ft	7,200	2,400	3,360
Solvent loss(1) \$ per lb U_3O_8	0.030	0.030	0.030
Stripping and acidification 0.4 lb Na_2CO_3 (2) and 0.1 lb H_2SO_4 per lb U_3O_8 produced	0.012	0.012	0.032
Maintenance and labour	0.025	0.065	0.055
Total operating cost	0.067	0.107	0.117

1. Solvent loss based on 0.13 lb amine per 1,000 gal feed containing 0.53 gram U_3O_8/litre
2. Cost of Na_2CO_3 - \$50 per ton
3. Freight to Uranium City \$100 per ton

Although tertiary amines have generally been used for the recovery of uranium, alkylphosphoric acids (Dapex process) have also been used(153). However, they are not as selective for uranium in the presence of such impurities as ferric iron and rare earths as is the amine solvent.

If we assume the same order of loss for the solvent extraction processing of base metals, the following conclusions become valid: (Prices are based on metal prices of July 5, 1971 of Oil, Paint and Drug Reporter.)

1. The recovery of copper @ $0.53/lb represents a solvent loss of 5.7% of its value.
2. The recovery of zinc @ $0.16/lb represents a solvent loss of 19% of its value.
3. The recovery of nickel @ $1.33/lb represents a solvent loss of 2.3% of its value.
4. The recovery of cobalt @ $2.20/lb represents a solvent loss of 1.4% of its value.

It can probably be estimated, therefore, that the cost of solvent loss for recovery of metals from very dilute solutions, where some metals are relatively inexpensive, could be of the order of 1 to 50% of the recovered value.

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 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 with the cost of extraction. At 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 acidity of the solution, with minimum loss of the organic phase to the aqueous phase. 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. This is demonstrated in Table 11, which shows some approximate solvent extraction processing costs on a few selected metal systems, where the feed solution has a flow rate of 100 gallons per minute. The equipment is depreciated over a straight-line, 10-year period, and no allowance is made for the solvent inventory. The systems exhibit a wide range of metal concentration, as well as a range of specialized treatment in order to achieve the desired extraction and separation, thus accounting for the great

TABLE 11

Approximate Solvent Extraction Costs for Recovery of Some Metals (Flow Rate at 100 gal/min)

Metal	Feed Conc. g/l	Aqueous System	Organic Extractant	A/O Ratio	Equipment Type	Processing Costs, ¢/lb Metal Produced							
						Acid. Adj.	Equip. and Inst.	Sol'v Treat.	Scrub-bing	Strip-ping	Est. Sol'v Losses	Labour and Maint.	Tot. SX Costs
Co-Ni	Co 20 Ni 9	H_2SO_4 pH 5-6	30% D2EHPA	1/1	Columns	3.0	0.23	2.2	--	0.3	0.7	0.2	6.6
Zr-Hf	Zr 95 Hf 1.5	HNO_3 7.5N	50% TBP	1/3	Columns	16.0	0.20	20.0	4.0	--	0.8	0.03	41.0
Cu	Cu 5.0	H_2SO_4 pH 1.5-2.0	20% LIX63+ 10% D2EHPA Mixture	2/1	Mixer Settlers	--	0.5	--	--	3.0	1.3	0.50	5.3
U	U 1.0	H_2SO_4 pH 1.5-2.0	5% Alamine 336	5/1	Mixer Settlers	--	2.5	0.5	--	1.2	3.0	2.5	9.7
*R. E. and Y	Y 0.10	H_2SO_4 pH 1.5-2.0	3.3% D2EHPA	20/1	Centrifuge and Columns	18.0**	0.6	--	--	30.4	7.0	25.0	81.0

*Assume separations of each of the rare earths and yttrium are being made.

**Neutralization and pH adjustment in the circuit divided among the rare earths and yttrium.

differences in total cost per pound of metal produced, ranging from 5.3¢ to 81.0¢.

4. COMPARISON OF ION-EXCHANGE AND SOLVENT-EXTRACTION PROCESSING COSTS

The choice of either ion exchange or solvent extraction is difficult because of such factors as the metal content of the liquor and the effect of other metal ions present. Normally, solvent extraction would be more suitable for small volumes of comparatively rich liquor, although the treatment of low-grade solutions for the recovery of rare earths has been demonstrated(165,166,169).

Liquid-liquid ion exchange (solvent extraction) can be operated as a truly continuous countercurrent operation in contrast to normal operations with solid ion-exchangers. This means a maximum utilization of exchange capacity. For example, one cubic foot of resin that can be loaded with 3 to 5 lb of U_3O_8 ordinarily produces 2 to 3 lb of U_3O_8 per day, while one cubic foot of 0.1 M organic extractant that can be loaded with only ¼ to ½ lb U_3O_8 will produce 4 to 8 lb U_3O_8 daily. A cubic foot of resin costs about $45.00, compared to $3.00 to $4.00 for a cubic foot of 0.1 M organic.

In Tables 12 to 14 are shown comparative costs for the treatment of a uranium ore (0.1% U_3O_8) in each of the three major uranium areas of Canada(63) and in which the daily tonnage has varied. The capital cost of resin inventory and equipment is depreciated over a straight-line, 10-year period, and a uranium recovery of 95% up to solution purification is assumed.

Table 12 shows the comparative inventory costs of resin and solvent for the three plants considered. The resin inventory, at approximately 20 times that of solvent, is obviously a considerable cost difference to consider.

Table 13 shows comparative costs of ion exchange columns and solvent extraction equipment. Although the solvent extraction equipment covers a wide range of costs, each type of equipment has certain advantages or disadvantages over another, depending upon feed solution clarity, throughput, interfering ions, head room and plant area. An average figure of $0.024 per lb U_3O_8 produced was estimated for the equipment costs for solvent extraction, as compared to about $0.022 per lb U_3O_8 produced for ion exchange.

Table 14 is an attempt to compare the cost of ion exchange with the costs of a solvent extraction operation in the Elliot Lake area. Obviously the major difference between the two systems is in the cost of elution, compared to stripping. On the other hand, an ion exchange system, using a weak-base exchanger such as the XE-270 already mentioned, could probably be operated as cheaply as the solvent extraction operation because of the lower eluting costs likely to be experienced with the weak-base resin.

TABLE 12

Cost of Resin vs Solvent Inventory for Treatment of Ore Containing 0.1% U_3O_8

	Elliot Lake (3,000 tpd)	Bancroft (1,000 tpd)	Saskatchewan (1,400 tpd)
Resin Cost (1), $	135,000	45,000	63,000
Solvent Cost (2), $	7,200	2,400	3,360

(1) Assume 1 cu ft resin loads 5 lb U_3O_8 and produces 2-3 lb U_3O_8 per day at an initial cost of resin at $45.00 per cu ft.

(2) Assume 1 cu ft 0.1 M organic loads 0.3 lb U_3O_8 and produces 5 lb U_3O_8 per day, at an initial cost of solvent at $6.00 per cu ft.

TABLE 13

Comparative Costs of Extraction Equipment

(For 3,000 tpd plant)

	Estimated Cost, $	Cost/lb U_3O_8 (cents)
Ion Exchange		
Columns (12 @ 8' x 14')	400,000	2.2
Solvent Extraction		
1) Sieve-plate pulse columns (12 @ 30" x 20')	660,000	3.7
2) Mixing columns (12 @ 30" x 16')	400,000	2.2
3) Reciprocating plate columns (8 @ 42" x 12')	440,000	2.4
4) Centrifugal contactors (3 @ 48" plus 2 @ 24")	450,000	2.5
5) Mixer-settlers	225,000	1.3

TABLE 14

Comparison of Total Costs of Ion Exchange and Solvent Extraction for Uranium-Ore Processing
(Elliot Lake ore, 0.1% U_3O_8)

	Cost Per Pound U_3O_8	
	Ion Exchange	Solvent Extraction
Resin or solvent loss	0.010	0.030
Elution or stripping reagents	0.057	0.012
Depreciation of equipment and instrumentation(a)	0.030	0.030
Maintenance and Labour	0.025	0.025
Total Costs	0.122	0.097

(a) 10-year straight-line of about $500,000 for either plant.

5. CONCLUSIONS

The successful introduction of solvent extraction or ion exchange to any operation will depend on a number of considerations. In all cases, the advantages of these separation processes lie in the possibilities of concentrating initially dilute values, of purification, and of separation of metals.

For future processing, the choice of ion exchange or solvent extraction will not be based on economics alone, as the two processes are similar in cost, provided that no fouling of the resin occurs and that elution costs can be brought closer to stripping costs. More likely, the choice will be dictated by considerations other than simply which one is the cheaper to operate. For example, in the uranium area, if it were specified that the final product be "yellow cake", then either ion exchange or solvent extraction would be equally acceptable. However, if UO_3 or UO_2 were in demand, solvent extraction together with ammonium carbonate or ammonium sulphate stripping would be desirable. Specifications on the product as set by the buyer, as well as pollution control considerations, will have a decided effect on the choice of whether to build an ion exchange or a solvent extraction plant. In present ion-exchange plants, it may be necessary to incorporate solvent extraction in order to decrease specific impurities in the product and to meet the local water-resources specifications against stream pollution.

To minimize the size of solvent extraction plants, the use of columns or centrifugal contactors may be more effective than the popular mixer-settlers. Columns have the advantage of providing many stages of contact, while the centrifugal contactor occupies a relatively small area, has a high throughput and relatively low solvent inventory.

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 or ion exchange.

In general, processing is simple so that operating costs 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 solvent 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. Automation of the extraction process will undoubtedly improve the recovery of the desired metal. The economics of applying solvent extraction or ion exchange cannot be generalized, and particular circumstances must be considered in every potential application.

Finally, if it were possible to apply either a solvent-in-pulp or resin-in-pulp system for solution purification, the expensive liquid-solid separation step that has been used in Canadian plants could be eliminated or greatly reduced in size.

6. GLOSSARY OF SOME SOLVENT EXTRACTION TERMS

A/O ratio - Refers to volumetric phase ratio of aqueous to organic phase. Also expressed as O/A. Generally, in practice the larger phase volume is the numerator.

Aqueous feed - Solution feed to the contactor containing the metal to be extracted.

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.

Continuous phase - The major phase in the contactor in which the minor phase is dispersed.

Crud - The condition that results from agitation of an organic phase, aqueous phase, and fine solid particles, resulting in a stable mixture of these components. Because of its density, which is heavier than the organic phase and lighter than the aqueous phase, the "crud" generally floats at the interface.

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.

Dispersed phase - The minor phase in the contactor in contact with the continuous major phase.

Equilibration - Pre-treatment of the solvent prior to extraction. The object of equilibration is to provide a solvent that will effectively extract the required metal ions, either because of the form of the active constituent of the solvent, or by maintaining the necessary extraction pH.

Extraction or stripping 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 stripping 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 - The active organic reagent.

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

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

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

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

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. Also inhibits third-phase formation and decreases emulsion tendency.

Raffinate - Generally the organic-soluble phase. See extraction raffinate and scrub raffinate.

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

Scrubbed solvent - The organic medium containing the desired metal solute after purifying by scrubbing undesirable solutes.

Scrub feed - The aqueous solution used to contact the loaded solvent for the removal of undesirable anions or cations.

Scrub raffinate - The aqueous phase after contacting the loaded solvent. Contains impurities removed during scrubbing.

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

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

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.

Solvent feed - 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.

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 the loaded solvent. Selective stripping refers to separate removal of specific metal solutes from an extract containing more than one metal solute.

Strip feed - Aqueous solution used to contact the loaded or scrubbed solvent to recover the extracted metal solute.

Strip liquor - Aqueous solution containing the recovered metal, generally in high concentration.

Stripped solvent - The organic phase after removal of the extracted solutes by stripping.

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

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