

Rhenium

By Larry J. Alverson ¹

Domestic rhenium production decreased but was adequate to meet the more greatly reduced demand for bimetallic platinum-rhenium catalysts, rhenium's major end use. As a result of decreased demand, there was a decline in the price of both metal powder and compounds, and an increase in stocks. Substitution of other metals for

rhenium in bimetallic catalysts was primarily responsible for the decreased demand. The rhenium supply was augmented during the year by the importation of a significant amount of ammonium perrhenate (NH_4ReO_4), primarily from Sweden, the United Kingdom, and West Germany.

DOMESTIC PRODUCTION

Production of rhenium, a secondary by-product material recovered primarily from molybdenite (MoS_2) associated with southwestern U.S. and Chilean porphyry copper ores, decreased in 1972 to an estimated 6,100 pounds of rhenium contained in rhenium salts. Cleveland Refractory Metals (CRM), a subsidiary of Kennecott Copper Corp., remained the leading rhenium producer in the United States. The company processed domestic molybdenite concentrates from operations of Kennecott and Magma Copper Co., a subsidiary of Newmont Mining Corp., as well as concentrates from Chilean sources, at its Garfield, Utah, roasting facility.

During 1972, Continental Rhenium Corp., a wholly owned subsidiary of Continental Ore Corp., became the nation's fifth rhenium producer, processing MoS_2 concentrate from Arizona, Canada (British Columbia), Chile, and Peru, at the corporation's Golden, Colo., plant. Preliminary information indicates recoveries in excess

of 95% have been achieved due to the application of a new patented process (see technology section) for recovering rhenium.

Production of rhenium bearing molybdenite from porphyry copper ore continued at Magma's San Manuel mine in Pinal County, Ariz. M&R Refractory Metals, Inc., at its Winslow, N.J., plant, produced rhenium salts from the MoS_2 of Magma's San Manuel copper operations for Engelhard Minerals & Chemicals Corp. on a contract-conversion basis. Shattuck Chemical Co., Denver, Colo., a division of Engelhard Minerals & Chemicals Corp., recovered rhenium salts from Arizona molybdenite concentrates. Molybdenum Corp. of America (Molycorp) recovered rhenium salts from MoS_2 concentrate associated with porphyry copper ores in Arizona and primary molybdenite from the Questa molybdenum mine in New Mexico. Molycorp de-

¹ Industry economist, Division of Ferrous Metals.

Table I.—Salient rhenium statistics
(Pounds of contained rhenium)

	1970	1971	1972
Mine production °	5,900	7,250	6,100
Consumption °	5,100	7,600	4,300
Imports (metal and scrap)	210	377	168
Imports (ammonium perrhenate) °	857	8,547	1,183
Stocks, Dec. 31 °	6,400	9,900	13,000

° Estimate. † Revised.

veloped a new hydrometallurgical process to produce molybdenum and rhenium compounds. This process, developed in cooperation with the Colorado School of Mines Research Institute, prevents sulfur dioxide (SO₂) pollution of the atmosphere, which occurs in conventional roasting of molybdenite. The new process is reportedly unique in its ability to produce high purity products at high yield from standard MoS₂ source material and has been successfully tested in a small production unit for several months. Molycorp applied for patents throughout the world and was holding licensing discussions with interested companies in the United States and Europe at yearend. The rhenium facilities at Washington, Pa., operating at minimal rates during the first half of 1972, were put on standby and remained that way for the remainder of the year owing to prevailing market conditions.

Newmont Exploration Ltd., a subsidiary of Newmont Mining Corp., installed a multihearth furnace for controlled atmosphere roasting tests at its Danbury, Conn., metallurgy research center as part of its research into a new method of molybdenum-rhenium separation. Much of the work will involve studies of molybdenite concentrate roasting. The molybdenite from the San Manuel mine of Newmont's wholly owned Magma Copper Co. has a high rhenium content, and a new roasting process could yield greater returns than currently obtained by selling concentrate to others for treatment.²

Other domestic molybdenite roasting facilities that might be adapted for rhenium recovery include those of Climax Molybdenum Co. at Langeloth, Pa., Duval Corp. at Mineral Park, Ariz., Duval-Sierra Corp. at Esperanza, Ariz., and Republic Steel Corp. at Canton, Ohio.

CONSUMPTION AND USES

Approximately 85% of estimated 1972 rhenium metal consumption of 4,300 pounds was used in alumina-based bimetallic platinum-rhenium catalysts for refining unleaded, high-octane gasoline. Atmospheric pollution considerations during the last few years have given this application added impetus; however, in 1972, consumption decreased considerably, owing primarily to the substitution of other metals (probably mostly iridium) for rhenium in bimetallic catalysts.

Engelhard Minerals & Chemicals Corp. developed a new series (E-600) of platinum-rhenium catalysts that initially prove to have better stability, better yield as activity declines, and an unlimited number of regenerations and reactivations without significantly impairing catalyst performance. Algeria and the Soviet Union contracted to use the new catalyst in major new complexes in their respective countries.³ The E-600 series catalysts supplement the older E-500 series catalysts, which are extensively used in the free world's reformers.

Mowhawk Petroleum Corp. completed 3 years of operation using Universal Oil Product's (UOP) bimetallic platinum-rhenium catalyst, type R-16, without a single regeneration or shutdown for catalyst screening. The catalyst service at the

end of this first cycle was equivalent to 300 barrels of naphtha per pound of catalyst. The charge rate during the 3 years of operation was essentially constant at 2,600 barrels of naphtha per stream-day.⁴

Two refiners, one Japanese and one domestic, have agreed to use Chevron's new type "D" catalyst for the manufacture of high-octane gasoline-blend stocks in new Rheniforming installations. Presently 29 refineries in the United States, Canada, Europe, and Japan are using type "A" and "B" Rheniforming catalysts.⁵

There are seven low-pressure (200 pound per square inch gauge) Rheniformers currently in service with a total capacity of 120,000 barrels per day.⁶ Presently, approximately one quarter of all petroleum reforming catalysts are of the bimetallic platinum-rhenium variety.

The straight platinum (monometallic) catalysts are rapidly being replaced by bi-

² Newmont Mining Corp. Annual Report 1972, 32 pp.

³ Engelhard Minerals & Chemicals Corp. Annual Report 1972, 28 pp.

⁴ The Oil and Gas Journal. Bimetallic Pays Off in 3-Year Run. V. 70, No. 36, Sept. 4, 1972, pp. 80-81.

⁵ The Oil and Gas Journal. Chevron Develops New Catalyst. V. 70, No. 47, Nov. 20, 1972, p. 48.

⁶ The Oil and Gas Journal. Cat-Reforming Pressure Drops Again. V. 70, No. 20, May 15, 1972, pp. 124-136.

metallic catalysts such as platinum-rhenium. However, research is continuing to find substitutes for the rhenium part of the catalyst. Gold, gallium, germanium, indium, and iridium are being tested and evaluated as replacements for rhenium. Iridium seems to have gained a foothold in the market, notably with the introduction by Exxon Research of its new KX-130 "multimetallic" reforming catalyst containing platinum, iridium, and possibly a third element.⁷

The remaining 15% of estimated domestic rhenium consumption was in X-ray tubes, refractory-metal alloys, high-temperature thermocouples, temperature controls, electronic devices, vacuum tube and flash-bulb filaments, coatings, electrical contacts, and research and development.

Tungsten-rhenium thermocouples are ex-

periencing increased usage for high temperature measurement, other than that in a nuclear environment, which use has been recently found to be better served by tungsten-molybdenum thermocouples, which exhibit less deterioration. It appears that tungsten-rhenium thermocouples may find additional application in measuring and controlling combustion chamber exhaust temperatures of turbine engines.

During the 1969-71 period, there was a decline in the use of fabricated devices of rhenium owing to curtailment of aerospace programs; however, rhenium is currently finding increased usage in the fabrication of devices for use in X-ray tubes.

A Bureau of Mines Information Circular was published in early 1973 that contains information on rhenium from geologic background and analysis to supply-demand patterns and trends.⁸

PRICES

Prices paid for rhenium metal powder used in rhenium metal wire and mill products during the year ranged from about \$975 to \$1,400 per pound, depending on quantity, decreasing toward the former by yearend. Prices paid for perrhenic acid used in catalytic applications ranged from about \$875 to \$1,350 per pound, trending toward the former in the second half of the year.

During the year, the country's leading rhenium producer, quoted rhenium metal powder and perrhenic acid prices closely within these ranges. In August, Shattuck Chemical Co. cut its price on rhenium metal powder to \$975 per pound, and that on perrhenic acid to \$875 per pound. The company claimed that its price reductions were made possible by its recent plant expansion.

FOREIGN TRADE

Imports of unwrought rhenium metal during 1972 decreased 55% from that of 1971, and totaled 168 pounds valued at \$125,751. These imports, all of which represented rhenium metal powder, came from West Germany (85%), and France (15%). There were no imports of scrap or wrought rhenium metal during the year. Unwrought rhenium imports are believed to have been recovered from byproduct molybdenite obtained from porphyry copper ore mined in Chile. The average price of unwrought rhenium metal imports, excluding U.S. duty, was \$749 per pound, and ranged from \$713 per pound (West Germany), to \$952 per pound (France).

A significant amount of rhenium in the form of ammonium perrhenate (NH_4ReO_4) salts was imported primarily from Sweden, the United Kingdom, and West Germany.

This material imported under the basket classification "Ammonium Compounds, not specifically provided for" (TSUS 417.44), totaled approximately 1,183 pounds of contained rhenium, valued at \$1,357,078.

The import duty on rhenium metal from non-Communist countries remained at the January 1, 1972, rate of 5% ad valorem for unwrought rhenium metal and scrap, and 9% ad valorem for wrought rhenium metal. The import duty on wrought and unwrought rhenium metal from Communist Bloc countries also remained unchanged at 45% ad valorem and 25% ad valorem, respectively. The duty on

⁷ Chemical Week. Catalysts. V. 111, No. 18, Nov. 1, 1972, pp. 23-33.

⁸ Shimamoto, K. Availability of Rhenium in the United States. BuMines IC 8573, 1973, 30 pp.

imports of ammonium perrhenate from Communist and non-Communist countries was 25% ad valorem and 4% ad valorem, respectively.

The import duty on waste and scrap remained temporarily suspended until June 30, 1973.

Table 2.—U.S. imports for consumption of rhenium (including scrap), by country
(Gross weight)

Country	1970		1971		1972	
	Pounds	Value	Pounds	Value	Pounds	Value
Belgium-Luxembourg	--	--	220	\$262,278	--	--
France	58	\$58,789	45	49,770	25	\$23,796
Germany, West	79	84,973	110	140,000	143	101,955
U.S.S.R.	73	23,467	--	--	--	--
United Kingdom	--	--	2	794	--	--
Total	210	111,629	377	452,842	168	125,751

Table 3.—Estimated imports for consumption of rhenium salts, by country¹
(Gross weight)

Country	1970		1971		1972	
	Pounds	Value	Pounds	Value	Pounds	Value
Germany, West	171	\$114,909	2,016	\$1,545,347	568	\$488,519
Japan	44	25,439	20	15,103	223	108,291
Sweden	1,027	658,933	2,965	2,201,568	687	563,506
United Kingdom	--	--	140	113,431	236	196,762
Total	1,242	799,281	5,141	3,875,449	1,714	1,357,078
Total (rhenium content)	857	799,281	3,547	3,875,449	1,183	1,357,078

¹ Figures are derived from the basket category "Ammonium compounds not specifically provided for" (TSUS 417.44).

WORLD REVIEW

Canada.—The Island Copper mine of Utah International Inc. (UI) on Rupert Inlet near Port Hardy, British Columbia, which contains some of the richest known rhenium concentrations in the world, continued to market rhenium and molybdenum concentrates. Two hundred and fifty tons of molybdenum concentrate was sold in 1972, about 14% of designed capacity. In some cases the molybdenum buyer purchased the contained rhenium, while in others, the rhenium was returned on a "toll" basis in order for UI to seek prospective buyers.⁹ The estimated rhenium content of the ore body based on copper ore reserves of 280 million tons with 0.53% copper and about 0.027% MoS₂, is over 270,000 pounds, assuming 90% recovery of rhenium from molybdenite.

The Lornex mine of Rio Algom Mines, Ltd., a subsidiary of the Rio Tinto-Zinc Corp., situated in the Highland Valley area of British Columbia, is Canada's newest and largest open pit copper-molybdenum producer. Estimates of the ore body

indicate reserves of 293 million tons of ore averaging 0.43% copper and 0.014% MoS₂.¹⁰ Rhenium is present in the ore body but its content has not been established. However, using the rhenium content of nearby operations as a rough base, an estimated rhenium content of about 75,000 pounds can be inferred.

Chile.—A new rhenium plant at Concepción was scheduled to come onstream in 1974-75. A Western European firm together with Cia. de Acero del Pacífico S.A., (CAP) financed a successful pilot plant at the Hazen Research Center in the United States. The industrial plant will be designed to deliver high-grade molybdenum chemicals with the byproduct rhenium as either a chemical-grade rhenium salt or perrhenic acid (HReO₄). The pro-

⁹ Utah International Inc. Annual Report 1972, 32 pp.

¹⁰ Mining Engineering. Island Copper Starts Up. V. 24, No. 7, July 1972, p. 8.

¹¹ Mining Magazine. Lornex. V. 128, No. 3, March 1973, pp. 154-163.

duction target calls for a yearly rhenium output of 3,300 pounds.¹¹

The privately owned Chilean firm Carbuero y Metalurgia S.A. (Carbomet) has been producing a technical-grade ammonium perrhenate (NH_4ReO_4) since December 1970. The firm is currently enlarging its plant facilities in Nos, Santiago, to increase rhenium capacity in 1973 from 2,000 to 2,700 pounds per year of rhenium contained in technical-grade ammonium perrhenate salt.¹²

Chilean molybdenum and rhenium resources show about 7,700 pounds per year of rhenium as a recoverable figure from the three big State-owned porphyry copper mines. There are additional potentially important rhenium resources from new Chilean porphyry copper deposits, such as Mocha, Cerro Colorado, El Abra, Andacollo, Loica, Pelambres, and others.

The Corporación del Cobre (CODELCO) announced commencement of feasibility studies on a plant to extract molybdenum, rhenium, and other rare metals from porphyry copper ore of the recently nationalized (1971) Rio Blanco copper deposit. The deposit was previously worked by the

Cerro Corp. of the United States. According to CODELCO, the plans envisage a \$2.6 million plant to be established in the Rio Blanco region about 90 miles northeast of Santiago. The plant is expected to become operational by mid-1973.¹³

Japan.—Shiba, Japan, is the site of Engelhard's newly commissioned magnaformer installation, utilizing the greatly improved E-601 platinum-rhenium bimetallic catalyst for the manufacture of unleaded, high-octane gasoline.¹⁴

Taiyo Mining and Industrial Co., Ltd., was granted an exclusive license for use of a new hydrometallurgical process developed by Molycorp to produce molybdenum oxide and rhenium compounds.

Mongolia.—The giant copper-molybdenum deposit at Erdenetiyn-ovoo was first investigated by a joint Mongol-Czechoslovak geologic expedition in 1964-65. In 1970, rhenium and other metals were identified in the deposit; however, the rhenium content has not yet been assayed. A new agreement with the Soviet Union for the exploitation of the deposit seems imminent.¹⁵

TECHNOLOGY

The Bureau of Mines electrooxidation technique was successfully applied to the recovery of molybdenum and rhenium from sulfide ores and concentrates at its Reno Metallurgy Research Center. Extraction of 99% of the molybdenum and rhenium was found to be feasible on a bench scale with an immersion-type electrode system. Similar results were obtained in larger experiments using a 1,260-ampere, bipolar, flow-through cell, except that the power requirements per pound of molybdenum were substantially reduced. This process eliminates the use of the conventional roasting techniques, which are the main factors contributing to sulfur dioxide pollution of the atmosphere.

Concomitant studies on the extraction and separation of molybdenum and rhenium from process solutions have resulted in development of an amine extraction-carbon adsorption system that is capable of recovering 99% of the rhenium as 99.99%-pure ammonium perrhenate, and 99% of the molybdenum as high-purity ammonium molybdate.

The Bureau also investigated hydrometallurgical processing of low-grade molybdenite rougher flotation concentrates as a means for improving byproduct molybdenum and rhenium recovery from porphyry copper ores. Several methods were investigated, and the best rhenium and molybdenum recoveries from the leach liquor were obtained by adsorption of the rhenium from the basic liquor with an anion exchange resin, acidification of the residual liquor, followed by recovery of the molybdenum by adsorption with activated charcoal. The rhenium was recovered from the loaded resin by stripping with ammonium thiocyanate.

Kennecott Copper Corp. received a patent for a process that simultaneously reduces atmospheric pollution and recovers

¹¹ Metals Sourcebook No. 9. Other Metals. May 7, 1973, p. 2.

¹² Intermet Bulletin. Rhenium Production in Chile. V. 2, No. 3, January 1973, p. 35.

¹³ The Mining Journal (London). Chile: New Plant? V. 278, No. 7136, May 26, 1972, p. 433.

¹⁴ Work cited in footnote 3.

¹⁵ Far Eastern Economic Review. Precious Cairn. V. 80, No. 14, Apr. 9, 1973, p. 24.

rhenum values in the gaseous effluent from copper smelting operations. The process involves scrubbing volatilized rhenum oxide and sulfur oxide with an aqueous alkaline solution to remove most of the sulfur oxide from the gas stream as a soluble sulfite and to dissolve the rhenum oxide in the resulting sulfite solution. The rhenum-bearing sulfite solution is treated by known means, such as ion exchange or solvent extraction, to recover the contained rhenum oxide.¹⁶

A patent was issued to Continental Ore Corp. for recovery of rhenum and molybdenum values from solution. The process involves extracting soluble molybdenum and rhenum values with an amine solvent, and stripping the values from the amine extract with an ammonium hydroxide solution. The rhenum is then concentrated and recovered from the crystallization mother liquor by amine solvent extraction. It is stripped from the resin using a sodium hydroxide solution and extracted into a pyridine solvent, which is distilled away leaving the desired rhenum salt.¹⁷

Early in the year, a patent was granted for a process that regenerates deactivated platinum-rhenum reforming catalysts to the condition of fresh reforming catalysts.¹⁸ Dependent on its cost and applicability, this or similar processes should attract the interest of many catalyst manufacturers and petroleum-refining companies.

Chevron Research Co., a subsidiary of Standard Oil of California, developed a new catalyst known as Rheniforming type "D" to help refineries meet no-lead and low-lead motor fuel requirements. The new catalysts reportedly will cost less, provide better yields, have greater stability, and require smaller amounts of platinum.¹⁹

Kennecott Copper Corp. was granted a patent on a new process for extracting molybdenum and rhenum from raw materials. In the process, molybdenum and rhenum values are recovered from molybdenite concentrate by roasting in the presence of calcium compounds to produce water-insoluble calcium molybdate and water-soluble calcium perhenate. The need for extensive gas-cleaning equipment to prevent SO₂ discharge is eliminated by the process. The calcine is leached with water to separate rhenum from the mo-

lybdenum values, and then leached with acid to solubilize the molybdenum. Alternatively, the calcine is leached with acid, and the dissolved rhenum and molybdenum values may be recovered separately from the clarified solution by use of extraction and stripping cells and/or ion-exchange resins.²⁰

A process was patented for the removal of rhenum and other metallic impurities from a sulfide-bearing molybdenite ore. The process, which does not evolve sulfur dioxide, thus eliminating a potential air pollution problem, comprises (1) roasting ore with alkali metal carbonate, (2) leaching 95% of the molybdenum from the resulting fusion mass, (3) oxidizing the leached mass, and (4) treating it with water to extract the rhenum and molybdenum from other metallic impurities before recovering the rhenum and molybdenum by conventional procedures.²¹

Engelhard Minerals & Chemical Corp. studied tungsten-rhenum thermocouple junctions to determine how and under what circumstances tungsten-rhenum wire could be joined and still maintain adequate handleability. It was found that a reliable, sound, and handleable thermocouple junction can be obtained by tightly twisting tungsten-rhenum wire and welding the ends. To be effective, there must be at least one and one half turns of wire prior to the weld. Repeated tests with over 75 junctions fabricated by this technique have resulted in no failures traceable to a properly executed twist.²²

A study was carried out in the Ledge-mont Laboratory of Kennecott Copper Corp. on the oxidative vaporization of

¹⁶ Spedden, H. R. (assigned to Kennecott Copper Corp., New York). Process for Recovering Volatilized Rhenum Oxides and Sulfur Oxides From Gas Streams. U.S. Pat. 3,723,595, Mar. 27, 1973.

¹⁷ Litz, J. E. (assigned to Continental Ore Corp., New York). Recovery of Rhenum and Molybdenum Values From Solution. U.S. Pat. 3,681,016, Aug. 1, 1972.

¹⁸ Moravec, Jr. V. J. Regeneration of Platinum-Rhenum Reforming Catalyst. U.S. Pat. 3,654,142, Apr. 4, 1972.

¹⁹ Work cited in footnote 5.

²⁰ Noy, J. M. (assigned to Kennecott Copper Corp., New York). Process for Extracting Molybdenum and Rhenum From Raw Materials Containing Same. U.S. Pat. 3,705,230, Dec. 5, 1972.

²¹ Martin, B. E., M. B. MacInnis (assigned to GTE Sylvania, Inc., Seneca Falls, N.Y.). Rhenum and Molybdenum Separation From Sulfide Ores. U.S. Pat. 3,725,524, Apr. 3, 1973.

²² American Metal Market. Tungsten-Rhenum Thermocouple Use Widening. V. 79, No. 14, Nov. 22, 1972, p. 14A.

rhenum from natural molybdenite concentrates under controlled conditions. The molybdenite oxidation and rhenium vaporization were measured, respectively, by the amount of $\text{SO}_2\text{-SO}_3$ and by the amount of rhenium collected in an aqueous absorber as a function of time. The rate of rhenium vaporization increased with the oxygen content of the reactant gas. Consistent with the molybdenite oxidation, rhenium volatilization increased markedly with tem-

perature. The experiments confirmed the general relationship between rhenium vaporization and molybdenite oxidation. With the volatility of rhenium shown under ideal conditions, it is suggested that in multiple hearth roasters, there is oxidation and vaporization in the lower hearths followed by reduction and recondensation of rhenium in the upper stages.²³

²³ Amman, P. R., and T. A. Loose. Rhenium Volatilization During Molybdenite Roasting. *Met. Trans.*, v. 3, No. 4, April 1972, pp. 1020-1022.

