

# RHENIUM

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**T**he increased demand for rhenium continued well into 2001 and was on a significant upward move until September 11. As has been well reported since the terrorist attack, the aircraft industry has reduced production of passenger aircraft and therefore engines (reduced rhenium consumption is a result). This is tempered to some extent by the war on terrorism and retrofitting of military aircraft. In addition, consumption of rhenium in the production of land-based or industrial gas turbines (IGTs) is on the decrease, but these alloys for industrial gas turbines are produced by the aircraft alloy producers, and in some cases the rhenium is purchased by the aircraft engine producers. This can distort the picture of use between aircraft engines and IGTs.

Total US imports of rhenium in 2001 increased nearly 20% over 2000, climbing from 39,710 lb to 47,255 lb Re contained. Ammonium perrhenate imports decreased by 43.6% from 12,352 lb to 6971 lb, while rhenium metal imports increased 47.2% from 27,358 lb Re to 40,284 lb Re.

Use in Europe was less clear in 2001 than it was in year 2000, but appears to have decreased, especially in alloys. However, catalyst use is on the increase as Pt-Re bi-metallic reforming catalysts increase in use in Eastern Europe, particularly in Russia.

## History

While their claims were disputed, Walter Noddack and Ida Take (who later became Mrs Noddack), along with Otto Berg, claimed the discovery of rhenium in 1925 and are consistently given credit for the discovery.

Recovery of significant quantities of rhenium for the limited industrial use at the time was from potash and copper smelter residues in Mansfield, Germany. These residues

remained the primary source of rhenium until World War II.

US rhenium production began in 1942 at the University of Tennessee. Professors A.D. Melaven and J.D. Bacon, along with graduate students, recovered rhenium from the Miami Copper Co. molybdenite roaster flue dusts. They patented their process in 1947.

Kennecott Copper Co. began rhenium production in 1956 at Washington, Pennsylvania, where Kennecott's molybdenite concentrates were being roasted. Kennecott researchers were issued numerous patents for their methods of recovery.

In 1961, Shattuck Chemical Co. in Denver, Colorado, and others, began recovery of rhenium including Starck in Germany and Carbuco y Metallurgia (now Molymet) in Chile. Molymet today is reported to be the world's largest producer.

## Occurrence

By- or co-product molybdenite recovered from porphyry copper deposits in the US and Chile continues to be the primary source of rhenium. There is significant production in Kazakhstan from a copper-rhenium sulphide deposit at Dzezhkazan. This was the primary source of rhenium in the Former Soviet Union and is the largest potential non-western source.

Reports about the occurrence of rhenium at high levels in the gases from the Kudriav volcano in the Kuril Islands north of Japan continue. There may now be production from Kudriav, where wooden collection devices are said to have been constructed over one of the volcano's vents. It was here in 1992 that rhenium sulphide chunks without contamination of other metals were discovered. It has been called rheniite, and was originally thought to be molybdenum

sulphide. This is the only place in the world where a purely rhenium mineral has been discovered. A specimen was recently presented to the National Mining Hall of Fame and Museum at Leadville, Colorado.

There are other sources of interest and possible recovery. These include oil shale and petroleum ash from Russia and other locations. Copper recovered from nickel operations at Norilsk is another possible source.

### 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.

The 187 isotope is also the radioactive isotope. The half life is reported as  $4.3 \times 10^{10}$  years. The radiation is very weak beta radiation (0.3 Mev). It cannot penetrate beyond the dead skin cells on the surface of the body and can be measured 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  $3,200^{\circ}\text{C}$ , second only to tungsten. The relative density of 21.02 is greater than tungsten and uranium and more than double that of molybdenum. Platinum and osmium are the only other natural elements with relative densities greater than rhenium.

Metallurgically, rhenium resembles the other refractory metals in many of its properties and reactions, but it does not form carbides.

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  $3,180^{\circ}\text{C}$ . 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 one to plus seven. 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 heptoxide 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  $400^{\circ}\text{C}$ . During the roasting/oxidation of molybdenite,  $\text{MoS}_2$ , to  $\text{MoO}_3$ , rhenium volatilises 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.

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.

It has been suggested that calling the salts of rhenium 'perrhenate' is a misnomer as perrhenates are not oxidisers as are permanganates. There are those, however, who insist on shipping any perrhenate as an 'oxidiser' despite tests to the contrary.

### Uses

Rhenium's physical properties were first utilised 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 with tungsten in the surface of higher energy X-ray targets.

During the early years following the discovery of rhenium, interest was in the chemistry of this new element. This continued through the 1940s. Beginning in the 1950s, particularly in the Former Soviet Union (FSU), the use of rhenium in alloys gained strong academic and commercial interest.

In the late 1960s, interest in rhenium moved again to the chemical properties, especially in catalysis. Chevron and UOP nearly simultaneously discovered that rhenium improved the life of platinum-reforming catalysts in the severe operating conditions necessary to produce greater volumes of lead-free high octane gasoline. Rheniforming was born. Rhenium consumption reached only 2,000 lb in 1968 prior to the use in catalysts. Consumption then grew to almost 8,000 lb/y Re by 1971.

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. 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.

There are continuing investigations into the use of rhenium in other catalysts, usually in combination with one or more other metals from the platinum group. At least two new

### Estimated Primary Rhenium Production (lb)

Company	Location	Estimated Source	Estimated Capacity	Estimated Recovery
Molymet	Chile	MoS <sub>2</sub> conc.	40,000	38,000
Codelco	Chile	MoS <sub>2</sub> conc.	8,000	0
Phelps Dodge	Sierrita AZ, US	MoS <sub>2</sub> conc.	16,000	11,000
Starck	Germany	Residue	8,000	5,000
Sumitomo	Japan	Cu conc.	8,000	0
Redsvetmet	Kazakhstan	Cu conc.	40,000	25,000
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>130,000</b>	<b>83,000</b>

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 rhenium use in alloys began in 1984 with the development of 3% rhenium-bearing nickel-based alloys for hot section aircraft engine turbine blades. This remains where the greatest volume of rhenium is used and is growing as alloys with a rhenium content of 5-7% begin to be 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% have been investigated. Little added benefit is said to be gained at this level unless a small amount of another unspecified platinum group metal is also added to the alloy.

### US Imports

Source	2000			2001		
	Lb Re	US\$ '000	Average US\$/lb Re	Lb Re	US\$ '000	Average US\$/lb Re
<b>Rhenium Metal</b>						
Chile	21,716	10,091	465	36,297	16,531	455
Kazakhstan	3,728	896	240	1,510	462	306
Germany	661	263	398	505	204	404
Others*	1,253	453	361	1,972	788	400
<b>Totals</b>	<b>27,358</b>	<b>11,703</b>	<b>428</b>	<b>40,284</b>	<b>17,985</b>	<b>446</b>
<b>Ammonium Perrhenate</b>						
Chile	-	-	-	-	-	-
Kazakhstan	9,720	2,100	216	5,562	2,926	526
Germany	403	130	322	611	338	553
Other*	2,229	671	301	798	342	428
<b>Totals</b>	<b>12,352</b>	<b>2,901</b>	<b>229</b>	<b>6,971</b>	<b>3,606</b>	<b>517</b>

\*UK, Eastern Europe, China

### Supply and Demand

There were ten Western producers of rhenium in 1987 with a production capability of about 40,000 lb. By 1992 the number had dropped to just six producers but the capacity had increased over 70% to 69,000 lb. Today, primary production capacity including the FSU is estimated at 130,000 lb Re, but actual production is now estimated at about 83,000 lbs Re contained:

Production and capacity data are estimates. Actual figures continue to be difficult to obtain. The above figures do not include recycle from petroleum and petrochemical catalysts and metal scrap.

Future production will be a function of demand. But use could be limited by production. The BHP property at San Manuel, Arizona continues closed and this has taken 6,000 lb/y primary rhenium out of available supply. Reduction of copper production at Phelps Dodge's Sierrita operation has also reduced molybdenite production and hence also rhenium.

From these supply and demand figures it would appear that there is now a 10% greater production than consumption caused by both increased production and reduced consumption.

### Pricing

Increased use and trader speculation had caused prices to increase prior to September 11 to levels above US\$800/lb Re for ammonium perrhenate. Now prices are in the range of US\$600-650/lb Re contained for ammonium perrhenate with metal pricing US\$750-800/lb.

With consumption down and production up, it is expected that prices will remain relatively stable for the near future. Some minor price increases or decreases may occur, but certainly no wild swings are expected.

### Outlook

Consumption has decreased since September 11, and there is today adequate rhenium available to supply that decreased market. What happens next looms as a large question with the result depending on the world's economic recovery and especially aircraft production. Should the recovery be rapid, a significant rhenium shortage could again develop quickly. It is, however, expected that there will be sufficient rhenium available to meet demand at least for the next few years. There is still sufficient capacity

available to increase production if the need arises and the molybdenite is available from which to recover the rhenium.

While there have been significant decreases in the production of molybdenite, most of those have come from primary mines where there is no recoverable rhenium in the concentrates. The primary mines are generally the swing producers today and are the first to curtail production while the copper co- and by-product mines with rhenium are cut back only when the copper market is bad. It is then the co-product mines which are the first to follow the primary mines in shutting down or reducing production. They may in turn then be followed by the high cost by-product mines.

### Expected Near Term World Wide Demand

Use	lb Re
Mill products & Powders	7,000
X-Ray Targets	6,000
Catalysts:	
Petroleum	10,000
Petrochemical	6,000
Aircraft Turbines	40,000
Land-based Turbines	6,000
<b>Total</b>	<b>75,000</b>