

## RHENIUM

*By Tom A. Millensifer  
VP, Powmet Inc*

**D**emand for rhenium began a noticeable journey upward in mid 2000 and continues at a moderate pace. Prices have escalated accordingly. Production of rhenium has been stable during this period and as a result has sparked some of the buying activity on the part of several traders.

Rhenium consumption has increased in the past year both metallurgically and chemically. Rhenium use in single crystal alloys has increased due to growing demand from the gas turbine sector. New catalyst applications, as well as changes in existing applications, has also created increased demand. It is anticipated that strong aircraft demand for rhenium will continue at least through 2002. However, there is some question about an adequate supply to satisfy the increased demand. Some believe that supply and demand are in balance for the near term, but show signs of an imbalance in the future. Many believe there is more than adequate availability to meet increased demand well into the future.

Total US imports in year 2000 increased 16.5% over 1999, with rhenium metal imports decreasing in year 2000 by about 3% from 28,129 lb to 27,358 lb. Ammonium perrhenate imports increased 107% from 5,953 lb Re contained to 12,352 lb Re contained. This was a result of a more than three-fold increase in ammonium perrhenate imports from Kazakhstan. These imports increased from 2,361 lb Re to 9,720 lb Re contained in year 2000.

Increasing quantities of rhenium are being used in Europe, and US imports can no longer be used as a true measure of total rhenium consumption, but only an indication.

### **Occurrence**

By- or co-product molybdenite recovered from porphyry copper deposits in the US and Chile remains the primary source of rhenium. Occurrences other than molybdenite are reported, especially in a copper-rhenium sulphide mined and processed in Kazakhstan. This was the primary source of rhenium in the former Soviet Union and is today the largest potential source outside the Western World.

The rhenium content of a molybdenite ore apparently varies with the temperature at which the mineralisation was formed. Molybdenite associated with copper was deposited at a lower temperature and contains much more rhenium than the primary molybdenites formed at much higher temperatures.

There continue to be reports of the discovery of rhenium at significant levels in the gases from several volcanoes in the Kurile Islands north of Japan. There are reports that attempts are being made to collect those gases and recover the rhenium. Recoveries are estimated to reach 2,000-3,000 lb/y. Other potential sources that continue to be investigated include petroleum ash and oil shales in Russia, as well as the copper recovered as a by-product of nickel from Russia's Norilsk Nickel operation. Uranium ores mined in Texas, south of San Antonio, were once a source of significant quantities of rhenium, but those mines ceased operation some time ago.

### **Properties**

Rhenium, element No. 75 in the Periodic Table, is composed of two naturally occurring isotopes. Rhenium 187 comprises 62.6% of natural rhenium while the other 37.4% is rhenium 185. The accepted atomic weight is

185.26 though values between 185.21 and 185.31 are reported.

The most abundant isotope, 187, is also the radioactive isotope. It is reported to have a half life of  $4.3 \times 10^{10}$  years. However, the radiation is very weak beta radiation (0.3 Mev) and cannot penetrate beyond the dead skin cells on the surface of the body. Radiation is so weak that it cannot be measured by typical field instruments, only by sophisticated laboratory equipment.

Rhenium chemicals and rhenium metal do exceed the 'specific activity' limits of US and international transport agencies. However, labelling regulations differ slightly and current regulations should be consulted for details. Because the radiation hazard from rhenium is so minimal, regulations governing shipping and exposure are very liberal.

Rhenium has physical properties similar to the refractory metals of Group IV of the Periodic Table, molybdenum and tungsten. However, chemical properties more closely resemble those of Group VII metals.

Rhenium is considered a refractory metal like molybdenum and tungsten and has a melting point of nearly 3,200°C, second only to tungsten. The specific gravity of 21.02 is greater than tungsten (19.25) and uranium (19.05) and more than double that of molybdenum (10.28). Platinum and osmium are the only other natural elements with specific gravities greater than rhenium. Metallurgically, rhenium resembles the other refractory metals in many of its properties and reactions, but it does not form carbides as do molybdenum and tungsten.

The unique metallurgical properties of rhenium and its improvement to alloys in which it is incorporated are a result of rhenium maintaining its hexagonal close-packed crystal structure to the melting point of 3,180°C. The improvement that rhenium imparts to alloys extends to additions of as little as 2-3% Re to as much as 50%.

Rhenium improves the ductility of both molybdenum and tungsten.

The electrical resistivity of rhenium is nearly four times that of both molybdenum and tungsten. Only osmium and iridium have a modulus of elasticity greater than rhenium. It is also more resistant to oxidation than tungsten.

Rhenium exists chemically in valence states from minus 1 to plus 7. A total of eight rhenium oxides are reported, but the most stable are rhenium dioxide,  $\text{ReO}_2$ , a black to brown oxide, red rhenium trioxide,  $\text{ReO}_3$ , and yellow rhenium heptoxide,  $\text{Re}_2\text{O}_7$ . This latter oxide is hygroscopic and takes water from the air very quickly to become perrhenic acid,  $\text{HReO}_4$ .

The recovery of rhenium from the primary source, molybdenite, is accomplished because of the fact that rhenium heptoxide melts and boils below 400°C. During the roasting/oxidation of molybdenite,  $\text{MoS}_2$ , to  $\text{MoO}_3$ , rhenium volatilizes as  $\text{Re}_2\text{O}_7$ . Recovery is then achieved by wet scrubbing of the molybdenite roaster stack gases and in at least two cases from copper smelting.

As with the refractory metals of molybdenum and tungsten, rhenium forms many perrhenates. Ammonium perrhenate is the most common and the primary commercial form. It is also the form in which rhenium is today recovered from chemical processing of stack gas scrub liquors, though original recovery methods relied on recovery as potassium or sodium perrhenates.

Many other perrhenates can be prepared, but none have the commercial importance of ammonium perrhenate which is the form used to reach the corresponding metal.

### Uses

Rhenium's physical properties were the first to be recognised through its combination with platinum in pen points. Additions of as little as 2% improved wear resistance. The

temperature resistance of rhenium later resulted in its use in heating elements, electrical contacts, thermocouples, special wire and components in electronic tubes. One important use today is as an alloy of 8-10% rhenium in the tungsten surface of higher energy X-ray targets.

During the early years following the discovery of rhenium, interest centered on the chemistry of this new element. This continued through the 1940s. Beginning in the 1950s, particularly in the former Soviet Union, the use of rhenium in alloys gained strong academic interest, as well as greater commercial interest.

In the late 1960s interest in rhenium moved again to the chemical properties especially in catalysis. It was found to improve the life of platinum-reforming catalysts in the severe operating conditions necessary to produce greater volumes of lead-free high octane gasoline. Rhenium consumption reached 2,000 lb in 1968 before its use in catalysts. Consumption then grew to almost 8,000 lb Re per year by 1971 due to its use in catalysts.

Consumption continued to climb to a peak of about 13,000 lb in 1978 as catalyst use grew. Recycling of rhenium from spent catalysts then slowed growth in primary consumption. Most recently, the development of a new platinum-tin catalyst for use in continuous catalyst regeneration (CCR) reactors further slowed the use of rhenium. While platinum-rhenium catalysts can be used in the new CCR reactors, the platinum-tin catalysts cannot be used in the original fixed-bed reformers.

Significant research and development continues into the use of other catalysts using rhenium in

combination with one or more other metals, usually those from the platinum group metals. At least two new catalysts are being used extensively in two new petrochemical applications, and others are being considered.

Rhenium metal and high temperature resistant alloys of rhenium continue to dominate rhenium use. Many of the rhenium-bearing, heat-resistant alloys retain their strength and hardness to temperatures of over 1,000°C. Many are also acid resistant. Significant quantities of rhenium in alloys began in 1984 with the development of 3% rhenium-bearing nickel-based alloys for use in hot section aircraft engine turbine blades. This remains today where the greatest volume of rhenium is used, and is growing as alloys with a rhenium content of 5-7% are used in some high performance engines. The result is an engine with possibly 6% in the first section blades and 3% in the second section. Alloys with a rhenium content as high as 10% are now being investigated. However, little added benefit is gained at this level unless a small level of another unspecified platinum group metal is also added to the alloy.

### Supply and Demand

In 1987, there were ten producers of rhenium in the Western World with a production

Estimated Primary Rhenium Production (lb)				
Company	Location	Source	Estimated Capacity	Estimated Recovery
Molymet	Chile	MoS <sub>2</sub> Conc.	38,000	35,000
Codelco	Chile	MoS <sub>2</sub> Conc.	8,000	-0-
Phelps Dodge	US	MoS <sub>2</sub> Conc.	16,000	14,000
Starck	Germany	Residue	8,000	5,000
Sumitomo	Japan	Cu Conc.	8,000	-0-
Samsung	Kazakhstan	Cu Conc.	40,000	20,000
Lurgi-Willowbank	Uzbekistan	MoS <sub>2</sub> Conc.	5,000	2,000
Various	Russia	MoS <sub>2</sub> Conc.	5,000	2,000
<b>Total</b>			<b>128,000</b>	<b>78,000</b>

Production and capacity data are estimates. Actual figures continue to be held confidential. The above figures do not include recycled material from petroleum and petrochemical catalysts and metal scrap.

capability of about 40,000 lb. By 1992, the Western World had only six producers but a capacity of 69,000 lb, an increase of over 70%. Today, primary production capacity including the former Soviet Union, is estimated at 128,000 lb Re, but actual production is now estimated at about 78,000 lb of contained rhenium.

Future production will be a function of demand. But use may be limited by production. The BHP property at San Manuel, Arizona continues closed and this has taken 6,000 lb/y of primary rhenium out of available supply.

<b>Expected Near Term World Wide Demand</b>	
<b>Use</b>	<b>lb Re</b>
Mill products & Powders	7,000
X-Ray Targets	6,000
<b>Catalysts:</b>	
Petroleum	10,000
Petrochemical	6,500
Aircraft Turbines	50,000
Land-based Turbines	3,000
<b>Total</b>	<b>82,500</b>

From these supply and demand figures it would appear that there is a slight annual rhenium deficit of perhaps 4,200 lb. This is probably compensated by rhenium obtained from the recycling of petroleum and petrochemical catalysts and metal scrap. Certainly the capacity to produce more rhenium is available.

**Pricing**

Increased demand has caused prices to increase, but speculation by traders could also be a cause. Prices in 1999 and early 2000 had decreased to below US\$300/lb for ammonium perrhenate. Metal prices were US\$500-550/lb on the average primarily due to contract agreements. Today prices in general have increased to US\$600-725/lb Re for ammonium perrhenate on the spot market, while spot metal is priced from US\$650-800/lb. There are reports of lower prices, but these are usually long term contracts and, as has always been the case, confidentiality clouds the picture.

**Outlook**

Demand has increased, and is likely to continue to increase, as more new catalyst uses develop and metallurgical use escalates in aircraft turbines and use begins in land-based turbines. Historically, increased prices have lagged demand. This

<b>Imports into the US for 1999 and 2000</b>						
Source	1999			2000		
	Imports (lb)	Value ('000 US\$)	(US\$/lb Re)	Imports (lb)	Value ('000 US\$)	(US\$/lb Re)
<b>Rhenium metal</b>						
Chile	22,227	11,209	504	21,716	10,091	465
Kazakhstan	-0	-	-	3,728	896	240
Germany	3,642	1,999	549	661	263	398
Others*	2,260	794	352	1,253	453	361
<b>Total</b>	<b>28,129</b>	<b>14,002</b>	<b>498</b>	<b>27,358</b>	<b>11,703</b>	<b>428</b>
<b>Ammonium perrhenate</b>						
Chile	1,720	691	402	-	-	-
Kazakhstan	2,361	614	260	9,720	2,100	216
Germany	-	-	-	403	130	322
Other*	1,872	380	203	2,229	671	301
<b>Total</b>	<b>5,953</b>	<b>1,685</b>	<b>284</b>	<b>12,352</b>	<b>2,901</b>	<b>229</b>

\*UK, Eastern Europe

rule seems no longer valid as currently prices have increased along with demand. Even though we have an increase in production in Kazakhstan with supply and demand relatively in balance, the long-term outlook could be grim. It remains a function of maintaining sufficient production as demand increases. Certainly, capacity is available for an increase in production. One of the challenges is to route the rhenium-bearing molybdenite to roasters where the rhenium can be recovered. There is a substantial volume of molybdenite

concentrates containing significant levels of rhenium being roasted where rhenium cannot be recovered. These have to be moved to other roasters, or given enough value, rhenium recovery facilities installed on those roasters where they do not now exist.

Many other new uses, chemical and metallurgical, continue to be investigated. Rocket thrusters made of rhenium through a new process to reduce time and cost of production are being investigated by NASA.