RHENIUM

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Since its discovery in the first quarter of the 20th Century, rhenium has often been described as a metal of the future. Some of that promise was realised in the 1970s and 1980s when rhenium became essential to two distinct products: as an addition in reforming catalysts and subsequently as an addition in complex super alloys. It is noticeable, though, that rhenium has been slow to make inroads into other industries – perhaps held back by price or perceived rarity.

Examining the market today, it is pertinent to ask whether rhenium has reached a moment of equilibrium in terms of supply and demand, whether possible future uses lie on the horizon, how the market is structured and what the impact would be of new uses on this small market.

This review emphasises the importance of Molybdenos y Metales SA of Chile (Molymet), the world's largest producer of rhenium, and Molymet's dominance of the rhenium market and its current market share. The manner in which other suppliers are developing their production is examined as are the steps that are being taken as regards recycling and better husbandry of by-product rhenium. Finally, we look at what the future may hold for new demand areas and thus also for prices.

A by-product

"Inhospitable and rough, guarded by high mountains, it hides in its entrails an inexhaustible treasure of mineral". In these words, Isabel Allende, cousin of the deposed President Salvador Allende, described the geology of Chile in her book, 'My Invented Country', written in 2003. She was undoubtedly referring to copper, of which a staggering 4.7 Mt of copper in concentrate was produced in the year that Isabel Allende wrote that sentence (up from 2.6 Mt ten years earlier). One of the first points then to make about rhenium is that it is recovered as a by-product of copper mining and that supply is governed entirely by copper output.

The development of copper mining in Chile has been impressive. In 1993, there were just five mines apart from the operations of state-owned Codelco. Today there are at least 15 other significant producers, including the extraordinary Escondida mine which, alone, produces about 1 Mt/y of copper in concentrates. Then there is Antofagasta Holdings plc, a London-listed company whose main asset in the early 1980s was its ownership of a railway (built by the British) that was able to provide the key to transporting copper from the newly discovered mines. Today, Antofagasta is the majority owner of three important copper mines, Los Pelambres, El Tesoro and Michilla which, together, produce just under 0.5 Mt/y of copper in concentrates.

As Isabel Allende was able to indicate in her book, despite a chequered political history, the great natural wealth of Chile generated through copper has contributed to making the country, in spite of everything, one of the few stable countries in South America. And Chile, through Molymet, is the world's largest producer of rhenium and the cornerstone of supply.

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 between 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

As noted, Chile is the world's principal source of rhenium but of the country's 16 main copper mines, only Chuquicamata, Disputada and Los Pelambres produce significant quantities of the necessary rhenium-bearing by-product molybdenum sulphide concentrates. These operations are the main sources of raw materials supplying Molymet's roasters in Chile.

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.

By its own account, Molymet produces and processes just under 50 Mlb/y of molybdenum in Chile, 15-20 Mlb/y in Mexico (Molymex) and, recently, via its acquisition of the Sadaci roaster, about a further 20 Mlb/y in Belgium.

Molymet has been involved with the manufacture of molybdenum products and the recovery of rhenium for over 40 years. Its position in rhenium is almost unassailable and it continues to invest in the rhenium recovery process.

In 2003, based on official figures from Banco Central de Chile, Molymet exported 16.6 t of rhenium in various forms (Table 1).

Overall deliveries in 2003 were down by 16% compared with 2002, suggesting a market in oversupply. The particularly steep fall in metal deliveries (down 28%) further suggests poor demand for super-alloy making. This in turn implies a slump in demand for aero-engines and industrial gas turbines.

During the same period, however other primary rhenium suppliers increased their production (Table 2).

Primary supply in 2003 reached the level of total supply (primary plus recycled material) reported for 2002. Largely responsible for this increase was the return to full production at Phelps Dodge's Sierrita mine, which had operated at 50% of capacity in the previous few years. Also, China began to emerge as a country trying to increase rhenium recovery. Kazakhstan (Dzhezkazganredmet) continued to produce at a high rate (8.5 t/y of rhenium contained in APR) despite any evidence of any increased uptake to justify the rise. Finally, Poland re-entered the market with a new circuit at the upgraded Lublin works of KGHM.

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 Hereaus 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. Over recent years, when the rhenium market appeared to be heading for a supply deficit, there was a push to recover more rhenium, for example, from scrap grindings of rhenium-containing super alloy, resins, tungsten-rhenium alloy from filament scrap and molybdenum-rhenium anodes from X-ray targets. Heraeus in Germany was 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 continues to recover Re from some resins, perhaps those from Sadaci, and grindings containing as little as 2.9% Re are processed at Heraeus.

(In China it has not been possible to establish whether rhenium supply figures represent primary or secondary material. For the moment the figures for China have been included only in the primary supply table in order to avoid double counting.)

In all, we estimate the supply of rhenium from recycling at about 4.0 t/y, bringing total supply in 2003 (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.

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.

Thus, when looking at why rhenium demand has slumped in the past couple of years, it is to the aerospace sector that we must turn to find the answer. It is not a coincidence that 2003 was regarded in the world of aerospace as the bottom of the trough in terms of demand. Boeing was 21% off on commercial airline sales at US$22.4 billion and EADS (owner of Airbus) was down 2% at US$21.523 billion. Amongst the engine-makers, Rolls-Royce was down 2% on civil engine sales but up 2% on defence. Pratt & Whitney was down 2% and General Electric down 1% across all engines.

Translated into rhenium sales, this fully explains Molymet's decline in rhenium metal deliveries from 17.8 t in 2002 to 12.9 t in 2003.

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 leaders 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$40/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 fuels. The resulting fuel is then blended with lower grade crudes in order to raise 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.

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 2003. 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 land-based 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 emphasizes, yet again, the importance of aerospace on rhenium demand; if that industry has a poor year, the consequences for rhenium are clear.

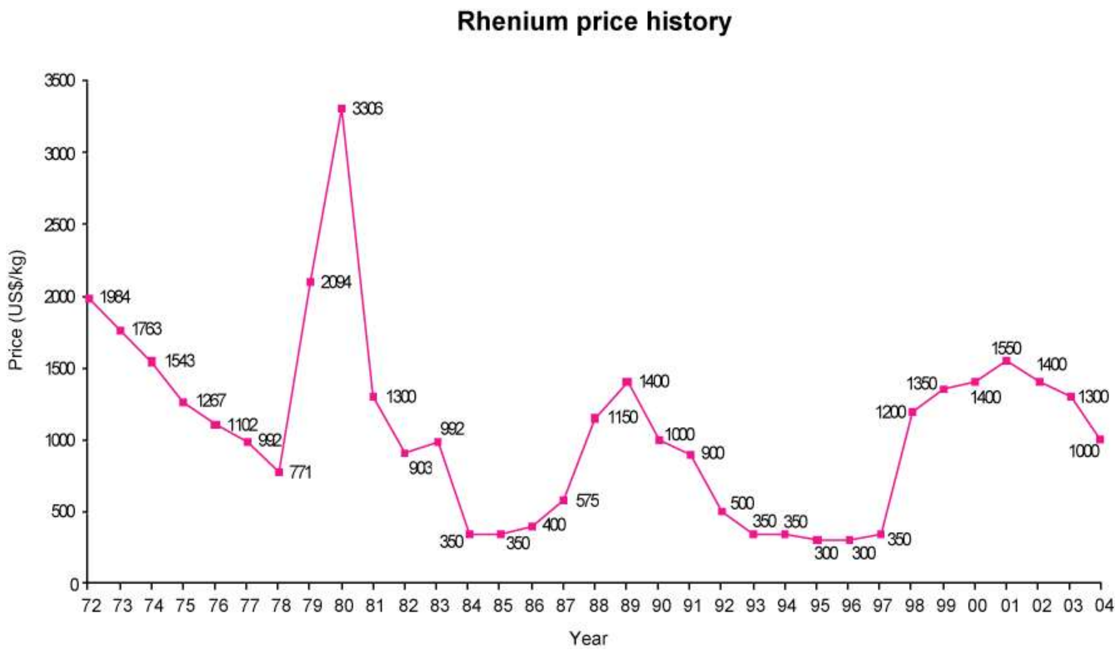
Prices

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. *Platts Metals Week* until recently carried a rhenium price but this was discontinued.

Neither the London *Metal Bulletin* nor *Mining Journal,* or Reuters, publish a price for rhenium other than in the context of an article.

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.

Meanwhile, prices for Russian/Kazakh origin material have remained in the doldrums around US$1,000/ kg Re for most of 2003 and into 2004.



Summary and conclusions

This survey commenced by drawing attention to the somewhat disappointing performance of rhenium in the marketplace. Despite its rarity in geological terms, and the dominant market share of one leading producer, the world has been slow to invest in great diversification of supply. In fact, Molymet's dominance has been without challenge for 40 years. Equally, the way in which rhenium is bought in the aerospace industry, although unusual, appears to work for all parties. Because the largest suppliers and consumers are somewhat similar in size the relationship is one of equals and has been remarkably stable.

The supply and demand figures indicate that rhenium was in oversupply by about 10 t in 2003, as a result of the downturn in the aerospace industry, over-production in Kazakhstan and increasing supply from new entrants in China.

However, although the oversupply in 2003 looks massive, 2004 is already looking much better for aerospace and there are excellent prospects on the horizon for a new generation of catalysts formulated for GTL.

Therefore, it is apparent that two factors will affect prices in the coming years. If the ever-growing rhenium production in Kazakhstan continues at the present rate without regard to the marketplace, then years of oversupply could be in prospect. However, if the drive towards GTL continues, predictions of requirements that could amount to as much as 5-10 t/y would help take up the slack. If GTL does indeed come on stream soon, it could not be at a more opportune time.

As regards price, if the overhang of APR generated by over-production continues it seems inevitable that prices will continue to ease during 2004. Currently, basic grade APR is trading either side of US$1,000/kg and it seems likely that US$800/kg or lower could be imminent until such time as both the aerospace and catalyst industries show signs of steady recovery.

In summary, rhenium remains intrinsic to two large and mature industries. In both, rhenium contributes to cleaner energy – via the type of gasolines generated by reforming and via the lower emissions resulting from fuel efficiencies in gas turbines. In so far as the 21st Century will doubtless be occupied with the problem of energy conservation, rhenium's general prospects remain positive, and we would expect the present weakness to be overcome in due course.

Table 1 Molymet exports	**2003**	**2002**
Rhenium metal pellets/briquettes	12.9 t	17.8 t
Ammonium perrhenate	2.9 t	1.2 t
Perrhenic acid	0.8 t	0.8 t
Total	**16.6 t**	**19.8 t**

Table 2 Primary suppliers (mine source)		
	2003	**2002**
Phelps Dodge (US)	7.0 t	4.0 t
Dzhezkasganredmet (Kazakhstan)	8.5 t	8.5 t
KGHM (Poland)	2.0 t	0.5 t
Uralelektromed (Russia)	1.0 t	1.0 t
Yerevan Pure Iron Plant (Armenia)	0.2 t	-
ZMMK (Armenia) Re bearing concs sold on the open market – Re mostly lost	-	-
Navoi (Uzbekistan)	1.0 t	1.0 t
China (various)	3.0 t	1.0 t
Sar Chesmeh (Iran) Re bearing concs sold on the open market – Re mostly lost		
Primary supply excluding Molymet:	22.7 t	16 t
Primary supply including Molymet:	39.30 t	35.8 t

Table 3	
Demand estimates	
Aerospace and super alloys	19-21 t
Catalysts	4 t
Other (incl X-ray targets,filaments, boosters	5 t
Total	**28-29 t**

Table 4										
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

