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Abstract

Rhenium is a unique, valuable and extremely rare chemical element currently used as an alloying element in high-temperature superalloys for aerospace and industrial gas-fired turbines and also as a catalyst in petrochemical industry. Moving towards a more competitive and sustainable economy requires access to this metal in adequate quantities and at competitive costs. However, minerals containing rhenium are generally found in very small quantities and are currently not commercially viable sources. Thus, the method and route for the extraction of primary rhenium is dependent on other metals (copper, molybdenum and uranium) of which rhenium is a by-product. In addition, focusing on alternative sources such as recycling of rhenium from waste alloy scrap and catalysts, is continually gaining attention in the research community. This paper has focused on the assessment of secondary sources of rhenium. The historical cost and also supply interruption indicators of rhenium were examined and assessed. Finally, opportunities of recovering and reusing existing stocks through Industrial Ecology are discussed.

Keywords: Rhenium, Supply interruption, Recycling, Industrial Symbiosis and Cost

1. Introduction

1.1. Background

Rhenium (Re) is one of the rarest and most dispersed naturally occurring elements in the Earth's crust, with estimates of average crustal abundance ranging from 0.2 to 2 part per billion Re) [1-8]. Re was discovered in 1925 by Ida Tacke, Walter Noddack and Professor Otto Berg [1, 6]. Early processing of rhenium from the roasting of molybdenite started in 1960 by Kennecott in the USA [3, 8]. Since then rhenium production has taken place in several other countries with Chile now the dominant supplier [1-3, 8]. Rhenium is currently used as an alloying element in super alloys in both aerospace and industrial gas-fired turbines and also as a catalyst. More than 80% of the rhenium consumed worldwide is used in super alloys [3-5, 8]. Nickel-base alloys contain 3-6% rhenium which is critical to the manufacture of turbine blades for jet aircraft engines and industrial gas turbine engines [8]. The work of Giamei [8] showed that additions of up to 6% (by weight) of rhenium resulted in a significant improvement in the creep resistance of single-crystal nickel-based turbine blade alloys. Subsequent research by Giamei and Anton [10] showed that this improvement was partly due to the reduction of the rate of coarsening of the γ' precipitates in nickel-based superalloys. The high-temperature properties of Re allow turbine engines to be designed with better tolerances and operate at temperatures higher than those of engines constructed with alternative alloying elements. These properties enhance the engine performance and the operating efficiency. The importance of rhenium to the aerospace industry is demonstrated by the fact that single-crystal superalloys are grouped into generations based on their rhenium content [1, 6-8]. The current generation of superalloys contains 5-6% rhenium by weight. Re is also used in the petrochemical industry as platinum-rhenium catalysts which account for about 10% of worldwide rhenium consumption [1-4]. The petroleum industry uses platinum-rhenium catalysts to produce high-octane, lead-free gasoline. These catalysts boost the octane level of refined gasoline and improve refinery efficiency. Other applications of rhenium include devices that control temperature, such as thermostats, heating elements and also therapeutic applications such as nuclear medicine, preparation of radiopharmaceuticals for radionuclide therapy, oncology, interventional radiology and cardiology [6-8]. For example, Re has been reported in countries such as, the United Kingdom, the United States, Germany, and China to be effective in treating tumours [6]. However, in many countries, the effective use of Re for medical purposes is in its emerging stages [1-6]. Lassner and Schubert [11] also reported on the use of tungsten-rhenium in rotating X-ray targets with graphite body and tungsten-rhenium focal track. Given the critical mega-trends of a rising global population and consumption, it can reasonably be expected that demand for Re will continue to grow for many decades [6]. The apparent trend of the growing consumption of rhenium might increase prices and enlarge the gap between supply and demand.

The fact that rhenium is an important alloying element in gas turbine blade superalloys has turned this transition metal into a strategic material with several countries wishing to establish secure supplies of it. In addition to its strategic importance, increases in its consumption, its high cost and low material resources have contributed to interest in the development of recycling processes for rhenium [1-13]. As a result, there has been research effort focused on the recycling of rhenium contained in alloy scrap such as nickel-base alloys and catalysts [1]. Through rhenium scrap recycling efforts, about 10 tons of rhenium are reportedly salvaged annually [12]. Recycling can provide energy conservation and improve economic process viability. Furthermore, considering the high environmental impact of primary production due to low ore concentrations and difficult mining conditions, recycling

becomes even more beneficial from the environmental viewpoint. Both recycling and improvement in separation technologies from raw materials such as copper and copper-molybdenum concentrates may be required to meet the growing demand for Re worldwide. The growing attention to developing a circular economy is structured so that policy makers and businesses seek to generate circular resource flows in ecosystems [15] by facilitating recovery and reallocation of materials and resources [16]. Processes such as industrial ecology and symbiosis may present new opportunities to source rhenium as a recycled resource addressing the problems of its being scarce.

Several authors reported on the different technologies for the production of rhenium from mineral deposit ores [1-9] Millensifer [8] reported assessment of the potential of future minerals sources of rhenium and on the promise of different mineral deposits. However, recycling from alternative sources such as alloy scrap and catalysts have not been examined. Furthermore, there is no study on the assessment of supply interruption indicators for rhenium. To better understand the global rhenium situation, this paper presents a comprehensive global assessment of rhenium recycling and process technologies. Attention has been given to recycling and assessment of different secondary sources of Re with possible commercial applications. Finally, the opportunities of recovering and reusing existing stocks through Industrial Ecology are discussed.

1.2.   Physical and chemical properties of Rhenium

Re is a silvery-white coloured transition metal and is element number 75 in the Periodic Table. It consists of two isotopes ^{187}Re and ^{185}Re. ^{187}Re, accounts for 62.6% of the total, while ^{185}Re accounts for 37.4 per cent [5, 8]. ^{187}Re is radioactive with a half-life of approximately 4.3×10^{10} years [8]. However, the beta radiation emitted is very low (0.3 M eV) and cannot penetrate human skin. The chemical properties of Re are like those of the metals in the manganese group (Group 7) of the Periodic Table. The physical properties, however, are similar to those of the refractory metals of Groups 5 and 6, particularly molybdenum and tungsten [1]. Re has a high melting point of about 3200 °C and is also considered as a refractory metal, with only tungsten having a higher melting point. However, in contrast to other refractory metals, rhenium does not form carbides [1, 8]. Platinum and osmium have greater specific gravities. Re exhibits several valencies from –1 to +7, the common once are +7, +6, +5 and +4 [1,8]. It easily changes from one valence to another, a property which makes it ideal for use as a catalyst. It has been reported in the literature that when rhenium is alloyed with molybdenum or tungsten, the resultant alloy exhibits or retains the 'best' properties of both metals individually and none of the 'poor' properties of either metal [1, 4, and 8]. For example, when tungsten is heated above its recrystallization temperature of about 1200 °C and also cooling it to room temperature causes it to become brittle [12]. The addition of rhenium to tungsten and molybdenum significantly reduces the brittle characteristics, increasing the recrystallization temperature, the ductility and the ultimate tensile strength of the alloys. Re does not exhibit ductile-to-brittle transition behaviour and it retains its ductility down to sub-zero temperatures, making it ideal for use in space propulsion applications such as rocket-thruster nozzles which have been reported to withstand more than 100,000 thermal fatigue cycles from room temperature to above 2225 °C without evidence of failure [8]. Re is also resistant to corrosion in sea water, hydrochloric acid and sulphuric acid [17]. Selected properties of rhenium are listed in Table 1.

Table 1: properties of rhenium

Property	Value	Units
Symbol	Re	

Atomic mass	75	
Atomic weight	186.21	
Density at 25 ºC	21023	kg/m³
Melting point	3180	ºC
Boiling point	5926	ºC
Hardness (Mohs scale)	7.0	
Specific heat cap at 25 ºC	0.14	J/(g ºC)
Electrical resistivity at 25 ºC	18.40	nΩm
Thermal conductivity	48	w/mºC
Young's modulus	463	GPa

2. Current sources of rhenium

2.1. Current supply: World resources and production

The world mine production of rhenium from the main known sources has been estimated to be 48 tonnes [1]. Re is among the rarest metals on earth. It does not occur as a mineral in nature but is mostly produced as a by-product of molybdenum production associated with porphyry copper and copper–gold deposits. Porphyry deposits account for roughly 85 to 90 per cent of primary rhenium production [1, 8, and 17]. The highest portion (26 tonnes Re) was produced in 2012 by Molymet in Chile, mainly from large porphyry deposits such as El Teniente and Collahuasi [1, 8]. Other sources include molybdenite concentrates from deposits in other countries including Mexico, Peru and the United States. The United States was the second largest producer (7 tonnes Re), with production mainly from Sierrita-Esperanza and Bagdad [17-21]. Other porphyry deposits from which Re was recovered include those at Kadzharan and Agarak in Armenia, Erdenet in Mongolia, Kal'makyr in Uzbekistan and Kounrad in Kazakhstan. Re is listed in China by Jiangxi Copper as one of the products from the Dexing porphyry copper–molybdenum deposit [8]. Even though a significant amount of rhenium is present in porphyry molybdenum deposits at places such as Climax in Colorado, the rhenium content of the molybdenite at Climax and other porphyry molybdenum deposits is generally too low to be recovered economically [1,8]. Re production from sediment-hosted copper deposits in 2011 is estimated to have been six to seven tonnes, about 3.5 tonnes from the Lubin deposit in Poland and a lesser amount from the Dzhezkazgan deposit in Kazakhstan [1, 8]. In addition, an unspecified amount, probably about 0.5 tonnes or less, was recovered at the Navoi metallurgical plant in Uzbekistan from the leach solutions associated with the in-situ mining of sandstone-hosted uranium deposits [1, 8]. In addition to porphyry deposits, other deposits include vein deposits, sediment hosted copper deposits, uranium deposits and magmatic nickel copper platinum group element deposits [2]. Table 2 shows the world rhenium reserves and production by country.

Table 2: World rhenium reserves and production by country [1]

Country	Mine production [kg]		Reserves [kg]
	2015	2016	
Chile	26000	26000	1300000
United states	7900	7900	390000
Canada	1800		32000
Russia	1500	1500	310000
Kazakhstan	1000	1000	190000
Aremenia	350	400	95000
Peru	5000	5000	45000

Poland	8900	7000	
China	2400	2400	
Other countries	1800	1800	91000
World total	48000	47200	2500000

2.2. Rhenium bearing minerals

A list of rhenium bearing minerals is shown in Table 3. Rheniite minerals are rich in rhenium but they are very small in quantity and are not commercially viable. The only documented occurrence of Re as a mineral, rheniite (ReS_2), was found near the Russian Kudryavyi and occurs in high-temperature volcanic fumaroles and, as the sulphide mineral rheniite [1]. In addition, rheniite occurs in other deposits including the Pagoni Rachi porphyry-type molybdenum–copper–tellurium–silver–gold prospect in northern Greece and the Phoenix nickel–copper–platinum-group element (PGE) deposit in Botswana [19]. Other rhenium sulphide minerals include dzhezkazganite, recognised in the copper ores of the Dzhezkazgan deposit, Kazakhstan [4] and tarkianite, identified in the Hitura nickel–copper–PGE deposit, Finland [21-23].

Even though rhenium has an affinity for sulphide phases, its concentration in most sulphide minerals is relatively low. The rhenium content of most molybdenites is generally within a range of a few ppm to several thousand ppm Re, although contents as high as 4.7 wt% Re occur in molybdenite at the Pagoni Rachi prospect [1] and up to 11.5 wt% Re has been recorded in molybdenite deposited in high-temperature fumaroles [18]. However, molybdenites, from which rhenium is currently recovered, commercially contain of the order of 200 to 1000 ppm Re [8, 21]. Other minerals in which rhenium may be concentrated in significant levels (i.e. >1 ppm Re) include uraninite, which can contain up to 2700 ppm Re and gadolinite [21].

Table 3: Rhenium bearing minerals. Most rhenium is produced from molybdenites

Name	Formula	Rhenium content
Rheniite	ReS_2	74%
Tarkianite	$(Cu.Fe)(Re.Mo)_4S_8$	49 -56%
Dzhezkazganite	$ReMoCu_2PbS_6$	22%
Molybdenite	MoS_2	<10 ppm to 11.5%
Castaingite	$CuMo_2S_5$	up to 1%
Uraninite	UO_2	up to 2700 ppm
Gadolinite	$Y_2Fe^{2+}Be_2Si2O_{10}$	up to 1ppm

3. World trade and historical cost of rhenium

3.1. World trade

Rhenium is generally traded in the form of ammonium perrhenate (APR). The Minor Metals Trade Association (MMTA) published specifications for basic-grade APR to contain a minimum of 69.00% Re and less than 0.05% by weight of impurities like Si, Fe, K, Mo, Al, Ca, Cu, Mg, Mn, Ni, Na, P and S, together with a maximum water content of 0.10% [8,24]. The international trade in rhenium is partly determined by the geological/geographical locations in which it arises and by the development of the industries that have commercialised its use. During the early cold war period (in the 1950s), rhenium was just beginning to be commercialised in catalyst applications and production in Kazakhstan and Armenia was used to supply the USSR and no exports were made to any Western countries [1]. The first commercial production in the USA was established around the same period to

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supply the oil-refining industry in the West [1, 8]. The processing plants were located at Shattuck Chemical in Denver, Colorado and Kennecott Copper, in Garfield, Utah. The key change to the structure of the trade occurred in the late 1970s when, due to a large build-up of stock at that time, (as much as 12 tonnes in 1974), the producers were discouraged out of the business and thus ceased production [8]. Philipp Brothers, a trading company then bought the technology for the recovery of rhenium from flue dusts from Shattuck Chemical and transferred operations to Santiago, Chile. This was a logical development as the plant was situated at the heart of the copper industry which supplied by-product rhenium-bearing molybdenite for rhenium recovery. This was the origin of Carburoy Metalurgia (now known as Molymet), today's leading producer of rhenium ([1, 8, 25].

Rhenium's unique properties have made it a vital part of the superalloy industry, most prominently in nickel superalloys used in both aerospace and industrial gas-fired turbines and also as a catalyst. Molymet's dominance has emerged by virtue of this strategic position, controlling the main world supply of rhenium via the recovery of rhenium units from the flue of their large molybdenite roasters. Production of rhenium here in 2012 was 24.68 tonnes that accounted for more than 55% of world primary supply [1, 8]. However, in keeping with the history of the initial over-production in the 1970s, Molymet, in the 1980s, pursued a policy of long-term fixed price contracts in order to encourage the commercialisation of rhenium in the aerospace industry [1]. During this period Molymet supplied more than 70% of the world's rhenium and free trade in rhenium was extremely limited. All this changed in the early 1990s because of two factors, (i) the break-up of the Soviet Union, and (ii) the rapid development of rhenium uses in modern jet engines. For the first time, Soviet stockpiles of rhenium flowed to the west from Kazakhstan, allowing companies in Europe such as HC Starck GmbH and WC Heraeus GmbH (now called Heraeus Precious Metals GmbH & Co. KG) to manufacture rhenium metal pellets suitable for the superalloy industry using non-South American rhenium raw material [1].

3.2. Historical cost of rhenium

Fig. 1 illustrates a combination of historical free-market rhenium prices from a variety of sources and shows periods of price fluctuation in the market. From the 1970s, at the starting of the wider trade in rhenium, prices ranged from US$3,000/kg Re contained, reducing to price as low as US$300/kg in the mid-1990s and subsequently peaking at US$12,000/kg in August 2008. The prices in the 1970s reflected first-time buying of rhenium as a raw material for bimetallic catalysts, prior to recycling that extended the efficiency of the industry [1, 8]. The next price hike arrived during the period following the OPEC oil crisis of the mid-1970s. In order to minimise dependency on oil, there was a drive for smaller cars. In addition, worldwide legislation, led to reduction of lead in petrol. The proliferation in demand for high-octane petroleum increased the demand for bi-metallic reforming catalysts. The trough in prices in the early 1990s, when prices reduced to near US$300/kg for almost five years, resulted from the disposal of redundant Soviet/ Kazakhstan stocks onto the Western market. The slow recovery from the late 1990s reflected the emerging use of rhenium in modern gas-turbine engines, while peak prices in 2008 of as high as US$12,000/kg, were attributed to Molymet's inability to meet demand from the aerospace industry [8]. The rhenium market went through a significant downward correction in 2009 after a period of strong demand growth and an escalation in prices up to the last quarter of 2008. The credit crisis and the resulting recession, particularly in North America and Europe, severely affected the major markets for rhenium and demand dropped by 16% in 2009 [1, 8]. In June 2010, rhenium metal prices were $4,500-5,000/kg. Those economies that were worst-affected following the credit crisis are now beginning to recover and the rhenium market is expected to follow suit.

With growing demand in the aerospace sector being the main driver for rhenium consumption, it is expected that prices are unlikely to decline. Despite past volatility, the future market for rhenium is expected to be more stable, largely as a result of increasing demand for more aircraft engines. Indeed the aerospace sector is expected to remain the largest end-market for rhenium and is predicted to account for more than 80% of global production. For the period 2018-22, the global rhenium market is expected to grow at a compound annual growth rate (CAGR) of more than 7% due to the demand for superalloy turbine blades.
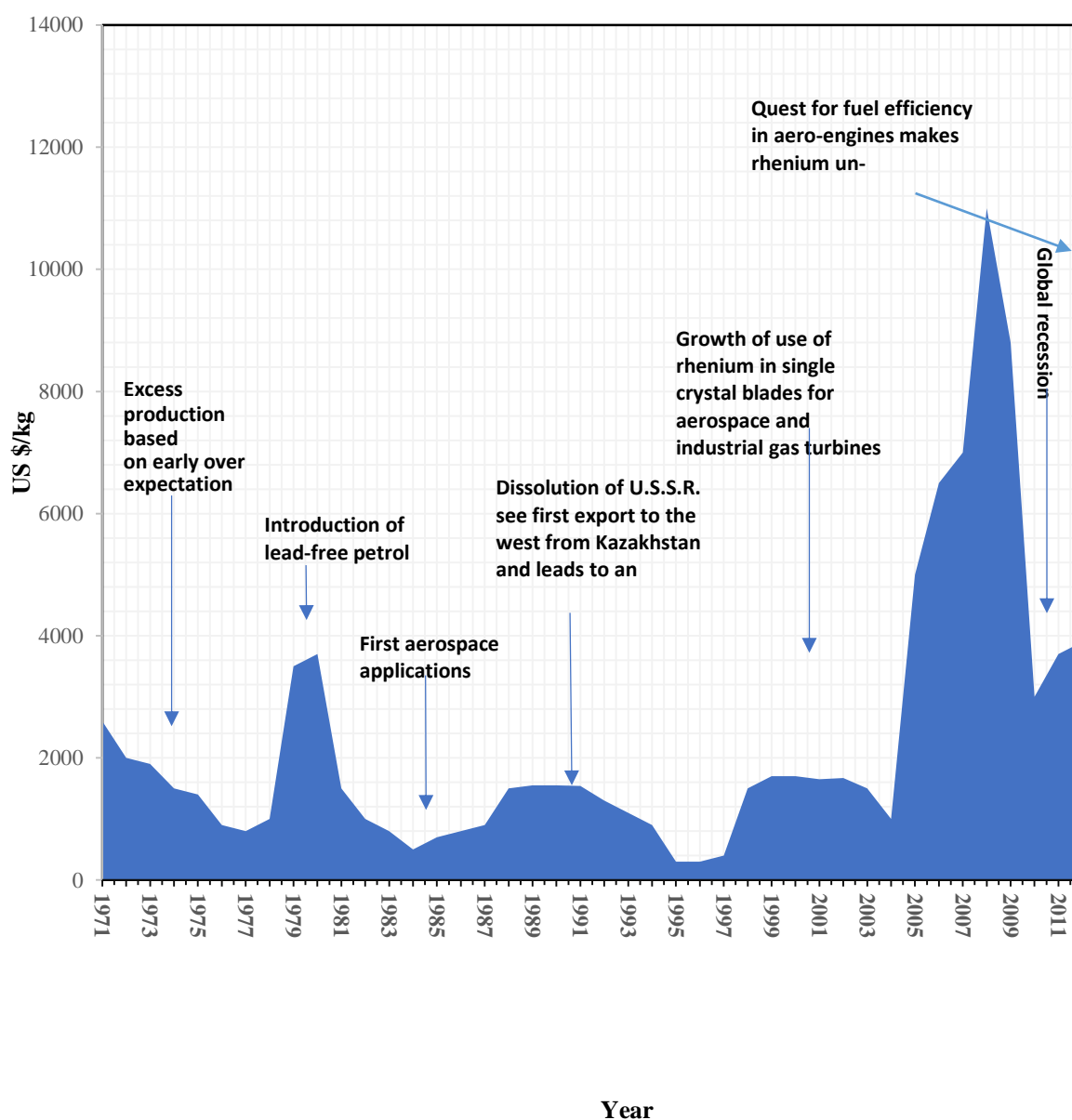

Fig 1: Rhenium price trend, 1971–2010.

3.3.   Supply interruption indicators of rhenium

Rhenium supply is derived as a by-product from molybdenite sludges, which themselves are a by-product of mining porphyry copper deposits. Thus, the supply of rhenium depends on

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factors that impact global copper production, or even the distribution of copper production among different deposits. Clearly as more copper and molybdenum are extracted, more rhenium concentrates will be available as well. Many factors can potentially interrupt supply of materials. However, by- product metals or companion metals typically have greater risk to supply disruption because the infrastructure may not be well established. Supply of raw materials can be threatened by different factors such as reserves, trade, ecological impact, processing, substitutability and recyclability. Table 4 shows the supply interruption indicators for Re and Table 5 outlines the criteria used to classify the major factors into a high (H), medium (M) or low (L) impact [25-27]. The indicators are noted for each element.

Table 4: Supply interruption indicators for Rhenium

Criteria	Rationale for the classification	Classification
Reserves	As the sole economic source of rhenium is as a by-product of molybdenum in copper mines, the reserves are totally linked to the availability of these metals.	High
Trade	Trade in rhenium is controlled by copper/molybdenum producers who exploit copper porphyry deposits. There are a limited number of companies in this position and by far the largest is Molymet, based in Chile, who produces almost half the world's supply. Large-scale porphyry mining also takes place in the US, but data is not currently available. The Polish company KGHM has joined the ranks of producers, fairly recently, with metal derived from its copper workings; the company reports an annual production capacity of 4 tonnes, equivalent to nearly 7% of world production.	High
Ecological impact	The ecological impact of the metal itself is therefore considered to be low to non-existent, although, as it is mostly produced as a by-product of molybdenum and copper mining, it could be associated indirectly with the impacts caused by the extraction of those metals.	Low
Processing	As mentioned above, most rhenium is extracted from molybdenum that is found in copper deposits. During the roasting of molybdenum, rhenium converts to rhenium pentoxide, which becomes deposited in the exhaust stacks of the roasting plant. This material is extracted by intensive washing and an ion-exchange process is used to recover rhenium. Copper roasting can also lead to the accumulation of rhenium pentoxide in the exhaust stack	High
Substitutability	The scarcity and price of rhenium have long driven efforts by major users to find substitutes but with limited success. Aero engine manufacturers,	

	including GE, have reduced the proportion of the metal needed in super alloys but have not been able to replace it. For use as a catalyst, rhenium can be substituted by elements including gallium, germanium, indium and selenium, unfortunately all critical materials themselves.	Medium
Recyclability	Rhenium recycling rates are reported to be steadily increasing, driven by the high cost of the metal and the supply rate being controlled by the copper and molybdenum industries. Recycling rhenium is facilitated by the fact that much of the metal is used in aero engines, which are fully accounted for throughout their existence	Medium

Table 5: Factors that can potentially interrupt supply of materials

Criteria	High (H)	Medium (M)	Low (L)
Reserves	• Reserves to production ratio (R/P) <20 years • Or R/P <100 years but semi monopolistic production	• R/P = 20 - 80 years • Or uncertain data	• R/P > 80 years • No monopolistic situation
Trade	• Element not traded on metal exchange • Semi-monopolistic (below)	• Element not traded on metal exchange • Semi-monopolistic production • Uncertain	• Traded on metal exchanges • No monopolistic production
Ecological impact	• Element is toxic • Ores contain low grade toxic or radioactive substances that might get enriched during processing • Risk of	• Low toxicity known • Uncertain data • Toxicity has been put/is in the process of getting into jurisdictional context	• No toxicity • No handling problem known

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	bioactivity is not refuted		
Processing	• Element is produced as by product	• The Element is main product and complex refining technologies are required • Uncertain data	• Element is main product • Technology proven
Substitutability	• No substitute of materials level available • Substitute available but itself considered critical	• Substitute available with degradation in performance • No substitute available on materials level but on systematic level	• Substitute available
Recyclability	• No Recycling technology in mass operation • Material concentration in the end of life production is low	• Recycling technology in place and logistics as limiting factor • Uncertain data	• Recycling technology in place • Global recycling rate >50%

4. Rhenium mineral extraction and recycling technologies

4.1. Rhenium mineral extraction

Rhenium is produced commercially from deposits associated with copper and molybdenum. Typically, rhenium exists in mixed copper/molybdenum deposits and is firstly separated from copper (accompanied with molybdenum) deposits using conventional concentration technologies such as froth flotation [1,25]. Following primary separation, molybdenum trioxide (MoO_3) is produced via pyrometallurgical roasting or hydrometallurgical pressure oxidation processes. The pyrometallurgical method involves roasting of molybdenum concentrates and the rhenium present is oxidized to rhenium heptoxide (Re_2O_7) as shown in equation 1:

$$2ReS_2 + 7.5O_{2(g)} = Re_2O_7 + 4SO_{2(g)} (\Delta G°_{298K} = -1701.6 \text{ kJ/mol}) \quad (1)$$

Rhenium heptoxide is extremely volatile and has a vapour pressure of (P_{vap} = 0.936 atm at 359.9 °C); It is expected that at the temperatures used for molybdenum roasting (627-679 °C),

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nearly all of the (Re_2O_7) present is volatilized. This volatile product exits the furnace with the flue gases and is subsequently recovered as perrhenic acid ($HReO_4$) after being scrubbed with water as illustrated by the reaction in equation 2:

$$Re_2O_7 + H_2O = 2HReO_4(aq) \quad (\Delta G°_{298K} = -63.5 \text{ kJ/mol}) \tag{2}$$
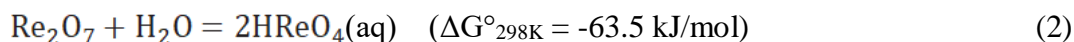
After scrubbing, the aqueous rhenium is typically recovered using solvent extraction or ion-exchange processes. Generally, the end product produced by these methods is ammonium perrhenate (NH_4ReO_4) which is formed by crystallization. Generally, repeated recrystallization is necessary to achieve the required ammonium perrhenate purity of 99.95 % by metal basis. Details of solvent extraction and ion exchanges processes for rhenium recovery are well explained in the literature [1, 25].

4.2. Recycling and re-use of rhenium

In addition to being produced as a by-product of the extraction of molybdenum, it is possible to recycle rhenium after usage. Processing of rhenium-laden manufacturing scrap and end-of-life materials, such as catalysts and superalloys, may present opportunities to source rhenium as a recycled material. A number of potential recycling approaches have been proposed which may include the utilization of primary processing techniques, as well as the implementation of end-of-life recycling programs. The following subsections illustrate a number of current technologies that might be used to recover rhenium from secondary sources.

4.2.1. Recycling from super alloys and alloy scraps.

Waste alloy scraps may be recycled using an oxidative pyrometallurgical roasting technique. The scrap material is first subjected to roasting at a high temperature of 1000° C, under an oxidizing atmosphere to produce rhenium heptoxide (Re_2O_7) and is subsequently condensed in the cooler section of the tube furnace [1, 25] The final product, aqueous rhenium (ReO_4^-) is subsequently precipitated as potassium perrhenate upon addition of potassium chloride as shown in the reaction equation [3]

$$KCl + ReO_4^- = KReO_4 + Cl^-(aq) \ (\Delta G°_{298K}) = -25.66 \text{ kJ/mol} \tag{3}$$
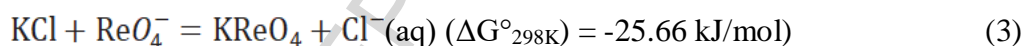
The potassium perrhenate is further subjected to purification by filtration and also dissolution and recrystallization. After purification, the salt is dried and sent for reduction under a hydrogen atmosphere at approximately 350° C. The experimental work of Heshmatpour and McDonald [14], demonstrated that 93.1% of the rhenium was recovered to produce a 99.98% pure Re° product.

In a similar study, Olbrich et al. [13] reported a process using elevated temperature digestion and recycling of rhenium-containing superalloys which are initially digested in a molten salt melt containing $NaOH$, Na_2CO_3, and Na_2SO_4 at temperatures between 850-1,100°C in a directly fired rotary kiln and also oxidizing agents such as nitrates and peroxides of the alkali metals are added. The melt from this process is then cooled down and sent to a comminution process for size reduction. The material is then leached using water as the lixiviant to selectively dissolve the 6th and 7th group elements present in the superalloy. The slurry is then filtered to separate the insoluble Co, Ni, Fe, Mn and Cr from the leach liquor. Magnetic separation is then applied to the insoluble components for further separation and concentration. The pregnant leach solution is sent to an ion exchange step, where the aqueous

rhenium is selectively adsorbed and can be recovered. An example of the flowsheet for this process is shown in Fig 2.

On the other hand, Stoller et al. [28] proposed a process based on the use of titanium baskets as electrodes. The baskets containing the superalloy scrap are fed to a polypropylene electrolysis cell containing 18% HCl solution. The electrolytic dissolution is carried out for 25 hours at a frequency of 0.5 Hz, current of 50 A, voltage of 3-4 V and a temperature of 70° C. The remaining scrap is then filtered from the pregnant solution and sent for further dissolution in sodium hydroxide/peroxide solution. After completion, this filtrate is sent to ion exchange for the recovery of rhenium and molybdenum. Rhenium is recovered using the ion exchange processes discussed previously [1]. An illustration of this process is shown in Fig 3. The authors have provided no details of the energy requirement for the two proposed recycling routes. However, the use of electrolysis for an extended period of 25 hours is likely to be expensive and with a high energy requirement. The need for titanium electrodes will further increase the cost.
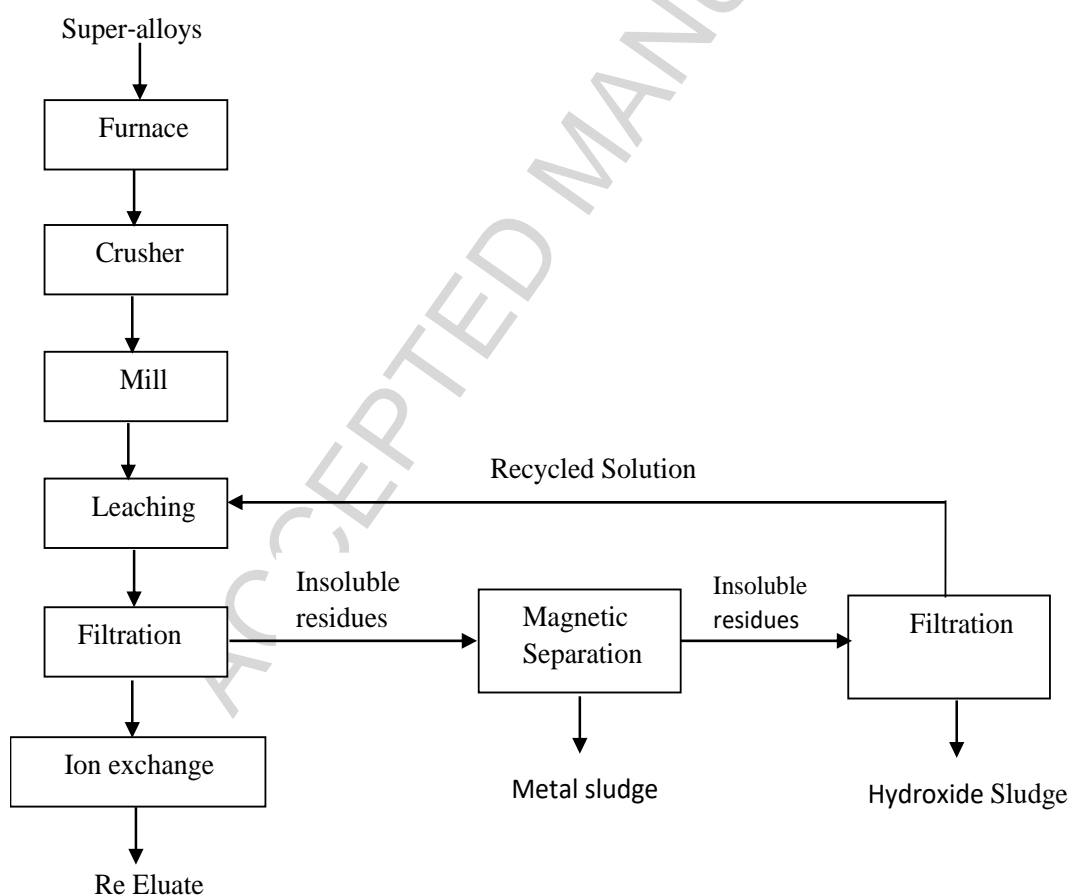

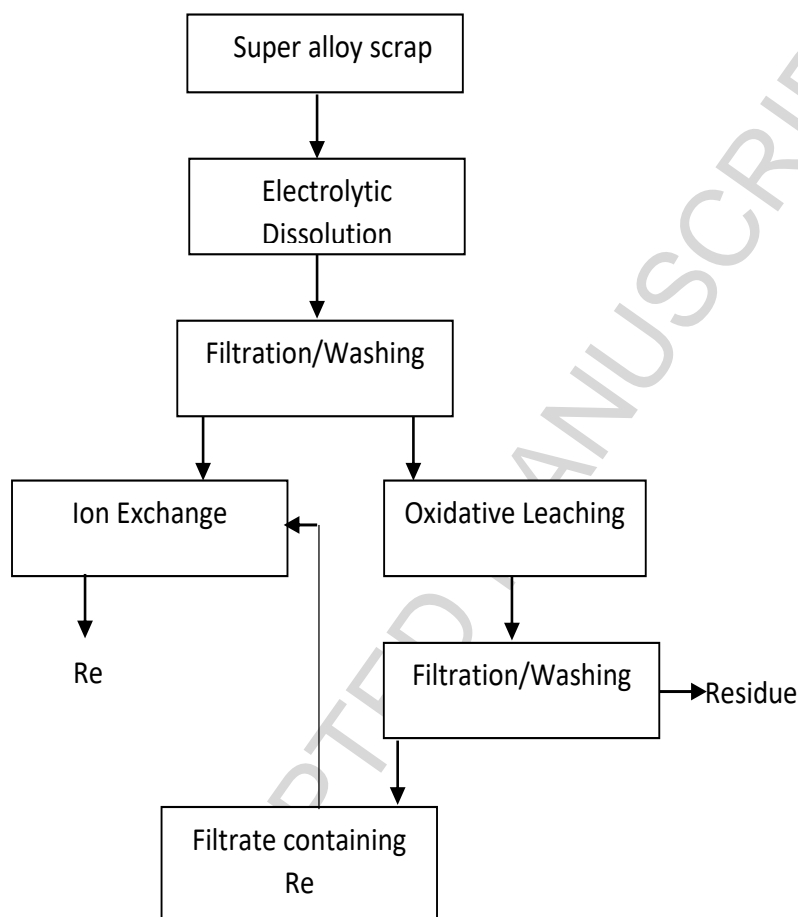Fig 2: The H.C. Starck process for superalloy recycling [13]

Fig 3: Electrochemical method for recycling of super alloy [28]

4.2.2. **Recycling of spent Pt-Re catalysts**

Petroleum-reforming catalysts containing rhenium and platinum on an alumina substrate are extensively used in the refining industry for the improvement of the octane level of fuels. Following use and deactivation, an effective method for the recovery of rhenium and other PGM metals is necessary. Two routes have been reported to be able to achieve this; these are illustrated in Fig. 4 and involve the following [29].

1. Complete dissolution of the alumina substrate.

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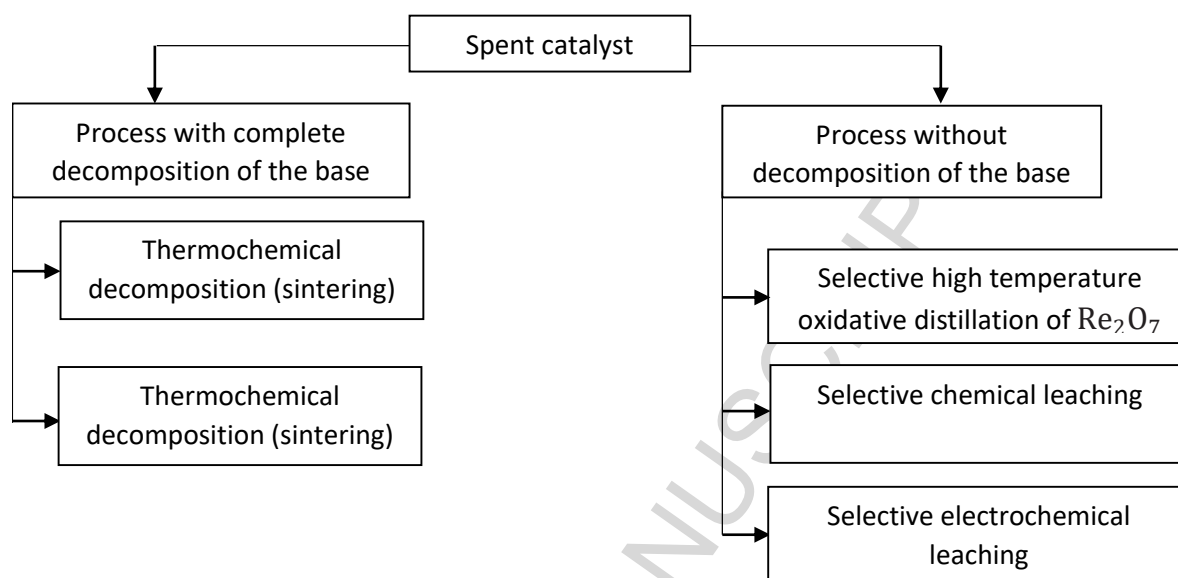2. Selective dissolution and recovery of rhenium and platinum.

Fig 4. Technologies for recycling of spent platinum rhenium catalyst

4.2.2.1. Complete dissolution of the alumina substrate

Complete dissolution of the alumina substrate can be conducted using sulphuric acid which also dissolves rhenium and to some extent, platinum [1]. H_2SO_4 has been demonstrated to be effective for leaching applications in the literature [3, 31]. The rhenium-rich solution is separated from the platinum-containing residue and aqueous aluminum using ion exchange. Rhenium is eluted from the organic amine resin by way of hydrochloric acid addition. After elution, the rhenium-rich eluate is neutralized using ammonium hydroxide. This solution is then evaporated to form a supersaturated perrhenate. After continued redissolution and recrystallization, a high-purity ammonium perrhenate precipitate is produced. The flowsheet for this process is summarised in Fig 5.

Sodium bicarbonate may also be used as a lixiviant in place of sulphuric acid. The proposed advantage of this process is the complete removal of the ion exchange circuit unlike the above process using H_2SO_4 as a leach solution. Experiments were performed on crushed and uncrushed catalysts in both packed columns and agitated leach vessels. Experimental results have shown that rhenium is preferentially leached in the sodium bicarbonate solution. Rhenium recovery has been reported to reach 97% for crushed catalysts and 87% for uncrushed catalyst samples. This result would be expected as the use of cruched catalysts leads to a greater surface area for the dissolution reaction. Following dissolution, the aqueous rhenium is crystallized via evaporative crystallization in the form of an ammonium perrhenate intermediate product [1].
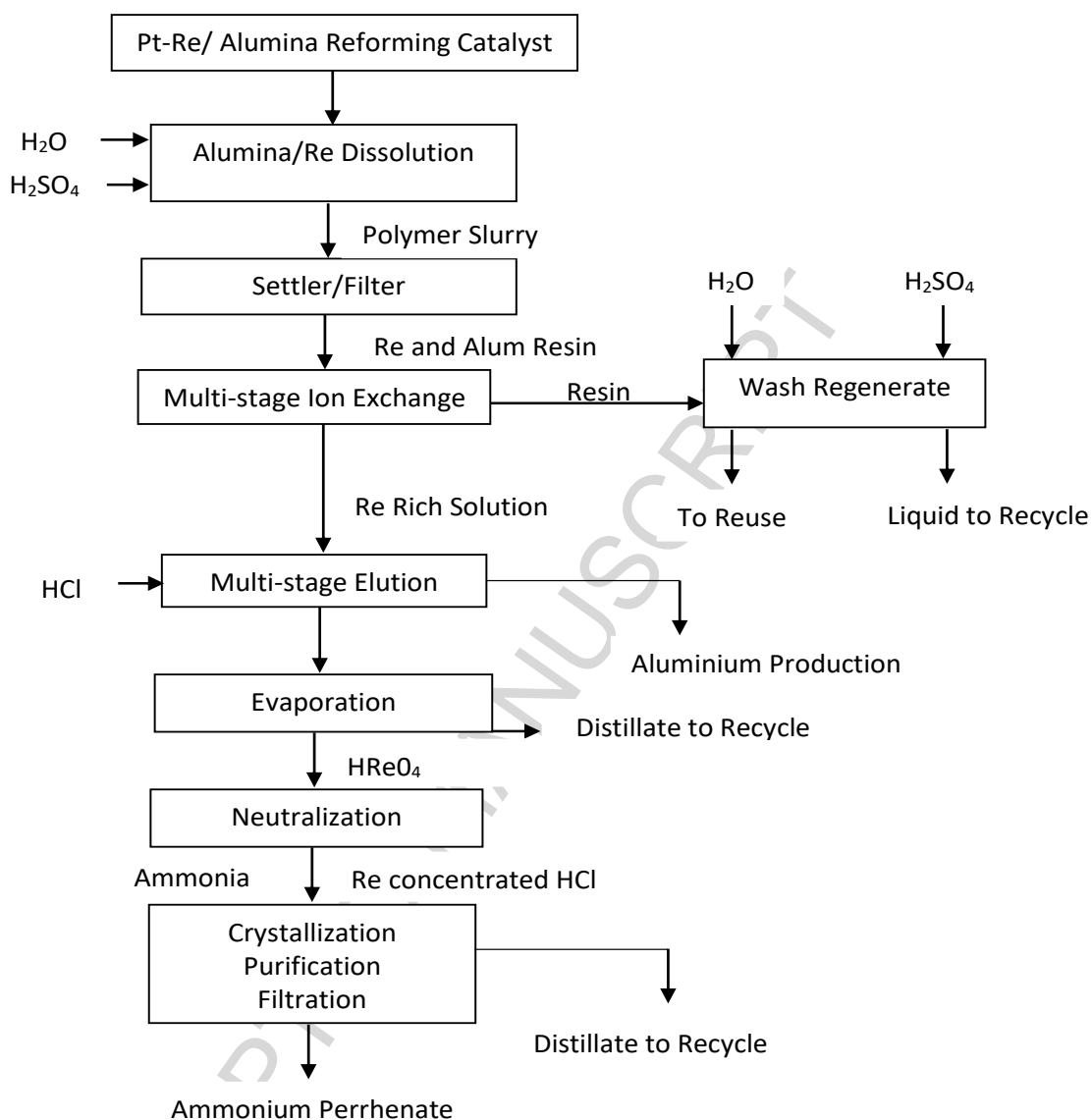
Fig 5 Method for rhenium recovery from spent reforming catalyst

4.2.2.2. Selective leaching of rhenium and platinum.

The methods used to selectively recover platinum and rhenium from spent catalysts without completely dissolving the alumina substrate vary from calcination of the catalysts to selective leaching in alkaline or acid conditions at ambient and elevated temperatures [29]. By calcining the catalyst at temperatures up to 1150°C, the γ-Al_2O_3 undergoes a phase transition to the chemically stable α-Al_2O_3 phase, lowering the dissolution of the alumina catalyst. The platinum and rhenium can then be selectively leached in concentrated (5 mol/L) sulphuric acid solutions containing sodium chloride and a potassium persulfate oxidant ($K_2S_2O_8$) [32].

By using this approach, it was reported that the recovery levels of rhenium and platinum are as high as 95.5% and 97%, respectively [32]. Additionally, a U.S. patent (US#: 5542957) has been granted involving the selective leaching of platinum and rhenium at elevated temperatures (50-300° C) and pressures (207-9,000 kPa). In this process, a dilute solution of sulphuric acid (0.001-1.0 mol/L) is used in the presence of ammonium iodide or bromide and oxygen to selectively leach Pt and Re, while leaving behind the alumina substrate. Han and Meng, [33] reported rhenium level recovery of 98% at 160° C and an oxygen overpressure of 800 kPa, which is higher than the amounts reported by the other techniques. Both methods of recovery (complete or selective dissolution) require high temperatures and therefore high energy consumption. In both cases high pressures are also needed. Thus, the resulting processing costs are likely to be high. Unfortunately, there has not been any study to investigate whether the proposed routes are likely to be economically viable. The viability will also be dependent on the number and continuous availability of spent catalysts. Having outlined Re production processes, the next sections explore strategies to acquire Re supply through circular economy networks.

4.3 Shaping a circular economy for rhenium

Considering the inherent scarcity of rhenium, the oligopolistic nature of the industry described in 4.1 with implications for stability of supply and the recovery in its demand, it is useful to return to the opportunities represented by a move to a circular economy, defined in Section 1.1. Section 4.2 explained that rhenium could be recovered after industrial use, and sections 4.2.1, 4.2.2 outlined possible recovered products that could be sources of rhenium. The question then arises of what processes additionally to the processing technologies explained are needed to ensure a steady supply of high quality rhenium. This would have to involve the identification of possible sources of scrap both of start and end-of life products which could be a source of Re.

In section 4.2.2 processes were prospected to recover by-products of refinery processes, this is an example of recovery from start of life-cycle processes. Sections 4.2.1 outlined end of life scrap as a source of Re through the processes outlined. Structured networks of industry players with roles of recovering, processing, supplying and reutilizing rhenium need to be designed to secure this steady supply. The field of industrial ecology is an operational strategy for sustainable development. Industrial Ecology "strives to optimize materials and energy sources in the industrial system in a fashion like the way natural ecosystems function [34]. Allied to Industrial Ecology is the concept of Industrial Symbiosis, the "development of working agreements between industrial and other organizations that, through the innovative reuse, recycling or sharing of resources lead to resource efficiency" [35].

The operationalization of these concepts features therefore the identification of organizations that can recover, recycle, share and supply rhenium. For example, components of industrial symbiosis networks would include:
1. logistics organizations able to collect start and end of life scrap from various sources, such as petrol refineries and aero engine manufacturers.
2. Organizations able to invest in plant and processes as illustrated in 3,2 and 3.2.2; and
3. Marketing organizations able to identify additional applications for Re, such as the therapeutic applications described in 1.1 and the organizations associated with manufacturing of these.

An important design criterion of these industrial symbiosis networks is the reduction of geographical concentration described in 4.1, which necessarily affects the oligopolistic nature of the industry. Careful design of structured networks of such organizations according to the principles of industrial ecology and industrial symbiosis, which take natural ecology as a model, where the waste of an organism is nourishment for another, present a unique opportunity to address problems of scarcity of rhenium whilst at the same time reducing waste and maximising resource efficiency.

5. Conclusions

Rhenium is a unique, extremely rare and strategic chemical element currently used as an alloying addition in high-temperature superalloys in aerospace, industrial gas-fired turbines and as catalysts in the petrochemical industry. Porphyry mineral deposits are expected to continue to be the main source of primary rhenium production for the foreseeable future, even though overall rhenium grades are low compared to other types of deposits, but rhenium production is feasible because of the large ore tonnage processed. As a result of increasing demand, it is expected that there will be dependency on recycling as well as a source as a by-product of molybdenum extraction. Another way to meet the increasing demand may be the reprocessing of rhenium-laden manufacturing scrap and end-of-life materials, such as Pt-Re catalysts and Ni-based superalloys. Most of the processes involved in the production of primary and secondary rhenium involve the use of elevated temperatures and pressures and large amounts of reagents; these requirements add to the high cost of rhenium. Thus, it is imperative that the extraction and recovery of rhenium is conducted as efficiently as possible.

The global rhenium market is expected to grow at a CAGR of over 7% during the period 2018-2022, while superalloy turbine parts for aero engines and industrial gas turbines will remain by far the largest end-market for rhenium at over 80% of total rhenium consumption. Given the oligopolistic and geographically concentrated nature of production and associated risks for security of supply, it is essential that additional, more geographically dispersed sources of supply be identified. This could be achieved for example through circular economic networks.
Systems and networks designed according to the concepts of Industrial Ecology and Symbiosis offer opportunities to manage rhenium stocks in a cost-effective, resource efficient manner.

6. Directions for research

Further research opportunities should be sought for the development of higher efficiency for both production and recovery processes in order to maintain rhenium supply. As reported in this paper, rhenium recycling presents a prime opportunity to source a rare and important material and research should focus on identifying spent products and industrial sectors that could potentially supply rhenium. Optimised sourcing and supply operations need to be established according to principles of Industrial Ecology and Symbiosis that may involve rhenium (i) as waste from processing and manufacturing and from (ii) faulty or returned products so that disassembly and recovery may take place as part of circular economic processes. Similarly, research should identify which products could be the best sources of rhenium for recycling. Both products and industries should be prioritized as acquisition targets, i.e. products and companies that could be approached or sourced with a view to develop a supply chain of recycled rhenium. Finally, research should explore how industrial ecology and symbiosis systems could assist the design of the said supply chains, including

the establishment of specialist waste processing companies that could collect waste materials and operate recovery processes for rhenium as explained in the sections above.

Acknowledgement

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Highlight

Rhenium is a refractory metal and is one of the rarest elements.

Due to its high cost, recycling of rhenium-containing scraps is of economic interest

The global rhenium market is expected to grow at a CAGR of over 7% during the period 2019-2022

Superalloy turbine and industrial gas turbines will remain by far the largest end-market for rhenium at over 80% of total rhenium consumption.