MSP REFRAM

Multi-Stakeholder Platform for a Secure
Supply of Refractory Metals in Europe

FACTSHEET

# RHENIUM

## SHORT DESCRIPTION

Rhenium, among all metals, has the second highest melting point, the third highest Young's modulus and the fourth highest density and high hardness, tensile strength and creep-rupture strength in the temperature range of up to 2000°C. It is also resistant to corrosion in seawater and hydrochloric and sulfuric acids and inert to most combustion gases apart from oxygen [18]. It is highly strategic for Europe for its applications in the aeronautic industry, although it has not been included among critical materials.

**Fig. 1 Rhenium metal [20]**

## APPLICATIONS

### *CURRENT APPLICATIONS*

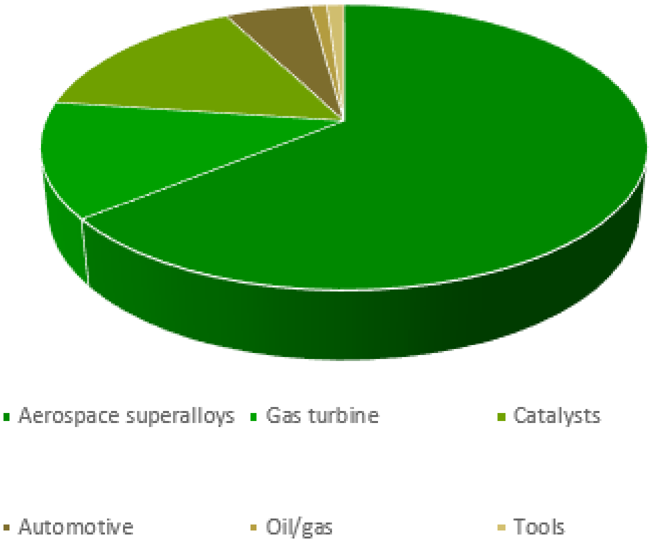

Fig. 2 Rhenium applications in 2011

Rhenium is consumed in several different forms, the most basic of which is ammonium perrhenate, which is the starting material for the production of perrhenic acid. Both ammonium perrhenate and perrhenic acid are used in the manufacture of Pt-Re reforming catalysts. Ammonium perrhenate is also the precursor of Rhenium powder, pellets and briquettes, and is also used in other superalloy and metallurgical applications. Rhenium is used in Nickel-based super alloys (3% Re content) and Platinum in bi-metallic reforming catalysts (0.3% Re), Turbine blades (0.03 kg/MW) and natural gas technology (12.5 tonnes/100,000 barrels) [3][1]. In 2011, the breakdown of the applications of Rhenium produced worldwide was as follows: aerospace superalloys (59%), gas turbines (12%), catalysts (14%), the automotive industry (5%), the oil and gas industry (1%), tool manufacturing (1%).

MSP-REFRAM has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 688993.

### *FUTURE APPLICATIONS*

Rhenium will be used in compounds, materials and composites for applications in the following developing economic sectors and industries: arms, aviation, pharmaceutical products and medicine, chemicals, drilling and mining. Innovative Rhenium products include:

- Electrochemical Rhenium-Nickel and Rhenium-Cobalt alloys containing W and/or Mo
- Electrochemical Rhenium-Nickel and Rhenium-Cobalt coatings with W and/or Mo
- Rhenium and non-ferrous metal powders
- Rhenium carbonyl and its derivatives-substrate for use in the manufacture of homogenous catalysts
- Homogeneous and heterogeneous Rhenium catalysts
- Inorganic Rhenium compounds with application properties that can be used in many industrial branches

## EU SUPPLY AND DEMAND: CURRENT AND FUTURE

Worldwide mine production of Rhenium in 2012 was 52.6 tons and about 27 tons were produced from porphyry Copper mines in Chile.

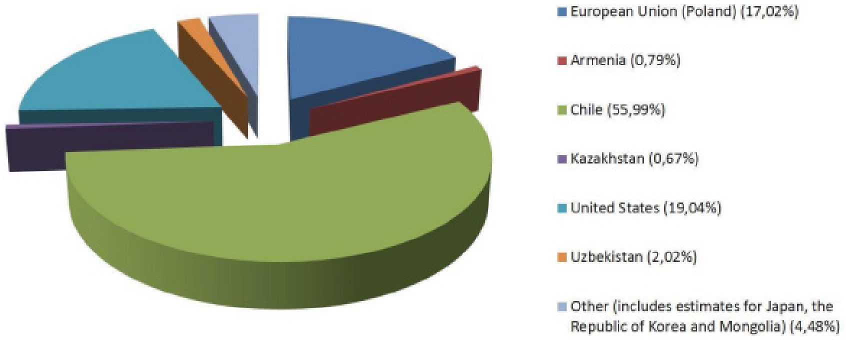

**Fig. 3 Rhenium production worldwide**

The demand for Rhenium is growing due to the demand for engines in both commercial and military jets. This is forecast to continue to rise strongly over the next twenty-five years, as the aerospace and defence industry are the biggest end-users of Rhenium, and aircraft manufacturers such as AIRBUS are directly affected. In 2016, Airbus estimated that there would be a demand of 6,508 new aircraft in Europe between 2016 and 2035, while another major manufacturer, Boeing, estimated a demand of 7,450 new airplanes for the period 2014-2033. Rolls Royce (UK) is another important user of Rhenium-containing Nickel superalloys. Considering an average demand of 50 kg of rhenium per aircraft, a demand up to 1,450 tons of Rhenium in the years leading up to 2033. Moreover, DERA (2016) estimates an expected demand of Rhenium for emerging technologies using superalloys of 120 t/year by 2035, which means 250% of the Rhenium production in 2013 (46 tons).

The use of Rhenium catalysts in reforming is also growing, albeit at a lower rate. Annual EU demand for Rhenium for advanced fossil fuel power generation is forecast at 0.6 tonnes/year in the period 2020-2030, which represents one of the greatest material requirements.

Roskill [21] states that demand for Rhenium will experience a period of sharp growth between 2015 and 2018 and should remain stable after that through to 2020. Demand growth for this period will average 6%/year and reach about 85 MT/year.

Rhenium production is feasible because of the large ore tonnage processed, the presence of sufficient molybdenite to make its recovery economically practical, and the presence of specialized facilities that allow Rhenium recovery from molybdenite. USGS estimated the total global source of Rhenium at 12,500 Mg, which corresponds to more than two hundred years of production at current extraction rates. Current reserves stand at approximately 2,500 tons, which is enough to sustain current production levels for some 50 years.

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## MAIN PRIMARY AND SECONDARY RESOURCES

### *PRIMARY RESOURCES*

Rhenium is the rarest element in the Earth's crust. Rhenium is probably not found free in nature, but occurs in amounts from 0.001% up to 0.2% in the mineral molybdenite, the biggest commercial source.

### *SECONDARY RESOURCES*

Rhenium is mainly extracted as by-product of copper-molybdenum deposits, with about 80 percent recovered from flue dust during the processing of molybdenite concentrates from porphyry copper deposits. The grade of Re-containing flue dust from Mansfel smelter in Germany is 63 g/t. Molybdenite, which commonly contains between 100 and 3,000 parts per million Rhenium, is the main source of Rhenium in porphyry deposits. The Molymet Mine in Chile dominates world Rhenium supply, producing 55.99% of the total world supply in 2014, followed by United States (19.04%), and Poland (17.02%).

Aitik is one of Europe's largest open-pit copper mines. Molybdenite grains contain up to 1,587 ppm Re, with an average of approximately 211 ppm of Aitik molybdenite and approximately 452 ppm of Salmijärvi molybdenite [25].

Rhenium secondary production takes place in Germany (Buss & Buss Spezialmetalle, H.C. Starck and Heraeus Precious Metals), and in Estonia (Toma Group) [2]. Recycling of Rhenium can be done using Pt-Re spent catalysts from reforming processes, Mo-Re and W-Re alloy scrap, used turbine blades from aircraft engines and waste and scrap from the production of nickel and cobalt-based superalloys. A small amount of Rhenium is also being recovered from medical equipment [12].

Other potential sources of Rhenium are:
- Volcanic gases in the Kuril Islands
- Oil shale in Russia
- Copper as a by-product of nickel production by the Russian Nickel company Norilsh
- Uranium ores in the USA and Uzbekistan

## MAIN RHENIUM PROCESSING AND EXTRACTING TECHNIQUES

Due to the high volatility of the oxidized forms of Rhenium during the processing of copper concentrates in pyrometallurgical processes, it accumulates in dusts and gases. In classical shaft furnace technology, Rhenium is partially distilled and accumulates in the sludge in a form of a sulphide. The rest remains in copper matte from which, after the Bessemer process, Rhenium as a Rhenium (VII) oxide transfers to the gas phase. After the gas phase, it is washed in the washing and cooling section of sulphuric acid plant (FKS). When fluidized-bed furnace technology is used, Rhenium is distilled as an oxide and then goes to the sulphuric acid plant along with other gases, where, in the washing and cooling installation of this plant, it is converted into a weak acidic waste effluent. Dusts from shaft furnaces, sludge from scrubbing, dusts from converters and dusts from fluidized-bed furnaces are directed to the lead smelter. During the smelting of lead in an oscillating-rotary furnace, Rhenium contained in processed gases passes partially to the gas phase, where it is recovered in secondary dusts. In the lead-recovery production cycle, the by-product, an Fe-As alloy, is formed [4].

Molybdenum roasters equipped to recover Rhenium are one of the main commercial sources for this metal. Rhenium can be recovered through liquid and solid ion exchange as presented in the following figure.

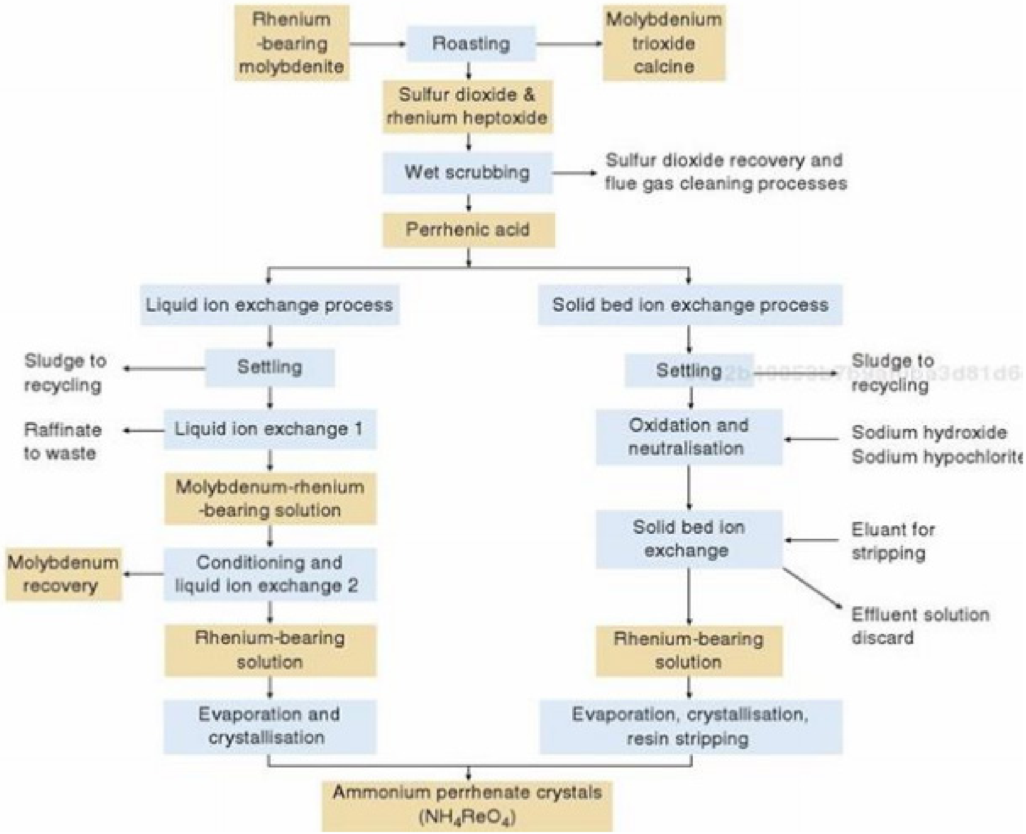


Fig. 4 Rhenium recovery by liquid and solid ion exchange [24]

Extractants commonly used for Rhenium are: trioctylamine, di-isododecylamine, or tributyl phosphate [11].

From W-Re scrap, Re may be recycled via an oxidative pyrometallurgical roasting technique. Initially, the scrap is roasted at 1000°C, under an oxidizing atmosphere to produce Rhenium heptoxide, which is after condensed in the cooler part of the tube furnace. This material is in turn sent for digestion in water. The aqueous rhenium is subsequently precipitated as potassium perrhenate upon the addition of potassium chloride. The potassium perrhenate is filtered and further purified via continued dissolution and recrystallization. After purification, the salt is dried and sent for reduction under an hydrogen atmosphere at approximately 350°C. Experimental results show that 93.1% of the Rhenium was recovered to produce a 99.98% pure Re product [22-23].

## ENVIRONMENTAL AND SOCIAL IMPACTS OF ITS EXPLOITATION

Rhenium is radioactive in all forms because of the content of the isotope 187Re. However, 187Re decays via the emission of very low-energy beta particles (electrons) that pose only a minimal risk to human health. There are few, if any, concerns related to radioactivity during the mining of copper-molybdenum ore or in the processing of the concentrates, as the concentration of Rhenium in these processes is extremely low. Only after the Rhenium is recovered could there be any potentially harmful exposure. However, even at this stage, huge quantities of Rhenium, of the order of several tonnes per annum, would need to be ingested for an occupational worker to exceed recommended annual limits.

The main environmental impact of sulfide deposits is related to drainage phenomena.

The quest for fuel efficiency affects many critical metals, and none more than Rhenium. In so far as Rhenium contributes to high operating temperatures, increased fuel efficiency of gas turbines, reduction of nitrous oxide emissions to the upper atmosphere, and blade longevity, it may be said that Rhenium is a green metal [26]. Rhenium is not included in The Best Available Techniques document published by the commission on tailings treatment and non-ferrous metals.

A life-cycle assessment of Re-recycling technology was conducted as part of the MSP-REFRAM EU Project, particularly as regards technology used for the treatment of Rhenium wastes from superalloy production and processing, with grain sizes ≤ 10 mm. This method is currently used for the production of ammonium perrhenate and consists of a multistage hydrometallurgical process. Compared to the virgin primary process of Re primary extraction, the impacts are very low (except for cumulative energy demand, which is almost the same):

- Global warming potential is about the half that of the virgin process, with the most significant stages being the leaching, the elution and the washing after elution
- Terrestrial acidification potential is about 15% of that of the virgin process, with the leaching stage being the most significant
- Almost null freshwater eutrophication (the virgin process has 35 kg P eq/kg)
- Almost null human toxicity (the virgin process has 6E-02)

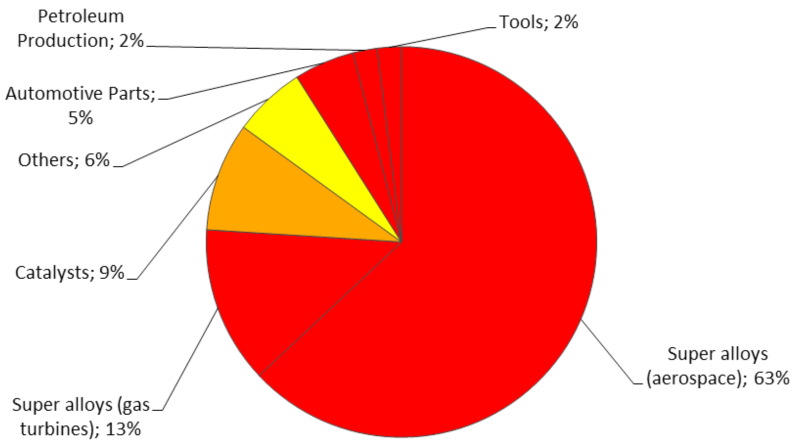
Compared to the other refractory metals, Rhenium has the highest global warming potential and terrestrial acidification (medium impact).

## SUBSTITUTION POSSIBILITIES

The substitutability index of Rhenium is given in the table below and presented in a more visual format in the pie-chart diagram:

| Application | Share | Megasector | Substitutability index |
|---|---|---|---|
| Super alloys (aerospace) | 63% | Transport-Other | 1.0 |
| Super alloys (gas turbines) | 13% | MechEquip | 1.0 |
| Catalysts | 9% | Chemicals | 0.7 |
| Others | 6% | Other | 0.5 |
| Automotive Parts | 5% | Transport-Road | 1.0 |
| Petroleum Production | 2% | Refining | 1.0 |
| Tools | 2% | MechEquip | 1.0 |

**Table 1. Substitutability of Rhenium given by application [27]**



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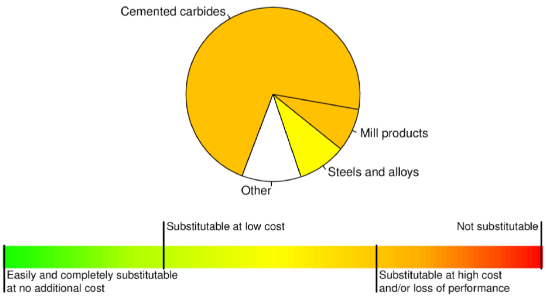

High Rhenium prices in the period 2007-2009 (10,000 $USA /kg) forced Rhenium users to search for methods to reduce Rhenium content in superalloys used in monocrystalline turbine blades situated near the combustion chamber in aero engines and other gas turbines. As a result of the research, several alloys were designed, including CMSX-8 and Rene515 which contain 1.5% Re, and Re-free CMSX-7. For the moment, however, the addition of Rhenium in superalloys still seems to be inevitable as no element has been found that can provide equal high-temperature (1600°C) creep resistance. Such temperatures and conditions are often found in large aero engines of twin-aisle civilian aircraft, as well as in land-based gas turbines used for continuous power generation.

Rhenium substitution is more common in the gas-to-liquid (GTL) catalyst market, using, for example, iron-based catalysts.

- **Substitutability in superalloys:** The advantage of using Rhenium in superalloys is that the addition of Rhenium allows for designing with closer tolerances, operating at higher temperatures, with prolonged engine life and increased engine performance and operating efficiency. It is difficult to find substitutes for it, although in 2008, General Electric announced that they will aim to reduce Rhenium content in production of jet engines in favour of ceramic matrix composites (CMC) [19].

- **Substitutability in catalysts:** Platinum-Rhenium on a silica or silica-alumina base are used in the reforming process of low octane petroleum refinery naphtas into high-octane liquids for high-octane gasoline [19].

## HEADING TOWARDS THE FUTURE: RECENT RESEARCH ACTIVITIES

Research activities in Rhenium extraction are and will continue to be focused on:

- Development of the **synthesis of new extractants** for Rhenium that are more selective, durable, ecological and economical [4].

- **New, more efficient methods of Rhenium recovery** based on solvent extraction and ion exchange, which will require a thorough examination of the latest available ion-exchange resins and organic extractants in order to optimize the Rhenium recovery process. Both methods generate large amounts of waste solutions. Membrane techniques have high industrial potential to reduce the amount of waste solution and to provide a more energy-efficient process [4].

- **Recovery of Rhenium from dust** [5], mainly using hydrometallurgical methods employing acid, base and sodium salts as leaching agents. An interesting alternative is to use the pressure method for recovery of Rhenium from dusts. This technique makes it possible to significantly improve the efficiency of Rhenium recovery, while minimizing leaching time and decreasing the leaching temperature [6].

More specifically, there have been recent studies on the following topics:

- **Rhenium extraction as by-product of Copper/Molybdenum production:** Rhenium recovery from direct leach liquors and from side-streams, as a direct ion-exchange recovery of Rhenium from Copper heap-leaching containing about 1 ppm Rhenium [7], Rhenium and Molybdenum recovery from a solution with tributylphosphate at acidic conditions and stripped with $NH_4OH$ to obtain an ammonium perrhenate solution [8].

- **Rhenium extraction from Spent Catalysts:** Pt-Re catalyst leaching with HCl-$HNO_3$ and selective precipitation [9], or milder treatment with $NaHCO_3$ to first extract Rhenium followed by complete dissolution with sulfuric acid [10].

- **Rhenium from scrap or spent catalysts:** Dissolution in sulfuric acid or hydrochloric acid solution, a mixture of HCl and $HNO_3$, or in aqueous acidic solution of sodium bicarbonate (catalysts), preceded by roasting in an oxidizing atmosphere or molten salts, followed by dissolution in an aqueous solution of ammonia or in water, and precipitated as $KReO_4$ through the addition of KCl, for example. Ion-exchange with selected ionites can be used to obtain a pure Rhenium compound [13-18].

## *EUROPEAN RELATED PROJECTS*

- **SPIN-PROJECT:** Technology which makes it possible to obtain ammonium perrhenate (VII) from solutions of a very low Rhenium concentration.

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