Kirk-Othmer Encyclopedia of Chemical Technology.

RHENIUM AND RHENIUM COMPOUNDS

1. Rhenium

Rhenium was the last natural element to be discovered (1). D. I. Mendeleev (1834–1907) predicted the existence of rhenium in 1860 as element number 75 during his development of the Periodic Table. He called it dvi (dwee)-manganese using the Sanskrit number two to identify the second undiscovered element in the manganese series. He called the first undiscovered element, number 43, eka-manganese using Sanskrit for the number one. Today eka-manganese, once known as masurium, is called technetium.

In 1925 Walter Noddack (1893–1960), Ida Tacke (1896–1978) along with Professor Otto Berg announced the discovery of element number 75. Ida Tacke became Mrs. Noddack in 1926. They called it rhenium after their Rhine River homeland. Rhine is Rhenus in Latin.

Controversy over the announced discovery surfaced early. Work of Berg and of the Noddacks was disputed by V. Dolejsek and J. Heyrovsky of the Charles University of Prague, Czechoslovakia (2). They claimed to have discovered rhenium in crude manganese compounds where the Noddacks and Berg reported their recovery of rhenium from platinum ore from the Urals.

At about the same time in the United Kingdom F. H. Loring and S. F. G. Druce announced their discovery of rhenium in pyrolusite, a manganese dioxide mineral (3). Eight years later in 1933 at the University of Wisconsin, Madison, L. C. Hurd questioned the work of both the Czech and English researchers (4). In 1962, K. B. Lebedev (5) reported on the work of S. Kern, a Russian chemist who discovered an element he called "Davyum" in honor of Sir Humphrey Davy, who was the first to isolate the alkali metals. Lebedev also reported that J. W. Mallet repeated and verified Kern's work. Lebedev expressed his belief that "Davyum" could actually have been rhenium. Lebedev also reported the work of other researchers who were unable to duplicate the Noddack's recovery of rhenium from platinum ore from the Urals.

Despite the controversy, the Noddacks and Berg are consistently credited with discovering rhenium. There is certainly no doubt they gave us the present and continuously recognized name for Mendeleev's dvi-manganese.

The Noddacks next devoted their efforts to process a quantity of molybdenite concentrates in order to obtain the single gram of rhenium they recovered for some of their studies (1).

Later, flue dusts from Mansfield, Germany, copper smelters became an important early source of rhenium and continued to be the primary source until World War II. Following the loss of Germany as a source of rhenium, A. D. Melaven and J. D. Bacon along with their graduate students at the University of Tennessee began producing rhenium from flue dusts which they obtained from the Miami Copper Company molybdenite roaster. In 1947 they were issued a patent for their process (6).

Then, in 1956 following several years of development and the granting of numerous patents to Zimmerly and his associates at Kennecott Copper, production of rhenium was begun at the Washington, Pennsylvania roaster of the Molybdenum Corporation of America, where Kennecott's molybdenite concentrates were being roasted. Kennecott was recovering molybdenite concentrates at their enormous Bingham Canyon copper mine.

It was also soon discovered that molybdenite concentrates from other Kennecott properties, Chino in New Mexico and McGill in Nevada, contained even larger concentrations of rhenium (7).

In 1961, The S. W. Shattuck Chemical Company, a small independent roaster in Denver, Colorado, began rhenium development work. Shattuck licensed the Kennecott technology, which was ultimately modified and improved to suit Shattuck's needs and ideas. Most of the Shattuck production was sold to Kennecott's Chase Brass and Copper Company located in Waterbury, Conn, Chase Brass was later moved to Cleveland, becoming Cleveland Refractory Metals.

Shattuck's production was acquired by Engelhard in late 1969 following the purchase of Shattuck by Philipp Brothers division of Engelhard Minerals and Chemicals Corporation. Philipp Brothers purchased Shattuck Chemical in order to acquire rhenium for Engelhard who by then was producing their version of the new Chevron Rheniforming catalyst. The Shattuck operations ceased in 1984 because of the high costs associated with a small molybdenite roasting operation. The plant has since been dismantled.

Kennecott was later taken over by petroleum giant Sohio. Sohio later sold Cleveland Refractory Metals (CRM) to F. Foyle, one of the CRM managers, who formed Rhenium Alloys at Elyria, Ohio. Foyle later sold the company to the Swedish company Sandvik, which has since sold the operation to several employees and other financial interests. Rhenium Alloys continues as a producer of rhenium mill products, including wire, rod, rocket components and alloys of molybdenum–rhenium and tungsten–rhenium.

In about 1965 Kennecott installed their own molybdenite roasters and rhenium recovery facilities. These were closed in a few short years after which Kennecott's molybdenite was sent to other roasters including Molymet in Chile where rhenium recovery was started in the early 1970s. Shattuck Chemical's technology was supplied to Carburo y Metalurgia in Chile (now Molybdenos y Metales or Molymet) through Philipp Brothers in the early 1970s.

As rhenium prices escalated with increasing demand caused by its use in petroleum catalysts, other producers entered the scene. H. C. Starck in Germany and other European roasters of molybdenite began to recover rhenium. M & R Industries, later known as Metec, installed rhenium recovery at their small Winslow, New Jersey roaster.

It is reported that rhenium was produced in the Soviet Union as early as 1930 (6), but other reports put significant production beginning in 1948 at the Balkash Metallurgical Combine in Kazakhstan (1).

In about 1972, Hazen Research of Golden, Colorado developed a process and built a plant for Continental Ore Corporation next to the Hazen facility. This was the only known plant where rhenium was the primary product, and off-grade molybdic oxide was the by-product. Operations ended in early 1973 due to operational and scale-up problems and a weak rhenium market.

Duval Corporation, a Pennzoil copper–molybdenum mining subsidiary, began investigations into rhenium recovery at their Esperanza copper mine and mill about 1975, but high costs, hazards of the chemicals to be used as well as cyclic prices stopped development. Then in 1980 at Duval's new Sierrita mine and mill a process was developed to recover rhenium from that portion of the roaster gas scrub liquors that escaped exposure to caustic. Duval licensed Kennecott's solid bed ion-exchange recovery technology and began production in 1981. Production ceased in 1983 due to low rhenium prices. It was resumed in 1984 only to stop again in 1985. The Duval Sierrita operation was sold by Pennzoil to Cyprus Minerals in 1986 and Cyprus soon resumed production which continues to this day.

Production in Russia is reported to have started at the Balkash metals complex in Kazakhstan where molybdenite from two copper porphyries was processed. There is also a very significant production in Kazakhstan from a deposit of sedimentary copper which contains a unique copper sulfide–rhenium sulfide mineral called Dhezkazganite. Recovery of rhenium is also reported from numerous other operations in the former Soviet Union: Chimkent Kazakhstan lead smelter; Khadzharan Armenian copper-moly plant; and Almalyk, Uzbekistan copper-moly plant.

Rhenium recovery also was instituted at Coldelco's molybdenite roasters in Chile in the early 1990's but soon fell victim to declining rhenium prices and has never been resumed.

1.1. Occurrence

Rhenium is reported to exist in the crust of the earth at 0.7–1 ppb (1, 8). It is one of the least abundant of all the elements and has no specific mineralogical specie, thus the late discovery of rhenium. The Noddacks and Berg claimed their discovery in platinum ore from the Urals while others claimed discovery in manganese ores. However, it was from molybdenite concentrates containing just two parts per million rhenium that the first gram of metallic rhenium was recovered (7).

It was eventually concluded that the greatest recoverable concentrations of rhenium could be found in molybdenite concentrates which were produced as a co-product or a by-product of porphyry copper mining.

Sutulov (7) reports the rhenium distribution in a variety of rocks and minerals varying from a low of 0.0001 ppm in silicates and oxides precipitated geologically before sulfide to as high as 0.2 ppm in an ore of columbium.

The rhenium content of molybdenite concentrates recovered from primary deposits varies from less than 10 ppm in some United States and CIS deposits to as much as 40 ppm in one Australian source (7).

By contrast, the content of molybdenite concentrates from porphyry copper ores varies from 125 ppm in Kennecott concentrates to as high as 1800 ppm in the now closed Island Copper operation of Utah International (now BHP) on Vancouver Island British Columbia. The also closed Ajo operation of Phelps Dodge had a similar concentration.

There are at least two cases of rhenium occurrence in sedimentary copper deposits, one of which was the former Soviet Union's primary source of rhenium. That ore body is a unique mineralization of copper sulfide and rhenium sulfide at Dzhezkazgan, Kazakhstan. This mineralization was appropriately named Dzhezkazganite. Prior to the break-up of the Soviet Union it may have been a source of ca 13,600 22,680 kg (30,000–50,000 pounds) of rhenium per year. Most of this was used in the former Soviet Union's military and space programs.

There was at least one nontraditional source of rhenium. Beginning about 1969 significant quantities of rhenium were found in uranium ores produced in the Falls City area of Texas south of San Antonio. This rhenium was associated with molybdenum also found in the uranium ore.

Recent reports from Russia (9) include the study of various carbonaceous materials, particularly oil shale and ashes from burning petroleum products, as sources of rhenium. Although the rhenium content is low, volumes are extremely high and could hold the promise as a significant source should demand and economics justify development. Rhenium is also reported in the condensates of gases from volcanoes in the Kurile Islands and in slags around the volcanoes (10). Deposits of other metals such as nickel may one day also become sources of rhenium.

Table 1 lists rhenium contents of molybdenite from various sources.

1.2. Properties

Naturally occurring rhenium, element number 75 in the Periodic Table, is composed of two isotopes. Rhenium 187 is the most abundant at 62.6% and is radioactive. Rhenium 185 at 37.4% is not radioactive (11). The half-life of rhenium 187 is 4.3×10^{10} years, perhaps slightly longer depending on the reference source used. The radiation though is a very weak 0.3 Mev, which cannot penetrate the skin. It also cannot be measured by the usual field instruments, but only by sensitive laboratory instruments. The radiation is so weak that the United States DOT regulations requiring no more than 3 curies per individual package would allow a package of 107,050 kg (236,000 lbs) rhenium metal. Based on calculations by health physicists, United Nations regulations would allow oral consumption of ca 21,320 kg/yr (47,000 lbs/year) and inhalation of nearly ca 3,585 kg (7,900 lbs), both levels well beyond anything practical. Those limits are based on the amount allowed before the beta radiation would cause any internal damage (12). These very high limits illustrate the extremely low hazard to human health.

Table 1. Rhenium Content of Molybdenite

Copper porphyries	ppm (100% MoS_2 basis)	Primary molybdenite	ppm (100% MoS_2 basis)
United States		*United States*	
Kennecott Utah Copper		Cyprus Climax	
Bingham Canyon	30	Climax	50
McGill	1600	Henderson	50
Cyprus Climax Metals		Thompson Creek	40
Bagdad	300	*Canada*	
Esperanza	180	Gibraltar	50
Pima	600	Brenda	90
Sierrita	150	Endako	50
Twin Buttes	600	*Other*	
BHP San Manuel	900	Sorsky Siberia	80
Pinto Valley	1000		
Island Copper	1800		
Phelps Dodge			
Ajo	1800		
Chino	600		
Morenci	700		
Asarco Mission	500		
Montana Resources, Butte	250		
Canada			
Lornex	250		
Island Copper	1800		
Mexico			
La Caridad	500		
Frisco	350		
Cananea	700		
South America			
Cuajone Peru	500		
Toquepala Peru	450		
Former Soviet Union			
Kounrad Kazakhstan	1300		
Almalyk Uzebekistan	900		
Kadzharan, Armenia	400		
Other			
Iran	1500		
Phillipines	1700		

The chemical properties of rhenium resemble the metals in the Manganese group, Group VII, where Mendeleev placed it. The physical properties, however, are much more similar to those of the refractory metals of Groups V and VI, particularly molybdenum and tungsten. This fact is what eventually lead the Noddack's to use molybdenum concentrates as their source for larger quantities of rhenium (1). Rhenium is considered a refractory metal because of its high melting point, of ca 3200°C. Only tungsten has a higher melting point. However, in contrast to other refractory metals, rhenium does not form carbides. Platinum and osmium have greater specific gravities.

Selected physical properties of rhenium are listed in Table 2.

Rhenium corrodes in hydrochloric acid (0.008 mg/min) and oxidizes rapidly in nitric acid (1.51 mg/min). It is attacked by sulfuric acid at high temperatures and is also attacked by dilute solutions of sodium chloride and sodium hydroxide.

Table 2. Selected Physical Properties of Rhenium

Property	Value
atomic number	75
atomic weight	186.2
mp, °C	3180
bp, °C	5926[a]
density, g/cm^3	21.02
crystal structure	hexagonal close-packed
lattice constants, nm	
a	0.2760
c	0.4458
metal radius, 12 coordinate, nm	0.1372
ΔH_{subl}, kJ/mol[b]	791
S°, crystal, J/(mol·K)[b]	37.2±1.2
specific heat, 20°C, J/(mol·K)[b]	25.1
ionization potentials, kJ[b]	
$\mathrm{Re} \rightarrow \mathrm{Re}^{+} + e^{-}$	757
$\mathrm{Re}^{+} \rightarrow \mathrm{Re}^{2+} + e^{-}$	1597
$\mathrm{Re}^{2+} \rightarrow \mathrm{Re}^{3+} + e^{-}$	2502
electrical resistivity, 20°C, $\mu\Omega\cdot$cm	19.3
thermal coefficient of electrical resistivity, °C^{-1}	3.95×10^{-3}
Richardson constant, kJ[b]	462[c]
thermal conductivity, 0–100°C, W/(cm·K)	0.400
module of elasticity, Pa[d]	0.46

[a] Estimated value.
[b] To convert J to cal, divide by 4.184.
[c] This value is equivalent to 4.8 eV.
[d] To convert Pa to mm Hg, multiply by 0.0075.

Rhenium has valences from 1 to 7 and easily changes from one to another. This characteristic is what makes it ideal for use as a catalyst.

In the 1960s it was observed that when rhenium is alloyed with molybdenum or tungsten, the resultant alloy exhibits or retains the best properties of both metals individually and none of the poor properties of either (13). It is almost true.

Rhenium does not have a ductile to brittle transition temperature. It retains its ductility from low sub-zero temperatures to very high temperatures, making it ideal for use in space propulsion applications. Rocket thruster nozzles have been reported to withstand more than 100,000 thermal fatigue cycles from room temperature to above 2225°C without evidence of failure (14).

Metallic rhenium varies from silvery-gray in appearance to dull gray as a function of its production. Powder is a relatively dark gray. Pellets pressed from powder and then sintered acquire a more silvery appearance. Parts coated with rhenium by plating or chemical vapor deposition have a very silvery appearance.

1.3. Sources and Supply

Rhenium is recovered primarily as a result of the roasting of molybdenite concentrates recovered from porphyry copper. Those facilities capable of recovering rhenium in the early 1970s with the estimated recovery capabilities then and now are listed in Table 3.

Table 3. Estimated annual capacity and Recovery of Rhenium

		Estimated annual capacity, kg. Re[a]		Estimated recovery
Plant/Company	Location	1970	1998	1999
Kennecott[b]	Garfield, Utah	1,814	0	
Cyprus Sierrita	Tucson, Arizona	1,814	5,449	4,535
Shattuck/Phibro[b]	Denver, Co.	1,360	0	
M&R/Metec[b]	Winslow, N.J.	907	0	
H. C. Starck[c]	Goslar, Germany	2,270	3,630	2,270
GFE/Metallurg[b]	Weisweler, Germany	1,360	0	
Mansfeld	Hettstedt, Germany	227	0	
Ferrolegeringar[b]	Trollhattan, Sweden (Metallurg)	2,270	0	
Hoboken[b]	Atwerpen, Belgium	136	0	
Sofrem[b]	LeGiffre, France	136	0	
Molymet	Santiago, Chile	6,350	17,235	13,638
Codelco		0	3,630	0
Balkhash	Kazakhstan	1,360		
Dzhezkazgan	Kazakhstan	13,608	18,190	2,270
Alaverdy	Uzbekistan	680	680	907
Sorsky	Siberia, Russia	907	907	909
Sumitomo	Japan	0	3,630	0
	Totals	*35,199*	*53,351*	*24,529*

[a] Actual production is a function of the rhenium content of the molybdenum concentrates being processed.

[b] Roasting plant dismantled.

[c] Roasting discontinued, production currently from residues from other roasters or secondary sources.

Recovery estimates are not based on reported figures because actual production is seldom revealed. Recovery is a function of molybdenite roasting, and there are roasters such as Mexico's La Caridad where rhenium is not recovered.

Aggravating today's availability of rhenium is the substantially reduced production of Dhezkazgan, Kazakhstan, where the operation is currently managed by Samsung of Korea. Copper concentrates that do not contain rhenium are being imported for processing in preference to the mining and processing of local rhenium-bearing copper concentrates.

Although rhenium is produced in the U.S. by Cyprus Climax Metals, that production is not adequate to meet domestic supply; therefore a substantial quantity of rhenium is imported into the U.S., primarily from Chile. It has also been imported from other producing countries. At the time of the break-up of the Soviet Union, a substantial volume of the Soviet stockpile of rhenium, estimated as high as 13,638 kg of rhenium contained in ammonium perrhenate, came into the market. United States rhenium imports are listed in Table 4.

Because the primary producers of rhenium-bearing petroleum reforming catalysts are located in the United States, much of the rhenium required is imported. Two of the three primary aircraft engine manufacturers are located in the U.S. and require much of their needs to be imported.

Since the break-up of the Soviet Union and the sale of their stockpiled rhenium from Russia and Kazakhstan, there is little or no rhenium in any inventory with the exception of petroleum refining company reserves. These reserves, estimated at 4,535–9072 kg. Re contained, have been recovered from spent reforming catalysts from which platinum has also been recovered and are in reserve for future catalyst production. In

Table 4. United States Rhenium imports, 1990–1997[a]

Year	Ammonium perrhenate, kg Re	Rhenium metal, kg Re	Total, kg Re
1990	10,633	6,055	16,688
1991	2,438	10,846	13,285
1992	5,694	6,385	12,079
1993	3,168	2,698	5,866
1994	2,327	5,876	8,204
1995	3,274	8,142	11,417
1996[b]	9,720	10,810	20,530
1997	6,557	8,510	15,067

[a] Ref. 15.

[b] Peak year of imports from the Former Soviet Union.

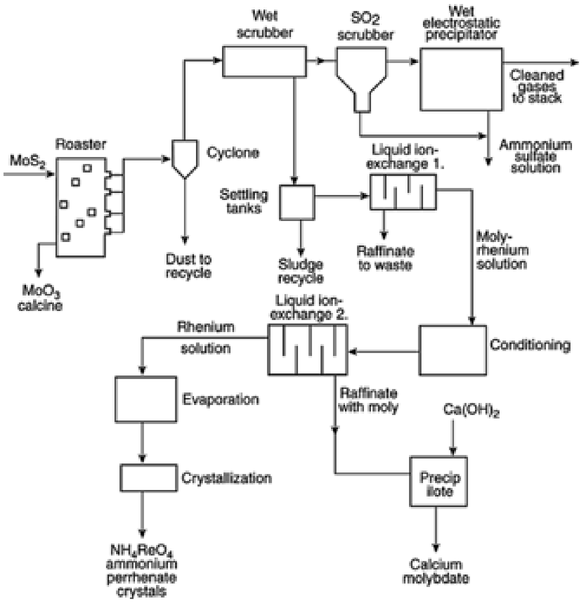

Fig. 1. Typical rhenium recovery process by liquid ion exchange.

order to avoid costly refinery downtime, a petroleum refinery always needs a supply of fresh catalyst to put into a reactor immediately following the removal of the spent catalyst. Oil companies, therefore, continuously retain a substantial inventory of rhenium to be available for production of new catalyst. It is generally rare for refineries to sell such inventories, but it has been done.

1.4. Manufacturing, and Production

When rhenium-bearing molybdenite is roasted, converting the MoS_2 to MoO_3 and SO_2, rhenium is oxidized to volatile Re_2O_7 which exists in the roaster with the SO_2. Scrubbing the exit gases with water dissolves the rhenium heptoxide as crude perrhenic acid, $HReO_4$. This solution is then treated to prepare for rhenium recovery by either solvent extraction (liquid ion-exchange) or solid bed ion-exchange (Figures 1 and 2). From either method, rhenium is stripped and crystallized as ammonium perrhenate, NH_4ReO_4. Generally, repeated recrystallization is required to achieve the required ammonium perrhenate purity of 99.95%, metal basis.

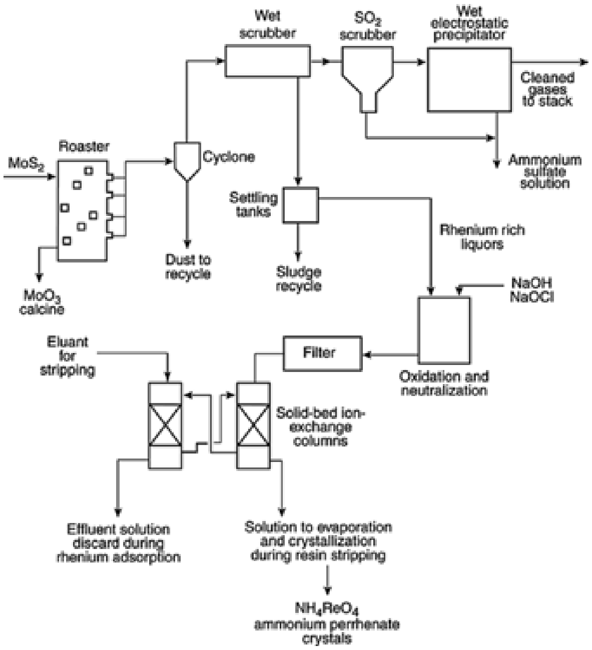

Fig. 2. Typical rhenium recovery process by solid-bed ion-exchange.

Ammonium perrhenate is the starting point for other rhenium chemicals and metal. The most important products beyond ammonium perrhenate are rhenium metal powder and pellets, and perrhenic acid (Fig. 3).

Rhenium metal powder is produced by traditional powder metallurgy techniques. Ammonium perrhenate is reduced using hydrogen in common boats-in-tubes type furnaces. Boats are filled with ammonium perrhenate and pushed through tubes countercurrently to a flow of hydrogen gas. The tubes are externally heated to the appropriate temperature.

Depending on the particle size of the rhenium powder required, the reduction may be a one or two stage process and the ammonium perrhenate may be specially ground before reduction.

Rhenium for alloy production is produced by pressing the powder into pellets of varying sizes but usually 5–8 mm in diameter by 3–5 mm in thickness. The pellets are then sintered to improve physical integrity as well as further reduce gases, especially oxygen.

Metal products such as wire and plate are made by pressing rhenium powder into bars or rods followed by resistance heating to sinter. The sintered rods or bars are then drawn into wire or rolled into sheets or plates. Rhenium can also be deposited on various types of parts and molds using chemical vapor deposition (CVD).

The production of catalysts sometimes requires the use of perrhenic acid, $HReO_4$. This is a solution of rhenium heptoxide, Re_2O_7, in water with a rhenium concentration of 35–50 wt% rhenium contained.

1.5. Shipment

Packaging of rhenium varies in accordance with customer requirements. Ammonium perrhenate is usually packed in plastic bottles of 2–10 pounds but can also be packed in plastic bags in fiber or steel cans. Rhenium powder and pellets are packed in plastic jars, almost always blanketed with argon gas to prevent oxidation and because nitrogen gas reacts with rhenium. Shelf life for powder is excellent. Pellets have an almost unlimited shelf life especially when blanketed with argon.

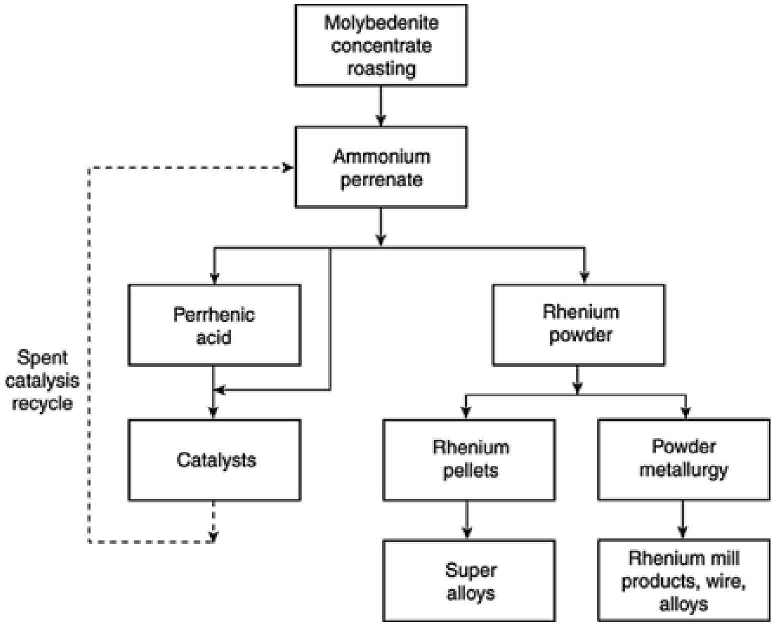

Fig. 3. Rhenium production flow diagram.

Perrhenic acid is generally packed in 1–2-liter plastic bottles but also in 3–5-gallon plastic pails or plastic 35-gallon drums inside 55-gallon plastic drums. All packaging must meet U.S. Department of Transportation regulations for domestic transportation or those of the International Air Transport Association for air transport overseas.

All shipments of other forms of rhenium must be made in accordance with the U.S. DOT regulations pertaining to radioactive materials.

1.6. Economic Aspects

The present low price of copper can also mean a reduction in rhenium production when copper processing facilities that also produce rhenium bearing molybdenite are closed. This has already occurred when BHP closed Pinto Valley and San Manuel, both in Arizona. However, as rhenium prices increase, recovery could be resumed at several locations. Prices have varied widely over the 29–30 years since substantial use began. Prices in the 1960s varied from ca $180–360 kg of Re, but as petroleum reforming catalyst use began, prices rose to a high of about $680/kg of Re. As petroleum requirements were satisfied, prices dipped to below $136/kg of Re. In 1979–1980 a new surge in petroleum requirements occurred and prices rose to ca $1,360/kg of Re. About this time alloy producers became interested in using rhenium but were cautious in their development due to high prices. Ultimately long term contracts were negotiated by aircraft engine producers at prices negotiated and deemed reasonable to producers and users.

Rhenium for use in catalysts is considered by the oil companies as an asset, a capital item and usually not depreciated. Only that portion lost during recycle is written off as the loss occurs. Depending on the price of rhenium and platinum, rhenium represents only 5–11% of the total cost of the catalyst.

As petroleum reforming catalysts are spent, they are removed from service and sent for recovery of the platinum and rhenium from the alumina base. The platinum and rhenium are recovered for recycling to fresh catalyst. The cost to recover the rhenium varies from $36/kg of Re to $82/kg over and above the cost for platinum

Table 5. Alloy Cost verses Rhenium Price

	Alloy cost $/kg			
Re Cost, $/kg Re	0	250	453	907
CMSX-3	4.10			
CMSX-4		12.03	18.16	31.76
CMSX-10		19.40	31.65	58.86
Rene N5		12.16	18.28	31.89

Table 6. Rhenium Portion of Alloy Cost

	Rhenium as % of total alloy cost		
Re Cost, $/kg. Re	250	453	907
CMSX-3			
CMSX-4	62	75	86
CMSX-10	77	86	93
Rene N5	62	74	85

recovery. There have been instances in periods of low rhenium prices when it was less costly for the petroleum user to purchase virgin rhenium than to pay for the recovered rhenium. It is likely though that the rhenium was recovered anyway and retained by the processor for their own use for make-up or later sale when prices rose.

Although petroleum or petrochemical companies may not have been concerned about the cost of rhenium, alloy and aircraft engine producers were most certainly concerned. Early in their development of commercial use, the aircraft engine producers decided to do their own contracting for their rhenium requirements rather than having their alloy melters or casters purchase the rhenium as is done with their other metal requirements. The engine producers negotiated long-term contracts with fixed or formula prices. Thus, they were assured of supply and price.

Using published figures for several super alloys (16) and recent metal prices one can see the price sensitivity of those super alloys to the price of rhenium in Tables 5 and 6.

In addition to the costs illustrated in Tables 5 and 6, the alloy is a direct expense to the engine producer as compared to an asset to a petroleum company. An alloy is not depreciated until it is in an engine on an airplane that is flying.

In addition to supply and demand strongly influencing rhenium prices, it is a costly material to produce. Early efforts at recovery by simple water scrubbing of roaster off-gases resulted in recovery of barely 25% of the rhenium content of the molybdenite. Changes in the roaster-gas scrubbing equipment to improve gas–liquid contact increased the recovery to about 40%. Subsequent improvements, some proprietary, increased recovery to near 80%. There are some reports of near 90%. Since about 10% of the rhenium content of the molybdenite being roasted will remain with the MoO_3 calcine, gas-phase recovery above 90% will probably never be possible.

The cost of capital equipment for rhenium recovery will vary by type of installation or process and degree of complexity. Best estimates for a complete facility to produce ammonium perrhenate and metal powder and pellets would vary from \$15 to $\$30 \times 10^6$ depending on size. This would equate to an annual cost of about \$91/kg Re. Operating costs will add another \$68–90/kg. An annual return on investment of 15% would add another \$90–136/kg and bring the total price to \$250–318/kg Re.

Table 7. Typical Ammonium Perrhenate (NH_4ReO_4) Specifications

Property	Value
appearance	white crystalline powder
purity	
NH_4ReO_4	99.95%
Re	69.35%
impurities, ppm[a]	
aluminum	<5
calcium	<5
copper	<7
iron	<20
lead	<5
magnesium	<1
molybdenum	<35
nickel	<7
potassium	<1
silicon	<10
sodium	<1
tin	<1

[a] Typical.

1.7. Grades and Specification

There is one principal grade of ammonium perrhenate produced in the Western World with only slight variations in Eastern European or CIS material. Sometimes CIS quality is better than Western material, sometimes it is not. Typical specifications are listed in Tables 7, 8, 9. Metal pellets will have an oxygen cap of 500 ppm because of oxygen reduction during sintering.

Rhenium metal powder is usually produced to special screen analyses and/or particle sizes as a function of a customer's requirements. Typical screen sizes are minus 200 or minus 250 mesh with a particle size of 4–6 microns by Fisher Sub Sieve Sizer, and minus 325 mesh with a Fisher number of 2–3 microns.

Rhenium pellets will vary in size depending on producer or customer requirements. Perrhenic acid can be made in various ways using different proprietary processes. The impurities will vary as a function of the raw material.

1.8. Analytical Methods

Rhenium in molybdenite concentrates may best be done by the method developed by Kennecott's Heaney and Malouf (16). That method is the solvent extraction of molybdenum from the rhenium and formation of rhenium thiocyanate complex, followed by ether extraction and spectrophotometric measurement. If this method is used on other materials, care must be exercised to eliminate interference by chromium, niobium, vanadium, and tungsten among others.

Other researchers have developed modifications to this procedure as well as alternative methods (17).

Rhenium content in ammonium perrhenate can be determined by dissolution and measurement by inductively coupled plasma (ICP) mass spectrometry. Another method is the hydrogen reduction of ammonium perrhenate to rhenium metal powder.

Rhenium is usually not determined in pure metal. Instead, Glo discharge mass spectrographic analysis or other spectrographic or spectrophotometric methods are used to determine impurities. Carbon, sulfur, oxygen, and other gaseous impurities are determined by standard gas analytical methods.

Table 8. Typical Rhenium Metal Powder Specifications

Element/impurity	Typical analysis, ppm
Re 99.95% minimum 99.97% typical (exclusive of gases)	
>Al	<5
As	<1
Bi	<1
C	20
Ca	5
Co	<10
Cr	<10
Cu	<10
Fe	<30
H	<10
K	<1
Mg	<1
Mn	<10
Mo	<50
N	<10
Na	<1
Ni	<10
O	<2000
P	<1
Pb	<5
S	<5
Sb	<1
Si	<15
Sn	<1
Ti	<5
W	<50

Table 9. Typical Perrhenic Acid Specifications

Property	Value
appearance	a colorless or straw colored solution
concentration	40% Re (38–42%) 54% $HReO_4$
specific gravity	1.8 gm/cc
	impurities, ppm
Al	<5
Ca	<5
Cu	<7
Fe	<20
Mg	<5
Mn	<10
Mo	<35
Ni	<10
K	<10
Si	<10
Na	<10

Rhenium content of perrhenic acid is determined gravimetrically by precipitation using tetraphenyl arsonium chloride. This method can also be used on ammonium perrhenate (18).

1.9. Recycling and Disposal

Recycling from spent petroleum catalysts was discussed earlier and is routine. Recycling from other sources is not routine and what is done is generally accomplished using the metal, if sufficiently pure in other alloy applications. However, aircraft gas-turbine blades are considered extremely critical with all elements used therein of the highest possible purity. This substantially eliminates the direct recycle of rhenium metal or rhenium alloys to gas turbine blades. Methods to reprocess recycled metal continue to be investigated.

1.10. Environmental Concerns

There are no known concerns about rhenium releases into the environment. Rhenium is considered radioactive in salts and pure metal because of the predominance of the isotope Re 187. However, the very weak beta radiation is not hazardous and because of the high value of rhenium, releases into the environment are unlikely.

1.11. Health and Safety Factors

Although the toxicity of rhenium is unknown, it is believed that hazards are low. Even the radioactivity is so low that it is not a human health hazard. Rhenium salts and metal are considered safe to handle in most ordinary conditions of application. No special precautions are needed beyond those normally used for any chemical or material of low or unknown toxicity. Rhenium is listed in the TSCA inventory but is not listed in CERCLA Section 103 nor in SARA sections 302, 304 or 313. It is also not listed by OSHA, 29CFR 1910.119 or in California Proposition 65.

Rhenium and its compounds must be shipped as radioactive materials in accordance with DOT regulations.

1.12. Uses

Early uses for rhenium were primarily metallurgical, taking advantage of the superior high-temperature resistance as well as improvement in properties of other metals when rhenium is alloyed with those metals. Those uses included pen points and thermocouples. One early use subsequent to World War II was in the 3% Re 97% W alloy used in the “guaranteed to flash” photo flash bulbs. Many other metallurgical applications use small quantities of rhenium, but X-ray targets or anodes were the largest metallurgical consumer until the development of the rhenium-containing nickel-based alloys for the latest generation of aircraft gas turbine engines. Table 10 lists uses of rhenium in 1999.

During the late 1960s rhenium was found to improve the performance of platinum reforming catalysts used to produce more of the high-octane components for gasoline which became necessary as the requirement came to remove lead from gasoline. Lead as tetraethyl lead was once added to 80 octane gasoline to improve the octane rating to 100 or higher. Once the lead could no longer be added, greater quantities of high-octane components such as benzene, xylene and toluene were required to produce 100 octane. Increased production of these components required processes using higher temperatures and pressures, which shortened the life of the mono-metallic platinum catalysts which were being used. Rhenium additions improved the life and performance of the catalysts. Platinum content in monometallic catalysts is 0.3% to 0.8% on an alumina base. Rhenium is added at equal or greater levels depending on the severity of the service.

Table 10. Uses of Rhenium in 1999

Use/market area	% of Total	$\times 10^3$ kg Re Estimated	
aircraft gas turbines	62.0	36	16.3
land based gas turbines	5.2	3	1.36
other metallurgical	10.4	6	2.72
petroleum catalysts	12.0	7	3.18
petrochemical catalysts	10.4	6	2.72
Total	*100.0*	*58*	*26.28*

Table 11. Composition of some of the Single Crystal Aircraft Gas-Turbine Blade Alloys Norminal Composition, wt%[a]

Alloy	Cb	Cr	Co	Mo	W	Ta	Re	Al	Ti	Hf	Ni
Rene N5		7	8	2	5	7	3	6.2		0.2	Bal
PWA1484		5	10	2	6	9	3	5.6		0.1	Bal
CMSX-3		8	5	0.6	8	6		5.6	1.0	0.1	Bal
CMSX-4		6.5	9	0.6	6	6.5	3	5.6	1.0	0.1	Bal
CMSX-10	0.1	2	3	0.4	5	8	6	5.7	0.2	0.03	Bal

[a] Ref. 15.

Development of bimetallic catalysts using less expensive tin with platinum instead of rhenium caused a short-term reduction in rhenium use. However, after several years use, it is recently reported that the Pt–Sn catalysts do not perform as well as expected, and some are now being replaced with Pt–Re catalysts.

The use of rhenium as an alloying agent in aircraft gas turbine components began in earnest in the mid to late 1980's. This is now the primary application of rhenium. Rhenium at 3% to 6% Re in the nickel based hot section turbine blades allows operation at temperatures of 100–200°F higher while maintaining performance and improved life. Early alloys and those in greatest use today are 3% Re while a new generation contains 6%. It is likely the 6% Re alloys will be used primarily in higher performance engines such as military or newer higher-capacity passenger planes because of cost.

Increased operating temperatures results in greater fuel efficiency and greater thrust, with improved overall performance. For a given thrust, lighter engines can be used and it is reported that each one pound saved in engine weight allows an eight pound savings in airframe weight, which in turn allows greater payloads and/or greater range (see Table 11 for composition of aircraft gas-turbine blade alloys).

An alternative to rhenium in the alloy is rhenium coating of blades and end tips. This would result in lower rhenium consumption and could be taken as a result of economics or lack of adequate supplies of rhenium. It has been said that the maximum pricing for rhenium for maximum use is $227–273/kg of Re. Above this price level other alternatives are available and could be used. There is however also the opinion that once incorporated, rhenium use will continue regardless of cost. Still other alternatives include fiber reinforced super alloy components using rhenium–tungsten fibers. These composites are said to provide substantially improved creep resistance as well as high-temperature strength.

Rhenium has proved successful in aircraft gas turbines, thus, manufactures of land-based gas turbines used for primary, as well as emergency power generation, are looking closely at the use of rhenium in those turbine blades. A large problem with these blades is their size and the volume of rhenium that could be consumed. The present limited supply of rhenium could well limit this use.

Other recent developments include new catalysts in petrochemical production. One has replaced silver in the production of ethylene oxide. Several large companies have developed new catalysts for the production of intermediates and precursors for several types of elastomeric materials for a variety of consumer products.

Table 12. Examples of Rhenium Compounds

Oxidation state	Electronic configuration	Coordination number	Metal atom geometry	Example[a]	CAS Registry Number
−I	d^8	5	trigonal bipyramid	$Na(Re(CO)_5)$	[33634-75-2]
0	d^7	6	octahedral	$Re_2(CO)_{10}$	[14285-68-8]
I	d^6		octahedral	$ReCl(CO)_5$	[14099-01-5]
				$K_5[Re(CN)_6]$	[39700-07-7]
				$(Re(CNC_6H_5)_6)I$	[81195-37-1]
				$Re(CO)_3(\eta\text{-}C_5H_5)$	[12079-73-1]
				$ReCl(dppe)_2(N_2)$	[25349-29-5]
II	d^5	6	octahedral	$ReCl_2(dppe)_2$	[109428-32-2]
III	d^4	6	octahedral	$ReCl_3(P(CH_3)_2C_6H_5)_3$	[15613-32-8]
			trigonal prism	$Re(S_2C_2(C_6H_5)_2)_3$	[14264-08-5]
		7		$K_4(Re(CN)_7)\cdot 2H_2O$	[59370-53-5]
			square pyramid	$K_2(Re_2Cl_8)$	[13841-78-6]
		7	capped octahedral	$ReH_3(dppe)_2$	[17300-50-4]
IV	d^3	6	octahedral	K_2ReCl_6	[16940-97-9]
				$ReCl_4$	[13569-71-6]
				$K_4(Re_2OCl_{10})$	[19979-02-3]
V	d^2	6	octahedral	Re_2Cl_{10}	[39368-69-9]
				$ReOCl_3(P(C_6H_5)_3)_2$	[17442-18-1]
				$K_2(ReOCl_5)$	[17443-52-6]
		8		$ReH_5(P(C_6H_5)(C_2H_5)_2)_3$	[12104-30-2]
VI	d^1	5	square pyramid	$ReOCl_4$	[13814-76-1]
		6	octahedral	ReF_6	[10049-17-9]
				$Re(CH_3)_6$	[56090-02-9]
		8	square antiprism	K_2ReF_8	[57300-90-0]
VII	d^0	4	tetrahedral	$KReO_4$	[10466-65-6]
				ReO_3Cl	[7791-09-5]
		4, 6	tetrahedral and octahedral	$(Re_2O_7)_x$	[1314-68-7]
		7	pentagonal bipyramid	ReF_7	[17029-21-9]
		9	tricapped trigonal prism	K_2ReH_9	[25396-46-7]

[a] dppe = 1,2-bis(diphenylphosphino)ethane.

2. Rhenium Compounds

As a general rule, elements in the second and third transition series have similar chemical properties. In contrast, the properties of the first member of the series are often different. This pattern of behavior is seen in Group 7 (VIIB). The properties of rhenium and technetium differ considerably from those of manganese.

Compounds of rhenium having metal oxidation states between -1 and $+7$ are known. As expected, the lower oxidation states $(-1,\ 0,\ +1)$ are encountered only with carbonyl groups and other π-acceptor ligands, and in these oxidation states all elements of this periodic group have fairly similar behavior. There is a significant difference between manganese and rhenium, however. Many more rhenium compounds than manganese compounds having oxidation states of $+4$, $+5$, $+6$, and $+7$ are known. Although rhenium(II) compounds are known to exist as solids and in nonaqueous solution, no aqueous chemistry of the Re^{2+} ion is known. The $+2$ oxidation state is common for manganese.

A particularly significant part of rhenium chemistry involves cluster compounds in which there is metal–metal bonding. This chemistry centers largely around the $+3$ oxidation state.

A survey of known types of rhenium compounds is presented in Table 12. The selected examples include a number of commonly encountered compounds and emphasize the diversity in structures.

2.1. Rhenium Carbonyls and Related Compounds

The parent compound of the low valent rhenium compounds is $Re_2(CO)_{10}$. Dirhenium decacarbonyl [14285-68-8], a white crystalline compound, mp 177°C, is volatile and soluble in most organic solvents. Its preparation in a high pressure reaction between Re_2O_7, H_2, and CO was reported in 1941. It has a molecular structure of two square pyramidal $Re(CO)_5$ groups linked by a metal–metal bond. This compound is available commercially as a specialty chemical. It is the precursor to other low valent rhenium carbonyl compounds, including the halides, $ReX(CO)_5$, where X = Cl, Br, or I; alkyl, aryl, and acyl compounds, $Re(R)(CO)_5$; the hydride complexes $ReH(CO)_5$ [16457-30-0], $Re_2(\mu\text{-}H)_2(CO)_8$ [38887-05-7], and $Re_3(\mu\text{-}H)_3(CO)_{12}$ [12146-47-3]; and hydrocarbon complexes, including $Re(CO)_3(\eta\text{-}C_5H_5)$ and $[Re(NO)(CO)_2(\eta\text{-}C_5H_5)]PF_6$ [12306-73-9]. Research in the 1980s and 1990s has focused on the photochemical activation of H_2 by $Re_2(CO)_{10}$, formation of metal atom clusters, and on the reduction of a coordinated carbon monoxide ligand to methane or methanol. The latter reaction has received much attention because it provides mechanistic information about the Fischer-Tropsch reaction (see Carbonyl; Coal conversion processes).

Pyrolysis of $Re_2(CO)_{10}$ at 400°C *in vacuo* or in an inert atmosphere has been used to obtain pure rhenium metal.

2.2. Oxides and Sulfides

Rhenium reacts with O_2 at moderate temperatures to give the yellow solid $(Re_2O_7)_x$, mp 220°C. This material contains tetrahedral and octahedral rhenium atoms in a lattice structure, so arranged that the formation of molecular Re_2O_7 can readily occur upon vaporization. Perrhenic acid, a strong acid, is formed when $(Re_2O_7)_x$ dissolves in water. It can be isolated upon evaporation of this solvent as crystalline $Re_2O_7{\cdot}2H_2O$ [41017-51-6]. Lower oxides of rhenium, such as ReO_3 [1314-28-9] and ReO_2 [12036-09-8], are formed by heating mixtures of $(Re_2O_7)_x$ and Re in the proper mole ratio. The hydrated compound, $ReO_2{\cdot}2H_2O$ [54706-20-6], is formed by hydrolysis of $[ReCl_6]^{2-}$. A black heptasulfide, Re_2S_7 [12038-67-4], is obtained when a $ReO^-{}_4$ solution in HCl is saturated with H_2S. This may be reduced to ReS_3 [12166-08-4] by H_2 or to ReS_2 upon heating at 750°C under nitrogen. Also, ReS_2 is the product formed by direct reaction of rhenium and sulfur.

Salts of perrhenic acid may be obtained in acid–base reactions, and may include the tetrahedral $ReO^-{}_4$ anion or the octahedral anion $ReO^{5-}{}_6$, eg, in $Ba_5(ReO_6)_2$ [13598-09-9]. Ammonium perrhenate and perrhenic acid, as well as rhenium metal, are sold by the primary suppliers of this element.

Rhenium oxides have been studied as catalyst materials in oxidation reactions of sulfur dioxide to sulfur trioxide, sulfite to sulfate, and nitrite to nitrate. There has been no commercial development in this area. These compounds have also been used as catalysts for reductions, but appear not to have exceptional properties. Rhenium sulfide catalysts have been used for hydrogenations of organic compounds, including benzene and styrene, and for dehydrogenation of alcohols to give aldehydes (qv) and ketones (qv). The significant property of these catalyst systems is that they are not poisoned by sulfur compounds.

2.3. Rhenium Halides and Halide Complexes

Rhenium reacts with chlorine at ca 600°C to produce rhenium pentachloride [39368-69-9], Re_2Cl_{10}, a volatile species that is dimeric via bridging halide groups. Rhenium reacts with elemental bromine in a similar fashion, but the metal is unreactive toward iodine. The compounds $ReCl_4$, $ReBr_4$ [36753-03-4], and ReI_4 [59301-47-2] can be prepared by careful evaporation of a solution of $HReO_4$ and HX. Substantiation in a modern laboratory would be desirable. Lower oxidation state halides $(Re_3X_9)_x$ are also prepared from the pentavalent or tetravalent compounds by thermal decomposition or chemical reduction.

Many coordination complexes of these halide complexes are known. More common examples have the formulas ReX_4L_2, $(Re_2X_8)^{2-}$, $Re_3X_9L_3$, and $(Re_3X_{12})^{3-}$, where L indicates a ligand and X is a halide ion.

Rhenium(IV) complexes form in reductive reactions between the ligand and Re_2Cl_{10}. For example, reduction occurs spontaneously when Re_2Cl_{10} dissolves in acetonitrile, giving the product $ReCl_4(NCCH_3)_2$ [116853-53-5]. The complexes of rhenium(III) are obtained from $(Re_3Cl_9)_x$, $(Re_3Br_9)_x$ [13569-49-8], and $(Re_3I_9)_x$ [15622-42-11] and added ligand. Rhenium(III) complexes contain metal–metal bonds. The structure of $[Re_2Cl_8]^{2-}$ has two square planar $ReCl_4$ units linked by a short (0.2237-nm) rhenium–rhenium quadruple bond. In salts of $[Re_3X_{12}]^{3-}$ there is a triangle of rhenium atoms, linked by metal–metal single bonds (ca 0.25 nm) and bridging halide atoms. The same triangular metal structural unit is retained in polymeric $(Re_3X_9)_x$.

2.4. Rhenium Hydrides and Alkyls

Reduction of $KReO_4$ by potassium in ethanol gives K_2ReH_9 [25396-46-7]. The identity of this compound was unknown until its structure was determined by a neutron diffraction study. The anion contains rhenium and nine hydride ligands in a tricapped trigonal prismatic arrangement. Reactions of this species with various phosphines give $(ReH_8L)^-$, ReH_7L_2, and ReH_5L_3, where L = tertiary phosphines. The neutral complexes are also formed from phosphine–rhenium halide complexes with $LiAlH_4$. Reactions of these complexes with unsaturated hydrocarbons have been much studied as models for various catalysts.

Compounds of the formulas $Re(CH_3)_6$, $ReO(CH_3)_4$, $Li_2[Re_2(CH_3)_8]$ [60975-25-9], $ReO_2(CH_3)_3$ [56090-011-8], and ReO_3CH_3 [70197-13-6] have been prepared. The first two compounds were obtained from reaction of rhenium halides or oxyhalides and methyllithium; the last three were formed from the species by oxidation or reduction reactions. The use of these hydride and alkyl complexes as catalysts is under investigation.

2.5. Health and Safety Factors

Little is known concerning the toxicology of rhenium or its compounds. Rhenium heptoxide is said to be an irritant if inhaled.

BIBLIOGRAPHY

"Rhenium and Rhenium Compounds" in *ECT* 1st ed., Vol. 11, pp. 721–730, by C. F. Hiskey, Polytechnic Institute of Brooklyn; "Rhenium" in *ECT* 2nd ed., Vol. 17, pp. 411– 423, by J. H. Port, Cleveland Refractory Metals Division, Chase Brass and Copper Co., Inc.; "Rhenium and Rhenium Compounds" in *ECT* 3rd ed., Vol. 20, pp. 249–258, by P. M. Treichel, University of Wisconsin; "Rhenium and Rhenium Compounds" in *ECT* 4th ed., Vol. 21, pp. 335–346, by Paul M. Treichel, Jr., University of Wisconsin, Madison; "Rhenium and Rhenium Compounds" in *ECT* (online), posting date: December 4, 2000, by P. M. Triechel, University of Wisconsin.

Cited Publications

1. F. Habashi, "Rhenium Seventy Years Old", in B. D. Bryskin, ed., *Rhenium and Rhenium Alloys*, TMS, 1996.
2. V. Dolejsek and J. Heyrovsky, *Nature* **116** (2926) 782–783 (Nov. 28, 1925).
3. F. H. Loring and J. G. F. Druce, *Chemical News* **131**, 337, (1925).
4. L. C. Hurd, *J. Chem. Ed.*, 605–608, (Oct. 1933).
5. K. B. Lebedev, *The Chemistry of Rhenium*, translated from the Russian by L. Ronson and A.A. Woolf, Butterworth's, London, 1962.
6. U.S. Patent 2,414,965 (1947) A. D. Melaven and J. A. Bacon.
7. A. Sutulov, *Molybdenum and Rhenium Recovery from Porphyry Coppers*, University of Concepcion, Chile, 1970.
8. A. Sutulov, *Molybdenum and Rhenium* 1778–1977, University of Concepcion, Chile, 1976.
9. A. M. Chekmarev and I. D. Troshkina, "Rhenium Recovery from Non-Traditional Resource", in B. D. Bryskin, ed., *Rhenium and Rhenium Alloys*, TMS, 1996.

10. A. D. Besser and co-workers, "The Perspectives of the Development of Rhenium's Production In Russia", in B.D. Bryskin, ed., *Rhenium and Rhenium Alloys*, TMS, 1996.
11. D. Lide, ed.-in-chief, *CRC Handbook of Chemistry and Physics*, 73d ed., CRC Press, Inc., 1992.
12. J. Johnson, Colorado State University, personal communication, 1989.
13. J. Port, Cleveland Refractory Metals, personal communication, 1965.
14. J. R. Wooten and P. T. Lanshaw, "The Enabling Technology for Long-life, High Performance On-Orbit and Orbit-Transfer Propulsion Systems: High Temperature Oxidation Resistant Thrust Chambers", *Proceedings JANNAP Propulsion Meeting*, Laurel, MD, 1989.
15. Based on information from the U.S. Bureau of Mines/USGS Mineral Information Service, J. W. Blossom, and U.S. Department of Commerce.
16. R. J. Heaney and E. E. Malouf, "The Spectrophotometric Determination of Rhenium, A Critical Evaluation", in B. W. Gonser, ed., *Rhenium, Proceedings of the Symposium on Rhenium of the Electrothermics and Metallurgy Division of the Electrochemical Society*, Elsevier, 1960.
17. S. Tribilat, "A Survey of the Different Methods for the Determination of Rhenium," in B. W. Gonser, ed., *Rhenium, Proceedings of the Symposium on Rhenium of the Electrothermics and Metallurgy Division of the Electrochemical Society*, Elsevier, 1960.
18. R. D. Peacock, *The Chemistry of Technecium and Rhenium*, Elsevier, 1966.

General References

19. R. D. Peacock in A. F. Trotman-Dickinson, ed., *Comprehensive Inorganic Chemistry*, Vol. **3**, Pergamon Press, London, 1973, p. 905.
20. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley-Interscience, New York, 1988, p. 847.
21. L. J. Alverson, "Rhenium," in *Minerals Yearbook*, Vol. **1**, Bureau of Mines, U.S. Government Printing Office, Washington, D.C., 1980, p. 743.
22. D. F. C. Morris and E. L. Short, *Handbook of Geochemistry*, Springer-Verlag, Heidelberg, Germany, 1965, p. 75–1.
23. R. D. Peacock, *The Chemistry of Technetium and Rhenium*, Elsevier, Amsterdam, the Netherlands, 1966.
24. R. Colton, *The Chemistry of Rhenium and Technetium*, Wiley-Interscience, New York, 1965.
25. G. Rouschias, *Chem. Rev.* **74**, 531 (1974).
26. K. A. Conner and R. A. Walton, *Rhenium*, in G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., *Comprehensive Coordination Chemistry*, Vol. **4**, Pergamon Press, London, 1987, p. 125.

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