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Review of rhenium extraction and recycling technologies from primary and secondary resources

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10 Abstract

11 Rhenium is a scarce and highly important metal, which is widely used in high-temperature superalloys 12 and platinum-rhenium catalysts due to its unique physicochemical properties. The substitution of 13 rhenium in its applications is very limited, and there is no suitable substitute without losing essential 14 performance. Furthermore, global extractable primary rhenium resources are predicted to deplete within 15 130 years. In this paper, rhenium extraction and recycling technologies from primary and secondary 16 resources are critically classified and reviewed. Rhenium is primarily produced as a by-product in 17 molybdenum, copper, lead and uranium production from the concentrates and ores. Rhenium is extracted 18 from roasting fume and dust, leaching residue, and aqueous solution to produce a rhenium bearing 19 solution. Subsequently, rhenium rich solution is generated by separation with solvent extraction, ion 20 exchange, adsorption, membrane techniques or chemical precipitation. Finally, rhenium is produced via 21 crystallization and reduction steps. Recycling rhenium from spent alloys and catalysts is a multi-step 22 process combining pyrometallurgical and hydrometallurgical techniques, where its separation and the 23 subsequent steps are similar to that of extracting rhenium from primary resources. The main challenges 24 in rhenium extraction and recycling are the enrichment of rhenium in the production and the collection 25 and classification of spent rhenium scrap, to identify suitable processes to recover the rhenium with a 26 high recovery. This paper contributes to better understanding the rhenium extraction and recycling 27 processes and enhances sustainability of rhenium production.

28 Key words: Primary resource; Spent alloys and catalysts; Extraction technology; Recycling; Separation

29 **1. Introduction**

30 With the continuous growth of population and economy in the world, the demand for metals that 31 were previously not produced in large amounts has become an increasingly urgent issue in recent years, 32 especially for those applied in high-tech products and emerging innovations (Gaustad et al., 2018; Wateri 33 et al., 2020; Zhang and Xu, 2018). Rhenium (Re) is one of the metals in this category, and is considered 34 as a scarce and highly important metal with its extractable global resources likely to be depleted within 35 100 years after 2050 (Henckens et al., 2014). The USGS Mineral Resources Program considers rhenium 36 as a rare metal critical to modern transportation (John, 2015). The British Geological Survey included 37 rhenium in high supply risk list in 2011, 2012, and 2015, with a very high supply risk index of 6.5, 6.2 38 and 7.1, respectively (BGS, 2011; 2012; 2015). Wateri et al. (2020) reported that rhenium is listed as the 39 fifth most critical metal based on a criticality evaluation at the global level using Yale University 40 methodology (Graedel et al., 2015).

41

Rhenium was discovered in 1925 by the German chemists Walker Noddack, Ida Tacke and Otto

42 Berg. They extracted this element, established its X-ray spectrum and named it as rhenium in honor of 43 the River Rhein (Eric, 2017). Rhenium has an extremely high melting point (3180 °C), only lower than 44 carbon (3500 °C) and tungsten (3422 °C) of all the elements. Rhenium has a heat-stable crystalline 45 structure and excellent ductility from freezing to very high temperatures, making it exceptionally 46 resistant to heat and wear (Millensifer et al., 2014; John et al., 2017). The two most important uses of 47 rhenium are in high-temperature superalloys and in platinum-rhenium catalysts (John et al., 2017). The 48 superalloys are mainly used to manufacture turbine blades for jet engines and in power-generation 49 applications, which consume over 80% of rhenium production. Catalysts in petrochemical industry 50 accounts for ~10%, and the remaining 10% is used as tungsten-rhenium and molybdenum-rhenium alloys 51 in manufacture of electrical contact points, heating elements, vacuum tubes, and X-ray tubes and targets 52 (John et al., 2017; John, 2015).

53 In addition, the substitution of rhenium in its applications is very limited, there is no adequate 54 substitute or the substitute is of high cost and loss of performance (Henckens et al., 2019). John et al. 55 (2017) pointed out in detail that substitutes for rhenium (such as gallium, germanium, indium, selenium, 56 silicon, tungsten, and vanadium) in platinum-rhenium catalysts are being evaluated on an ongoing basis, 57 which might someday decrease the rhenium use in the existing catalyst market; however, this decrease 58 would be likely offset due to the use of rhenium being considered in several proposed gas-to-liquid 59 projects. Similarly, even though aerospace superalloy producers continue to research new alloys with 60 smaller quantities of rhenium, it has proven difficult to develop alloys with lower rhenium content for 61 use in jet engines without a loss in performance (John et al., 2017).





Fig. 1. The estimated world reserve (a) and mine production (c) of rhenium over the last 10 years and
their illustrated information of 2018 (b) and (d) for example (data from USGS, 2011-2020).

As one of the rarest metals, the estimated average crustal abundance of rhenium is about 0.4 part
per billion (ppbw) (Millensifer et al., 2014; John et al., 2017). According to U.S. Geological Survey

67 (USGS, 2011-2020), the world reserve and mine production of rhenium over the last 10 years are 68 presented in Fig. 1, where the detailed information in 2018 is picked out as an example. As shown in Fig. 69 1 a and b, the total rhenium reserve in the world is ~2500 tons, mainly located in Chile (>50 % reserve, ~1300 tons), United States, Russia, and Kazakhstan. The annual world mine production of rhenium has 71 stayed stable with ~50 tons, in spite of the slight fluctuation caused by political and environmental 72 features (Fig. 1 c). In 2018 as shown in Fig. 1 d, the rhenium mine production is principally supplied by 73 Chile (55.03 %), United States (16.92 %) and Poland (12.4 %).

74 Rhenium primarily exists as a solid solution in molybdenite, and its resources are mainly contained 75 in porphyry Cu-Mo-Au deposits (Millensifer et al., 2014; John et al., 2017). The natural rhenium mineral 76 is mainly in the form of rheniite (ReS₂, 74 wt.% Re), and others are in the form of sulfides combined 77 with other metal elements (Millensifer et al., 2014). Due to rhenium rarely occurring on its own sulfide 78 mineral, rhenium is usually extracted as a by-product of molybdenum, copper and other metals (Free, 79 2011). Molybdenite, especially from porphyry copper ore deposits, is the host rhenium-bearing mineral. 80 In molybdenum concentrates, the rhenium contents are typically in the range of 200-800 ppm, and its 81 content in copper concentrates is about 10-50 ppm (Gabashi, 1997; Nadler, 2012).

82 Besides the natural resources, recycling rhenium from spent scrap can relieve the stress of 83 requirement for primary rhenium, and avoid mining costs, mining wastes and serious environmental 84 problems in mineral processing (Bian et al., 2012; Beck and Graedel, 2012). Due to the life cycle of ~10 85 years for turbine blades(John et al., 2017), a significant quantity of used blades containing 3-6 wt. % 86 rhenium can be recycled and used to manufacture new blades (Kesieme et al., 2019). Rhenium can be 87 recovered together with tungsten, molybdenum, platinum and other valuable metals from spent catalysts, 88 which contain about 0.3 wt. % Re. Every year, at least 10 tons of rhenium is recycled from spent scrap 89 in the world (John et al., 2017; Kesieme et al., 2019). Recycling rhenium has an enormous potential as 90 for the ultimate recyclability of rhenium can be more than 80% (Heneckens et al., 2019).

91 Due to strategic importance, increasing consumption, high cost and scarce raw materials, the supply, 92 extraction and recycling of rhenium have drawn a remarkable attention from governments, industries and 93 academics. As extraction and recycling of rhenium from primary and secondary sources are of vital 94 importance to the supply of rhenium in the industrial chain, there is a large amount of research carried 95 out on rhenium extraction, recycling, and separation. Kasikov and Petrova (2008) reviewed the 96 processing methods for spent platinum-rhenium catalysts. Abisheva et al. (2011) summarized the 97 recovery technologies of rhenium from mineral raw materials in Kazakhstan, focusing on the recovery 98 of rhenium as by-products of copper, lead and uranium production. Anderson et al. (2013) reviewed the 99 commercial processing technologies of extracting rhenium from primary and secondary sources. Yagi 100 and Okabe reviewed the smelting technologies of recovering rhenium from various ores (Yagi and Okabe, 101 2016a), the characteristics of Re-containing materials, and the current Re recycling status and 102 technologies (Yagi and Okabe, 2016b), but both in Japanese. Wang and Wang (2018) reviewed the recent 103 processes of separating and enriching rhenium in China. Kesieme et al. (2019) assessed the rhenium 104 recycling and processing technologies.

105 This paper focuses on a comprehensive review of metallurgical technologies for extracting and 106 recycling rhenium from primary and secondary resources, respectively. First, the paper has collected the 107 available literature related to extraction technologies of rhenium in molybdenum, copper and other metals 108 production lines, as well as the rhenium recycling from spent alloys and catalysts. Then, the collected 109 literature has been classified and reviewed critically. Relevant information has been correlated from110 books, journal papers, patents and reports on the internet. Additionally, the problems, challenges, and

111 recommendations are proposed for the sustainability of rhenium metallurgy.

112 2. Extracting Re from primary resources

113 2.1 Re extraction processes

As rhenium dominantly exists in molybdenum and copper concentrates after flotation, rhenium is typically extracted as a by-product in molybdenum and copper production. Additionally, rhenium is also recovered from lead and uranium production. The rhenium extraction processes and the existing forms

of primary resources were collected and summarized in Table 1.

118	Table 1 The	process, technology	and existing	form of rhenium	extracted from	primary resources.
-						1 2

Production	Deseuree type	Extraction technology	Do ovisting form	
process	Resource type	Extraction technology	Re existing for m	
		Oxidation roasting-	Re2O7 in roasting fume and dust;	
Ma una daratian	Re-containing Mo	hydrometallurgical leaching	Residue	
Mo production	concentrates	Hydrometallurgical	In a lastice to a sthemarith Ma	
		methods	In solution together with Mo	
		Pyrometallurgy-	Constant from and death Clima	
	Re-containing Mo concentrates	hydrometallurgical leaching	Smelling lume and dust; Slime	
Cu production		Hydrometallurgical	Aqueous solution together with	
		methods	Cu	
DI 1 (י ומיי מ	Oxidation roasting-		
Pb production	Re-containing Pb slime	hydrometallurgical leaching	Dust	
U production	Re-containing U ores	Insitu leaching	In solution together with U	

119 2.1.1 Pyrometallurgical processes

Pyrometallurgy is the traditional method to extract by-product rhenium from concentrates, still employed in commercial production. It includes molybdenum roasting at about 600-650 °C, copper smelting process at ~1200-1300 °C and lead (galena) roasting process at ~900-1000 °C. The early literature is available in a patent by Melaven and Bacon (1947) for the pyrometallurgical processes to extract rhenium, since then the technologies have been developed to increase the efficiency and accommodate the different Re-containing concentrates. A conceptual flowsheet is shown in Fig. 2.

126



- 128 Fig. 2. Conceptual flowsheet for rhenium extraction from pyrometallurgical wastes of Re-containing
- 129 concentrates in accordance with the literature (Anderson et al., 2013; Yagi and Okabe, 2016a).

130 In pyrometallurgical processes, rhenium existing in concentrates is oxidizes to rhenium heptoxide 131 (Re_2O_7) according to Eq. (1). Due to the high volatility property of Re_2O_7 ($P_{\text{vap}} = 0.936$ atm at 360 °C), 132 nearly all Re₂O₇ volatilize at the pyrometallurgical temperatures for molybdenum, copper and lead 133 production (Ammann and Loose, 1972). The volatile Re_2O_7 in the furnace flue gas is subsequently 134 scrubbed with water and recovered as soluble perrhenic acid (HReO₄), as illustrated by Eq. (2) (Anderson 135 et al., 2013; Kesieme et al., 2019). A detailed process was described by Tarasov et al. (2001) for roasting 136 molybdenite in a fluidized bed. The flue dust is captured in a cyclone, an electrostatic separator and 137 finally by a wet gas scrubbing.

138
$$2\text{ReS}_2 + 7.5\text{O}_2(g) = \text{Re}_2\text{O}_7 + 4\text{SO}_2(g)$$
 (1)

(2)

139
$$Re_2O_7 + H_2O = 2HReO_4$$
 (aq)

140 In order to increase rhenium recovery in this process, some additives are used in the solution to 141 oxidize the low valence rhenium oxide in the flue gas when using water scrubbing for pyrometallurgical 142 rhenium streams (Zhang and Zhao, 2007). The solution also contains ~ 50 g/L H₂SO₄ after washing the 143 gases. Part of rhenium remains in the calcines as perrhenates if concentrates contain metals such as 144 calcium and potassium, and subsequently goes into solution in the later leaching step. A small part of 145 rhenium remaining in the residue or slime is returned back to roasting or leaching steps. After partial 146 neutralization, a counter-current extraction, filtration or decantation is used to remove impurity elements 147 (primarily iron). The final Re-bearing solution is obtained after filtration.

148
$$2MoS_2 + 6Ca(OH)_2 + 9O_2(g) = 2CaMoO_4(s) + 4CaSO_4 + 6H_2O$$
 (3)

149
$$2\text{ReS}_2 + 5\text{Ca}(OH)_2 + 9.5\text{O}_2(g) = \text{Ca}(\text{ReO}_4)_2(s) + 4\text{CaSO}_4 + 5\text{H}_2O$$
 (4)

150 Juneja et al. (1996) investigated molybdenum and rhenium extraction from a low grade molybdenite 151 concentrate by roasting in the presence of lime and soda ash. The molybdenum and rhenium reacted 152 according to reactions (3) and (4), respectively. 74% of rhenium was extracted from the lime-roasted 153 calcine by water leaching. Zagorodnyaya et al. (2010) revealed that the formation of interphase 154 substances during rhenium extraction from acid solutions was due to the presence of a black fine 155 rhenium-containing precipitates in the form of insoluble sulfides and oxides. These precipitates generate 156 in the gas phase and in scrubbing of copper smelter metallurgical gases. Lessard et al. (2014) proposed a 157 new technology platform called 'Looping Sulfide Oxidation', in which volatile Re₂O₇ produced during 158 pyrometallurgical processing of molybdenum and copper concentrate was directly reduced to rhenium 159 metal by S2. Sun et al. (2020) used a pretreatment of Re-bearing molybdenite concentrate to increase the 160 Mo and Re grades by leaching with a solution of HCl and CaCl₂, then co-volatilized of 99.9% Re and 161 90.4% of Mo at 1050 °C, subsequently the volatile molybdenum oxide was condensed above 500 °C to 162 obtain highly pure MoO₃ (99.9%) with almost no rhenium while high-content Re₂O₇ was collected at 163 lower temperature.

Today, rhenium is mainly produced through the molybdenum roasting and copper smelting processes. However, compared to hydrometallurgical process, pyrometallurgical process consumes more energy and discharges larger amounts of waste gas, requiring expensive gas treatment or causing serious environmental problems. Due to its recovery as a by-product from the gas phase in smelting and roasting, the total recovery of rhenium in those processes is of key importance.

170 2.1.2 Hydrometallurgical processes

171 In order to reduce off gas treatment costs and adapt different ore types for extracting rhenium from 172 Re-containing concentrates, some alternative hydrometallurgical methods have been developed in recent 173 years. In these hydrometallurgical processes, rhenium compounds were oxidized to perrhenate (ReO4-) 174 entering into solution together with the main metals e.g. Mo, Cu, and U in a leaching process. The 175 schematic diagram is presented in Fig. 3. The hydrometallurgical process of treating Mo/Cu ores included 176 e.g. oxygen pressure leaching, acid or alkali leaching with an oxidation agent, and oxidative leaching 177 (using chlorine-based oxidizing species) (Anderson et al., 2013; Yagi and Okabe, 2016a). Oxygen 178 pressure leaching was developed to oxidize molydenite to molybdenum oxide in water with air or oxygen 179 at >150 °C (Barry et al., 1972; Ketcham et al. 2000). Dresher et al. (1956) studied the leaching of 180 molybdenite by KOH solution in the pressure range 0-700 psia of oxygen at 100-170 °C. Sutcliffe et al. 181 (2012) used hypochlorite-containing solution to leach molybdenum-rhenium sulfide ores and 182 concentrates in a closed reactor vessel at ambient temperature and pressure. Mollerstedt and Backius 183 (1976) employed the two leaching steps with nitric acid at 60-120 °C to convert molybdenum sulfide to 184 molybdic acid. Most of the molybdic acid forms a solid phase, and the residual part in the solution is 185 extracted through the solvent extraction technique.



186

187 Fig. 3. Extracting rhenium by hydrometallurgical processes from rhenium-containing concentrates.

188 In uranium production by in-situ leaching, rhenium dissolves into leaching solutions together with 189 uranium when using sulfuric acid, carbonates and sodium or ammonium bicarbonates for treating 190 uranium ores (Abisheva et al., 2011; Chekmarev et al., 2004). Amer (2008) developed an oxidation 191 leaching method to treat a rhenium-containing lead slime produced in copper manufacture. More than 192 90% rhenium was extracted in the form of perrhenic acid under leaching conditions with oxygen partial 193 pressure <1.0 MPa, temperature <90 $^{\circ}$ C, particle size \leq 23 μ m and leaching time <90 min. Helbig et al. 194 (2018) tested the extraction of rhenium in different acidic and alkaline media with oxidizing agents from 195 a flue dust from former copper shale processing, together with zinc, copper, germanium and molybdenum 196 extraction. It was found that the H₂SO₄-H₂O₂/O₃ system is the most efficient lixiviant to extract these 197 metals.

Additionally, Askari Zamani et al. (2005) tested the bioleaching of a molybdenite concentrate to extract rhenium, with a low rhenium yield of only 7.3 %. Abdollahi et al. (2019) optimized the operational parameters of dissolving Cu, Mo and Re from molybdenite concentrate through meso-acidophilic bioleaching using an artificial neural network (ANN), with the maximum recovery of Cu, Mo and Re of 73%, 2.8% and 27.17% on the 30th day, respectively.

203 2.2 Separation of Re from solution

204 The separation of rhenium from Re-bearing solution is another important step in the rhenium 205 production. The reported methods of separating rhenium involved e.g. solvent extraction, ion exchange, 206 adsorption, membrane techniques, and chemical precipitation.

207 2.2.1 Solvent extraction

208 Solvent extraction is a mature technology used in the industry to selectively separate metals from 209 aqueous solutions. A flowsheet of separating rhenium from a Re-bearing solution is shown in Fig. 4. 210 Through the solvent extraction step, ammonium perrhenate is usually obtained for subsequent rhenium 211 production. Different extraction solvents can be used to separate rhenium and reused after regeneration, 212 with a similar extraction mechanism. The development of separating Re from Re-bearing solution by 213 solvent extraction is illustrated in Table 2.



214

Fig. 4. A flowsheet of rhenium separation from rhenium-bearing solutions by solvent extraction 216 method.

217 Karagiozov and Vasilev (1979) separated rhenium and molybdenum by solvent extraction with 218 mixtures of trioctylamine and Aliquat 336. Zhou et al. (1982) employed the amide type extractant A101 219 for rhenium and molybdenum separation. Yu et al. (1985) separated Re(VII) from Mo(VI) in alkaline 220 solutions by synergistic extraction with a primary amine and neutral phosphorus esters. Sato and Sato 221 (1990) extracted rhenium (VII) from hydrochloric acid solutions using tributyl phosphate (TBP) and 222 trioctyl phosphine oxide (TOPO) with trioctylamine (TOA) and trioctylmethylammonium chloride 223 (TOMAC). Gerhardt et al. (2000, 2001) employed diisododecylamine (DIDA) to separate rhenium from 224 acidic molybdenum-tungsten solutions, and compared it with two other extractants, trioctylamine (TOA) 225 and dioctylamine (DOA). Cao et al. (2009) selectively extracted rhenium from alkaline solutions 226 containing rhenium and molybdenum by solvent extraction using a mixture of tributyl phosphate and 227 triotylamine as extractant. Xiong et al. (2010) separated Re(VII) and Mo(VI) by mixtures of tri-228 alkylamine (N235) and tri-n-butylphosphate (TBP) dissolved in heptane. Ali et al. (2012) selectively 229 extracted perrhenate anion from nitric acid solution using 2,20-(imino)bis(N,N0-dioctylacetamide) as

²¹⁵

230 extractant. Keshavarz Alamdari et al. (2012) separated Re and Mo from roasting-dust leach-liquor using 231 solvent extraction technique by TBP. Kim et al. (2015) used a solvent of 10 v/v.% tertiary amine (Alamine 232 304-1), 10 v/v.% Isodecanol and 80% Anysol-150 to extract rhenium from a liquor containing 260-280 233 mg/L Re and 80-90 mg/L Mo. Srivastava et al. (2015) addressed the extraction of rhenium(VII) from a 234 HCl solution using Cyanex 923 diluted in kerosene. Petrova and Kasikov (2016) extracted rhenium(VII) 235 from sulfate media by mixtures of tri-iso-octylamine (TIOA) and oxygencontaining reagents (2-octanol, 236 2-octanone, phenetole). Lou et al. (2015, 2016) studied the extraction of Re(VII) from Re-Mo 237 hydrochloric acid solutions by TritonX-100/N235/IAA/n-heptane/NaCl microemulsion or N263/TBP/n-238 heptane/NaCl microemulsion systems. Cheema et al. (2018) used tri-butyl phosphate (TBP) as organic 239 extractant in kerosene to separate rhenium from molybdenite flue-dust leach liquor. Salehi et al. (2019) 240 recovered molybdenum and rhenium from scrubber liquors of fumes and dusts in molybdenite 241 concentrate roasting using D2EHPA-TBP. Hong et al. (2020a) separated perrhenate ions from industrial 242 acidic or chlorine leach solutions produced in a copper smelting process, using a synergistic solvent 243 extraction system of Trioctyl amine (Alamine 336) and tributyl phosphate (TBP). Quijada-Maldonado et 244 al. (2020) selectively separated molybdenum and rhenium by solvent extraction using kerosene and 1-245 octyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide as diluents and di(ethylhexyl) phosphoric 246 acid and trioctylmethylammonium bis(2-ethylhexyl) phosphinate as extractants.

247 Table 2 Development of rhenium separation from solution by solvent extraction

	1	1				
Separation	Bulk	Extractant	Selective	Extractive	Separation	Reference
elements	solution		stripping	yield	coefficient	
Re-Mo	Acidic	A mixture of	nitric acid	99.44%	-	Karagiozov
	media	trioctylamine and				and Vasilev,
		Aliquat 336				1979
Re-Mo	Sulphuric	Amide type extractant	-	Recovery	667	Zhou et al.,
	acid	A101		increasing		1982
	solution			2%		
Re-Mo	Alkaline	Synergistic extraction	-	-	Up to	Yu et al.,
	solutuons	with primary amine and			100000	1985
		neutral phosphorus esters				
Re	Hydrochlor	Tributyl phosphate or	10%	-	-	Sato and
	ic acid	trioctyl phosphine oxide	dimethyla			Sato, 1990
	solutions	with trioctylamine	mine			
		(TOA) or				
		trioctylmethylammoniu				
		m chloride				
Re-Mo-W	Sulphuric	Dioctylamine DOA	Aqueous	99.5	-	Gerhardt et
	acid media		ammonium			al., 2000;
			solution			2001
Re-Mo	Alkaline	A mixture of tributyl	18%	96.8%	1700	Cao et al.,
	solution	phosphate and	ammonia			2009
7	D1	triotylamine	lıquor		1.5.0	
Re	Rhenium	Mixtures of tri-	-	-	15.36	Xiong et al.,
	stock	alkylamine and tri-				2010
D 14	solutions	nbutylphosphate		0.001	450	
Re-Mo	Molybdenu	Tri-butyl phosphate	Ammonia	98%	450	Alamdari et
	m oxide	(1BP)	solution			al., 2012
	leaching					
D	liquor	2.20 (* *)1 * 01)20				A 11 / 1
ке	INITIC acid	2,20-(imino)bis(in,in0-	-	-	-	All et al.,
	solution	diociylacetamide)				2012

Re	A scrub liquor of molybdenit e roaster fume	A 10 v/v.% tertiary amine, 10 v/v.% Isodecanol in 80% Anysol-150	30% ammonium hydroxide	96.4–99%	-	Kim et al., 2015
Re	An acidic chloride solution	Cyanex 923 diluted in kerosene	1.5 mol∙L ^{−1} NH₄OH solution	99.2%	-	Srivastava et al., 2015
Re-Mo	Hydrochlor ic acid solutions	TritonX- 100/N235/IAA/n- heptane/NaCl microemulsion	HCl or/and NH ₄ SCN solutions	94.9-96.6	1801-2795	Lou et al., 2015; 2016
Re	Sulfate media	Mixtures of tertiary amine and oxygen-containing extractants	ammonia solution	-	-	Petrova and Kasikov, 2016
Re	Molybdeni te flue-dust leach liquor	Tri-butyl phosphate (TBP)	-	>99.6%	-	Cheema et al., 2018
Re	Scrub liquors of fumes and dusts from roasting molybdenit e concentrate s	Trioctyl amine	32% ammonium hydroxide	99.6%	-	Salehi et al., 2019
Re-Mo-Cu	a synthetic pregnant leach solution	Di(ethylhexyl) phosphoric acid and IL trioctylmethylammoniu m bis(2-ethylhexyl) phosphinate	-	Almost 100%	-	Quijada- Maldonado et al., 2020
Re-Cu-As-Bi	An acidic washing solution present in the copper smelting process	Alamine 336 and TBP	4 mol/L ammonium solution	98.78%	-	Hong et al., 2020a

249 Table 2 summarizes research in rhenium extraction from various rhenium-containing solutions by 250 employing different extractants. The separation is mainly between rhenium and molybdenum or/and 251 copper. The extractants include tertiary amine, tri-butyl phosphate, oxygen-containing extractants or their 252 mixtures. Selective stripping is carried out by using ammonium solution or acid solution depending on 253 elements to be separated, bulk solution and used extactants. The separation yield is very high, usually 254 above 96%. In total, the advantages of solvent extraction are its easy operation and high efficiency. 255 However, large amounts of acid or alkaline solution and water are consumed during solvent extraction 256 process, resulting in the discharge of huge high-salinity wastewater. Additionally, the toxicity and 257 environmental hazards of organic extractants and diluents or the interaction of organic phase with 258 concentrated acid and strong oxidants need to be considered.

259 *2.2.2 Ion exchange*

Another separation technology is ion exchange used in the industry for extracting rhenium from Rebearing solutions. As shown in Fig. 5, ammonium perrhenate solution is usually generated after adsorption-desorption steps. Several types of resins have been adopted in the rhenium separation, which can be reused after reactivation. The reported examples of separating Re from solution by ion exchange are summarized in Table 3.





Fig. 5. Rhenium separation from rhenium-bearing solutions by ion exchange.

267 Kholmogorov et al. (1999) synthesized weak base anion resins AN-82-14G and AN-105-14G to 268 recover rhenium from salt solutions. Lan et al. (2006) employed a strong base anion resin to absorb Re 269 from a Mo-Re containing solution. Xiong et al. (2008) used 4-amino-1,2,4-triazole resin (4-ATR) for 270 Re(VII) separation. Nebeker and Hiskey (2012) recovered rhenium from a copper leach solution by ion 271 exchange using a weak base anion exchange resin Purolite® A170. Zagorodnyaya et al. (2013, 2015) 272 separated rhenium and uranium from their concentrated solutions by a weak base anion exchange resin 273 AN-21 and a strong base anion exchange resin Ambersep A920U, respectively. Laatikainen et al. (2015) 274 studied the extraction of rhenium from nitrate, chloride and sulfate solutions using weak base anion 275 exchangers using Gel-type IRA-67 and WP-1 resins. Virolainen et al. (2015) investigated the recovery 276 of Re from sulfate solutions containing Mo and As by weak anion exchangers with Purolite A170 and 277 gel-type A172 resins. Zhang et al. (2017) used a weak base resin ZS70 with complex amine as the 278 functional group to recover rhenium from copper leach solutions. Cyganowski et al. (2019) used a 279 microwave-assisted method for the synthesis of Re(VII)-selective anion exchange resins to adsorb ReO₄⁻ 280 ions from acidic solutions containing Re(VII), Mo(VI), V(V) and Cu(II). Guo et al. (2019) prepared 281 coated solvent-impregnated resins containing ionic liquid Aliquat 336 to recover rhenium from industrial 282 acidic waste waters with low rhenium content, with 99.85% rhenium recovery.

Bulk solution	Separation	Resin type	Desorption	Efficiency	Reference
Sulphuric and nitric–sulphuric acid solutions Molybdenite calcine leaching	Re-Mo Re-Mo	Weak basic anion exchange resins AN-82- 14G and AN-105-14G Resin D216 and gel type resin 201X7	reagent 5% NaOH 10% NH4OH solutions HNO3 solution	>99.5% >90%	Kholmogorov et al., 1999 Lan et al., 2006
solution Re-Mo solution with pH 2.6-6	Re-Mo	4-amino-1,2,4-triazole resin	$1.0\sim5.0 \text{ mol}\cdot\text{L}^{-1}$ HCl solution	Separation coefficient	Xiong et al., 2008
Copper-bearing leach solutions	Re	Weak basic anion exchange resins Purolite®A170	1 M NaOH solution	~90%	Nebeker and Brent Hiskey, 2012
Solutions with different anion compositions	Re	Strong base anion exchange resin Ambersep A920U	-	97.7-99.6%	Zagorodnyaya et al., 2013
Solutions containing Re, U and salts	Re	AN-21 weakly basic anion exchange resin	-	33.0-99.2%	Zagorodnyaya et al., 2015
Nitrate, chloride and sulfate matrices	Re	Gel-type IRA-67 and Macroporous WP-1	-	-	Laatikainen et al., 2015
Sulfate solutions containing Mo and As	Re-Mo/As	IRA-67, A172 and 170 resins	NH₄OH solution	95.3 and 53.6 for Re/Mo and Re/As separation ratios	Virolainen et al., 2015
Copper leach solutions	Re	Weak base resins ZS70	2.5% aqueous ammonia	97.13%	Zhang et al., 2017
Solutions acidified at 0.1M HCl containing oxoanions of Re(VII), Mo(VI) and V(V), as well as Cu(II)	Re	Anion exchange resins synthesized using microwave heat	-	Maximum Re(VII) adsorption capacity of 303 mg/g	Cyganowski et al., 2019
Industrial waste water terms with of low rhenium content and high sulfuric acidity	Re	Coated solvent- impregnated resins containing ionic liquid Aliquat 336	3.5 mol/L KCl solutions	99.85%	Guo et al., 2019

284	Table 3 The reported	l example of	separating Re	e from solution by	y ion exchange.

Compared to solvent extraction, ion exchange can also ensure a high recovery efficiency of rhenium, and this approach is more appropriate on separating the target metal with low concentration in the solution. Similar to solvent extraction, large amounts of high-salinity wastewater are generated, which can cause serious environmental issues if not properly dealt with.

290 *2.2.3 Other methods*

Adsorption and membrane techniques have also been studied to recover metal anions from the industrial solutions. 293 Seo et al. (2012) used activated carbon to extract rhenium from molybdenum solutions, obtaining a 294 rhenium recovery of 91.5% and a concentrated rhenium solution. Hu et al. (2018, 2019) synthesized Cu-295 coated biochar composites and nano-ZnO functionalized biochar to adsorb low concentration Re(VII) 296 from acidic solutions. Lou et al. (2018) prepared a novel chitosan adsorbent modified by imidazolium-297 based ionic liquid to selectively adsorb Re(VII), and synthesized a series of solid copolymers with 298 vinylimidazolium-based ionic liquid as functional group and divinylbenzene (DVB) as the basic 299 framework (Lou et al., 2019). Vosough et al. (2016) used Para-magnetic Nano-particles of Fe₃O₄ to 300 absorb rhenium ions, and Gaete et al. (2019) used magnetite nanoparticles functionalized with amine-301 derivative groups to separate rhenium and molybdenum from aqueous solutions. Xiao et al. (2017) 302 synthesized two silica gel based adsorbents for Re(VII) capture, with the monomer of 1-vinyl imidazole 303 and 4-vinylpyridine grafted by methacryloxy propyl trimethoxylsilane, respectively. Xiong et al. (2017) 304 synthesized the adsorbents of diisobutylamine-functionalized graphene oxides to efficiently adsorb 305 Re(VII). Zhang et al. (2012) prepared a novel adsorbent of NH4HCO3-modifying nanoalumina dioxide 306 to separate Re(VII) ions from aqueous solutions.

307 Charewicz et al. (1991) proposed pressure reduction to recover rhenium from acidic aqueous 308 solutions by gaseous hydrogen and sulfur dioxide as the reductants. Chekmarev et al. (2004) extracted 309 rhenium from an underground uranium leaching solution by precipitation and membrane methods using 310 cationic water-soluble polyelectrolytes. Hori et al. (2015; 2019) developed a photochemical technique to 311 selectively precipitate rhenium as ReO₂ and ReO₃ from a solution in the presence of 2-propanol as the 312 electron donor, with rhenium recovery of ~95%. Meschke et al. (2017; 2020) studied the concentration 313 of rhenium and target elements from the solution by membrane techniques, including microfiltration, 314 nanofiltration and reverse osmosis. Hong et al. (2020b) investigated the recovery of rhenium from the 315 high arsenite wash acid solution obtained in the copper smelting process using sulfide precipitation.

316 2.3 Re chemical and metal production

The ammonium perrhenate solution obtained in a separation step is crystallized via evaporation crystallization to produce a high-quality ammonium perrhenate product (Gabashi, 1997; Millensifer et al., 2014; Nadler, 2012). The remaining rhenium in the mother liquor can be recovered by adding zinc sulfate and ammonia to precipitate a complex salt $[Zn(NH_3)_4](ReO_4)_2$, which can be dissolved by sulfuric acid to prepare ammonium perrhenate (Zagorodnyaya and Abisheva, 2002). Rhenium metal powder can be produced by reducing with hydrogen or other reducing gas at a high temperature (Gabashi, 1997; Millensifer et al., 2014; Nadler, 2012).

Additionally, Melaven and Bacon (1947) produced KReO₄ salt by adding KCl into Re-bearing solution. Churchwood and Rosenbaum (1963) used electrodeposition to produce rhenium metal from a solvent extraction stripping solution. Agapova et al. (2001) produced concentrated rhenium acid by electrodialysis of ammonium and potassium perrhenate solutions. Casas et al. (2012) obtained sodium perrhenate with induced crystallization of aqueous solution by adding ethanol at 25 °C.

329 3. Recycling Re from secondary resources

The secondary resources of rhenium include Ni-Re superalloys (~1-20 wt. % Re, and most commonly 3-6 wt. % Re), W-Re and Mo-Re alloys (3-5 wt. % Re), and spent Re-containing catalysts (~0.3 wt. % Re) (Mishra et al., 2012). Rhenium recycling is a multi-step process combining pyrometallurgical and hydrometallurgical techniques.

Reference	Raw material	Method	Year
		Leaching with a ammonium halogen salts-iodide	
Han and Meng, 1996*	Particularly spent catalysts	and bromide solution in presence oxygen and/or sulfuric acid	1996
Elutin et al., 1997*	Spent catalysts	Roasting, the acid- or alkali-assisted leaching	1997
Angelidis et al., 1999	Spent catalysts	Dilute NaHCO3 leaching	1999
Allison et al., 2003	Spent catalysts	Sublimation	2003
Thomas, 2008*	Spent catalysts	Dissolving in a halogen acid with the corresponding halogen element	2008
Stoller et al., 2008	Rhenium-containing superalloys	Electrochemical decomposition with 15-25 wt. % HCl, and further oxidizing leaching by NaOH- H ₂ O ₂	2008
Olbrich et al., 2009	Rhenium-containing superalloys	Digesting in a salt melt containing 60-95 wt.% NaOH and 5-40 wt.% Na ₂ SO ₄	2009
Dasan et al., 2011	Rhenium-containing superalloys, usually a nickel- based superalloy	Oxidizing to convert rhenium into a volatile rhenium oxide	2011
Delent et el			2011;
2011.2013.2014	Re-containing nickel	Electrochemical processing in H ₂ SO ₄ /	2013;
2011,2013,2014	superalloy	H ₂ SO ₄ +HCl/HNO ₃ electrolytes	2014
Bryukvin et al., 2016			2016
Luederitz et al., 2013*	Rhenium containing materials alloy residue and cermet catalysts	Solubilization in HCl solution or a mixture of HCl and HNO ₃	2013
Ferron and Seeley, 2015*	Alloys, super-alloys	Using an oxidizing acid solution or a mixture of HCl and HNO3	2015
Singh Gaur et al., 2015	Tungsten-rhenium wire	Roasting at 900 °C in the presence of air	2015
Srivastava et al., 2016	Reverted Turbine-Blade Superalloy	A two-step HCl leaching process followed by the liquid-liquid separation	2016
Britton and Markarian, 2017a; 2017b*	Particularly superalloys	Digestion with 50-1000 g/L H ₂ SO ₄ and a halide- free oxidant; further digesting in an oxidizing and complexing milieu	2017
Kim et al., 2018	Nickel-based superalloy	Pyrometallurgical pretreatment with Al powder- selective two-step HCl leaching	2018
Levin and Levchuk, 2017 Kuznetsova et al., 2018: 2020	W-Re alloys	Anodic dissolution of W-Re alloys, precipitation of calcium tungstate from the electrolyte, and electrodialysis of rhenium in the form of HReO ₄	2017 2018; 2020
Mamo et al., 2019	Nickel-based superalloy	Leaching with aqua-regia	2019
Ye et al., 2020	Tungsten-rhenium wire	Decomposition by KOH-K ₂ CO ₃ molten salt at 800 °C	2020

Table 4 Recent developments in recycling of rhenium from secondary resources.

*The method can also treat other Re-containing materials as reported, including alloys, spent catalysts, concentrates and
 ores.

In 1997, Ward and Dillard (1997) reviewed the information on rhenium recycling from secondary sources using various approaches, covering the patent literature of 1957-1993 and technical publications from 1977 to 1995. Drobot and Bukin (1997) summarized the publications of rhenium extraction from alloys and catalysts. According to them, recovery methods from alloys can be divided into a) oxidation roasting, b) alkaline fusion with alkali nitrites, c) fluoride treatment, and d) electrochemical dissolution, while the spent catalysts were usually treated by roasting with soda ash, and followed by sulfuric acid leaching.

344 Technological developments have been covered in many publications and patents reported recently.345 The recycling technologies included e.g. digestion in molten salts, selective leaching with a

pyrometallurgical pretreatment, and halogen acid dissolution. Their brief review is summarized in Table
4. Due to the different compositions of secondary rhenium resources, the choice of rhenium recovery
process needs also to take into account the recycling of other valuable metals.

349 3.1 Re recycling from superalloys

Stoller et al. (2008) proposed a process to treat superalloy scrap with electrolytic decomposition in
a very low-frequency electrolysis cell containing a 15-25 wt. % HCl solution. The remaining scrap after
filtration is further treated by oxidizing leach in a sodium hydroxide-hydrogen peroxide solution.
Rhenium is recovered from the filtrate using ion exchange.

Olbrich et al. (2009) reported a process for digesting rhenium-containing superalloys in molten salt
containing 60-95 wt. % NaOH and 5-40 wt.% Na₂SO₄ (preferably 70-80 wt. % NaOH and 20-30 wt. %
Na₂SO₄) at temperatures between 800-1200 °C, preferably at 900-1050 °C. The addition of 5-8 wt. %
Na₂CO₃ and some oxidizing agent including NaNO₃, K₂S₂O₈ and Na₂O can promote the digestion. Then,
the digestion product was dissolved in water at < 80 °C to obtain a metal rich solution, which is upgraded
by hydrometallurgical methods for separating the individual metal values.



360

Fig. 6. Technological scheme for recovering rhenium from Re-containing nickel superalloy developed by Palant et al. (2011; 2013; 2014).

Based on physicochemical studies, Palant et al. (2011; 2013; 2014) developed a process flow sheet (Fig. 6) for recovering rhenium and other metals from a rhenium-containing nickel superalloy by a complex electrochemical process using H_2SO_4 , H_2SO_4 +HCl, or HNO₃ electrolyte. After electrochemical dissolution, ~70% of rhenium is concentrated in the anode slimes, from which Re is leached by ammonia solution. The other 25–30% of rhenium is transferred to a sulfuric acid electrolyte, from which it is reextracted by solvent extraction to obtain ammonium perrhenate solution. Finally, KReO₄ crystals are produced through liming precipitation, filtrate, evaporation and precipitation steps. This process can also
 treat re-melted nickel–rhenium alloys with a specified Ni/Re weight ratio (Bryukvin et al., 2016).

371 Dasan et al. (2011) applied for a patent to recycle rhenium-containing superalloy scrap, by first
372 grinding the scrap to a particle size of around 5 μm to increase the surface area of particles and then
373 oxidizing it to convert rhenium into a volatile rhenium oxide.

In 2013, Luederitz et al. (2013) applied for a patent for selectively recovering rhenium and other metals from rhenium containing materials, such as alloy residue and wastes, ore materials, waste materials and cermet catalysts. All metals in the Re-containing materials are solubilized in a HCl solution or a mixture of HCl and HNO₃ to form their corresponding aqueous salts. Rhenium is then selectively precipitated as Re₂S₇, which is later oxidized and sublimed as Re₂O₇. The subsequent process is similar to rhenium extraction in molybdenum production.

380 Ferron and Seeley (2015) patented a hydrometallurgical process of recovering rhenium from Re-381 bearing materials including superalloys, metallurgical residues, ore and/or a mixtures of Re-containing 382 solids. Re-bearing materials were subjected to an oxidizing acid solution at a redox potential of > 500383 mv vs. Ag/AgCl or a mixture of HNO3 and HCl to convert rhenium and other metals, such as nickel and 384 cobalt, to their soluble salts. Other metals in the materials, such as tantalum and tungsten, remained in 385 the solid leaching residue phase. Rhenium was separated from the leach solution by sulfide precipitation 386 as Re₂S₇, absorption on activated carbon or an absorbent resin, or by solvent extraction. Finally, the solid 387 intermediate NH₄ReO₄ was obtained.

388 Srivastava et al. (2016) developed a two-step HCl leaching process followed by the liquid-liquid 389 separation using two different P-based organic solvents for rhenium recovery from an engine-reverted 390 superalloy. In the first leaching step, the base metal nickel and thermal-barrier elements (e.g., Al, Cr, Co 391 and W) were leached out using 4 mol/ L^{-1} HCl at 90 °C, rhenium selectively remained unleached in the 392 residues. Then, the residues were leached in the presence of in situ generated chlorine to solubilize the 393 rhenium. Under the optimized leaching condition, >98% rhenium could be leached in 4 mol/ L^{-1} HCl to 394 yield a rhenium-bearing leach solution. Subsequently, the selective recovery of rhenium over other base 395 metal impurities was achieved by solvent extraction to yield a pure NH₄ReO₄ product.

Britton and Markarian (2017a, 2017b) patented a hydrometallurgical method to treat rheniumcontaining materials, particularly superalloys. The raw materials were digested with $50-1000 \text{ g/L H}_2\text{SO}_4$ and a halide-free oxidant including air, ozone, oxygen, peroxide and persulfate salts. After filtration, the filter cake was further digested in an oxidizing and complexing milieu to extract the unreacted targeted metal. Finally, rhenium and platinum were separated by an ion exchange resin.

Kim et al. (2018) investigated a selective two-step leaching process for nickel and rhenium from
nickel-based superalloy scrap in hydrochloric acid solutions. Superalloy scrap with particle size < 150
µm was pyrometallurgically pretreated with aluminum granule at 1500 °C to form Al3Ni intermetallic
compound. In the first leaching step, the pretreated scrap was leached in a 4.0 mol/L HCl solution to
extract nickel together with aluminum, cobalt and chromium, remaining most rhenium and tantalum in
the residue. Rhenium was leached from the residue by using electrogenerated chlorine as an oxidant in
4.0 mol/L HCl solution, leaving tantalum in the residue.

408 Mamo et al. (2019) studied the recovery of rhenium and other metals from nickel-based superalloy409 with aqua-regia. The separation of rhenium and other metals from the solution was achieved by two

410 stages of precipitation. Oxides of aluminum, chromium, molybdenum and titanium were first precipitated 411 at pH = 5.05, then mixed hydroxides of cobalt and nickel were obtained at pH = 7.0. Finally, a rhenium 412 enriched solution was further processed to recover rhenium.

413 3.2 Re recycling from W-Re and Mo-Re alloys

414 In 1982, Heshmatpour and MaDonald (1982) developed a prototype method for recovering rhenium 415 from W-Re and Mo-Re alloy scraps based on the different volatilization properties of Re4O7 referred to 416 WO₃ and MoO₃ at high temperatures. Flowsheet of this process is shown in Fig. 7. Re-containing alloy 417 scrap is first oxidized by gaseous oxygen at 1000 °C, and the resulting rhenium oxide vapors are 418 condensed in the cooler region of the reaction chamber. Then, rhenium oxide is dissolved in water and 419 treated with potassium chloride to form potassium salt which is reduced in gaseous hydrogen to pure 420 rhenium metal powder. The oxides of tungsten or molybdenum are treated with boiling water, dried and 421 reduced in hydrogen to their respective pure metal powders.



422

Fig. 7. Flowsheet of rhenium recovery from W-Re and Mo-Re alloys developed by Heshmatpour and
MaDonald (1982).

Allison et al. (2003) patented a method to recover rhenium from spent catalysts by conversion of rhenium to a sublimable oxide via oxidation by heating in an oxidizing atmosphere and then isolation of rhenium from the volatized oxide.

428 Singh Gaur et al. (2015) used a similar roasting method to Heshmatpour and MaDonald (1982) to 429 recovery of rhenium form tungsten-rhenium wire scrap at 900 °C in the presence of air. Then the 430 volatilized Re₂O₇ solid was recovered as a NH₄ReO₄ solution, and was further treated by crystallization 431 and hydrogen reduction of NH₄ReO₄ to rhenium metal power. Ye et al. (2020) decomposed W-Re wire by a KOH-K₂CO₃ molten salt at 800 °C to form KReO₄. Subsequently, the decomposed product was
leached by water, and treated by crystallization to obtain high purity KReO₄ crystals which were reduced
by H₂ at 350 °C to produce Re powder.

In addition, Levin and Levchuk (2017) proposed a flow-sheet for Re recovery from W-Re alloys. W-Re alloys were firstly treated in NaOH solution with anodic dissolution, then tungsten was precipitated as calcium tungstate from the electrolyte by adding Ca(OH)₂, subsequently KReO₄ precipitate was obtained by adding KOH to the NaReO₄ solution. This was further treated by electrodialysis to produce perrhenic acid. Kuznetsova et al. (2018; 2020) simplified this scheme to directly produce perrhenic acid by electrodialysis of neutralized NaReO₄ solution.

441 3.3 Re recycling from spent catalysts

Spent rhenium-containing catalysts typically contain ~0.3 wt. % rhenium, ~0.3 wt. % platinum, and
alumina. These can be treated for selective recovery of rhenium and platinum. Kasikov and Petrova (2008)
reviewed the decomposition methods and divided them into two groups, selective extraction of rhenium
without the carrier material decomposition and incorporating decomposition of catalyst aluminum oxide
carrier.

447 Han and Meng (1996) have been granted a patent for selective pressure leaching of platinum and 448 rhenium from spent catalysts in a solution containing ammonium halogen salts (iodide and bromide) in 449 the presence of oxygen and/or sulfuric acid at elevated temperatures (50-300 °C) and pressures (207-450 9000 kPa). Subsequently, rhenium and platinum group metals could be recovered from the leaching 451 solution by electrowinning, cementation, solvent extraction, precipitation or adsorption. Elutin et al. 452 (1997) reported a process of selectively recovering rhenium from spent catalysts through the steps of 453 roasting, acid- or alkali-assosiated leaching, and ion exchange, to prepare high-purity NH₄ReO₄. The 454 method is similar to the pyrometallurgical-hydrometallurgical technique for recovering rhenium from alloys as mentioned above. El Guindy (1997) discussed the techniques and methods for processing of 455 456 spent catalyst to recover rhenium. Before early 80's, spent rhenium-containing catalysts were primarily 457 treated by caustic dissolution. But it is difficult to recover rhenium from caustic solutions and residues. 458 Thus, sulfuric acid dissolution has become the most favorable processing route today to treat spent 459 rhenium-containing catalysts. A typical flowsheet is shown in Fig. 8. Rhenium and aluminum were 460 extracted in H₂SO₄ or NaOH solution together leaving the platinum in the solid residue by adding 461 appropriate reducing agents. Then rhenium was extracted from aluminum sulfate solution by ion 462 exchange or solvent extraction.

Angelidis et al. (1999) simplified the conventional Re recovery process in Fig. 8 by employing
dilute NaHCO₃ solution to firstly dissolve rhenium from reforming catalysts, with the recovery up to 97%
for crushed and up to 87% for uncrushed scrap. Then, the unreacted platinum and alumina left after
NaHCO₃ dissolution were recovered by H₂SO₄ leaching.



468 Fig. 8. Flowsheet of rhenium recovery from spent catalyst developed by El Guindy (1997).

Thomas (2008) applied for a patent to extract rhenium, gold, and platinum group metals from their raw materials in an acid solution, preferably containing a halogen acid and the corresponding halogen element. Then, the metals were extracted by a non-cross linked polyamine composite resin, and separated using solvent extraction. Additionally, the methods of acid leaching (Luederitz et al., 2013; Ferron and Seeley, 2015; Britton and Markarian, 2017a and b) mentioned in Table 4 can also be used to recover rhenium from spent catalysts according to the report.

475 In total, the rhenium content present in secondary resources is much higher than that of primary 476 resources. Recycling of rhenium from secondary resources can contribute to a sustainable, low carbon, 477 resource efficient economy. As Heneckens et al. (2019) pointed out, recycling rhenium has an enormous 478 potential with the ultimate recyclability of more than 80%. The first step in the rhenium recycling is to 479 collect end-of-life goods and classify different types of spent rhenium scrap, then a suitable process can 480 be determined with thorough consideration of economic feasibility, recycle efficiency, environmental 481 factors, and potential recycling of other metals. Furthermore, the process should make full use of the 482 existing industrial equipment to reduce the investment.

483 4. Conclusion

484 Regarded as a precious and scarce metal, rhenium was the last naturally occurring stable element to 485 be discovered. Rhenium is primarily used in superalloys for high-temperature applications and platinum-486 rhenium catalysts. Annual production of rhenium is about 50 tonnes globally, and its demand will 487 continue to increase steadily due to the development of emerging high-tech innovations. However, the 488 potential for substitution of rhenium in many applications is very restricted, and no acceptable 489 substitute has been found so far. Furthermore, the extractable global rhenium resources have been 490 predicted to deplete within about 130 years. This creates a challenge to achieve sustainable rhenium 491 production requiring an increase of extraction yield from primary resources and recycling rate from

492 secondary resources.

With the science and technology development, the rhenium metallurgy industry has made great
progress. A flowsheet summarizing the rhenium extraction and recycling technology route is presented
in Fig. 9.



496 497

Fig. 9. Flowsheet of rhenium extraction and recycling technology route.

498 The occurrence of rhenium as a primarily sulfide ore mineral is rare, instead, it co-exists as a solid 499 solution with molybdenum, copper and other metal sulfide minerals. Thus, rhenium is obtained as a by-500 product in industrial production of molybdenum, copper, lead and uranium from ores and concentrates. 501 Rhenium is extracted from pyrometallurgical roasting fumes and dusts, and from leaching solutions and 502 residues in hydrometallurgical processing to obtain a rhenium-bearing solution. Separation technologies, 503 mainly solvent extraction and ion exchange, are employed in commercial practice for separating rhenium 504 to a rhenium-rich solution. Finally, rhenium metal is produced via crystallization and hydrogen reduction 505 steps.

506 Spent rhenium scrap, including spent rhenium alloys and catalysts, contains higher rhenium contents 507 than the natural resources. Recycling rhenium from spent scrap can avoid the mining costs and its wastes. 508 Recycling rhenium from spent alloys and catalysts is a multi-step task that can involve pyrometallurgical 509 and hydrometallurgical techniques. The main step is separating rhenium and other metals from the scrap 510 matrix, after which the purification steps are similar to that of extracting rhenium from the primary 511 resources.

The challenge of rhenium extraction in molybdenum, copper, lead and uranium processing is the enrichment of rhenium fractions in the production, while the recycling of spent rhenium scrap focuses on the collection and classification of different spent rhenium-containing scraps. Then, a suitable and efficient process flow sheet can be determined to recover rhenium from various sources with a high efficiency. Additionally, extraction and recycling of rhenium should also consider the practical policy to increase the efficiency. The critical evaluations, similar to those for tungsten and molybdenum production 518 proposed by some researchers (Leal-Ayala et al., 2015; Henckens et al., 2018), should be carried out for 519 the processes to determine the most sustainable options. Thus, an efficient and healthy supply chain is 520 hopefully built for the sustainability of rhenium industry.

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