SOURCES AND RECOVERY METHODS FOR RHENIUM

By P. E. Churchward and J. B. Rosenbaum

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SOURCES AND RECOVERY METHODS FOR RHENIUM

by

P. E. Churchward[1] and J. B. Rosenbaum[2]

ABSTRACT

Rhenium sources and recovery methods were investigated by the Bureau of Mines to delineate potential resources of the metal. The only significant rhenium resource appears to be about 28,000 lb of rhenium contained in the domestic annual output of approximately 20,000 tons of byproduct molybdenite concentrates from porphyry copper operations. An estimated 70 to 80 pct of this rhenium is potentially recoverable by processing the rhenium-bearing fumes and dusts obtained during conventional roasting of molybdenite concentrate. At 70 pct recovery this would amount to 19,600 lb of rhenium. A more conservative estimate by the Committee on Refractory Metals of the National Research Council (15)[3] is that 12,000 lb of rhenium metal could be produced annually from current production of molybdenite from porphyry copper operations in the United States.

A procedure was developed in the laboratory for recovering rhenium in the form of electrolytic flake by electrowinning the metal from a solvent extraction strip solution. The procedure included (1) water leaching of molybdenite roaster flue dust, (2) selective extraction of rhenium from the leach liquor by contacting it with a kerosine solution of a quaternary amine, (3) stripping of rhenium from the loaded organic solution by a perchloric acid solution, and (4) electrodeposition of rhenium from the loaded strip liquor.

Raw material for the studies was flue dust containing 0.48 pct Re, 35 pct Mo, and 23 pct S in sulfide and sulfate form, and small amounts of numerous metallic impurities. Water leaching dissolved 85 pct of the Re and yielded a solution that was 1 N in sulfuric acid and contained, 1 g/l Re and 16 g/l Mo.

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

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The solvent extraction strip solution that was electrolyzed for rhenium deposition was 1 molar in perchloric acid and 1 molar in ammonium sulfate and contained 13 g/l Re and 0.01 g/l Mo.

INTRODUCTION

A reconnaissance for rhenium resources and research into recovery methods was initiated at the Salt Lake City Metallurgy Research Center to further the Bureau's program for conserving and utilizing mineral resources. Rhenium's principal known occurrence as a trace element in molybdenite from certain porphyry copper deposits and the lack of established uses for it has resulted in a permanent loss of most of the rhenium that has been mined. Rhenium is high-priced as a direct result of this continued wastage and of its scarcity and limited use.

Rhenium's occurrence in the earth's crust has been estimated to be 4 parts per billion--about as rare as iridium and 15,000 times more rare than molybdenum (13). Of the metals, only tungsten has a higher melting point than rhenium's 3,180° C. Rhenium's density of 21 g/cm^3 is exceeded only by iridium, osmium, and platinum. Its electrical resistivity is several times that of tungsten, permitting the use of larger diameter, and consequently stronger, filaments in lamps and tubes.

Mechanically, rhenium develops tensile strength of up to 300,000 lb/in^2 and has better ductility than either tungsten or molybdenum. The mechanical properties of tungsten-rhenium and molybdenum-rhenium alloys also are outstanding, especially at elevated temperatures.

Uses for rhenium are being developed in filaments for mass spectrographs and ion gages, in magnets under cryogenic conditions, in electrical contacts and resistance heaters, in thermocouples for temperatures of up to 2,750° C, in welding rods, and in catalysts (2, 4, 13, 15).

Molybdenite concentrate prepared from copper ores in the Western States contains 0.4 to 4 lb of rhenium per ton of molybdenite concentrate. Industrial practice is to roast the concentrate in air at about 650° C to convert molybdenum sulfide to the oxide. In doing so, rhenium is oxidized to the heptoxide, which is volatile at 350° C and consequently sublimes from the charge (10, 18). Part of the sublimed rhenium may be recovered from cool sections of the roaster flues in the form of dust containing up to 1 pct rhenium. Additional rhenium may be recovered by scrubbing the roaster flue gas with water. As the rhenium heptoxide is soluble in water, leaching of the roaster dust or water scrubbing of the flue gas yields solutions of perrhenic salts and acid. These are heavily contaminated with salts of molybdenum and other metals.

A review of rhenium extraction procedures is contained in "A Survey of the Literature on Rhenium" by Sims (19). Rhenium recovery from potash residues and copper smelter dusts in Germany is summarized therein.

In the United States, rhenium was prepared initially by Professors Melaven and Bacon, University of Tennessee, from molybdenite roaster-dust leach solution by repeated crystallizations of potassium perrhenate followed by hydrogen reduction of the salt to metal (13). However, rhenium powder prepared from the potassium salt always contains some potassium, which is a detrimental impurity (17). Later Kennecott Copper Corp. developed an ion-exchange procedure for processing the impure rhenium-bearing solutions (10, 22-26). In the Kennecott procedure, solutions are clarified, oxidized, and then passed through a column of a strong base anion-exchange resin. Impurities such as molybdenum and selenium that are coabsorbed with the rhenium are selectively eluted with sodium hydroxide solution. Rhenium then is eluted with perchloric acid solution, and hydrogen sulfide gas is passed through the eluate to precipitate rhenium sulfide. Next, the sulfide is dissolved in ammonium hydroxide solution containing an oxidizing agent. Subsequently, ammonium perrhenate is crystallized from the solution by cooling. Reaction of ammonium perrhenate with hydrogen at 700° to 800° C yields rhenium metal powder.

Ammonium perrhenate is sold for about $400 a pound. The metal powder, depending upon purity, is sold for $470 to $580 a pound. Metal fabricated into strip is priced at about $1,000 a pound (4).

Solvent extraction is another method that might be useful in the recovery of rhenium. A number of analytical methods employing solvent extraction appear in the literature (1, 11, 14, 20). A patent issued to Suzanne Tribalat and Marcel Bertolus (21) claims the use of compounds of the formula R_4M, in an organic solvent such as chloroform, to complex and extract rhenium from aqueous solutions. R is an alkyl group and M is arsenic, antimony, or nitrogen.

Research on rhenium recovery by the Bureau of Mines at Salt Lake City centered on solvent extraction because exploratory tests and subsequent development work showed it to be a technologically feasible alternative to the crystallization and ion-exchange procedures employed industrially. Further research developed a procedure for direct recovery of rhenium as metal by electrowinning in conjunction with solvent extraction.

To conduct a survey of rhenium sources, the Bureau needed an analytical procedure sensitive to about 1 ppm rhenium in rocks and metallurgical products. Fortunately, the early experiments in rhenium solvent extraction evolved a procedure that was adaptable to analytical routine. The analytical procedure that was developed is described in a Bureau publication (16). Results of the resources survey and the development of a solvent extraction-electrodeposition method for recovering rhenium as metal from impure solutions are described herein.

RECONNAISSANCE OF RHENIUM SOURCES

Selected samples of ores and mill products available at the Bureau's Salt Lake City Metallurgy Research Center or especially acquired for the survey were analyzed for rhenium. Although established analytical methods were satisfactory for determining rhenium in molybdenite concentrate, considerable

modifications in procedure were necessary for determining rhenium in the range of 1 to 10 ppm in other materials, especially in siliceous ores and ores containing uranium. Development of an analytical procedure for rhenium accurate to less than 1 ppm (0.0001 pct) is described in a separate report (16).

Analysis of an array of mineral types revealed positive findings of rhenium only in those materials that contained molybdenum. Therefore, particular attention was given to materials containing molybdenum either as a major constituent or as an impurity. Rhenium occurred randomly in all molybdenite concentrates and in most molybdenum-bearing ores. Molybdenite concentrates from porphyry copper operations contained as much as 1,700 ppm of rhenium. These concentrates appear to be the only significant source of readily available rhenium.

Rhenium in Manganese Ores

Search for rhenium in manganese ores was logical because rhenium and manganese are in the same group of the periodic table, and such neighboring elements are often associated with each other in nature. No rhenium was found in manganese oxide ore from the Artillery Mountains, Ariz., or in rhodonite ores from San Juan County, Colo. However, composites from the GSA stockpiles at Wenden, Ariz., and Deming, N. Mex., and ore from Manganese, Inc., Henderson, Nev., contained 0.5 to 1 ppm rhenium. In common with all other rheniferous materials, the rhenium-bearing manganese ores contained 400 to 1,000 times as much molybdenum as rhenium.

Samples of various products from the Manganese, Inc., mill were assayed to determine if the rhenium concentrated at some point in the flowsheet, particularly in the fumes from the nodulizing kiln. Less than 1 ppm rhenium, however, was found in any of the samples. Only 1 lb of rhenium is contained in 1,000 tons of manganese ore that assays 0.5 ppm rhenium. Owing to the low tenor of the rhenium in the manganese ores and the absence of enrichment in any product in the processing circuit, the possibility of its economic recovery appears remote.

Rhenium in Uranium Ores

As molybdenum is a common impurity in Colorado Plateau uranium ores, the presence of rhenium in these ores appeared probable. Ores from the Front Range district of Colorado that assayed as much as 0.6 pct molybdenum (6,000 ppm) contained up to 3 ppm rhenium. A sample from Lakeview, Oreg., that assayed 0.04 pct molybdenum contained only 0.3 ppm rhenium. The highest concentration of rhenium found in naturally occurring material was 20 ppm in a sample of subgrade uranium ore from the Sun Valley mine, Coconino County, Ariz., that contained 0.34 pct molybdenum, partly in the form of ilsemannite, a hydrated oxide. This was a handpicked sample and is not believed to represent a significant tonnage.

Rhenium in Alkaline Leach Process Mills

The uranium ores from the Front Range district, Colorado, that contain up to 3 ppm rhenium, are routinely processed by alkaline leaching in a 200-ton-a-day plant at Canon City, Colo. Most of the molybdenum and rhenium in the ore are dissolved along with the uranium. If it were economically attractive, molybdenum could be recovered as a byproduct (9), and rhenium probably could be recovered as well. With an average rhenium content of 1 ppm, the 200 tons of ore treated per day contains a total of only 0.4 lb of rhenium. About 3,000 tons of ore are treated daily by alkaline leaching at two mills in the Ambrosia Lake area, New Mexico. The molybdenum content of Ambrosia Lake ores averages about 0.02 pct, and the rhenium content probably is less than 0.5 ppm (equivalent to 3 lb/day). Slurry feed to an alkaline leach resin-in-pulp plant at Moab, Utah, contained 0.5 ppm rhenium. The uranium-barren slurry from anion exchange contained 0.25 ppm rhenium, indicating that half of the rhenium was coabsorbed with the uranium.

Rhenium in Acid Leach Process Mills

The rhenium content of acid leach liquors ranged from 0.03 ppm in an Ambrosia Lake mill to 1 ppm in a Gas Hills, Wyo., mill. About half of the rhenium was removed from the leach liquor by passing it through a bed of activated carbon, by treating it with anion-exchange resins, or by treating it with secondary or tertiary amines. Alkaline scrub liquors used for removing molybdenum from activated carbon, resins, and amine extractants contained 2 to 4 ppm rhenium along with 2 to 5 g/l molybdenum. If an aggregate of 1,000 tons of alkaline scrub liquor assaying 3 ppm rhenium were produced daily in uranium acid leach mills, the rhenium potential of these solutions would be about 6 lb/day. A maximum rhenium accumulation of 400 ppm in dried resin was found by spot checking resins in prolonged use in different uranium mills. Using the maximum figure, a resin inventory of 1,000 cu ft of wet settled resin, equivalent to about 10 tons of dry resin, would contain 8 lb of rhenium. The resin containing 400 ppm rhenium also analyzed 5 pct molybdenum.

Rhenium Potential of Domestic Uranium Ores

Domestic uranium mills currently process a total of about 20,000 tons of ore daily. At an assumed average rhenium tenor of 0.5 ppm, the daily feed to the mills contains 20 lb of rhenium. The technical and economic aspects of recovering rhenium would depend upon the flowsheets of the individual mills and on other factors. Except for those uranium mills that may recover byproduct molybdenum, the prospects for recovering rhenium from uranium ores appear remote.

Rhenium in Carbonaceous Shales

Samples of uraniferous Chattanooga shale from Tennessee contained 0.05 pct molybdenum and about 1 ppm rhenium. Vanadiferous shale from Dry Creek, Wyo., that assayed 0.06 pct molybdenum similarly contained 1 ppm rhenium. Because of the complex mineral assemblage in the shales and the large amount or organic material present, efforts in the laboratory to collect an enriched product by roasting the shales and collecting the fume were unsuccessful.

Rhenium in Miscellaneous Concentrates and Ores

Selected samples of copper, lead, zinc, and iron sulfide concentrates were essentially devoid of rhenium, as were a variety of vanadium, tungsten, and nickel ores.

Rhenium in Molybdenite Ore and Concentrate

The only materials in which rhenium was present in appreciable amounts were molybdenite ores and concentrates. It is perhaps significant that in this reconnaissance no rhenium was found except in materials containing molybdenum. No definite relationship was apparent between the molybdenum and rhenium content. The molybdenum-to-rhenium ratio ranged from about 50,000 to 1 in Climax concentrate to 400 to 1 in San Manuel molybdenite concentrate. Rhenium analysis of Arizona and Nevada molybdenite concentrate ranged from 340 to 1,700 ppm. South America and Utah concentrate ranged from 200 to 600 ppm rhenium. Climax concentrate contained only 10 ppm rhenium, and California concentrate, only 5 ppm rhenium.

Rhenium Potential of Molybdenite Concentrate

The rhenium of commerce is recovered from molybdenite roaster fume and roaster gases. Rhenium volatilization and recovery in fume and scrub solutions is related to the rhenium grade of the roaster feed and the degree of sulfur removal in roasting (15). About 55 pct of the rhenium was volatilized in commercial roasting of molybdenite to a residual sulfur content of 0.2 to 0.4 pct, whereas 90 to 95 pct of the rhenium was volatilized when molybdenite concentrate was roasted to a lower residual sulfur content in the laboratory (10, 18, 26).

The same bench-scale studies showed that 95 pct of the volatilized rhenium can be recovered as fume or in scrubber solutions. Ion-exchange treatment extracted 90 pct of the rhenium from solution (10). In summary, rhenium recovery, in a plant designed and operated for byproduct recovery of rhenium in conjunction with molybdenite roasting, is estimated as (1) 90 pct volatilized in roasting, (2) 95 pct scrubbed from roaster gas and fume, and (3) 90 pct adsorbed from the scrub liquor. This is equivalent to a net recovery of 77 pct.

Approximately 20,000 tons of molybdenite concentrate was derived from porphyry copper-type operations in 1960 (12). Assuming that the average rhenium grade was 700 ppm, these concentrates contained a total of 28,000 lb of rhenium.

Recapitulation of Rhenium Resources

The principal rhenium-bearing materials delineated by this survey are listed in table 1. Only the rhenium present in molybdenite from porphyry copper operations is considered as a promptly available resource. A long-range possibility exists of recovering rhenium from other molybdenum concentrates and from uranium leach solutions. Recovery of molybdenum from

Chattanooga shales and from the carbonaceous shales of the Phosphoria formation is highly speculative.

TABLE 1. - Rhenium content of domestic potential sources (annual basis)

Resource	Rhenium, ppm	Rhenium content, lb
Molybdenite concentrates from porphyry copper operations, 20,000 tons.....	700	28,000
Molybdenite concentrate, Colorado, 40,000 tons.....	10	800
Uranium ores, milling rate, 6 million tons.....	.5	6,000
Chattanooga and vanadiferous shales...	.5	([1])

[1] No ore production. If these materials were processed for uranium or vanadium, some byproduct rhenium might be produced.

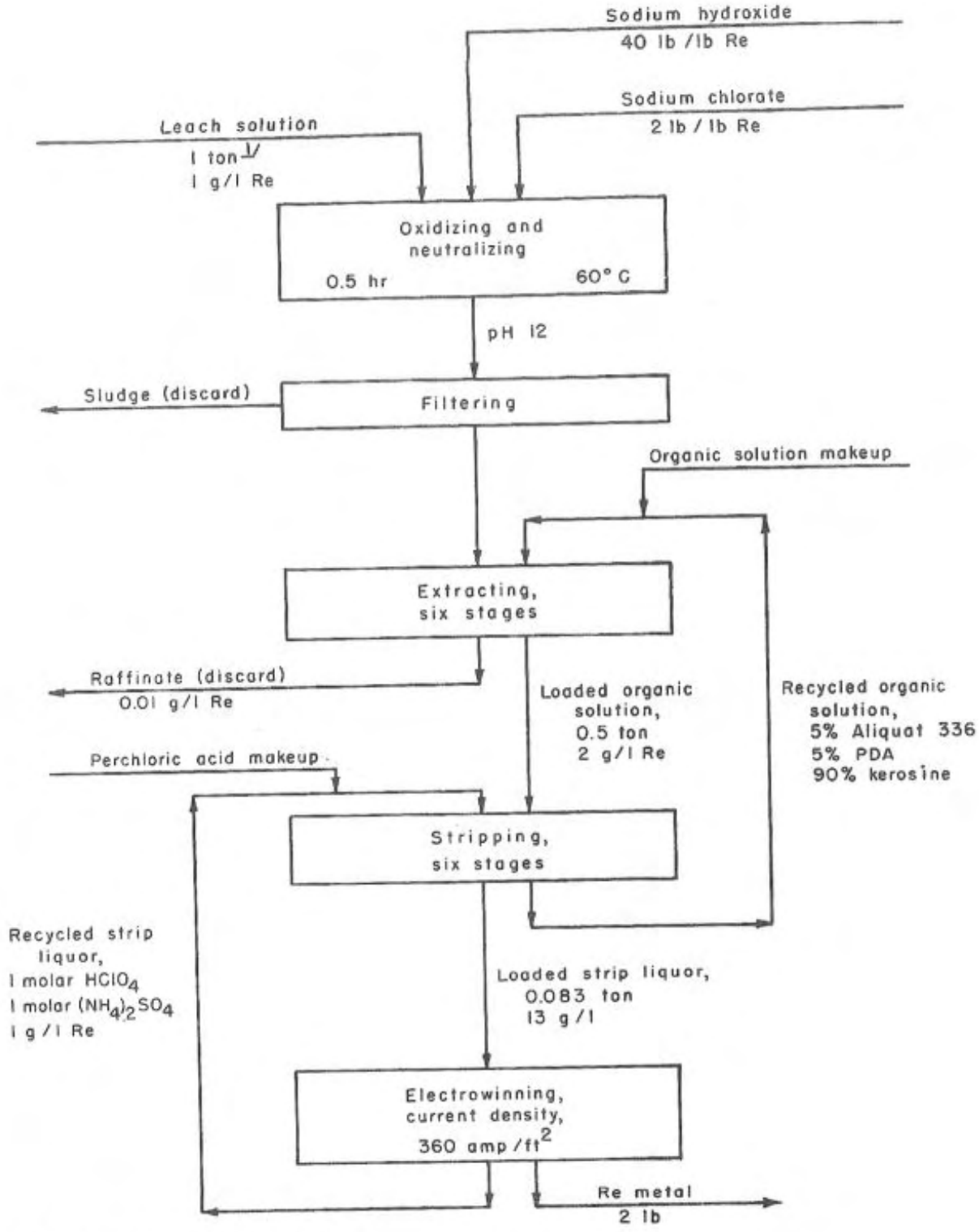
DEVELOPMENT OF A SOLVENT EXTRACTION-ELECTROLYTIC PROCEDURE FOR RHENIUM RECOVERY

The process developed by the Bureau of Mines for recovering rhenium from impure solutions is portrayed in block diagram form in figure 1. Attractive features are the small number of unit operations and their relative simplicity. The metal prepared in the laboratory contained about 0.1 pct total impurities, most of which was molybdenum. As such, it was intermediate between two commercial grades of metal powder that contain less than 0.01 and less than 1.0 pct metallic impurities, respectively (4).

Preparation of Solvent Extraction Feed Solution

Feed solution for the process development studies was prepared by batchwise leaching of Miami Copper Co. molybdenite roaster dust containing 0.48 pct rhenium.

Chemical analysis of the dust is shown in table 2. Spectrographic analysis revealed traces of arsenic, barium, chromium, lead, magnesium, manganese, potassium, silver, sodium, strontium, and thallium.



1/ Solution quantities in volume-tons of 240 gallons.

FIGURE 1. - Flowsheet of Combined Rhenium Solvent Extraction and Electrolysis Treatment.

TABLE 2. - Chemical analysis of flue dust

Components:	Analysis, pct
Molybdenum	35.0
Rhenium	.48
Sulfide sulfur as sulfur	16.6
Sulfate sulfur as sulfur	7.0
Silica (SiO_2)	3.7
Iron	3.6
Selenium	1.0
Copper	.45
Aluminum	.26
Calcium	.10

The dust was leached by agitating it in water in the proportion of 4 parts liquid to 1 part solid by weight for 1 hour at 65° C. Undissolved solids, composed principally of molybdenum oxides and sulfides, were filtered from the leach slurry, washed with about 0.5 ton of water per ton of dust, and discarded. The filtrate, which was about 1 N in sulfuric acid, was reheated to 60° C, and sodium chlorate was added to oxidize the rhenium and molybdenum. Sodium hydroxide then was added to adjust the pH to 12, and the small amount of precipitate formed was filtered out. The clarified leach liquor analyzed as follows:

Components:	Grams per liter
Rhenium	1
Molybdenum	16
Copper	.03
Selenium	.03
Sulfate	50
Manganese[1]	1 - .1
Sodium[1]	1 - .1
Calcium[1]	.1 - .01
Magnesium[1]	.1 - .01
Potassium[1]	.1 - .01
Silicon[1]	.1 - .01
Strontium[1]	.1 - .01
Chromium[1]	.01
Gallium[1]	.01
Lithium[1]	.01
Titanium[1]	.01

[1] Impurities revealed by spectrographic analysis.

The liquor contained 85 pct of the rhenium in the flue dust. Because the Miami roasters were no longer operating, the dust was only a temporary and convenient feed material. Detailed leaching studies were not warranted.

Rhenium Solvent Extraction

Pyridine, alkyl phosphoric acids, and aliphatic amines were used in probing experiments to find an extractant suitable for recovering rhenium from sulfate leach solution containing molybdenum, copper, and selenium as principal impurities. Batch shaker tests were made at room temperature, employing feed solution over a range of pH from acidic to basic, and organic solutions over a range of concentrations in kerosine. Pyridine was used in undiluted form. Similarly, the loaded organic solution was stripped batchwise with appropriate aqueous solutions, employing a range of conditions.

Pyridine (C_5H_5N) has been reported to be an effective extractant for heptavalent rhenium (8). In tests using a 2-to-1 ratio of feed liquor (3 N in NaOH) to pyridine, 99 pct of the rhenium and only 0.3 pct of the molybdenum were extracted. The pyridine, however, was too miscible in the aqueous solution to warrant its use as a rhenium extractant because organic solution losses would be excessive.

A number of monoalkyl and dialkyl phosphoric acids react with cationic species of uranium, vanadium, molybdenum, beryllium, and other metals to form organic-soluble species (3). None of the alkylphosphates tested extracted rhenium from the perrhenate leach solution. Extraction of molybdenum from the rhenium-bearing solution, however, was worthy of investigation. Extraction coefficients, E_a^o, of 40 to 50 for molybdenum were obtained when contacting equal volumes of feed liquor at pH 1 to 2 with 0.1 molar solutions of dodecyl or heptadecyl phosphoric acid. Unfortunately, a residual molybdenum content of 0.03 g/l remained in the raffinate despite repeated contacts with fresh organic solution. The presence of part of the molybdenum in the form of a stable unextractable polymer was postulated. The use of alkylphosphates for rhenium recovery did not appear promising because of the persistent retention of part of the molybdenum in the aqueous phase.

The long-chain aliphatic amines extract metal species by an anion-exchange mechanism. Primary amines extract ferric iron, molybdenum, scandium, thorium, zirconium, and other metals from acidic sulfate solutions (5, 6). Secondary and tertiary amines are used commercially in uranium extraction from sulfuric acid solutions (5, 6). Secondary and tertiary amines are used commercially in uranium extraction from sulfuric acid solutions (5, 6). Quaternary amines are powerful extractants for numerous metallic anionic species (9). Unlike the other amine types, quaternary amines may be used in alkaline as well as acid solutions. All the amines strongly extracted both rhenium and molybdenum from acidic liquors. Extraction of rhenium and molybdenum by the primary, secondary, and tertiary amine types was maximum at a pH of 1 or 2, but decreased to very low values in neutral or alkaline solutions. The molybdenum extraction coefficient when using a 5-pct solution of the chloride salt of quaternary tricaprylyl amine (R_3CH_3NCl, Aliquat 336)[4] at equal volumes of aqueous and organic phases, decreased from 160 at pH 1 to 0.03 at pH 12. On the other hand, the rhenium extraction coefficient decreased only from 480 to 140 when the quaternary amine was used. The quaternary amine, therefore, appeared to have promise for the recovery of rhenium. Addition of 5 pct primary decyl alcohol (PDA) to the quaternary amine solution proved necessary to avoid the

[4]Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

precipitation of an insoluble salt, probably amine perrhenate, in the organic solution.

Stripping tests employing a variety of acid and salt solutions showed that only perchloric acid and perchlorate salt solutions effectively removed rhenium from the loaded organic solution. A minimum perchlorate ion concentration of about 1 molar was necessary for stripping the rhenium at a practical rate while simultaneously yielding an enriched rhenium solution.

Reuse of the organic solution in the perchlorate form for extracting rhenium from leach solution resulted in sharply lowered extraction coefficients of 6 for rhenium and 0.001 for molybdenum. The coefficient for rhenium was still high enough to assure substantially complete rhenium recovery by employing several countercurrent stages. The separation of rhenium from molybdenum was improved by using the amine in the perchlorate form.

Preparation of Ammonium Perrhenate

An exploratory test was made to prepare ammonium perrhenate from perchloric acid strip solution containing 13 g/l rhenium and 0.01 g/l molybdenum.

Treatment corresponding to that employed in processing rhenium-loaded ion-exchange eluate was used as follows (10):

1. Forty milliliters of 12 N HCl was added to the 400-ml batch of solvent extraction strip liquor.

2. The solution was heated to 70° C and gassed with H_2S for 10 min to precipitate rhenium sulfide.

3. The rhenium sulfide was removed by filtration, washed on the filter with water containing H_2S, and then redissolved in 80 ml of 30 pct H_2O_2 by heating at 80° C for 1 hour.

4. Twenty milliliters of 15 N NH_4OH was added.

5. Sulfur that formed during oxidation of the sulfide was removed by filtration.

6. The filtrate was concentrated to a volume of about 20 ml by evaporation and cooled overnight at 5° C. Twelve grams of mixed ammonium perrhenate and ammonium sulfate crystals were obtained that represented 98 pct of the rhenium.

7. The crystals were redissolved in 80 ml of water, and ammonium perrhenate was recrystallized by evaporation and cooling. This yielded 7 grams of ammonium perrhenate representing 90 pct of the rhenium in the solvent extraction strip liquor.

Analysis of the ammonium perrhenate showed that 3.2 pct sulfate was the major impurity. The only metallic impurities were 0.01 pct molybdenum and 0.001 to 0.0001 pct each of silicon, calcium, and magnesium.

Electrodeposition of Rhenium From Perchlorate Solution

Electrowinning of rhenium from perchloric acid strip solution was investigated as an alternative to the conventional practice of precipitating rhenium as the sulfide, redissolving the sulfide in ammonium hydroxide-hydrogen peroxide solution, crystallizing ammonium perrhenate, and reacting the salt with hydrogen to prepare rhenium metal powder. Electroplating of rhenium from aqueous solutions of the sulfate, citrate, and perchlorate and from other baths has been reported (7). Electrowinning, however, involved different and more restrictive parameters than plating because (1) deposits of strippable metal had to be obtained, (2) the electrolyte had to be of a composition suitable for stripping the loaded organic solution, and (3) electrodeposition had to be feasible over the range of rhenium concentration from about 15 to 1 g/l, corresponding to depletion of the loaded strip liquor for reuse in stripping.

The cell used for the initial tests was a 250-ml beaker fitted with a 0.125-inch-diameter copper wire cathode and a concentric platinum anode spaced 0.5 inch from the cathode. Only thin deposits, nonmetallic in appearance, were obtained over a wide range of current density, electrolyte pH, and temperature, when electrolyzing unmodified 1 molar perchloric acid strip liquor containing 13 g/l rhenium.

The key to deposition of adherent, bright metallic deposits from the perchlorate strip liquor was found to be in the addition of sodium or ammonium sulfate to yield an electrolyte 1 molar in sulfate. A current density of about 180 to 360 amp/ft^2 also was necessary. Gray-appearing deposits occurred at a lower current density, and dark, rough deposits at a higher current density. Results were about the same at the ambient temperature of 45° C (the electrolyte was heated by the passage of current) as when the cell was cooled to 35° C or heated to 60° C. Similarly, electrodeposition was as good at the natural pH of the strip liquor, 0.25, as at lower or higher pH.

The current efficiency was 17 pct initially, dropping off to 1 pct upon depletion of the rhenium from 13 to 0.5 g/l. Cell voltage at 360 amp/ft^2 was 3 volts. Blistering occurred in deposits thicker than 0.1 mm. The rhenium metal was readily removed in the form of flakes by flexing the cathode.

Integrated Solvent Extraction-Electrodeposition Tests

The combined solvent extraction and electrodeposition operations were tested on a semicontinuous basis, involving continuous countercurrent solvent extraction and batchwise electrolysis. A compartment-type mixer-settler provided six stages of extraction and six stages of stripping (3). Electrolysis was performed batchwise in a 250-ml beaker containing a type 316 stainless steel cathode with 2 sq in of submerged area per side and platinum anodes.

In processing 36 liters of leach liquor containing 1 g/l rhenium, 6 liters of the organic extractant and 1 liter of strip solution were recycled three times. The extractant was composed of 5 pct Aliquat 336, 5 pct PDA, and 90 pct kerosine. Strip liquor was 1 molar each in perchloric acid as well

as in ammonium sulfate. With prolonged reuse of the strip liquor it would be necessary to make up perchlorate ion losses in the raffinate, but supplemental additions were not required in these tests.

Individual mixers and settlers had volumes of 60 and 120 ml, respectively. Flow rates of the aqueous feed, organic solution, and strip liquor were 24, 12, and 2 ml/min, respectively. A scrub stage employing 1 pct NaOH solution was tried for a short time on the loaded organic solution but was discontinued because it did not remove the contaminating molybdenum. Recent experiments show that alkaline NaCl solution is an effective scrubbing agent. Neither copper nor selenium was extracted. The rhenium and molybdenum content of the solvent extraction streams are shown in table 3.

TABLE 3. - Composition of solvent extraction streams

Solvent extraction streams	Analysis, g/l	
	Re	Mo
Feed liquor	1.0	16.0
Raffinate	.012	16.0
Stripped organic solution	.014	.009
Loaded organic solution	2.0	.011
Loaded strip liquor	13.0	.01
Depleted strip liquor	1.0	.001

Loaded strip liquor was electrolyzed in 200-ml batches, and the depleted electrolyte was reused for stripping the loaded organic solution. When operating at 360 amp/ft^2, the ambient temperature of the electrolyte was 45° C and the voltage 3.0 volts. Electrolysis for 2.5 hours depleted the rhenium content from 13 to 1 g/l with simultaneous deposition of 2.2 grams of rhenium. Metal from three successive batches were deposited on the same cathode to build up a thickness of about 0.12 mm before the metal was removed by flexing the cathode. Energy requirements were 13.6 kwhr/lb of rhenium. The deposited metal contained 0.1 pct molybdenum, 30 ppm copper, and spectrographically determined traces of aluminum, calcium, chromium, iron, platinum, and silicon.

CONCLUSIONS

Molybdenite concentrate from porphyry copper operations seems to be the only significant source of rhenium. Domestic production of about 20,000 tons of byproduct molybdenite concentrate contains an estimated 28,000 pounds of rhenium.

Rhenium metal can be prepared from impure solutions grossly contaminated with molybdenum by a novel solvent extraction-electrodeposition procedure. The metal is recovered in the form of electrolytic flake containing only 0.1 pct molybdenum and spectrographic traces of other impurities. Further improvement in purity may be possible by refinements in the procedure; for example, employing a higher rhenium loading in the organic extractant to more completely displace molybdenum.

Reagent, energy, and equipment requirements are modest. A comparison of this procedure with the conventional ion exchange-hydrogen reduction process would first require information on the nature of the solutions to be treated and on the scale of the proposed operation.

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