RHENIUM

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Unlike many other elements in the periodic table, rhenium, from a commercial point of view, is still young. Only discovered in 1925, it is not yet a hundred years since it was first separated. However, partly because of rhenium's military and space applications, there has been considerable opacity when it comes to publishing supply and demand figures. In future years this is likely to change as civil industrial uses dominate.

In the 2002 edition of *Mining Annual Review*, my predecessor focused on the then confluence of demand for rhenium from the aerospace and industrial gas turbine (IGT) sectors which ended with the collapse of Enron and the events of September 11 2001. The main overriding factor in this report will be to explain why, given the recent negative factors for the business environment, rhenium's continued growth, commercialisation and prices have been maintained.

History and background

The name *Rhenium* comes from the Latin for the River Rhine, the largest river in the country where rhenium was first discovered – Germany. It was first separated by Walter Noddack and Ida Tacke who, in 1925, were working at the Physico-Technical Laboratory in Berlin. They recovered the metal as a 10 ppm trace in gadolinite. However, as well as this initial breakthrough, they pursued their studies further and managed to recover a gram of Rhenium from 660 kg of Scandinavian-origin molybdenite. Thus Noddack & Tacke added to their scientific achievement the commercial discovery that the world's main industrial source of rhenium would be as a by-product of molybdenite (MoS_2), which it remains to this day.

Properties

Rhenium is No. 75 in the periodic table – a member of Group VII. It has a high melting point of 3,180°C, the second highest of all metallic elements after tungsten. It is the fourth densest of all elements at 21 g/cm^3 (more than twice that of molybdenum) and its resistivity is almost four times greater than tungsten. It also has a great affinity for oxygen, readily forming Re_2O_7. When collected, it is usually processed into a stable salt (white free-flowing powder), ammonium perrhenate (NH_4 ReO_4) containing 69.2-69.4% Re.

Uses

Rhenium's early uses were in filament wires in lamps and, when alloyed to tungsten, used for thermocouples for, amongst other things, the measurement of furnace temperatures. Its density has also proved useful to the X-ray industry where Mo-W-Re targets are generally used to reflect the X-rays.

Subsequently, it was found that rhenium is a good stabiliser alongside platinum in alumina-based catalysts. In the early 1970s rhenium's greatest commercial-isation took place when Chevron developed a set of catalysts that would not react to sulphur and would assist the production of aromatic gasolines. These catalysts are known as rheniforming catalysts and contain typically 0.3% Re and 0.3% Pt on an alumina base.

Rhenium's main use today, by volume, is in nickel-based alloys known as *single crystal* because of the way in which they are grown through a ceramic core and precision cast into the shape of a turbine blade. These alloys, called second and third generation in the super alloy industry, are covered by patents lodged by General Electric, Pratt & Whitney and Cannon Muskegon, all of the US. In broad terms, this group of alloys is much sought after in the development of ever more efficient gas turbines engines as they bring the quality of 'creep resistance' – resistance to deformation after great variations of temperature. When used in the centre of the turbine, they enable consistent operating temperatures above 1,200°C resulting in greater and more efficient burning of fuel and lower emissions of nitrous oxide gases. At the same time, the use of these alloys ensures greater longevity of the engine in this testing environment.

Developments in making larger castings, using precision-casting methods, mean that ever more parts of the engine are being 'colonised' by this group of alloys.

Occurrence
The crustal abundance of rhenium is no more than 0.4 ppb (the 77th rarest element); but in areas where rhenium is contained in molybdenum ores, the occurrence can rise to 0.025% (250 ppm) or sometimes as high as 0.07% (700 ppm).

Nowhere in the world is rhenium mined as a primary product. This means that, like several other by-product metals, rhenium depends to a large extent on the fortunes of the base metal(s) with which it is found.

Rhenium is most frequently found in porphyry copper deposits in association with molybdenum, for example in Chile, Peru, US (Arizona), Canada (British Columbia) and Mongolia. Rhenium also occurs in trace amounts in some cupriferous sandstone deposits in Kazakhstan and Russia. In Kazakhstan, the rhenium-containing mineral is dhezkasganite, named after the town in the middle of the Kazakh steppe where it was first discovered.

Although almost all rhenium is recovered as a by-product of copper mining, the amount of rhenium in copper deposits varies considerably. In Chile, for example, the world's largest copper producer, Codelco, mines copper deposits possessing relatively low rhenium content, running at about 250 ppm per tonne in the by-product MoS_2.
In other deposits in other parts of the world, the rhenium content can be much higher; the copper deposits at Sar Cheshmeh in Iran and at Agarak and Kadsharan in Armenia, are good examples, averaging around 650 ppm in MoS_2. The highest commercial concentrations ever recovered were at BHP's

San Manuel Mine in the US which ran at 900 ppm and at Island Copper in Canada at 1,000 ppm, but both operations are now closed.

The only other geological host for rhenium, apart from copper porphyry and sandstone type deposits is alleged to be an active volcano in Russia's Kurile Islands where a questionable ore, named rhenite, is said to exist. It was named thus because Russian scientists claimed that it is the world's only source of primary rhenium ore. It occurs on the lip of the Kudryavy volcano. However, there is considerable scepticism over this source and samples of rhenite sent to the Mining Museum in Denver Colorado, after testing, were said to contain no rhenium. Furthermore, the problem of commercial recovery of rhenium in gaseous form from a volcanic vent has still to be overcome and no commercial recovery is yet reported. Nevertheless, developments in the Kurile Islands need to be monitored closely because if rhenium were to be successfully recovered, this could sharply alter the supply/demand balance of rhenium, a relatively small market.

Methods of recovery

Rhenium's usual method of recovery first involves the milling and concentrating of copper ore, separation of the by-product molybdenum by flotation in the form of MoS_2 (molybdenite) and roasting of the MoS_2 to remove the sulphur and form molybdic oxide. At this point, most of the rhenium is also oxidised to form rhenium heptoxide (Re_20_7) which is carried off with the roaster flue gas and subsequently removed from the flue gas by wet scrubbing. Wet scrubbing is used primarily for environmental reasons to convert the sulphur into sulphuric acid and prevent its release into the atmosphere. Without wet scrubbing, rhenium is not recovered. Those companies that do use wet scrubbing at their roasters include Molymet (Chile), Molymex (Mexico), Sierrita (Arizona, US), Rozenberg (Holland), Sadaci (Belgium), Pobedit (North Ossetia) and a few other smaller operations in China and the CIS.

Production (Table 1)

In Chile, **Molybdenos Y Metales SA** (Molymet) became a rhenium producer in the 1970s when technology, once developed at Shattuck Chemical in US, was transferred to Chile by, trader, Philipp Brothers, in return for an agency to market rhenium. This situation appears to have continued for some years until the demise of Philipp Brothers or when rhenium appeared (in the late 1970s/early 1980s) to be a declining commodity. Today, Molymet, which is a private company, and leading producer of a range of molybdenum products, is the world's largest source of rhenium, which is derived as a valuable by-product of its molybdenum roasting operation (three roasters). The rhenium is sold under long- term contracts into the US aerospace and super alloy industry as rhenium briquettes, pellets or powder. According to official Chilean export statistics, Molymet's exports of rhenium products last year were as follows:

- rhenium metal (incl. pellets, powder, briquettes): 17.8 t (99%+ to US)
- perrhenic acid: 886 kg Re (80% to US, balance EC)
- ammonium perrhenate: 1,153 kg Re (75% EC, 25% others).

Total rhenium exports were 20.57 t, equivalent to 58% of primary world supply (or 50% of total supply if recycled material is included)

In the US**, Phelps Dodge** is the largest copper producer and the country's only producer of by-product rhenium. This came about when Phelps acquired the Sierrita mine and Fort Madison facilities from Cyprus Amax in 1999. Since then, with copper prices relatively weak, and the general migration of copper production into South America, this co-product mine (where income is derived equally from copper and molybdenum) has been under pressure from high costs. It is thought that 1 lb of copper mined at Sierrita costs nearly US$0.70/lb, compared with US$0.41/lb at Codelco's operations in Chile. Nevertheless, in spite of this, and mounting losses for the parent company, Sierrita continues to operate at 50% of capacity.

The Sierrita processing facilities also take in residues containing rhenium from Phelps' wholly-owned European Molybdenum Roaster located at Rozenberg in Holland. With this, and locally processed material, production of Rhenium is thought to have declined from around 8.0 t in 1998 to nearer 4.0 t today. This still represents 11% of primary supply. If copper prices do not recover in the next few years, there remains a serious question over whether Sierrita (already 20 years old) can continue, although rhenium processing at the Sierrita facility and at Fort Madison might conceivably soldier on, using imported concentrates.

In Kazakhstan, the world's second largest producer of rhenium, **Dzheskasgan**, was a gulag in Soviet times, and the mine and smelter were run by slave labour. Today, the copper operation has been privatised and is run by **Kazakhmys** (KCC), with annual copper production running at some 425,000 t/y (taking together the mines of Balkhash and Dhezkasgan). The ore is acid leached and rhenium passes directly into solution. The acid is then sent to Dzheskasgan-redmet, another plant within the copper complex, for rhenium recovery. Commensurate with the level of copper production, rhenium output has increased during recent years. As recently as 1996, output had slumped to 1.5 t/y but, today, production is around 8.5 t/y, produced in the form of ammonium perrhenate (24% of primary supply).

Rhenium output elsewhere in the CIS is associated with the processing of molybdenite concentrates in North Ossetia, Uzbekistan and Russia. In a unique production at Navoi, in Uzbekistan, 500 kg–1,000 kg/y of rhenium is recovered as a by-product from uranium ores.

In Iran, Armenia and Mongolia, rhenium is only recovered when delivered to roasters with a rhenium circuit. Often, though, this is not the case and rhenium- bearing MoS_2 from these regions is sent to China where treatment charges have been low and, as a result, rhenium is generally lost.

The recent acquisition by Molymet of the world's second largest molybdenum roaster, **Sadaci** in Belgium, may redress this situation, enabling good rhenium-bearing MoS_2 to be husbanded.

Consumption (Table 2)
Catalysts: demand for rhenium rose dramatically in the late 1970s when platinum–rhenium reforming catalysts were first commercialised. With no large stocks of rhenium in the system, rhenium was acquired by oil companies and catalyst makers in what might be described as 'virgin demand'. During a decade from, say, 1975 until 1985, this was the principal demand application for rhenium, responsible for about 75% of total demand. In subsequent years, due to the value of the platinum, a highly-efficient recycling industry developed around these catalysts. Spent catalysts began to be recycled in the 1980s and served to reduce demand for virgin material. Today, it is thought that the amount of platinum and rhenium in current use is about 5,000 t (containing 15 t of rhenium) and that this material is regularly recycled in 3-5 year intervals, with only 10% yield loss in recovery.

Nevertheless, due to mismatches in the timing and disposal of spent catalysts versus new requirements, anomalies frequently occur. As a result, rhenium consumption for reforming catalysts usually outstrips the theoretical 10%. This, together with demand from new refineries and for new types of catalyst in the process chemical industry, mean that global consumption in this field is about 9 t/y (22% of demand). Some of this is accounted for by the fact that platinum exports are prohibited from the CIS except via government-controlled routes. In these instances rhenium is often lost when platinum is recovered locally. Perhaps as much as 2-3 t/y of rhenium in ammonium perrhenate now moves back into the CIS each year to replace such losses.

Super alloys: rhenium's success has meant that no modern gas turbine engine – neither aero nor land-based, is designed without rhenium-bearing alloys in the hot turbine section. Consumption in this area is also growing as further parts are colonised by these alloys and the new policy of retro-fitting older engines with new rhenium-containing alloy adds to rhenium's growing use in this field. Newer engines, such as the Rolls-Royce Trent 500 or Trent 900 also contain rhenium in two blade ring-sections. Although not the originator of rhenium-bearing alloys, the greatest exponent is Cannon Muskegon in the US, which consumes more rhenium than any other party in the world. Its most popular alloy is CMSX-4 (Re 3%) a second generation alloy whose patents in the US and Europe expire in 2004 and 2005 respectively. Their CMSX-10 (Re 6%) is third generation. Worldwide consumption of rhenium in alloy is thought to be about 27 t (65-66% of all consumption) of which Cannon Muskegon consumes approximately half. No substitute has yet been found for rhenium in these applications.

Recycling
A strong and efficient recycling industry has grown up around Pt/Re catalysts encouraged not so much by the wish to recover rhenium but by the much more valuable platinum. The market leader is W.C. Heraeus GmbH & Co. KG, which has expanded its activities in the past five years by acquiring the old Degussa capability in Hanau, as well as PGP Industries in the US. In Europe, Pt/Re recovery also takes place at Engelhard-CLAL in France (now owned by Metalor), while in the US the largest recycler is Gemini Industries.

In the metal field, H.C. Starck is thought to recover rhenium from some Mo-based materials and resins, and rhenium from tungsten-rhenium or molybdenum-rhenium alloy is recovered at Toma in Estonia. However, as yet, no rhenium is recovered anywhere from complex nickel-bases super alloy solids, such as blades or bars. These units have mainly been lost to the stainless-steel industry where they have been dumped as poor nickel scrap. Some limited use of these complex alloys has been made as revert – where a proportion of a new melt may contain such material. Grindings from blades containing as little as 2% Re may be recovered at Heraeus but the quantity available of such material is small, and limited by capacity.

Substitution

Although substitution has been explored in both of rhenium's main markets, no successful commercial solution has yet been found. In the case of reformers, Pt-Sn catalysts were tried in the 1980s but are said to have been less reliable. In the case of super alloy, it is possible that ruthenium or other platinum group metals may have a role to play. But, in each case, the substitute is either the same price, or more expensive, than the metal it is intended to replace.

Pricing (Figure 1)

The pricing of rhenium is opaque, like its supply-demand figures. The largest proportion of world trade is conducted direct from the main producer (Molymet) to the world's largest consumers in the US under long-term contracts. The exact nature of these contracts is not known but it is fair to say that they contain a fixed price that is lower than spot-market activity. The spot market centres on Kazakh and Russian ammonium perrhenate (69.2-69.4% Re) defined as 'basic grade' by the Minor Metals Trade Association (MMTA). It comes into Europe under 'duty suspension' and generally requires upgrading before end use.

Over the past few years, free-market prices for rhenium have been recorded by traders, such as ourselves, but there is no generally accepted published price for rhenium. Metal-Pages Ltd in London (www.metal-pages.com) has started to record CIS ammonium prerrhenate (APR) prices from 2003 and these may be taken as a guide. Purified catalyst-grade APR is referred to on www.thebulliondesk.com.

In general, prices for basic grade APR experienced a serious trough between 1994 and 1998 when prices barely rose above US$300–350/kg Re. This was caused by massive de-stocking in the Former Soviet Union. As the 1990s progressed, commercialisation of the second- and third-generation rhenium-bearing nickel- base alloys began to accelerate and prices rose dramatically, peaking at US$1,550-1,600/kg Re in 2000 for basic grade APR.

Since then the market has formed a steady platform above US$1,000/kg Re for the past four years and it is expected that this level will remain intact. Certainly, due to the high costs of recycling, rhenium, needs to be at this minimum level in order to encourage the commercial recovery of rhenium from complex nickel base alloys.

Conclusions

Rhenium is a metal still in its early stages of commercial development - it has now passed its 'first flush of youth' and shown early success. But its era of greatest maturity may yet be ahead.

Rhenium is, at present, the servant of two important and rich masters – the oil industry and the aerospace/power generation industries. In both, rhenium contributes to processes which make energy production cleaner and more efficient. Thus it is a truly modern metal, with applications highly-desired by society in the 21st century. Unfortunately, methods to recover rhenium remain little changed from the earliest processes developed by Arthur Melaven and John Bacon in 1947. As regards the important area of recycling, its main consumption area of super alloys still has no regular commercial process for recovering rhenium from spent complex alloy.

Thus, the danger for rhenium is that its growth in popularity may be held back by an inefficient supply industry. Efforts in this direction will, therefore, be required over the next few years in order to meet ever growing demand. The areas where growth may be predicted are at Molymet, the market leader, which is currently investing in its new acquisition in Europe (Sadaci) and from the CIS where capacity at Dzheskasgan in Kazakhstan is not fully utilised. In other areas in the CIS, knowledge about rhenium is higher than in other parts of the world and with local costs low, there is hope of further primary recovery and recycling from these areas.

As regards consumption, the US$236 billion Joint Strike Fighter project in the US (3,000 planes and more than 6,000 engines) will be an important long-term consumer of rhenium-bearing alloy, and all supply will have to come from the open market because the US Defense Logistics Agency Stockpile contains no rhenium. Meanwhile, demand for the development of ever more efficient ways of burning fuel means that rhenium's use in civil aero engines will grow irrespective of the general health of the aero industry as a whole.
Finally, it is mooted that some new catalysts are being developed in the 'gas to liquids' conversion field which may contain some percentage of rhenium. Although this industry is in its infancy too, it may grow to be a factor in years to come.

All in all, rhenium remains a metal that miners should be prepared to count as a credit, rather than as an inconvenience in their ores. After all, who would give away palladium today?

Notes:

In order to compile this report, a questionnaire was sent to 80 parties identified within the rhenium trade worldwide – producers and consumers of alloy and catalyst, oil companies, aero and land-based gas turbine makers, traders and recyclers. The questionnaire asked each recipient to detail quantities of rhenium handled and also offered a supply-demand balance for any party to challenge. Where replies were received, no major figures were seriously challenged and, instead, a number of figures were confirmed. Although the world's largest producer, Molymet, did not reply in any detail, replies were received from other producers representing at least 30% of world primary supply. Also, one of the three largest aero engine makers, several super alloy makers and a number of catalyst recyclers replied in full. The conclusions reached in this report were assisted by these findings and I am grateful to them all for their positive response.

Acknowledgements:-
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Tables on following pages

Table 1
A Summary of Primary Sources of Rhenium

Producer	Country	Raw material	Typical Re content in MoS_2 or ore	Production (t)
Molybdenos y Metales	Chile	Codelco and imported MoS_2	250 ppm in Chile 400 ppm+ in imported ores	20-21
Phelps Dodge	US	MoS_2 from Sierrita mine in Arizona, Mo by-product residues from Rozenberg Roaster in Netherlands	250 ppm in US	4.0
Dzheskasganredmet	Kazakhstan	Dzheskazgan and Balkhash copper ores	X	8.5
Navoi	Uzbekistan	Ex nuclear process		0.5-1.0
Unknown	China	X	X	1.0
Uralelectromed	Russia	Mednogorsk, Gaisky Ore complex	X	1.0
KGHM Metale SA	Poland	Local copper concs		0.5
Pobedit	N. Ossetia	Armenian Mo concs. Mongolian and Sorsk concs.	200-400 ppm	Nil production – lack of concs. supply
TOTAL				**35.5—37.0**

Table 2

Production (t)	
Chile (incl Mexico)	20-21
US	4.0
Kazakhstan	8.5
Uzbekistan	0.5-1.0
Russia	1.0
Poland	0.5
China	1.0
Recycling (W Europe, CIS, China)	4 .0
Total	**39.5 – 42.5**

Consumption (t)	
Super alloys (incl. powder alloys)	27
Catalysts (incl. petrochemical)	9.0
Other (incl. X-ray targets/filaments/ boosters)	5.0
Total	**41 Mt**

Note: These figures do not include material recycled from the closed circuit 5,000 t/y Pt/Re catalysts in operation at the world's oil refineries. The impact from this sector is only felt when:

a) an oil company resells rhenium it no longer needs, or
b) b) an oil company requires virgin rhenium for a new refinery.

Figure 1