IC 8502

PB 198 134

Bureau of Mines Information Circular/ January 1971

# Metallurgical Application of Solvent Extraction

## (In Two Parts)

## 2. Practice and Trends

UNITED STATES DEPARTMENT OF THE INTERIOR

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

23

Information Circular 8502

# Metallurgical Application of Solvent Extraction

## (In Two Parts)

## 2. Practice and Trends

By Joe B. Rosenbaum, D. R. George, and Joan T. May

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

This publication has been cataloged as follows:

Rosenbaum, Joe B

Metallurgical application of solvent extraction (in two parts). 2. Practice and trends, by Joe B. Rosenbaum, D. R. George, and Joan T. May. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1971]

19 p. illus., table. (U.S. Bureau of Mines. Information circular 8502)

Includes bibliography.

Pt. 1 is Information circular 8139.

1. Extraction (Chemistry). I. George, D'Arcy R., jt. auth. II. May, Joan T., jt. auth. III. Title: Metallurgical application of solvent extraction: Pt. 2. Practice and trends. (Series)

TN23.U71 no. 8502 622.06173
U.S. Dept. of the Int. Library

## CONTENTS

## ILLUSTRATIONS

## TABLE

# METALLURGICAL APPLICATION OF SOLVENT EXTRACTION

## (In Two Parts)

## 2. Practice and Trends

by

Joe B. Rosenbaum,[1] D. R. George,[2] and Joan T. May[3]

## ABSTRACT

New applications and concepts of solvent extraction as a unit operation in extractive metallurgy have been developed in the last decade. Wider use is being made of established solvent extraction techniques in processing spent nuclear fuel elements and in winning columbium-tantalum, hafnium-zirconium, thorium, tungsten, uranium, and vanadium. Commercial application has been extended to recovery of beryllium, boron, bromine, copper, molybdenum, phosphorus, rare-earth metals, and rhenium. Systems in use and proposed typically extract metals or salts as anion, cation, or neutral species from aqueous media by reaction with a recycleable organic reagent.

## INTRODUCTION

This is the second Bureau of Mines Information Circular dealing with solvent extraction as a unit process of growing importance in minerals processing. The first circular (3),[4] issued in 1962, covered the history, chemistry, equipment, and terminology of the uses and metallurgical development of solvent extraction. Since then, its use for recovery of columbium-tantalum, hafnium-zirconium, tungsten, uranium, and vanadium has expanded, and application of solvent extraction techniques has extended to industrial processing of beryllium, boron, bromine, copper, molybdenum, phosphorus, and rare-earth elements. Additionally, a plant which will recover potassium nitrate by solvent extraction is being constructed (19).

Laboratory studies of extractants and procedures for recovery of aluminum, arsenic, cadmium, cesium, gallium, germanium, nickel-cobalt, scandium, selenium, thallium, and zinc have been reported. These are cited in a review article of the solvent extraction literature by Zakarias (34) and Cahalan.

---

[1] Research director.

[2] Supervisory metallurgist.

[3] Research chemist.

All authors are with the Salt Lake City Metallurgy Research Center, Bureau of Mines, Salt Lake City, Utah.

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

A review of the literature on laboratory developments in solvent extraction of the common base metals also was assembled by Ritcey (27). Recent laboratory developments in solvent extraction for aluminum and cobalt were reported by the Bureau of Mines (4, 16).

Some solvent extraction costs, both actual and projected, are given by Cahalan (7) and Agers (1). The recovery of fission products from depleted nuclear fuel elements is comprehensively reported in the literature and need not be discussed here. This paper reviews the status of solvent extraction in industrial practice and summarizes the chemistry of typical systems. As published information on many commercial operations is absent, meager, or outdated, personal communications have been helpful in supplementing published data.

## INDUSTRIAL PRACTICE

The earliest metallurgical use of solvent extraction in commercial practice was in the recovery and refining of uranium. Its next use was in separating columbium from tantalum and hafnium from zirconium, and in processing nuclear fuel elements. Subsequently, solvent extraction processes were applied in the production of vanadium, thorium, tungsten, rare-earth metals, molybdenum, boron, bromine, phosphorus, beryllium, rhenium, and copper. The current applications are summarized in table 1, located at the end of this report, and the significant features are briefly reviewed in the accompanying text. Organic extractants are listed in table 1 by class or by trade designation and are more fully described in the text.

### Beryllium

The Brush Beryllium Co. extracts beryllium as a cation from an acid sulfate solution with a kerosine solution of di-2-ethylhexyl phosphoric acid, hereafter referred to as EHPA. The loaded organic is stripped with ammonium carbonate solution, then reacidified by scrubbing with dilute sulfuric acid before recycling.

Brush has practiced beryllium solvent extraction on a small scale for several years as part of its beryl processing facility at Elmore, Ohio. In 1969, the company's Lynndyl, Utah, plant began recovery of beryllium from volcanic tuffs mined at Spor Mountain, Utah. Ore containing 0.5 to 1 percent BeO as bertrandite, a hydrated silicate, is treated by sulfuric acid leaching, countercurrent decantation washing, and solvent extraction. The aqueous feed has a pH of less than 1 and contains much more aluminum than beryllium. Aluminum loads first and is displaced by beryllium as the organic flows countercurrent to the aqueous stream. About eight mixer-settler extraction stages are needed,with a relatively long mixing time of 20 minutes or more in each stage.

Ammonium carbonate solution is used for stripping the loaded organic. Loaded strip liquor is heated in stages. First, part of the ammonia and carbon dioxide is driven off, and coextracted impurities, principally ferric iron and aluminum, are precipitated. These are removed by filtration. Further heating under partial vacuum eliminates more ammonia and carbon dioxide and precipitates a hydrated beryllium oxide. This is shipped to Elmore, Ohio, for refining, if needed, and conversion to metal (8, 11, 21).

## Boron

The American Potash and Chemical Co. at Searles Lake, Calif., extracts boron as a sodium borate molecule from a natural brine with a phenyl glycol-kerosine mixture. The loaded organic is stripped with dilute sulfuric acid to yield a solution from which boric acid and sodium sulfate are recovered by evaporation and fractional crystallization. The plant processes about 5,000 gallons per minute of brine containing 1 percent sodium borate. A single extraction stage suffices. Four mixer-settler stages are used in stripping. The loaded strip solution contains about 6 percent boric acid (15, 18).

## Bromine

Israel Mining Industries extracts bromine as a neutral bromine molecule from Dead Sea brine with tetrabromoethane. Sparging chlorine into the brine as it comes from the sea liberates the bromine for extraction. The bromine-rich extract is then treated with acetylene, with which the bromine reacts to form more tetrabromoethane, in which form the bromine is marketed (19).

## Columbium-Tantalum

Columbium (niobium) and tantalum are purified and separated from hydrofluoric-sulfuric acid solution by methyl isobutyl ketone (MIBK) solvent extraction. The process chemistry and operating techniques were demonstrated in a Bureau of Mines pilot plant in the early 1950's (23). Subsequently, Wah Chang, Union Carbide, and Fansteel Metallurgical Co. in the United States; Murex, Ltd. in England; and plants in Belgium, Germany, and Japan adopted the process with individual modifications.

The Bureau of Mines process coextracted columbium and tantalum from a strong hydrofluoric-sulfuric acid solution. By scrubbing the loaded MIBK with dilute acid solution to remove columbium and by reextracting the scrub liquor in an interlocked system, separate columbium and tantalum fractions were obtained.

The Union Carbide Co. uses either sequential extraction or coextraction in a mixer-settler cascade. When extracting sequentially, tantalum is extracted first; the aqueous feed is then made more acid, and the columbium is extracted (9).

In another version of the process, columbium and tantalum are coextracted, and then columbium is selectively stripped by introducing the loaded MIBK at the center of a mixer-settler cascade, with fresh MIBK entering at one end and dilute sulfuric acid at the other end. Finally, tantalum is stripped from the loaded organic by addition of potassium fluoride, which quantitatively precipitates potassium tantalum oxyfluoride. Columbium is recovered from the dilute acid strip liquor by reextracting with MIBK and adding potassium fluoride to the loaded organic to precipitate potassium columbium oxyfluoride (6).

## Copper

Copper solvent extraction was initiated on a commercial scale in 1968 by Rancher's Exploration Co. at the Bluebird property near Miami, Ariz. A cupric cation is extracted from a sulfuric acid leach solution by a kerosine solution of General Mills Co. reagent LIX-64N,[5] a mixture of hydroxyoximes. Free sulfuric acid in the spent electrolyte from the subsequent copper electrowinning step is used for stripping.

The feed liquor, containing about 2.9 grams of copper per liter, is prepared by heap leaching of silicate ore with recycled raffinate fortified with added sulfuric acid. About 1,100 gallons per minute of the feed liquor is contacted with 2.5 times as much of a 7-volume-percent solution of LIX-64N in kerosine. Extraction takes place in three mixer-settler stages. About 0.3 gram of copper per liter remains in the raffinate. Loaded organic, containing 1.8 grams of copper per liter, is stripped in two stages at an organic-to-aqueous ratio of about 3 to 1 with depleted electrolyte that is 1.5 molar in $H_2SO_4$ and that contains about 32 grams of copper per liter.

The strip liquor, containing 35 grams of copper per liter, is electrolyzed at a current density of 17 to 20 amperes per square foot to produce 15 tons per day of cathode copper containing 99.9 percent copper. Organic loss in the solvent extraction circuit is 0.16 gallon of the 7-percent LIX-64N solution per 1,000 gallons of leach solution. Assuming the cost of the LIX-kerosine mixture is $1.40 per gallon, the organic loss is equivalent to 1.2 cents per pound of copper recovered (<u>26</u>).

Figure 1 shows a solvent extraction plant. Leach solution storage and clarifying filters are at the left in the photograph. The mixer-settlers for extraction and stripping are in the center, and the electrolytic tankhouse is at the right. Flotation cells for removing entrained organic from the loaded strip liquor before electrolysis are in the structure in the center foreground.

In July 1970, the Bagdad Copper Co. started operation of an LIX-64N solvent extraction-electrowinning plant to produce 25 tons of copper per day from waste dump leaching solution (<u>24</u>). N'Changa Consolidated Copper Mines, Ltd., has announced plans to construct a plant in Zambia that will recover 60,000 tons of copper per year from oxide ores by sulfuric acid leaching and solvent extraction.

The Capital Wire and Cable Co. extracts copper from cupric ammonium carbonate solution by the following reaction, in which R represents the LIX-64N anion:

$$Cu(NH_3)_4(OH)_2(Aq) + 2RH(Org) \longrightarrow R_2Cu(Org) + 2H_2O + 4NH_3(Aq).$$

Feed solution, containing 30 grams of copper per liter, is prepared by leaching copper metal scrap or cement copper with an aerated solution of

---

[5] Reference to specific company or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

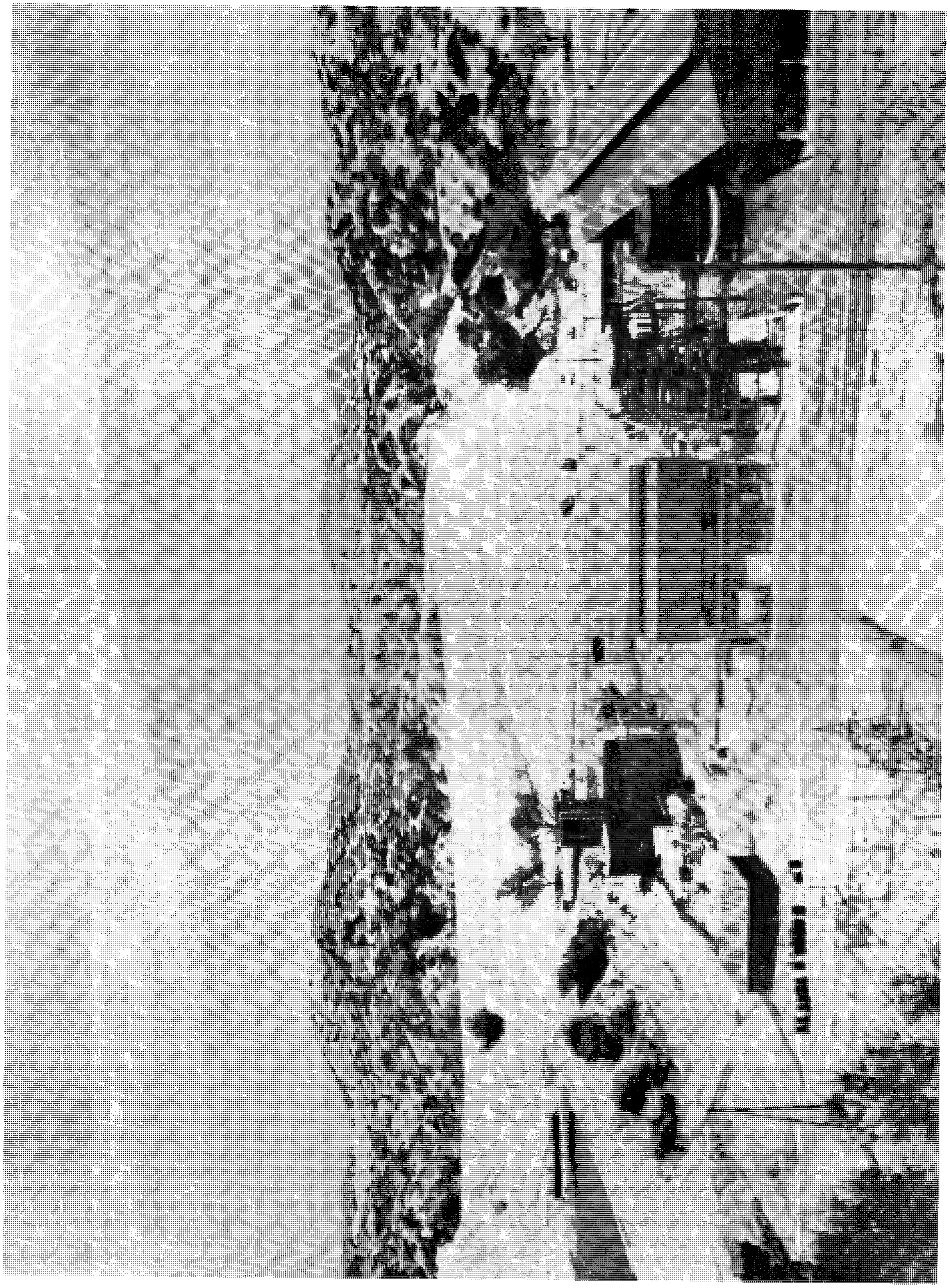

FIGURE 1. - Rancher's Bluebird Solvent Extraction Plant.

solvent extraction raffinate. The leach liquor contains 30 grams ammonia per liter, evenly divided between ammonium hydroxide and ammonium carbonate, and has an initial copper content of 15 grams per liter. Two mixer-settler stages are used in extracting the copper with a 10-percent solution of the LIX reagent in kerosine. Loaded organic contains 4 grams copper per liter. Depleted electrolyte, containing about 170 grams sulfuric acid and 30 grams copper per liter, is used for stripping the loaded organic in two mixer-settler stages. Loaded strip liquor, containing about 40 grams copper per liter, is electrolyzed to produce copper of 99.9-percent purity.

## Hafnium-Zirconium

Hafnium and zirconium are purified and separated by solvent extraction at two plants in the United States and at several foreign plants. Zirconium, occurring naturally as the mineral zircon, usually contains about 2 percent hafnium. In its principal use of cladding nuclear fuel elements, the zirconium must be freed of neutron-absorbing hafnium. The hafnium is used in the nuclear industry for reactor control rods.

Either a methyl isobutyl ketone-thiocyanate system (MIBK-HCNS) or a tributyl phosphate-nitrate system (TBP-$HNO_3$) is used in hafnium-zirconium extraction. The two operating U.S. plants and those in Germany, Great Britain, and Japan use MIBK-HCNS. One plant in the United States, now on standby, and plants in France and Canada use TBP-$HNO_3$ (25).

Feed solution for the MIBK-HCNS plants is prepared by chlorinating zircon concentrates and dissolving the mixed chlorides in 1 molar HCl-1 molar thiocyanic acid solution. A hafnyl thiocyanate molecule, perhaps $HfO(CNS)_2$, is selectively extracted with MIBK, which was previously contacted with HCNS, to give a thiocyanic acid loading of about 3 moles per liter.

Loaded organic is first lightly scrubbed with dilute HCl to remove the coextracted zirconium, which is recycled. The organic is then stripped of hafnium with 5 molar sulfuric acid. Pulse column contactors are used for both extraction and stripping. Figure 2 shows the pulse columns and pumps originally installed at the Wah Chang plant, Albany, Oreg. The initial columns were mainly of glass construction. New columns for replacement and plant expansion are constructed of welded zirconium and plastic.

Hafnium is recovered by neutralizing the strip liquor with ammonia to precipitate the hydroxide. This is calcined and chlorinated and the chloride is reduced to metal by reaction with magnesium. Zirconium, in the solvent extraction raffinate, is similarly precipitated, chlorinated, and reduced to metal by reaction with magnesium. The resultant zirconium contains less than 50 parts per million hafnium. The hafnium, however, contains 2.5 to 4 percent zirconium, but metal containing less zirconium can be made if the market requires.

As MIBK solubility in aqueous solutions is about 20 grams per liter, organic losses can be a significant cost factor.

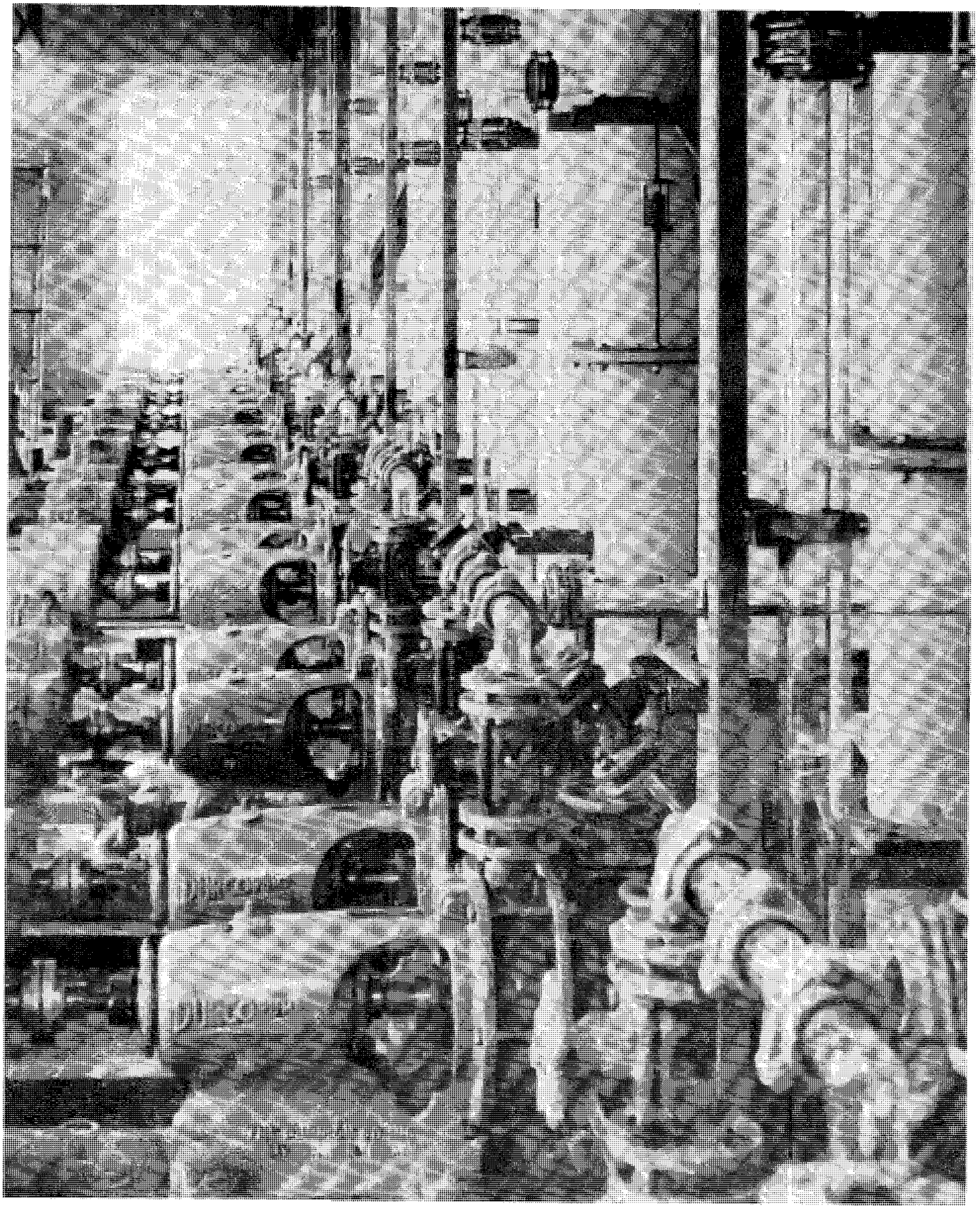

FIGURE 2. - Pulse Columns and Pumps Originally Installed at the Wah Chang Plant, Albany, Oreg.

Feed solution for the TBP-$HNO_3$ process may be prepared from zircon concentrate by alkaline fusion or chlorination. The zirconium products are then dissolved in nitric acid to yield a feed liquor that is 8 molar in nitric acid and 1 molar in zirconium plus hafnium. A zirconium nitrate molecule, perhaps $Zr(NO_3)_4$, is selectively extracted with a 50-percent solution of TBP in n-heptane. The loaded organic is scrubbed with 5 molar $HNO_3$ to remove impurities, then stripped of zirconium with water. Both raffinate and strip liquor, containing the hafnium and zirconium, respectively, can be distilled to recover nitric acid and then neutralized to precipitate the hydroxides of hafnium and zirconium for conversion to metal.

## Molybdenum

Molybdenum is recovered as a byproduct in solvent extraction processing of sulfuric acid-uranium ore leach liquor by Kerr-McGee at Grants, N. Mex. The molybdenum is coextracted with uranium as anion complexes by a tertiary amine extractant, but resists stripping by the sodium chloride solution that removes the uranium. After the uranium is stripped, a bleed stream of the organic is scrubbed with ammonium hydroxide to remove the molybdenum. Addition of phosphoric acid to the scrub solution precipitates an ammonium phosphomolybdate, which is marketed in that form.

Recovery of molybdenum by solvent extraction is also accomplished by Kennecott Copper Corp., in connection with the processing of molybdenite flotation concentrate. Molybdenum oxide, prepared by roasting the concentrate, is leached with sulfuric acid to remove copper. Some molybdenum is solubilized with the copper and is recovered from the solution by solvent extraction with a trilauryl amine. Molybdenum is stripped from the loaded organic with aqueous ammonia, from which it is recovered as ammonium molybdate by evaporation and crystallization.

## Phosphorus

Israel Mining Industries extracts phosphorus in the form of phosphoric acid from a phosphoric acid-calcium chloride solution by a $C_4$-$C_5$ industrial alcohol. The loaded organic is stripped with water. To prepare the feed solution, phosphate rock is acidulated with HCl solution rather than the conventional sulfuric acid. A plant in Brazil also uses the Israel Mining Industries procedure to prepare pure phosphoric acid solutions, and one in Japan formerly did so (19).

## Rare-Earth Metals

The rare-earth metals are fractionated from a chloride solution by EHPA extraction and HCl stripping at the Molybdenum Corp. of America plant in Mountain Pass, Calif. Selectivity is obtained by use of numerous countercurrent extraction stages and close pH control of the aqueous feed. Rare-earth metals are also separated and purified by a variety of solvent extraction procedures at the Molycorp plants in Denver, Colo. and York, Pa.; Dennison Mines, Ltd., in Canada; Thorium, Ltd. in England; and Nippon Yttrium Co. in Japan.

Illustrative of rare-earth fractionation is the recovery of europium at Mountain Pass, Calif. The source mineral is bastnasite, a rare-earth fluorocarbonate. Flotation is used to recover a bastnasite concentrate, which then is roasted to drive off $CO_2$ and to oxidize the cerium to the tetravalent form. Leaching of the calcine with HCl solution dissolves all the rare earths except the cerium. After removal of the undissolved residue, the leach liquor is diluted to a rare-earth content of 100 grams per liter, and the pH is adjusted to about 2 by adding soda ash. Europium, samarium, and gadolinium are coextracted as cations with a kerosine solution of EHPA in eight mixer-settler stages. The other rare-earth constituents, mainly lanthanum, praseodymium, and neodymium, are recovered from the solvent extraction raffinate by precipitation with sodium hydroxide.

The loaded organic is stripped with strong HCl solution, and the strip liquor is in turn contacted with amalgamated zinc to reduce europium from the trivalent to the divalent state. Addition of sulfuric acid precipitates europous sulfate, which is removed by filtration and then further refined to a 99.99-percent $Eu_2O_3$ material. Samarium and gadolinium are recovered by neutralizing the filtrate with sodium hydroxide (33). Figure 3 shows the mixer-settlers in the Mountain Pass solvent extraction plant.

## Rhenium

The Shattuck Chemical Co. in Denver, Colo., extracts rhenium as an anion complex from a sulfate solution with a quaternary or tertiary amine. Loaded organic is stripped with perchloric acid.

The rhenium source is byproduct molybdenite concentrates recovered from porphyry copper ores. In roasting the sulfide concentrate to oxide, rhenium is volatilized and recovered as an acidic solution containing copper, molybdenum, and other impurities by water-scrubbing the roaster offgas. Sodium chlorate is added to the scrub solution to oxidize the rhenium. Rhenium can be extracted from an acid solution at pH 2 to 3 by a tertiary amine, but if it is to be extracted from alkaline solution, a quaternary amine must be used.

Ammonium perrhenate, $NH_4ReO_4$, can be obtained by neutralizing the strip liquor with ammonia. Thermal decomposition of ammonium perrhenate yields an oxide that is readily reduced with hydrogen to rhenium metal powder. When the Bureau of Mines first developed the rhenium solvent extraction process, rhenium was electrodeposited from the strip liquor, thus regenerating the perchloric acid for reuse in stripping (10). The Kennecott Copper Co. uses both ion exchange resin and solvent extraction processes in recovering rhenium. A Kennecott patent application covers substitution of ammonium thiocyanate for perchloric acid in stripping resin or the amine. This is desirable to avoid the risk of a violent reaction of perchloric acid with organic materials.

## Thorium

Although thorium recovery is listed here as representative of current solvent extraction practice, the single plant that recovered thorium by solvent extraction has been shut down owing to the lack of a thorium market.

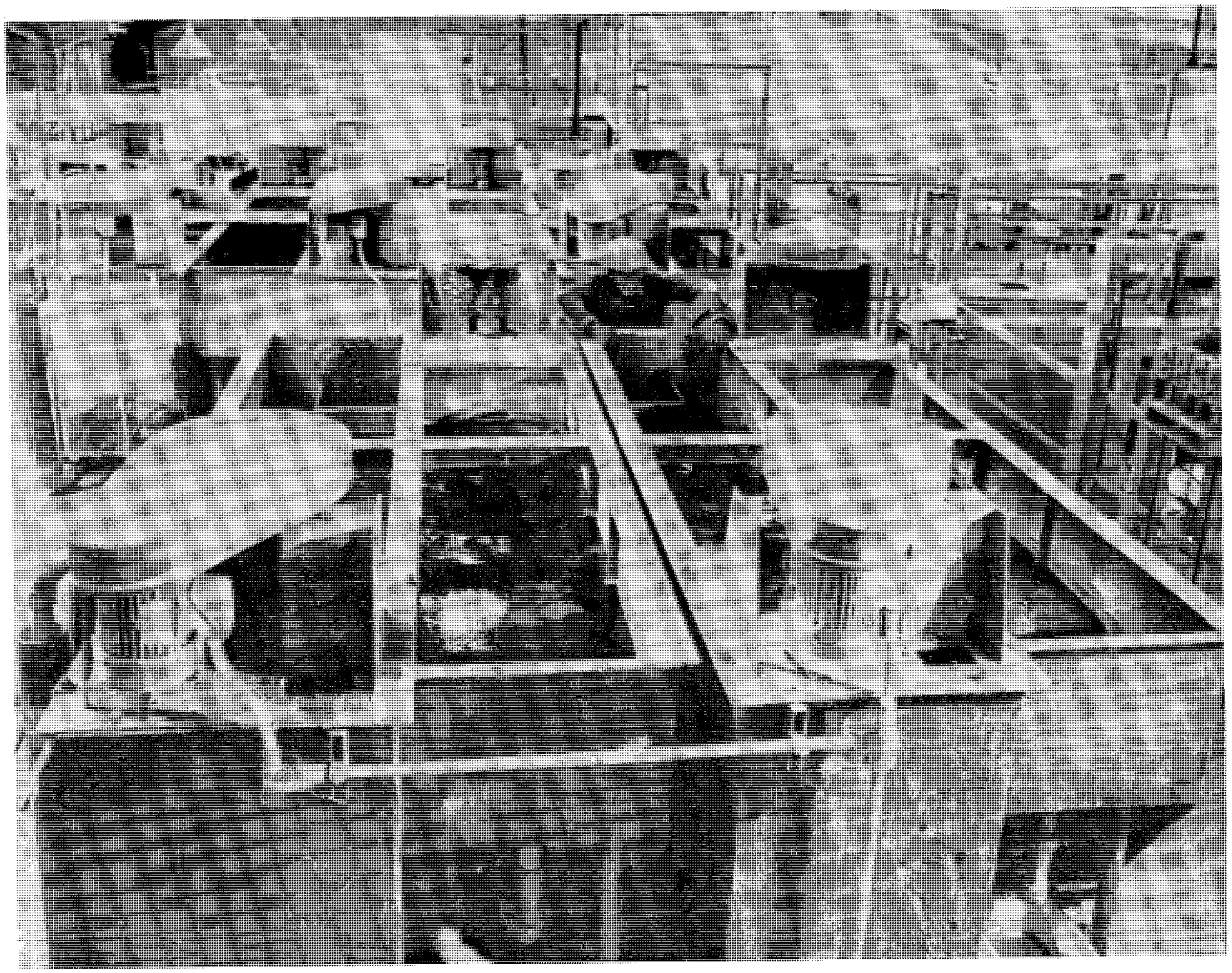

FIGURE 3. - Mixer-Settlers in the Mountain Pass Solvent Extraction Plant.

Rio Tinto-Dow originally built and operated a plant at Elliot Lake, Ontario, Canada, which produced about 150 tons per year of thorium as the sulfate. The feed liquor was uranium-barren solution at a pH of 1.5 to 2.0 from an ion exchange resin circuit. Thorium was extracted as a cation by a solution of heptadecyl phosphoric acid (HDPA) in kerosine. The loaded organic was stripped with a strong sulfuric acid solution. A precipitate of thorium sulfate formed and was removed from the strip liquor (32).

## Tungsten

High-purity tungsten compounds are produced by Union Carbide Corp. at Bishop, Calif., using solvent extraction. The feed liquor is prepared by digesting scheelite concentrates in soda ash solution, acidifying with sulfuric acid, and then gassing with $H_2S$ to remove molybdenum as the sulfide. An acidic anion, perhaps pentavalent $HW_6O_{21}$, is extracted from the sulfate liquor with a secondary amine in kerosine. The loaded organic is stripped with ammonium hydroxide, and ammonium tungstate is crystallized and removed from the loaded strip liquor (20).

## Uranium

On a dollar basis, uranium processing remains the largest application of solvent extraction in the minerals industry. In uranium ore processing, either an anion is extracted from a sulfate feed liquor with a tertiary amine, or a cation is extracted from sulfate or chloride feed liquor with EHPA. In refining uranium concentrate, a neutral complex is extracted from a nitrate feed liquor with tributyl phosphate (TBP).

Seven of the 14 operating uranium mills in the United States use an amine solvent extraction circuit. Of these, three use amine solvent extraction on the primary sulfuric acid leach liquor (13), and the other four use amine solvent extraction on the sulfuric acid eluate after primary resin-in-pulp or column ion exchange processing (14). Five South African plants recently changed from ion exchange resin to amine solvent extraction, and four more are scheduled to do so (12). Most new acid process plants now proposed in the United States are being designed with amine solvent extraction in the flowsheets. Figure 4 shows a mixer and settler unit in the Petrotomics mill.

The amines used are symmetrical trialkyl tertiary amines of the tricaprylyl type. They are employed as a 2- to 5-volume-percent solution in kerosine which contains 2 to 3 percent of a long-chain alcohol such as isodecanol to improve phase disengagement properties. Some of the South African plants dilute the kerosine with an aromatic solvent instead of isodecanol to inhibit growth of fungus in the organic. If allowed to accumulate, the fungus increases the loss of organic in the raffinate. When extracting with amines at the usual leach liquor pH of about 1, four mixer-settler stages will yield a raffinate barren of uranium. Uranium may be stripped from the loaded amine in two or three stages with slightly acid chloride or nitrate solutions, and then precipitated from the strip liquor by neutralizing with ammonia. A sodium carbonate solution also may be used for stripping. Usual practice, however, is to strip in three stages with warm ammonium sulfate solution maintained at a pH of 4.3 by addition of ammonia. Further addition of ammonia to the strip solution precipitates uranium as a mixed hydrated oxide and basic sulfate which is centrifuged and calcined.

Three operating mills in the United States recover uranium and vanadium from carnotite ores that are salt-roasted to solubilize the vanadium as the initial processing step. Union Carbide Co. at Rifle, Colo., and Climax Uranium Co. at Grand Junction, Colo., subsequently extract the uranium from a mixed sulfate-chloride leach solution at pH 1 with 0.1 molar EHPA in kerosine. Excessive iron extraction is avoided by reducing $Fe^{+3}$ to $Fe^{+2}$ with iron powder or $SO_2$ before solvent extraction. Two to three percent TBP or isodecanol is added to the organic to provide adequate solubility of the sodium salt of EHPA that forms when the loaded organic is stripped with sodium carbonate solution.

Climax recovers uranium from the loaded strip liquor by acidifying and then adding hydrogen peroxide to precipitate uranium peroxide. Union Carbide uses sodium hydroxide to precipitate uranium as sodium diuranate. Cotter Corp. at Canon City, Colo., extracts uranium from a sulfuric acid solution with EHPA. The feed material is a uranium refinery residue containing uranium, iron, copper, nickel, cobalt, and a large amount of nitrate (17).

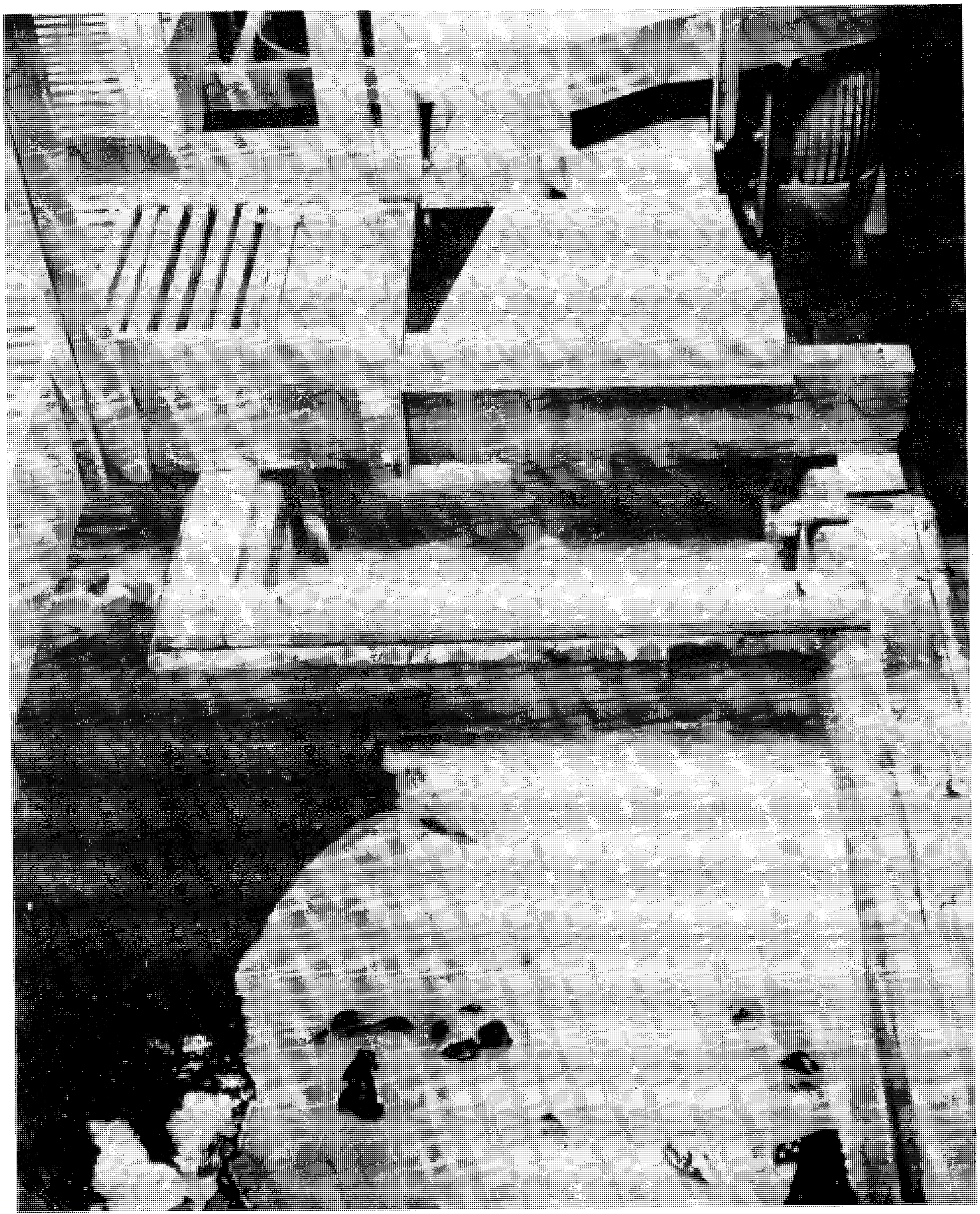

FIGURE 4. - Mixer and Settler Unit in the Petrotomics Mill.

Two plants in Florida formerly extracted uranium as a tetravalent cation from phosphoric acid solution using a 1- to 2-percent solution of nonyl pyrophosphoric acid in kerosine. The loaded organic was stripped and the uranium was simultaneously precipitated as an impure fluoride by contacting with an aqueous solution containing 8 percent HF and 16 percent $H_2SO_4$ (22).

Feed solution for the TBP refining process to make a nuclear-grade product is prepared by dissolving uranium concentrates in nitric acid to yield liquor containing 350 to 400 grams $U_3O_8$ per liter. The uranium is extracted as an anhydrous neutral molecule, possibly $UO_2(NO_3)_2$, with a 30-percent solution of TBP in kerosine or hexane. Loaded organic is first scrubbed with 4 molar $HNO_3$ to remove impurities, and then stripped with slightly acidified deionized water to prepare a concentrated solution of pure uranyl nitrate (2, 31). In the United States, the strip solution is evaporated to dryness, and the crystals of uranyl nitrate hexahydrate that form are calcined to produce an orange oxide ($UO_3$) and $HNO_3$. An alternative method is to precipitate the uranium from the aqueous nitrate solution by adding $H_2O_2$ or $NH_3$. The precipitate that forms is subsequently calcined to produce $UO_3$.

## Vanadium

Solvent extraction is employed in four plants for production of most of the U.S. vanadium output; about 10,500 tons of $V_2O_5$ is produced annually from domestic ores.

Union Carbide Co. at Rifle, Colo., extracts vanadium as a $V^{+5}$ anion complex with a tertiary amine in kerosine. Salt-roasted calcine is water-leached and the solution is acidified to pH 2 to 3 for solvent extraction. Loaded organic is stripped with soda ash solution, and vanadium is subsequently recovered as ammonium metavanadate by adding ammoniacal chloride or sulfate compounds to the strip solution (5). Susquehana Western at Edgemont, S. Dak., processes uranium ore tailings by acid leaching and EHPA solvent extraction for vanadium (29). Also, imported metallurgical slag and petroleum ash that have been salt-roasted and water-leached join the uranium ore tailings circuit for additional vanadium recovery.

A vanadium-bearing shale is processed by salt roasting, water leaching, and solvent extraction in Wilson Springs, Ark. (30). The slightly alkaline salt roast liquor is acidified with sulfuric acid to a pH of 2 to 3. Pentavalent vanadium in the form of a vanadic acid anion is extracted with a tertiary amine. As vanadic acid, a strong oxidizing agent, attacks the organic, centrifugal contactors are employed to minimize the contact time. The loaded organic is stripped with a solution of ammonia and ammonium chloride. Ammonium metavanadate of high purity is crystallized from the strip liquor.

Solvent extraction with a tertiary amine in mixer-settlers is used by Kerr-McGee, Soda Springs, Idaho, in scavenging vanadium from a red-cake precipitation tailing liquor. Kerr-McGee feed material is vanadium-bearing ferrophosphorus. This is roasted with salt and limestone, and the calcine is then water-leached to yield a sodium vanadate solution for red-cake precipitation followed by solvent extraction for recovering residual vanadium.

Another solvent extraction system formerly used in Colorado Plateau uranium-vanadium mills that are not now operating was coextraction of a uranyl cation and a vanadic acid anion from acidified salt roast solution using a synergistic mixture of heptadecyl phosphoric acid (HDPA), tertiary amine, and TBP in kerosine. This system was designed to cope with the high chloride content and to take advantage of pentavalent vanadium in the salt roast leach liquor. Ferric iron extraction was suppressed by the mixed organic (28).

## CHEMISTRY OF TYPICAL SYSTEMS

The chemistry of the different types of applied solvent extraction systems is typified by extraction and stripping of a beryllium cation, a uranium anion, and a boron neutral molecule.

Cation extraction by organophosphates is illustrated by use of EHPA in beryllium processing. Equation 1, in which X is the anion (2 ethyl hexyl$)_2PO_4^-$, shows the theoretical reaction of a $Be^{+2}$ cation with two molecules of EHPA to yield beryllium EHP and two hydrogen ions. In practice, however, EHPA forms a dimer in kerosine solution. One of the hydrogens in the dimer is so tightly bonded that it does not exchange with beryllium. The stoichiometry of the working system is therefore represented by equation 2. Here the beryllium cation reacts with two molecules of the dimer ($H_2X_2$) to form $BeH_2X_4$ plus two hydrogen ions.

Stripping with 2 moles of ammonium carbonate is shown in equation 3. Both beryllium and hydrogen are released from the organic, and ammonium EHP is formed. Equation 4 shows regeneration of the organophosphate to the hydrogen dimer. If the aqueous feed liquor contains enough free acid, regeneration may be done simultaneously with extraction in the first organic feed stage. Otherwise a separate acid scrub stage is needed between the strip and extraction circuits.

$$Be^{+2}(Aq) + 2HX(Org) \longrightarrow BeX_2(Org) + 2H^+(Aq) \tag{1}$$

$$Be^{+2} + 2H_2X_2(Org) \longrightarrow BeH_2X_4(Org) + 2H^+(Aq) \tag{2}$$

$$\begin{aligned} BeH_2X_4(Org) + 2(NH_4)_2CO_3(Aq) \longrightarrow\ & BeCO_3(Aq) + H_2CO_3(Aq) \\ & + 4(NH)_4X(Org) \end{aligned} \tag{3}$$

$$4(NH)_4X(Aq) + 2H_2SO_4(Aq) \longrightarrow 2H_2X_2(Org) + 2(NH_4)_2SO_4(Aq) \tag{4}$$

Anion extraction by tertiary amines is illustrated by uranium extraction and stripping. Equation 5, in which $R_3$ is a tertiary alkyl cation, shows the reaction of 2 moles of tertiary alkyl amine ($R_3N$) with 1 mole of sulfuric acid to form amine sulfate. This reaction occurs in the first organic feed extraction stage, assuming that the aqueous feed solution contains enough free acid. Otherwise, an acid scrub stage is needed. Equation 6 shows the reaction of a uranyl sulfate anion with an amine sulfate molecule to yield amine uranyl sulfate and a sulfate anion. Although nitrates have been used for stripping amines in the past, and while stripping with chlorides is still practiced, most of the mills strip with $NH_3$ in an aqueous ammonium sulfate solution at pH 4.3. Stripping with 2 moles of ammonia is shown in equation 7. An aqueous solution of uranyl and ammonium sulfates is obtained and free amine is liberated for recycling.

$$2R_3N + H_2SO_4 \longrightarrow (R_3NH)_2SO_4 \qquad (5)$$

$$UO_2(SO_4)_2^{-2}(Aq) + (R_3NH)_2SO_4(Org) \longrightarrow (R_3NH)_2UO_2(SO_4)_2(Org) + SO_4^{-2}(Aq) \qquad (6)$$

$$(R_3NH)_2UO_2(SO_4)_2(Org) + 2NH_3(Aq) \longrightarrow 2R_3N(Org) + UO_2SO_4(Aq) + (NH_4)_2SO_4(Aq) \qquad (7)$$

Extraction of a neutral molecule is portrayed by the extraction and stripping equations for boron. Equation 8, in which $R(OH)_2$ is an aromatic polyol, shows the reaction of sodium borate with an aromatic polyol such as phenyl glycol, which yields a sodium borate organic complex and water. As shown in equation 9, stripping is accomplished with dilute sulfuric acid, which regenerates the free organic and yields a solution of boric acid and sodium sulfate.

$$NaB(OH)_4(Aq) + 2R(OH)_2(Org) \longrightarrow NaR_2BO_4(Org) + 4H_2O \qquad (8)$$

$$NaR_2BO_4 + 1/2H_2SO_4 + 3H_2O \longrightarrow 2R(OH)_2(Org) + H_3BO_3(Aq) + 1/2Na_2SO_4(Aq) \qquad (9)$$

## SUMMARY

Not counting the recovery of fission products from nuclear fuel elements, solvent extraction techniques are used in commercial production of the rare earths and 15 other metals or chemicals. This is about twice the number of applications listed in the 1962 Bureau of Mines report on solvent extraction in metallurgy.

TABLE 1. - Solvent extraction applications in minerals processing

| Element | Extracted species | Feed solution | Organic solution | Strip solution |
|---|---|---|---|---|
| Beryllium | Cation | Acid sulfate | EHPA | $(NH_4)_2CO_3$. |
| Boron | Neutral | Alkaline brine | Phenyl glycol | $H_2SO_4$. |
| Bromine | ..do | Brine | Tetrabromoethane | $C_2H_2$. |
| Columbium-tantalum | Neutral columbium<br>Neutral tantalum | $H_2SO_4$-HF | MIBK | Cb, $H_2SO_4$.<br>Ta, KF. |
| Copper | Cation | Acid sulfate or $NH_4OH$-$(NH_4)_2CO_3$. | LIX-64N | $H_2SO_4$. |
| Hafnium-zirconium | Neutral hafnium<br>Neutral zirconium | HCl-HCNS<br>$HNO_3$ | MIBK<br>TBP | $H_2SO_4$.<br>$H_2O$. |
| Molybdenum | Anion | Acid sulfate | Tertiary amine | $NH_4OH$. |
| Phosphorus | Neutral | $H_3PO_4$-$CaCl_2$ | $C_4$-$C_5$ alcohol | $H_2O$. |
| Rare earths | Cation | Acid chloride | EHPA | HCl. |
| Rhenium | Anion | Alkaline sulfate | Quaternary amine | $HClO_4$ or $NH_4SCN$. |
| Thorium | Cation | Acid sulfate | HDPA | $H_2SO_4$. |
| Tungsten | Anion | .....do | Secondary amine | $NH_4OH$. |
| Uranium | Anion<br>Cation<br>Neutral | .....do<br>Acid sulfate-chloride<br>Acid nitrate | Tertiary amine<br>EHPA<br>TBP | $NH_3$-$(NH_4)SO_4$.<br>$Na_2CO_3$.<br>$H_2O$. |
| Vanadium | Anion<br>Cation | Acid chloride<br>Acid sulfate-chloride | Tertiary amine<br>EHPA | $NH_3$-$NH_4Cl$.<br>$H_2SO_4$. |

# REFERENCES

1. Agers, D. W., and J. E. House. Basic Economic and Technical Considerations in the Extraction of Metals Using Amine Solvents, Unit Processes in Hydrometallurgy. Proc. 1963 AIME Met. Soc. Conf. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1964, pp. 836-850.

2. Arnold, D. S., and B. G. Ryle. Reactor Grade Uranium by Extraction of Slurries. Chem. Eng. Prog., v. 53, February 1957, pp. 63:F-64:F.

3. Bridges, D. W., and J. B. Rosenbaum. Metallurgical Application of Solvent Extraction, Part I: Fundamentals of the Process. BuMines Inf. Circ. 8139, 1962, 45 pp.

4. Brooks, P. T., G. M. Potter, and D. A. Martin. Chemical Reclaiming of Superalloy Scrap. BuMines Rept. of Inv. 7316, 1969, 28 pp.

5. Brown, K. B., C. F. Coleman, D. J. Crouse, C. A. Blake, and A. D. Ryan. Solvent Extraction Processing of Uranium and Thorium Ores. Proc. 2d UN Internat. Conf. on the Peaceful Uses of Atomic Energy, Geneva, v. 3, September 1958, pp. 472-484.

6. Butters, P. A. The Separation of Tantalum and Niobium by Solvent Extraction. Chem. and Ind. (London), Apr. 15, 1967, pp. 613-615.

7. Cahalan, M. J. Solvent Extraction for Metal Recovery--Some Process Economics. Ch. in Advances in Extractive Metallurgy. Institute of Mining and Metallurgy, London, 1968, pp. 716-721.

8. Chemical Engineering News. Brush Beryllium Co. Uses Solvent Extraction. Apr. 19, 1965, pp. 70-71.

9. Chilton, C. H. Columbium and Tantalum Process Flowsheet. Chem. Eng., v. 65, No. 22, Nov. 3, 1958, pp. 105-107.

10. Churchward, P. E., and J. B. Rosenbaum. Sources and Recovery Methods for Rhenium. BuMines Rept. of Inv. 6246, 1963, 16 pp.

11. Crocker, Laird, R. O. Dannenberg, D. W. Bridges, and J. B. Rosenbaum. Recovery of Beryllium From Spor Mountain, Utah, Ore by Solvent Extraction and Caustic Stripping. BuMines Rept. of Inv. 6173, 1963, 27 pp.

12. Faure, A., and T. H. Tunley. Uranium Recovery by Liquid Extraction in South Africa. Proc. Symp. on Recovery of Uranium From Its Ores and Other Sources, Internat. Atomic Energy Agency, Sao Paulo, Brazil, August 1970.

13. Garbella, E. J. The Petrotomic Co. Deco Trefoil, Winter 1968-1969, pp. 11-18.

14. Garbella, E. J. The Split Rock Mill, Western Nuclear, Inc. Deco Trefoil, May-July 1967, pp. 11-22.

15. Garrett, Donald E., Friedrich J. Week, Adam J. Marsh, and Herbert R. Foster, Jr. Boron Extractants. U.S. Pat. 3,111,383, Nov. 19, 1963.

16. George, D. R., K. E. Tame, S. R. Crane, and K. B. Higbie. Recovery and Production of Alumina From Waste Solutions by Solvent Extraction. J. Metals, September 1968, pp. 59-63.

17. Harrah, H. W. Cotter Corporation. Deco Trefoil, Spring 1969, pp. 11-22.

18. Harrighorst, C. R. AP & CC's (American Potash and Chemical Co.) New Process Separates Borates From Ore by Extraction. Chem. Eng., v. 70, No. 23, Nov. 11, 1963, pp. 228-232.

19. Ingham, J. Solvent Extraction in Israel. Chem. and Ind. (London), Nov. 4, 1967, pp. 1363-1367.

20. Kurtak, Charles R. Purification of Tungsten Solutions by Amine Extraction. U.S. Pat. 3,158,438, Nov. 24, 1964.

21. Maddox, Robert L., and Raymond A. Foos. Producing Basic Beryllium Material of High Purity. U.S. Pat. 3,259,456, July 5, 1966.

22. Manning, P. D. V., I. M. Baron, and F. Crampton. Recovery From Phosphate Rock. Ch. in Uranium Ore Processing, ed. by J. W. Clegg and D. D. Foley. Addison-Wesley Pub. Co., Inc., Reading, Mass., 1958, pp. 375-377.

23. May, S. L., J. L. Tews, and T. N. Goff. Separation of Tantalum From Columbium by the Hydrofluoric Acid-Sulfuric Acid-Methyl Isobutyl Ketone System. BuMines Rept. of Inv. 5862, 1961, 31 pp.

24. McGarr, H. J. Solvent Extraction Stars in Making Ultra Pure Copper. Chem. Eng., v. 77, No. 17, Aug. 10, 1970, pp. 82-84.

25. Nielsen, R. H. Separation of Hafnium and Zirconium. Ch. in The Metallurgy of Hafnium, ed. by D. E. Thomas and E. T. Hayes. U.S. Atomic Energy Commission, 1960, pp. 49-54.

26. Power, Kenneth L. Operation of the First Commercial Copper Liquid Ion Exchange and Electrowinning Plant. Proc. Extractive Metallurgy Division Symposium on Copper Metallurgy, AIME, Denver, Colo., February 1970, pp. 1-26.

27. Ritcey, G. M. Application of Solvent Extraction to Common Base Metals (A Review). Dept. of Energy, Mines, and Resources (Canada), Inf. Circ. 213, January 1969, 28 pp.

28. Rosenbaum, J. B., S. R. Borrowman, and J. B. Clemmer. Solvent Extraction for Recovering Uranium and Vanadium From Salt Roast Process Solutions. Proc. 2d UN Internat. Conf. on the Peaceful Uses of Atomic Energy, Geneva, v. 3, September 1958, pp. 505-509.

29. Seeton, F. A. Solvent Extraction Recovers Vanadium From Waste Stream. Chem. Eng., v. 71, No. 4, Feb. 17, 1964, pp. 112-115.

30. Taylor, I. R. Union Carbides Twin-Pit Vanadium Venture at Wilson Springs. Min. Eng., April 1969, pp. 82-85.

31. Thayer, Harold E. The Newest United States Uranium Processing Plant. Progress in Nuclear Energy, Series III, Process Chemistry, by F. R. Bruce, J. M. Fletcher, and H. H. Hyman. Pergamon Press, New York, 1961, pp. 86-97.

32. Vermeulen, L. W. Recovery of Thorium From Uranium Solutions. J. Metals, v. 18, January 1966, pp. 22-25.

33. World Mining, U.S. Edition, v. 2, March 1966, pp. 16-19.

34. Zakarias, J. J., and M. J. Cahalan. Solvent Extraction for Metal Recovery. Inst. of Min. and Met. Trans. (London), v. 75, secs. A-C, 1966, pp. C245-C259.