# Rhenium

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At the time of writing, autumn 2005, questions are being asked about the link between global warming and extreme weather, and it is, perhaps, not a bad time to consider a metal whose two main consumption areas are in the fields of energy and energy savings. Rhenium's main applications are in high-temperature alloys used in aerospace, and in catalysts for oil.

This year's review examines how the supply side is coping with these twin demands and whether any new applications are coming through. Some of the politics behind rhenium supply are described and the outlook for rhenium prices is examined.

**Mode of occurrence**
In 1925 two young German physicists, Walter Noddack and Ida Tacke (who were later to marry) separated 10 parts per million of material from a sample of gadolinite, and named the material rhenium after their native River Rhine. Subsequently, they produced a gram of rhenium from 660 kg of molybdenite from Scandinavia, establishing for the first time that most rhenium would be recovered from molybdenite, itself mainly produced as a by-product of copper mining.

Today, rhenium ranks with the platinum group metals as one of the most precious traded mineral commodities. It is rare, averaging not more than 4 parts per billion in the Earth's crust and nowhere is rhenium mined as the main product.

It occurs principally in porphyry copper deposits but is only recovered at those mining operations that generate by-product molybdenum sulphide concentrates, and then, only when a circuit exists at the molybdenum roaster that employs wet scrubbing of the flue dusts (which contain the rhenium in oxide form as $Re_20_7$). The exception to the rule is in Kazakhstan where a unique sedimentary ore, dzezhkazganite contains rhenium but no molybdenum.

**Recovery**
The roasting of molybdenum sulphide concentrate produces molybdenum trioxide. Rhenium's greater affinity for oxygen, however, means that it passes up the flue with the sulphur emission. The sulphur is captured and turned into sulphuric acid and when the flue dusts are wet scrubbed, the rhenium passes into the acid for subsequent recovery. Where environmental rules are relaxed and no desulphurisation occurs, the rhenium is lost to the atmosphere.

In Chile, molybdenum sulphide concentrate is separated from copper concentrate by conventional flotation and contains an average of about 250 g/t Re, close to the minimum required for viable recovery. The highest commercially recorded level of rhenium in $MoS_2$ was 1,000 ppm at Island

Copper in Canada (now closed). The highest commercially viable rhenium contents in $MoS_2$ at existing operations are found at Sar Cheshmeh in Iran (650 ppm) and at Kadzharan and Agarak in Armenia (700 ppm).

**Products**

The most common form in which rhenium is precipitated prior to conversion or upgrading is ammonium perrhenate ($NH_4ReO_4$). This is a white crystalline, free-flowing, stable and non-hazardous powder containing 68.5-69.4% Re. A typical specification of 'basic grade' ammonium perrhenate (APR) is issued by the London-based Minor Metals Trade Association (MMTA), which provides industry-guideline chemistries for a wide range of minor metals. (These can be found under the 'Metal Norms' section on the MMTA's website: www.mmta.co.uk) The MMTA also publishes a specification for 'metal' and 'catalyst' grades of APR, each of which requires precise control of a range of other elemental impurities. In alloying applications, APR, once purified, is usually reduced to rhenium metal powder and then sintered into small 20-25 gram pellets for exact additions. In catalyst applications, APR is sometimes converted into perrhenic acid.

**Primary supply**

Rhenium is recovered as a by-product of copper mining and hence the supply of rhenium is governed entirely by copper output. It is not possible to talk of rhenium and not refer to Molybdenos y Metales SA of Chile (Molymet) although the company gives out very little information publicly about its rhenium recovery or production.

Molymet is the world's largest producer of rhenium and dominates the market. Through Molymet, Chile is the world's largest producer of rhenium and the cornerstone of supply. Three big copper mines – Chuquicamata, Disputada and Los Pelambres – are the main sources of rhenium-bearing by-product molybdenum sulphide concentrates for Molymet's roasters.

Molymet's roasting capacity in Chile is situated at Nos, 35 km south of the capital, Santiago. A large proportion of its concentrates comes from Chuquicamata, Codelco's largest operation. Codelco does have its own molybdenum roaster on site at Chuquicamata but its rhenium recovery circuit was dismantled more than ten years ago, hence any rhenium contained in the $MoS_2$ roasted there is now lost.

At Nos, rhenium is obtained at the wet scrubbing stage, when flue dusts are recovered and sulphuric acid produced as a by-product. This is done for environmental reasons but at the same time has the effect of capturing the potentially lost rhenium, which otherwise would be lost to the atmosphere. Molymet operates the largest roaster of molybdenum sulphide concentrates in South America (with an annual capacity of 46 Mlb/y of contained molybdenum) and is also the largest producer of rhenium. In 2005, rhenium production is expected to be back to around 20 t, up from less than 16 t in 2004.

Molymet plans to expand in its roasting capacity. Although this is primarily a response to the current strong demand for molybdenum, it also means that greater quantities of rhenium are likely to be produced. Certainly, the market will depend upon such an increase in the supply of rhenium units as consumption of rhenium grows year-on-year.

Molymet produces and processes close to 50 Mlb/y of molybdenum in Chile, plus 15-20 Mlb/y in Mexico (Molymex) and a further 20 Mlb/y at its Sadaci roaster in Belgium. The company has been recovering rhenium for more than 40 years and its position is almost unassailable. Based on official figures from Banco Central de Chile, Molymet exported 15.95 t of rhenium in various forms in 2004, and 12.9 t in the first half of 2005 (Table 1). The supply of rhenium has risen as a result of the strong demand (and prices) for copper and molybdenum, and output in Chile would have been higher but for some decline in the rhenium content of the ore

Primary supply in 2004, excluding Molymet, is estimated at 22.5 t (2003: 22.7 t). Phelps Dodge has maintained full production at its Sierrita mine in the US, and in Europe the Polish producer KGHM, which re-entered the market in 2003 following the introduction of a new circuit at its Lublin works, continues to produce around 2 t/y. China has yet to become a significant producer but this is likely to be only a matter of time.

The key development on the supply side has been in Kazakhstan, where politics has always had an influence on rhenium production. Since the end of the Soviet era, the mine and smelter at Dzhezkazgan have been under separate ownership from the Dzhezkazganredmet rare-metals plant (which recovers rhenium) but the two entities have had an equal share of rhenium exports. However, the owner of the copper mine and smelter, Kazakhmys (recently admitted to the London Stock Exchange with a £661 million IPO, and a market capitalisation of some £2.75 billion) is reported to have blocked all rhenium deliveries to Dzhezkazganredmet. The dispute is continuing and has reportedly halved the supply of rhenium from Kazakhstan. Importantly, the West relies almost entirely on Kazakhstan for its spot purchases, which meet approximately 25% of the West's rhenium needs. In 2004, primary rhenium supply from Kazakhstan amounted to about 8.5 t ( contained in APR) but in the first half of 2005, exports are estimated at no more than 2 t. This shortfall has been a factor in the rapid rise in free market rhenium prices in recent months

**Secondary supply**

The recycling of rhenium falls into two categories which reflect rhenium's two main applications – in catalysts and alloys.

The recovery of rhenium from spent reforming bi-metallic catalysts is a mature business. It is thought that about 5,000 t of reforming catalysts containing about 15 t of rhenium are rotating within the oil-refining system. As spent catalysts emerge, they are sent for recovery, essentially to recuperate the more valuable platinum. If it were not for the value of platinum, it is doubtful that the recovery industry for rhenium would be nearly as efficient. However, it is, and these catalysts are recovered with less than 10% yield losses at W C Heraeus GmbH & Co KG in Hanau, Germany, Heraeus-owned PGP Industries in California, Engelhard-CLAL (now called Platexcis) in France and Gemini in the US. The largest percentage is recovered by Heraeus. These units are then returned to oil companies or catalyst makers to manufacture new catalyst and few units ever pass into the free market.

Without an expensive metal like platinum to provide the incentive, the recovery of rhenium from complex alloys or resins is an extremely marginal process requiring prices for basic grade APR to be maintained at a minimum of US$1,000/kg Re in order to be viable.

However, with the developing shortage of rhenium from Kazakhstan and the attendant price rise, there is a growing incentive for secondary producers to increase their rhenium output, and at two or three locations in Eastern Europe, nickel-based scrap turbine blades, scrap grindings and resin scrap from ferro-molybdenum are now being recycled, with rhenium recovery running at as much as 2 t/y.

Heraeus in Germany is able to recover rhenium from metallic forms and Toma in Estonia can recover Re from W-Re and Mo-Re solids. H C Starck & Co recovers Re from some resins, perhaps those from Sadaci, and grindings containing as little as 2.9% Re are processed at Heraeus.

In all, the supply of rhenium from recycling is estimated to be running at about 4.5 t/y, bringing total supply in 2004 (primary and secondary) to about 43 t.

**Alloying demand**

Demand for rhenium in the alloying sector relies to a great extent on the fortunes of the aerospace industry. For it is here that rhenium is used, as either a 3% or 6% addition in a range of complex nickel-based alloys which are precision cast into single crystal turbine blades for the hot core of the gas turbine. The leading exponent is Rolls-Royce plc, whose Trent family of engines has the largest share of new engine orders for civil airframes. The Trent 500 engine has two rings in the hot turbine section (with over 100 blades per ring) and uses both alloys.

The market leader with patents on two industry-standard alloys is Cannon Muskegon of the US, which developed its range of rhenium-bearing alloys with Rolls-Royce in the early 1980s. The specifications of their two main alloys are listed in table 4. At the time of writing, there are signs that the pace of development of a fourth generation of alloys, containing rhenium and ruthenium, is picking up, suggesting that these alloys will be used in the newest generation of gas turbine engines.

The addition of rhenium gives the necessary structure to crystal growth which, in turn, increases the precision-cast alloy's resistance to deformation under large variations of temperature. This property, referred to as 'creep resistance', means that a typical gas turbine aero engine using CMSX alloy blades may burn gas at something like 1,200°C continuously on transcontinental flights, and withstand temperatures that are higher than the melting point of previous generations of alloy. The gain to the engine maker and airlines is in fuel efficiency (higher burn, lower sulphur emissions), greater blade longevity, savings on fuel costs and possible noise reduction attributes.

**Catalyst demand**

Until recently, when referring to the catalyst market for rhenium, we were mainly talking of a group of catalysts called 'reformers'. These are the group of catalysts, originally developed in the 1970s by Chevron, which became the market leader in the processes for making aromatics (benzene, toluene & xylene) and high-octane gasolines. Typically, these were bi-metallic Pt-Re catalysts containing 0.3% Pt and 0.3% or (sometimes) 0.4% Re on an alumina substrate.

As mentioned earlier, because of its highly efficient levels of recycling, this industry has no need to be a large consumer of virgin rhenium units. Nevertheless, owing to the fact that rhenium is rather the poor sister to platinum (about 18 times cheaper at present), it is imperative, for fear of contamination, that only the highest grades of rhenium in APR are used. It is for this reason that a two-tier market in APR exists, in which Western 'catalyst grade' APR trades at a considerable premium to all other grades (including Kazakh production).

In the apparently stable market of catalysts a new entrant has appeared on the horizon. With oil prices in the past few years above US$30/bbl, and above US$50/bbl at the time of writing, oil companies have been considering ways in which previously uneconomic fields of gas can be brought to the market. One means is the growing industry known by the generic term 'gas-to-liquids' (GTL). What this actually means is that in the case of previously stranded gas, a process may be installed, possibly using the Fischer-Tropsch process (or similar), in which gas may be catalysed and condensed into low sulphur fuel. This fuel is then blended with lower-grade crudes in order to improve quality. Some of the catalytic formulations will use rhenium. How much is not known. However, if those plants at the planning stage come to fruition, it is predicted that GTL could one day become as large a consumer of rhenium as the reforming industry is today. At the moment not more than 1t/y of rhenium enters this field. However, if plants are put into operation it is not inconceivable that this sector could consume as much as 5-10 t/y within about five years. Prevailing high oil prices in 2005 have served to accelerate the pace of development of GTL catalysts, and this is expected to attract new demand over the next 12 months.

**Demand summary**

Taking into account the exact figures for Molymet deliveries obtained from Banco Central in Chile it is possible to get a fairly good feel of real sales and demand for rhenium in 2004. Estimates are given in Table 3.

Included in the aerospace figure in Table 3 are purchases made under long-term contract from Molymet and Phelps Dodge by GE, Pratt & Whitney, Cannon Muskegon and other alloy makers, and by aero-engine and landbased gas turbine makers worldwide. The catalyst figure includes the top-up quantities of rhenium required in catalyst making, where new material is required in lieu of material available through recycling.

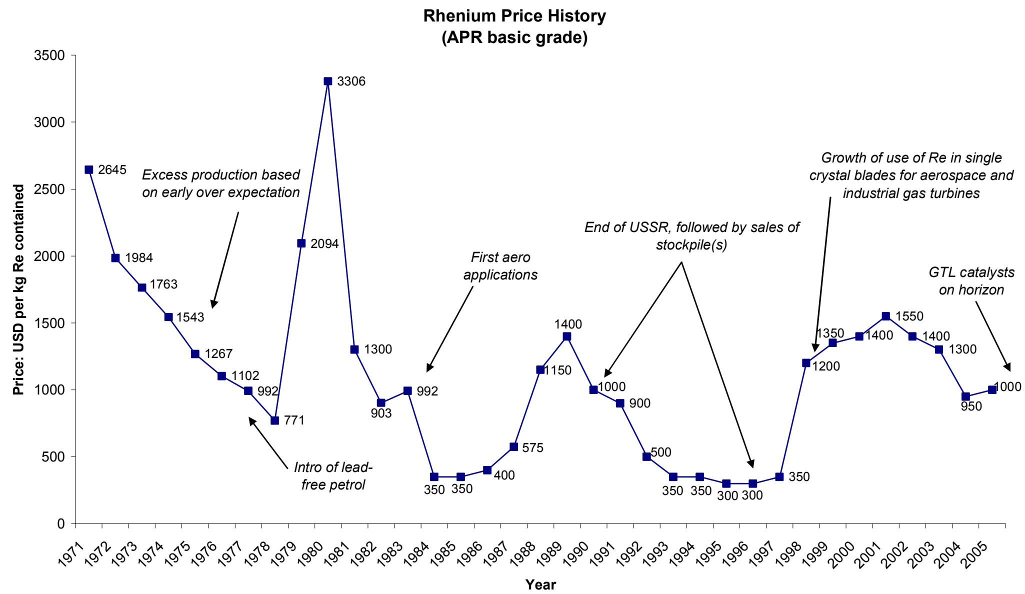
The amount of rhenium used in medical X-ray target sectors, and filament wires and boosters coated with rhenium via chemical vapour deposition, is not thought to have changed from the previous year. This emphasises, yet again, the importance of aerospace on rhenium demand; if that industry has a poor year, the consequences for rhenium are clear.

**Prices**

Price promulgation for rhenium continues to remain obscure; but slightly less so than it was ten years ago. Nowadays it is possible to obtain some guidance of price online from two main sources: www.thebulliondesk.com, which quotes a range referring to the price for catalyst-grade APR expressed in US$/kg of contained Re, and www.metal-pages.com (by subscription only), which provides a quote based on basic grade APR traded on the free market and originating from Kazakhstan.

Lipmann Walton & Co Ltd tracks the price of rhenium mainly in the form of APR (basic grade) because it regards this material as the largest ingredient of free market trade. Because a large proportion of the market (that traded by Molymet and Phelps Dodge) is in the form of rhenium metal pellets, and moves directly from producer to consumer via long-term contracts, the market has been opaque. It is thought that most rhenium metal pellet business in the past year was transacted at around US$600/lb (US$1,322/kg) Re. Meanwhile, catalyst-grade APR, which is often bought for immediate delivery on the spot market, has consistently traded at around US$1,500-1,600/kg Re (a healthy premium). Part of the explanation for this is the haphazard nature of the purchasing, which is unpredictable. Also, the need for super-pure material and the cost of finance, is not inconsiderable.

Although prices for Russian/Kazakh origin material remained in the doldrums around US$1,000/ kg Re for most of 2003 and until mid-2004, the lack of adequate supply from Kazakhstan is now being felt and has propelled the spot price towards US$1,500/kg. In November 2005, there was still no sign that the dispute between the two Kazakh suppliers had been resolved.




## Summary and conclusions

As we draw to the end of 2005 a confluence of events seem ready to propel rhenium into the next phase of its economic development and commercial use.

With regard to applications, the anticipated use of rhenium in GTL catalysts seems highly likely, and the further use of rhenium in 4th generation alloys (with ruthenium) is on the edge of commercialisation. Both consumer blocks will have to vie for the same supply. It is thought that one aero-engine maker alone is now using 8 t/y of rhenium in alloy, and a single new GTL plant might require as much as 10 t/y of rhenium.

These quantities would, perhaps, be available were it not for the supply problems in Kazakhstan, towards which the West looks for 8.5 t/y or rhenium, equivalent to around 23% of consumption. The dispute between Kazakhmys (the copper producer) and Dzhezkasaganredmet (the rare earth plant) has led to material being blocked for export. As an immediate consequence, it is thought that current production at the plant has been halved, meaning that only 4-4.5 t/y of rhenium per year is now being generated.

To offset this, temporarily, it is thought that just over one year's supply, or about 10 t of rhenium in APR is in stockpile in Kazakhstan but this material is also the subject of dispute and therefore currently unavailable to the market.

These matters aside, the key to rhenium's next phase of consumption growth appears to be linked to climate change and energy considerations. In all senses, rhenium may be regarded as a 'green element'. Thus far, no substitute has been found for its use in nickel-based, single-crystal turbine blades, the main means by which operating temperatures and thus fuel efficiency in aircraft engines is achieved. As concern grows about the pollution of the upper atmosphere, combustion technology has focused on the material science to reduce nitrous oxides, and the use of rhenium (and soon ruthenium too) is the main means to achieve this end. As regards fossil fuels, developments requiring the use of lower-sulphur fuel are to the fore, and it is thought that rhenium-bearing catalysts will be used to convert stranded gas into premium and clean derivative products.

These developments are likely to place considerable pressure on a supply system that has seen little expansion or investment over the past ten years. It seems probable, therefore, that a rise in price will have to be the spur to encourage more efficient recovery of rhenium from scrap and perhaps new circuits to recover primary rhenium at those molybdenum roasters where it is currently lost. In terms of price, when it is understood quite how rare rhenium is, and when its commercial applications are more fully appreciated, it seems likely that rhenium will gradually move towards price levels more akin to the platinum group metals with which it shares so many properties.

All in all, rhenium remains, par excellence, the great 21st century metal, still not 100 years since its discovery, and now at last being commercialised in environmentally-positive applications.

| **Table 1: Molymet exports (tonnes)** | **H1 05** | **2004** | **2003** | **2002** |
|---|---|---|---|---|
| Rhenium metal pellets/briquettes | 11.2 | 12.9 | 12.9 t | 17.8 t |
| Ammonium perrhenate (APR) | 1.4 | 2.8 | 2.9 t | 1.2 t |
| Perrhenic acid | 0.3 | 0.25 | 0.8 t | 0.8 t |
| **Total** | **12.9** | **15.95** | **16.6 t** | **19.8 t** |

| Table 2: Primary suppliers (tonnes, mine source) | | | |
|---|---|---|---|
| | **2004** | **2003** | **2002** |
| Phelps Dodge (US) | 7.0 | 7.0 t | 4.0 t |
| Dzhezkasganredmet (Kazakhstan) | 8.5 | 8.5 t | 8.5 t |
| KGHM (Poland) | 2.0 | 2.0 t | 0.5 t |
| Uralelektromed (Russia) | 1.0 | 1.0 t | 1.0 t |
| Yerevan Pure Iron Plant (Armenia) | 1.0 | 0.2 t | - |
| | | | |
| Navoi (Uzbekistan) | 1.0 | 1.0 t | 1.0 t |
| China (various) | 2.0 | 3.0 t | 1.0 t |
| | | | |
| | | | |
| **Primary supply excluding Molymet:** | **22.5** | **22.7 t** | **16 t** |
| **Primary supply including Molymet:** | **38.45** | **39.30 t** | **35.8 t** |

| Table 3: Demand estimates (t) | |
|---|---|
| | |
| Aerospace and super alloys | 25 t |
| Catalysts | 10 t[1] |
| Other (incl X-ray targets,filaments, boosters, powder alloys) | 5 t |
| **Total** | **40 t** |

**Table 4: Examples of rhenium content (%) in two Re-bearing alloys**

| **Alloy** | Cr | Co | Mo | **Re** | W | Al | Ti | Ta | Nb | Hf |
|---|---|---|---|---|---|---|---|---|---|---|
| CMSX-4 | 6.5 | 9.0 | 0.6 | **3.0** | 6.0 | 5.6 | 1.0 | 6.5 | - | 0.1 |
| CMSX-10 | 2.2 | 3.3 | 0.4 | **6.2** | 5.5 | 5.8 | 0.2 | 8.3 | 0.1 | 0.03 |

[1] Based on expected demand for GTL.