

Rhenium

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In 1978, consumption of rhenium increased 71% over that of 1977, reaching a record level of approximately 12,500 pounds. In 1979, consumption fell to about 9,500 pounds as supply remained extremely tight. Demand came primarily from bimetallic catalyst manufacturers as the need for

high-octane, low-lead gasoline increased. Imports of ammonium perrhenate reached a record 11,192 pounds in 1978, an increase of 83% over the prior record year of 1977, but declined significantly in 1979. Prices increased in 1978, and reached \$2,000 per pound by late 1979.

Table 1.—Salient rhenium statistics
(Pounds of contained rhenium)

	1975	1976	1977	1978	1979
Mine production ^e -----	2,000	1,500	--	W	W
Consumption ^e -----	6,000	8,300	7,300	12,500	9,500
Imports (metal) -----	59	82	148	449	927
Imports (ammonium perrhenate) -----	^e 966	4,047	6,111	¹ 12,042	8,299
Stocks, Dec. 31 ^e -----	21,000	18,300	17,300	W	W

^eEstimate. W Withheld to avoid disclosing company proprietary data.

¹ Includes 850 pounds of perrhenic acid.

DOMESTIC PRODUCTION

Rhenium was recovered from domestic ores by three companies in 1978 and by one company in 1979. Most of the rhenium recovered in the United States was toll-refined from Canadian molybdenite concen-

trate (MoS₂) and returned to the owner for sale. Kennecott Corp. resumed recovery of rhenium in late 1978 after being inactive since 1975 and was the sole producer of rhenium from domestic ores in 1979.

CONSUMPTION AND USES

Estimated consumption of rhenium in 1978 increased over 71%, compared with that of 1977, reaching a record level of approximately 12,500 pounds. Consumption dropped to about 9,500 pounds in 1979 as stocks became depleted and supply could not keep pace with demand. The increase in demand over previous years was due to strong demand for bimetallic petroleum reforming catalysts used in producing unleaded and low-lead, high-octane gasoline. The petroleum industry uses several types

of catalytic reformers to produce high-octane, low-lead gasoline. Aggregate capacity of semiregenerative bimetallic reformers increased nearly 13% from 1977 to 1979, to a record 58% of total reforming capacity. Capacity of cyclic bimetallic reformers increased over 120% during the same period, and capacity of all other types of reformers increased 55%. In 1972, semiregenerative bimetallic reformers comprised only 28% of total reforming capacity, compared with 45% for comparable monometallic reform-

ers. In 1979 the semiregenerative monometallic reformers' share of capacity was eroded to 9%, as platinum-rhenium catalysts continued to gain in use over platinum catalysts.

Together the three basic types of rhenium-utilizing reformers comprised a record 73% of domestic reforming capacity, or 2,883,700 barrels per stream day, while conventional platinum catalysts accounted for the remainder.²

It is estimated that platinum-rhenium catalysts now account for about 85% of bimetallic reforming capacity, or about 62% of total domestic reforming capacity. The trend for platinum-rhenium catalysts to capture more of the market should continue for several years.

The 20 largest oil companies held 84% of total domestic catalytic reforming capacity, while 147 smaller companies held the remaining 16%.³

In 1978, the estimated market for reforming catalysts was about 5 million pounds. Approximately 70% of the market was for bimetallic catalysts, which were selling for \$4.80 per pound without the precious metal. The cost of bimetallic replacement catalysts was nearly \$17 million. In addition, an estimated \$5.7 million was spent on monometallic platinum replacement catalysts, \$1.9 million on recovering precious metal from catalysts, \$8.8 million for replacing metal lost in recovery, and \$2.2 million for metal used in new capacity scheduled to come onstream during the year. Thus, nearly \$27.5 million was spent in the reforming catalyst market, approximately 70% of which was for bimetallic catalyst to replace the older monometallic type.

Gross weight of existing catalysts in domestic reformers totaled about 15.5 million pounds in 1978, with about 5 million pounds replaced during the year. Bimetallic catalysts generally contained 0.3% rhenium and 0.3% platinum. The newest generation of catalysts contain 0.6% or more rhenium, which helped increase demand for rhenium.

Recovery of metals from reforming catalysts has become a strongly competitive business. Recovery of platinum averages 98% to 99%, and rhenium recovery reportedly averages about 93%. Platinum recovery costs for one company averaged \$1.90 per pound. Engelhard Metals & Minerals Corp. and UOP Inc. were leading processors for domestic and foreign operations.⁴

The bimetallic platinum-rhenium catalysts employed in the reformers of the Cities Service Co. at Lake Charles, La., were

licensed by two companies to Cities Service. Catalyst for one of the units has been regenerated 10 times and is reportedly functioning well. The ability to be regenerated is one of the attractions of the bimetallic over the monometallic catalysts. Under normal conditions these catalysts can be regenerated almost indefinitely. However, conditions prevailing in 1978-79 were not normal. Refiners were trying to maintain high octane levels in low-lead and lead-free gasolines, which put a greater strain on the catalyst than occurs under more normal conditions. In view of this, 3 years between catalyst regenerations was considered a good performance.

UOP had 12 continuous Platformers in operation with continuous catalyst cycles in which the initial catalyst charge reportedly was performing well. Four units have been operating in excess of 3 years, and an additional six units were scheduled to begin operation in 1979.

Engelhard Minerals and Chemicals Corp. catalysts have been in use for many years and have undergone many regenerations. Over 60 units currently use the E-500 and E-600 series bimetallic catalysts.

Most of the increased rhenium demand came from converting monometallic reformers to bimetallic reformers and increasing the charge capacity of existing bimetallic reformers. The following additions to charge capacity were made (barrels per stream day): Chevron Oil Co., 2,800, to the Bakersfield, Calif., refinery; Murphy Oil Co., 1,500, to the Meraux, La., refinery; Amoco, 1,000, to the Texas City, Tex., refinery; Arco, 3,000, to the Carson, Calif., refinery; Exxon Co., 60,000, to the Baytown, Tex., refinery; and Shell Oil Co., 1,500, to the Wood River, Ill., refinery. Phillips Petroleum Co. converted the 21,000-barrel-per-stream-day reformer at Kansas City, Kans., from monometallic to bimetallic operation, and Pennzoil Corp. converted the 5,000-barrel-per-stream-day refinery at Shreveport, La., from monometallic to bimetallic operation.

Texaco Inc. was building a new 40,000-barrel-per-stream-day reformer at Port Arthur, Tex. The \$180 million project was expected to be completed by 1983. The new unit will increase Texaco's production of gasoline by about 2 1/2%, or 475,000 gallons per day, and boost the company's ability to make unleaded gasoline.⁵

Champlin Petroleum Co. was adding a new continuous catalytic reformer at its Wilmington, Calif., refinery; this was part

of a \$120 million modernization and expansion program to be completed in early 1981. Gulf Oil Co. added a \$60 million refiner to its Port Arthur, Tex., refinery which will boost unleaded gasoline capacity by 30,000 barrels per day. Hill Petroleum Co. was expanding catalytic reforming capacity by 15,000 barrels per day at a cost of \$20 million at the Krotz Springs, La., refinery. Completion was expected by mid-1980. Vickers Petroleum Corp. was upgrading its Platformer at Ardmore, Okla., to a continuous catalyst regeneration type, which will result in more capability for producing unleaded gasoline.

Based on total reforming capacity, 8 States have entirely bimetallic reforming capacity; 21 States have none. The remaining 21 States have bimetallic reforming capacity ranging from 12% of total capacity (Indiana) to 94% (Mississippi).

Platinum-rhenium catalysts are also used in the production of benzene, toluene, and xylenes by reforming. Reformate accounts for nearly one-half of domestic benzene production; however, the production utilizes only a small proportion of the rhenium used in catalysts.

The United States is the world's leader in catalytic reforming, averaging 3.84 million barrels per calendar day in 1978. Japan was second with 557,000; followed by the United Kingdom, 452,235; Canada, 450,000; France,

441,050; and the Federal Republic of Germany, 439,772. These countries account for the majority of world consumption of bimetallic platinum-rhenium catalysts, a large portion of which was produced in the United States.

An estimated 8% of rhenium consumption was accounted for by use in high-temperature thermocouples, vacuum tube and flashbulb filaments, X-ray tubes and targets, electrical contacts, heating elements, crucibles, semiconductors, electromagnets, metallic coatings, ionization gages, and high-temperature nickel- and cobalt-base alloys.

Rhenium coatings were used on electrical contacts to resist wear and arc erosion. Rhenium reportedly performed better in this application than either tungsten or platinum-ruthenium, which were also used. Rhenium was applied to contacts for various engine magnetos because of its resistance to material transfer. On initial interruption of a current, a thin oxide film is produced that prevents sticking or welding of the contacts or the transfer of metal across the gap. Restoration of the current causes layering of the oxide film at a thickness that does not significantly impair the efficiency of the contact. The resistance of rhenium to salt water corrosion is an important additional advantage in marine engine magnetos.

PRICES

In early 1978, the price for rhenium metal powder was about \$375 per pound, and for perrhenic acid, \$350 per pound. These prices fell to nearly \$300 per pound by late summer; however, by yearend, unofficial prices rose to about \$475 per pound for metal powder and \$425 per pound for perrhenic acid. In 1979, the price rose dramatically as demand for bimetallic catalysts

outpaced available supply. By yearend 1979, the price for rhenium metal powder rose to about \$2,000 per pound, depending on grade, quantity, and buyer-seller relationship. The reduction of tetraethyl lead in gasoline to meet air quality standards set by the Environmental Protection Agency exacerbated the rhenium price increases.

FOREIGN TRADE

In 1978, U.S. imports for consumption of ammonium perrhenate reached the record level of 11,192 pounds, valued at nearly \$2.2 million. In 1979, 8,299 pounds was imported, valued at \$3.3 million. Smaller amounts of metal powder and wrought rhenium were also imported. Chile and the Federal Republic of Germany continued to be the major

sources, together supplying over 99% of total imports in 1978, and 94% in 1979.

The import duty on ammonium perrhenate from countries with market economies was 4% ad valorem; the duty on that from countries with central economies was 25% ad valorem. The duty on rhenium metal from countries with market economies was

5% ad valorem for unwrought metal and 9% ad valorem for wrought metal. The duty on wrought and unwrought metal from countries with central economies was 45%

and 25% ad valorem, respectively. There is no duty on rhenium contained in molybdenite concentrate.

Table 2.—U.S. imports for consumption of ammonium perrhenate, by country
(Rhenium content)

Country	1975 ^e		1976 ¹		1977 ¹		1978 ¹		1979 ¹	
	Quantity (pounds)	Value (thousands)	Quantity (pounds)	Value (thousands)	Quantity (pounds)	Value (thousands)	Quantity (pounds)	Value (thousands)	Quantity (pounds)	Value (thousands)
Chile -----	--	--	1,280	\$606	4,187	\$1,087	5,855	\$889	4,335	\$1,380
Germany, Federal Republic of ---	401	\$165	2,767	801	1,924	533	*6,187	1,512	3,898	1,854
Poland -----	--	--	--	--	--	--	--	--	66	25
Sweden -----	565	277	--	--	--	--	--	--	--	--
Total ---	966	442	4,047	1,407	6,111	1,620	12,042	2,401	8,299	3,259

^eEstimate.

¹Adjusted by Bureau of Mines.

*Includes 850 pounds of perrhenic acid.

Table 3.—U.S. imports for consumption of rhenium metal, by country
(Gross weight)

Country	1975		1976		1977		1978		1979	
	Quantity (pounds)	Value	Quantity (pounds)	Value	Quantity (pounds)	Value	Quantity (pounds)	Value	Quantity (pounds)	Value
Belgium-Luxembourg ---	28	\$11,136	17	\$8,687	18	\$4,120	15	\$6,075	238	\$97,836
France -----	--	--	--	--	--	--	--	--	--	--
Germany, Federal Republic of ---	30	15,760	65	29,060	130	51,734	434	161,920	468	426,735
U.S.S.R. -----	--	--	--	--	--	--	--	--	220	82,594
Other ¹ -----	1	300	--	--	--	--	--	--	1	478
Total -----	59	27,196	82	37,747	148	55,854	449	167,995	927	607,643

¹Includes Austria and Switzerland.

WORLD REVIEW

World production of rhenium totaled an estimated 15,700 pounds in 1978 and 16,000 pounds in 1979. Canada, Chile, and the Federal Republic of Germany accounted for the majority of production in both years.

Porphyry copper deposits in Canada, Chile, and the U.S.S.R. were the major sources of rhenium. Known recovery facilities outside the United States were located in Belgium-Luxembourg, Bulgaria, Chile, France, the German Democratic Republic, the Federal Republic of Germany, Poland, Sweden, the United Kingdom, and the U.S.S.R.

Canada.—All of Canada's rhenium production came from the Island Copper Mine of Utah International Inc. In 1978, an esti-

mated 2,200 tons of MoS₂ concentrate, containing approximately 5,000 pounds of rhenium, was shipped to the United States and Western Europe. The contained rhenium was toll-processed into ammonium perrhenate and perrhenic acid and returned to Utah International. Other porphyry copper mines in British Columbia have significant quantities of rhenium in molybdenite, but rhenium has not been recovered.

A prefeasibility study of several aspects of a major copper-molybdenum-gold-silver-rhenium deposit on Gambier Island, British Columbia, was being carried out by 20th Century Energy Corp. The study will include extensive metallurgical testing to determine specifications for mill design, and

will include determination of metal recoveries as well as grades of concentrates of copper and molybdenum. A basis will also be determined for estimating rhenium content of the ore.⁶ Ore reserves are estimated at 282 million tons to a depth of 300 feet below sea level, having an overall mean average grade of 0.27% copper and 0.014% molybdenite.

Chile.—Production of rhenium in Chile in 1978 was estimated at 4,400 pounds, contained in approximately 7,000 pounds of ammonium perchlorate. The molybdenite-roasting plant of Molibdenos y Metales, S.A. (MOLYMET), which processes concentrate from the Chuquicamata, El Teniente, El Salvador, and Andina mines, is the only Chilean firm that recovers rhenium. These four mines have rhenium concentrations of approximately 230 ppm (parts per million), 440 ppm, 570 ppm, and 350 ppm, respectively, and are a major source of the world's rhenium supply.

The El Teniente mine, south of Santiago, holds the world's largest reserve of rhenium, an estimated 1.5 million pounds (enough to supply current world demand for 100 years). The ore contains an average 1.5% copper and 0.04% molybdenum.

Los Pelambres is a porphyry copper-molybdenum deposit located about 125 miles north of Santiago and 25 miles east of Salamanca at an altitude greater than 10,000 feet above sea level. Reserves are estimated at 472 million short tons of ore grading 0.78% copper and 0.03% molybdenum. Assuming 300 ppm rhenium in MoS_2 , rhenium content would total over 140,000 pounds. The property was purchased by Anaconda Co. in late 1979, for an estimated \$20 million. Anaconda plans to spend between \$6 million and \$8 million over the next 3 years on exploratory drilling.

China, Mainland.—One of the world's largest copper deposits will be developed by Fluor Corp. and is to begin operation in 1984. The deposit has proven reserves of 8.8 million tons of copper with recoverable quantities of rhenium. It is located in Tensing County, about 100 miles east of Nanchang in Kiangsi Province in east-central China. Exploration was continuing at the site, and additional reserves seemed likely to be verified.

Hungary.—Exploration drilling in the late 1960's led to the discovery of the Reesk porphyry copper deposit. This deposit, in the Matra Mountain area of northern Hungary, is now being developed for mining. The copper mineralization is in the form of

chalcopyrite with associated pyrite. Molybdenum and rhenium are present in the ore in reportedly recoverable quantities. By selective mining of the skarn and porphyry ores, the operators plan to maintain an average grade of 1.3% copper for a production of up to 2.5 million tons of ore annually. Eventually, twice this quantity may be mined.⁷

Mexico.—The Caridad copper mine came onstream on June 2, 1979, about 1 year behind schedule. At full capacity, the mine was expected to produce 600,000 tons per year of concentrate, averaging 32% copper. A flotation plant was expected to be onstream in early 1981 to produce 2,000 tons per year of molybdenum sulfide concentrate. It is not known whether recovery of the contained rhenium will be attempted. Proven reserves are 680 million tons of ore, grading an average 0.67% copper and 0.02% molybdenum. Assuming 250 ppm rhenium in MoS_2 , rhenium content would total over 100,000 pounds.⁸

Poland.—A new method of recovering rhenium from ore reportedly was developed by the Non Ferrous Metals Institute at Gliwice. The process was put into practice at the Huta Miedzki copper works at Glasgow, which now produces several hundred pounds of rhenium per year.

Romania.—Romanian Chemical Enterprises (ROMCHIM) and UOP Inc. reached agreement for the foreign trade company to license 13 process units at several locations in Romania. Included in the agreement are three Platforming process units, each with a 500,000-ton-per-year naphtha feed for production of high-octane gasoline. Similar UOP bimetallic catalysts are used extensively in reforming operations worldwide.

U.S.S.R.—Oil shales in the Tadzhikistan and Uzbekistan regions of central Asia contain concentrations of molybdenum and rhenium. These concentrations may be extracted by acid solutions. The rhenium concentration in the Tadzhikistan region ranges from 0.74 ppm at the Rauat deposit to 12 ppm at the Garauty deposit; in the Uzbekistan region the concentration ranges from 0.2 ppm in the Baysum deposit to 21 ppm in the Urtabulak deposit.⁹

Yugoslavia.—The Bor and Majdanpek porphyry copper mines in mideastern Yugoslavia contain recoverable quantities of molybdenum and rhenium as well as other minor metals such as germanium and gallium. Additional porphyry deposits are found at Dunitri Potok, Valja Stary, and Cerova, northwest of Veliki Krivelj. They

are generally low in molybdenum content but have a comparatively high rhenium content.¹⁰ To date no molybdenum or rhenium is believed to have been recovered;

however, plans are being made to recover molybdenum and several other minor metals in the next few years.

TECHNOLOGY

The Bureau of Mines published the final report in its series on recovery of molybdenum and rhenium from offgrade molybdenite concentrates. The Bureau determined that current leakage losses that occur in operation of bipolar flow-through electro-oxidation cells can be minimized by incorporating cell design factors that increase the current leakage path. This could be accomplished by sealing the edges of the electrodes in the sides of the cell enclosure and adding nonconductive extensions on the top and bottom of each electrode.

Overall molybdenum and rhenium recoveries of 97% were obtained from flotation concentrates containing 16% to 35% molybdenum. Molybdenum-rhenium extraction was unaffected by the presence of chalcocite in the molybdenite concentrate; however, molybdenum extraction declined if the copper content, as chalcocite, exceeded 7%. High-purity molybdenum and rhenium compounds can be recovered from the electrolyzed reaction mass by liquid-solid separation, solvent extraction, and crystallization steps.¹¹

Research was conducted to find new methods of warm-rolling work-hardened thin wires of high-strength refractory alloys such as molybdenum-rhenium and tungsten-rhenium into metallic tapes. Different methods of heating were tried. One method involved heating the wire with argon preheated to the desired temperature. The heated gas stream was directed into the space between the rolls, heating both the wire and the rolls. Due to the large difference between the masses and the heat-removal capacities of the rolls and the wire, the wire attained the maximum temperature, not in the deformation zone (at the point of contact with the rolls) but some distance away from the entry point. This resulted in some improvement in the form coefficient (width-to-thickness ratio) of the molybdenum-rhenium alloy wire and in the quality of its surface and edges. Similar results were obtained when both the rolls and the wire were indirectly heated by an electrically heated tungsten spiral. It was

possible to obtain a molybdenum-rhenium tape with form coefficients of 20 to 25 and higher, retaining all strength and elastic properties with good quality of surface and edges. Also, for the first time, it became possible to cold-roll a difficult material like the tungsten-rhenium alloy (VR27-VP) and obtain a tape with a form coefficient of 10 to 12 from highly cold-hardened wire of 0.08 millimeter diameter, while retaining strength and elasticity.¹²

The need to construct reliable special-purpose electrovacuum devices created demand for new materials for cores of oxide cathodes and for other parts of the cathode unit. Alloys of nickel with magnesium, silicon, calcium, aluminum, tungsten, and other metals had certain deficiencies. All suffered from a high ratio of volatilization, inadequate stability of form, and low strength at elevated temperatures. To meet the complex property requirements, a series of nickel-rhenium alloys with various additions was developed. It was found that rhenium improved the strength properties and the stability of nickel. Also, activating additions of elements of the IV-A group and rare-earth elements improved the emission characteristics of the cathode. The stability of the new alloys increased the rigidity of the cathode and ensured the stability of the emission characteristics of valves with short interelectrode distances. In pulse devices, valve life more than doubled. At 1,000°C the strength of nickel-10% rhenium alloys containing activating additions exceeded the strength of a nickel-vanadium cathode alloy by about 90% and exceeded its rigidity by 1.5 to 2 times. It was shown that in nickel-rhenium alloys an intermediate layer of rhenium compounds did not form, and the service life of the valve increased several times.¹³

The catalytic properties of rhenium catalysts were studied in the process of liquid-phase reduction of nitrobenzenes (NB). It was found that the specific activity of rhenium depends little on the concentration of the active component in the catalyst and was close to that of palladium and much

superior to that of nickel. A study of the effect of NB concentration and hydrogen pressure on the activity and stability of a 5% rhenium catalyst (percent metal on charcoal) showed that in the concentration range of 10% to 50% NB, the reaction proceeded almost at a constant rate, with apparent activation energy of about 7,000 calories per mole. Total conversion of NB was obtained at 180° to 200°C. A considerable advantage of rhenium catalysts in NB reduction is their high selectivity. Being superior to palladium and nickel catalysts in productivity, the 5% rhenium catalysts showed a high working capacity over a wide range of contact loads, which is of great importance in its industrial use in column-type contact reactors. A comparison of the relative costs of rhenium-base catalysts with the cost of nickel-, platinum-, and palladium-base hydrogenation catalysts on granulated carbon showed that the 5% rhenium catalyst is competitive with 1% platinumized carbon. The 2% rhenium catalyst is a promising substitute for 0.5% platinum or 2% palladium catalysts in the reduction of temperature-stable nitrocompounds.¹⁴

A patent was applied for in 1978 on a catalytic composition for the reforming of petroleum hydrocarbons. The catalyst consists of 0.1 to 2.0 weight-percent rhenium and 0.1 to 2.0 weight-percent gallium. The catalyst was supported on a solid, porous, refractory, inorganic oxide material. This and similar research was intended to obvi-

ate the need for expensive platinum in bimetallic catalysts without sacrificing desirable qualities that platinum imparts.¹⁵

¹Industry economist, Section of Ferrous Metals.

²Oil & Gas Journal, Octane Emphasized in Refining Capacity Gains. V. 78, No. 12, Mar. 24, 1980, pp. 75-77.

³Page 77 of work cited in footnote 2.

⁴Chemical Week. A \$600-Million Market In Cars and Refineries. V. 124, No. 13, Mar. 28, 1979, pp. 42-54.

⁵Chemical Engineering. V. 86, No. 26, Dec. 3, 1979, p. 45.

⁶The Northern Miner. New Funds Provided 20th Century for Gambier Island Copper-Moly. V. 65, No. 38, Nov. 29, 1979, p. 18.

⁷World Mining. Reesk, Hungarians Prove Big, Deep Porphyry Copper. V. 31, No. 12, November 1978, pp. 40-47.

⁸Mining Magazine. La Caridad, Mexico, Ceremonially Opened. July 1979, p. 9.

⁹International Molybdenum Encyclopedia. Volume I, Resources and Production. Geochemistry. Alexander Sutulov Publications, Santiago, Chile, November 1978, p. 168.

¹⁰World Mining. European Copper Deposits. V. 33, No. 1, January 1980, pp. 52-55.

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¹⁵Bertolacini, R.J., and D.K. Kim (assigned to Standard Oil of Indiana, Chicago, Ill.). Catalyst and Hydrocarbon Conversion Process. U.S. Pat. 4,136,060, Jan. 23, 1979.

