

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

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

Shen, Leiting; Tesfaye, Fiseha; Li, Xiaobin ; Lindberg, Daniel; Taskinen, Pekka

Published in:
Minerals Engineering

DOI:
[10.1016/j.mineng.2020.106719](https://doi.org/10.1016/j.mineng.2020.106719)

Published: 15/01/2021

Document Version
Accepted author manuscript

Document License
CC BY-NC-ND

[Link to publication](#)

Please cite the original version:

Shen, L., Tesfaye, F., Li, X., Lindberg, D., & Taskinen, P. (2021). Review of rhenium extraction and recycling technologies from primary and secondary resources. *Minerals Engineering*, 161, Article 106719. <https://doi.org/10.1016/j.mineng.2020.106719>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

Leiting Shen^{a,*}, Fiseha Tesfaye^b, Xiaobin Li^{a,**}, Daniel Lindberg^c, Pekka Taskinen^c

^a Central South University, School of Metallurgy and Environment, Changsha 410083, China

^b Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Turku FI-20500, Finland

^c Aalto University, School of Chemical Engineering, Metallurgical Thermodynamics and Modelling, Espoo FI-00076, Finland

*Corresponding author: shenleiting@csu.edu.cn

**Corresponding author: x.b.li@csu.edu.cn

Abstract

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

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

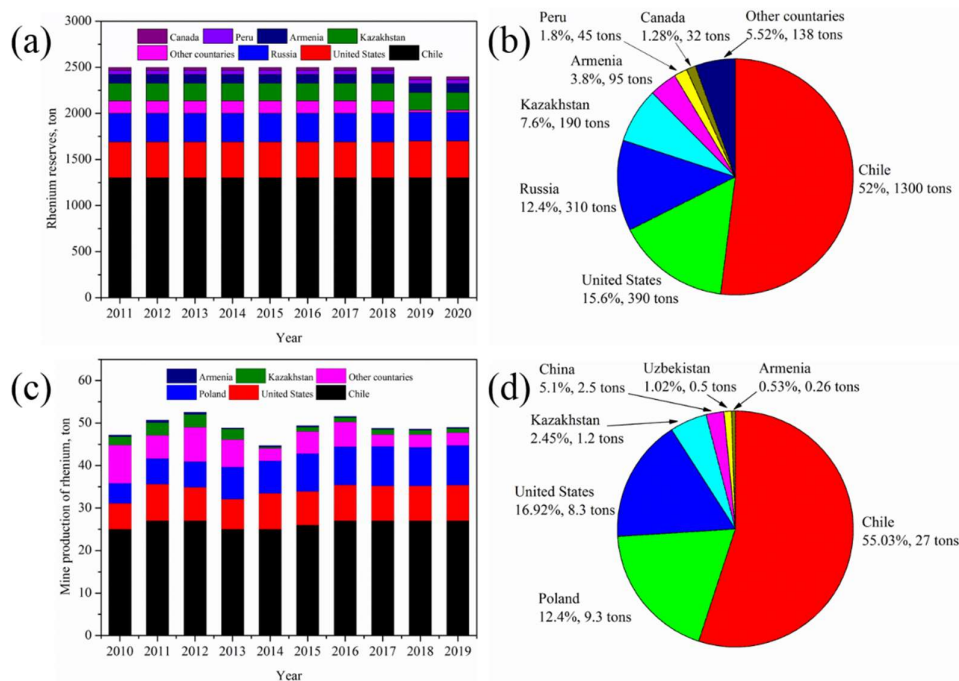
1. Introduction

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

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).



62
 63 **Fig. 1.** The estimated world reserve (a) and mine production (c) of rhenium over the last 10 years and
 64 their illustrated information of 2018 (b) and (d) for example (data from USGS, 2011-2020).

65 As one of the rarest metals, the estimated average crustal abundance of rhenium is about 0.4 part
 66 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,
70 ~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 (ReS_2 , 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 from
 110 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

114 As rhenium dominantly exists in molybdenum and copper concentrates after flotation, rhenium is
 115 typically extracted as a by-product in molybdenum and copper production. Additionally, rhenium is also
 116 recovered from lead and uranium production. The rhenium extraction processes and the existing forms
 117 of primary resources were collected and summarized in Table 1.

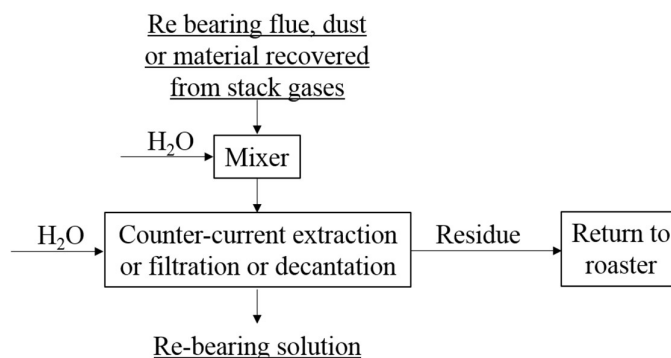
118 **Table 1** The process, technology and existing form of rhenium extracted from primary resources.

| Production process | Resource type | Extraction technology | Re existing form |
|--------------------|-------------------------------|--|--|
| Mo production | Re-containing Mo concentrates | Oxidation roasting-hydrometallurgical leaching Hydrometallurgical methods | Re ₂ O ₇ in roasting fume and dust; Residue In solution together with Mo |
| Cu production | Re-containing Mo concentrates | Pyrometallurgy-hydrometallurgical leaching Hydrometallurgical methods | Smelting fume and dust; Slime Aqueous solution together with Cu |
| Pb production | Re-containing Pb slime | Oxidation roasting-hydrometallurgical leaching | Dust |
| U production | Re-containing U ores | Insitu leaching | In solution together with U |

119 2.1.1 Pyrometallurgical processes

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

126



127

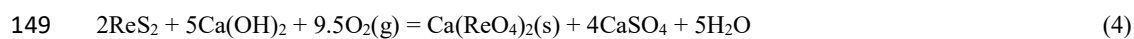
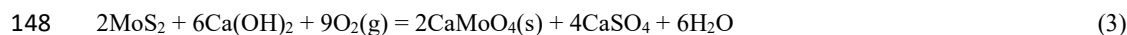
128 **Fig. 2.** Conceptual flowsheet for rhenium extraction from pyrometallurgical wastes of Re-containing

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 Re_2O_7 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 (HReO_4), as illustrated by Eq. (2) (Anderson
135 et al., 2013; Kesime 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.



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 H_2SO_4 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.



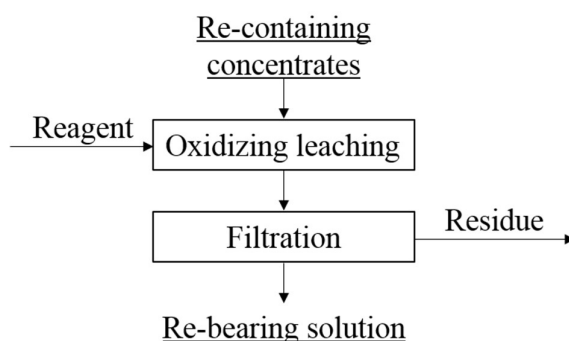
150 Juneja et al. (1996) investigated molybdenum and rhenium extraction from a low grade molybdenite
151 concentrate by roasting in the presence of lime and soda ash. The molybdenum and rhenium reacted
152 according to reactions (3) and (4), respectively. 74% of rhenium was extracted from the lime-roasted
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 Re_2O_7 produced during
158 pyrometallurgical processing of molybdenum and copper concentrate was directly reduced to rhenium
159 metal by S_2 . 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 CaCl_2 , 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 MoO_3 (99.9%) with almost no rhenium while high-content Re_2O_7 was collected at
163 lower temperature.

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

169

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 (ReO_4^-)
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 $>150^\circ\text{C}$ (Barry et al., 1972; Ketcham et al. 2000). Drescher et al. (1956) studied the leaching of
180 molybdenite by KOH solution in the pressure range 0-700 psia of oxygen at $100\text{-}170^\circ\text{C}$. 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 $60\text{-}120^\circ\text{C}$ 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 $<1.0\text{ MPa}$, temperature $<90^\circ\text{C}$, particle size $\leq 23\ \mu\text{m}$ and leaching time $<90\text{ min}$. 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 $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2/\text{O}_3$ system is the most efficient lixiviant to extract these
197 metals.

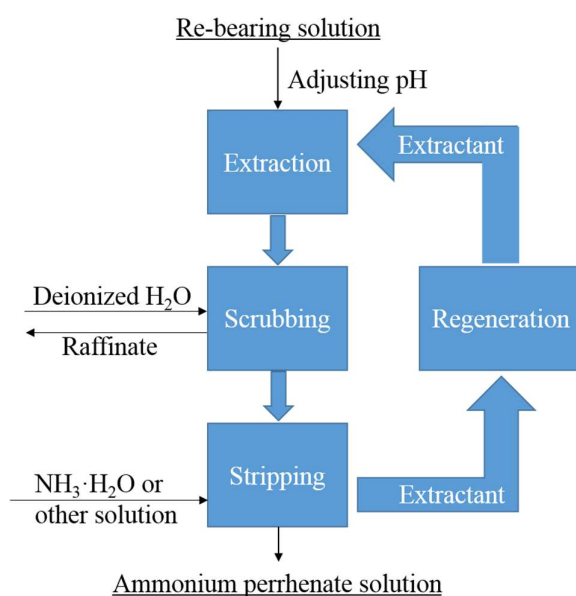
198 Additionally, Askari Zamani et al. (2005) tested the bioleaching of a molybdenite concentrate to
199 extract rhenium, with a low rhenium yield of only 7.3%. Abdollahi et al. (2019) optimized the operational
200 parameters of dissolving Cu, Mo and Re from molybdenite concentrate through meso-acidophilic
201 bioleaching using an artificial neural network (ANN), with the maximum recovery of Cu, Mo and Re of
202 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

215 **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 trioctylamine 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

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

| Separation elements | Bulk solution | Extractant | Selective stripping | Extractive yield | Separation coefficient | Reference |
|---------------------|----------------------------------|--|---------------------------|------------------------|------------------------|------------------------------|
| Re-Mo | Acidic media | A mixture of trioctylamine and Aliquat 336 | nitric acid | 99.44% | - | Karagiozov and Vasilev, 1979 |
| Re-Mo | Sulphuric acid solution | Amide type extractant A101 | - | Recovery increasing 2% | 667 | Zhou et al., 1982 |
| Re-Mo | Alkaline solutions | Synergistic extraction with primary amine and neutral phosphorus esters | - | - | Up to 100000 | Yu et al., 1985 |
| Re | Hydrochloric acid solutions | Tributyl phosphate or trioctyl phosphine oxide with trioctylamine (TOA) or trioctylmethylammonium chloride | 10% dimethylamine | - | - | Sato and Sato, 1990 |
| Re-Mo-W | Sulphuric acid media | Dioctylamine DOA | Aqueous ammonium solution | 99.5 | - | Gerhardt et al., 2000; 2001 |
| Re-Mo | Alkaline solution | A mixture of tributyl phosphate and triethylamine | 18% ammonia liquor | 96.8% | 1700 | Cao et al., 2009 |
| Re | Rhenium stock solutions | Mixtures of tri-alkylamine and tri-nbutylphosphate | - | - | 15.36 | Xiong et al., 2010 |
| Re-Mo | Molybdenum oxide leaching liquor | Tri-butyl phosphate (TBP) | Ammonia solution | 98% | 450 | Alamdari et al., 2012 |
| Re | Nitric acid solution | 2,20-(imino)bis(N,N0-dioctylacetamide) | - | - | - | Ali et al., 2012 |

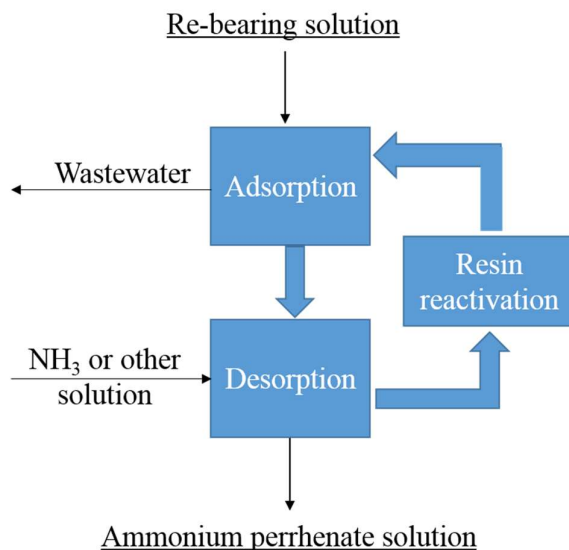
| | | | | | | |
|-------------|---|--|---|-------------|-----------|--------------------------------|
| Re | A scrub liquor of molybdenite roaster fume | A 10 v/v.% tertiary amine, 10 v/v.% Isodecanol in 80% Anysol-150 | 30% ammonium hydroxide | 96.4-99% | - | Kim et al., 2015 |
| Re | An acidic chloride solution | Cyanex 923 diluted in kerosene | 1.5 mol·L ⁻¹ NH ₄ OH solution | 99.2% | - | Srivastava et al., 2015 |
| Re-Mo | Hydrochloric 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 | Molybdenite flue-dust leach liquor | Tri-butyl phosphate (TBP) | - | >99.6% | - | Cheema et al., 2018 |
| Re | Scrub liquors of fumes and dusts from roasting molybdenite concentrates | 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 trioctylmethylammonium 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 |

248

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 extractants. 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

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



265
266

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 ReO_4^-
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.

283

284 **Table 3** The reported example of separating Re from solution by ion exchange.

| Bulk solution | Separation elements | Resin type | Desorption reagent | Efficiency | Reference |
|---|---------------------|---|---|---|--------------------------------|
| Sulphuric and nitric-sulphuric acid solutions | Re-Mo | Weak basic anion exchange resins AN-82-14G and AN-105-14G | 5% NaOH or 10% NH ₄ OH solutions | >99.5% | Kholmogorov et al., 1999 |
| Molybdenite calcine leaching solution | Re-Mo | Resin D216 and gel type resin 201X7 | HNO ₃ solution | >90% | Lan et al., 2006 |
| Re-Mo solution with pH 2.6-6 | Re-Mo | 4-amino-1,2,4-triazole resin | 1.0~5.0 mol·L ⁻¹ HCl solution | Separation coefficient β _{Re/Mo} =17.3 | 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 | NH ₄ OH 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 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 |

285

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

290 2.2.3 Other methods

291 Adsorption and membrane techniques have also been studied to recover metal anions from the
 292 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 trimethoxysilane, 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**

317 The ammonium perrhenate solution obtained in a separation step is crystallized via evaporation
318 crystallization to produce a high-quality ammonium perrhenate product (Gabashi, 1997; Millensifer et
319 al., 2014; Nadler, 2012). The remaining rhenium in the mother liquor can be recovered by adding zinc
320 sulfate and ammonia to precipitate a complex salt [Zn(NH₃)₄](ReO₄)₂, which can be dissolved by sulfuric
321 acid to prepare ammonium perrhenate (Zagorodnyaya and Abisheva, 2002). Rhenium metal powder can
322 be produced by reducing with hydrogen or other reducing gas at a high temperature (Gabashi, 1997;
323 Millensifer et al., 2014; Nadler, 2012).

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

329 **3. Recycling Re from secondary resources**

330 The secondary resources of rhenium include Ni-Re superalloys (~1-20 wt. % Re, and most
331 commonly 3-6 wt. % Re), W-Re and Mo-Re alloys (3-5 wt. % Re), and spent Re-containing catalysts
332 (~0.3 wt. % Re) (Mishra et al., 2012). Rhenium recycling is a multi-step process combining
333 pyrometallurgical and hydrometallurgical techniques.

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

| Reference | Raw material | Method | Year |
|--------------------------------------|---|--|------------|
| Han and Meng, 1996* | Particularly spent catalysts | Leaching with a ammonium halogen salts-iodide 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 NaHCO ₃ 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; |
| Palant et al., 2011;2013;2014 | Re-containing nickel superalloy | Electrochemical processing in H ₂ SO ₄ /H ₂ SO ₄ +HCl/HNO ₃ electrolytes | 2013; 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 HNO ₃ | 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 | | Anodic dissolution of W-Re alloys, precipitation of calcium tungstate from the electrolyte, and | 2017 |
| Kuznetsova et al., 2018; 2020 | W-Re alloys | electrodialysis of rhenium in the form of HReO ₄ | 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 |

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

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

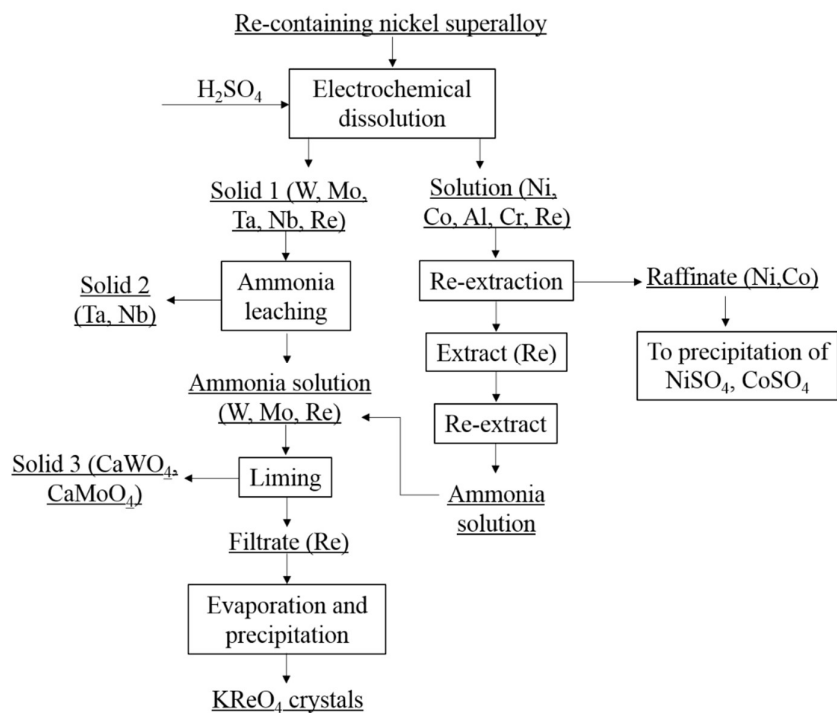
344 Technological developments have been covered in many publications and patents reported recently.
345 The recycling technologies included e.g. digestion in molten salts, selective leaching with a

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

349 3.1 Re recycling from superalloys

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

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



360

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

363 Based on physicochemical studies, Palant et al. (2011; 2013; 2014) developed a process flow sheet
 364 (Fig. 6) for recovering rhenium and other metals from a rhenium-containing nickel superalloy by a
 365 complex electrochemical process using H₂SO₄, H₂SO₄+HCl, or HNO₃ electrolyte. After electrochemical
 366 dissolution, ~70% of rhenium is concentrated in the anode slimes, from which Re is leached by ammonia
 367 solution. The other 25–30% of rhenium is transferred to a sulfuric acid electrolyte, from which it is re-
 368 extracted by solvent extraction to obtain ammonium perrhenate solution. Finally, KReO₄ crystals are

369 produced through liming precipitation, filtrate, evaporation and precipitation steps. This process can also
370 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.

374 In 2013, Luederitz et al. (2013) applied for a patent for selectively recovering rhenium and other
375 metals from rhenium containing materials, such as alloy residue and wastes, ore materials, waste
376 materials and cermet catalysts. All metals in the Re-containing materials are solubilized in a HCl solution
377 or a mixture of HCl and HNO_3 to form their corresponding aqueous salts. Rhenium is then selectively
378 precipitated as Re_2S_7 , which is later oxidized and sublimed as Re_2O_7 . The subsequent process is similar
379 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 > 500
383 mv vs. Ag/AgCl or a mixture of HNO_3 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 Re_2S_7 , absorption on activated carbon or an absorbent resin, or by solvent extraction. Finally, the solid
387 intermediate NH_4ReO_4 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 NH_4ReO_4 product.

396 Britton and Markarian (2017a, 2017b) patented a hydrometallurgical method to treat rhenium-
397 containing materials, particularly superalloys. The raw materials were digested with $50\text{--}1000 \text{ g/L}$ H_2SO_4
398 and a halide-free oxidant including air, ozone, oxygen, peroxide and persulfate salts. After filtration, the
399 filter cake was further digested in an oxidizing and complexing milieu to extract the unreacted targeted
400 metal. Finally, rhenium and platinum were separated by an ion exchange resin.

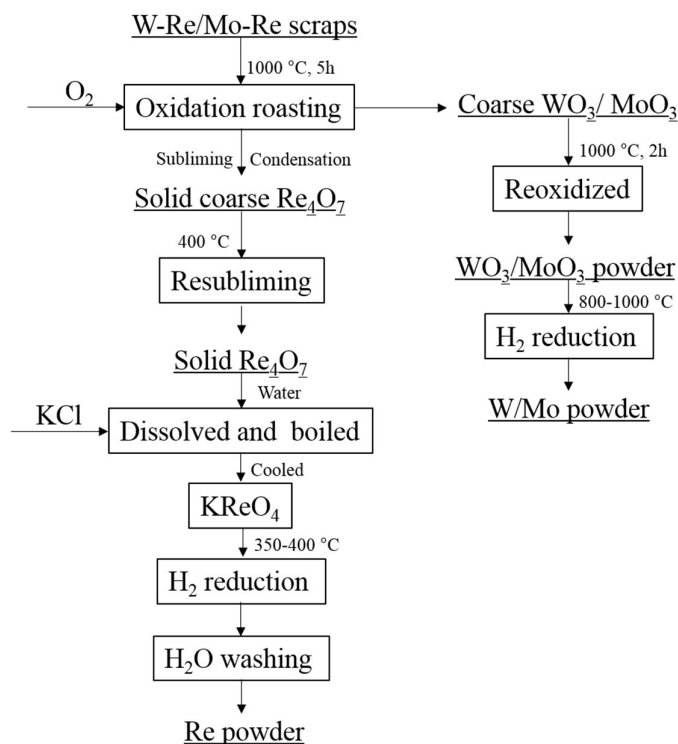
401 Kim et al. (2018) investigated a selective two-step leaching process for nickel and rhenium from
402 nickel-based superalloy scrap in hydrochloric acid solutions. Superalloy scrap with particle size < 150
403 μm was pyrometallurgically pretreated with aluminum granule at 1500°C to form Al_3Ni intermetallic
404 compound. In the first leaching step, the pretreated scrap was leached in a 4.0 mol/L HCl solution to
405 extract nickel together with aluminum, cobalt and chromium, remaining most rhenium and tantalum in
406 the residue. Rhenium was leached from the residue by using electrogenerated chlorine as an oxidant in
407 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 superalloy
409 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 Re_4O_7 referred to
 416 WO_3 and MoO_3 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

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

425 Allison et al. (2003) patented a method to recover rhenium from spent catalysts by conversion of
 426 rhenium to a sublimable oxide via oxidation by heating in an oxidizing atmosphere and then isolation of
 427 rhenium from the volatilized 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 Re_2O_7 solid was recovered as a NH_4ReO_4 solution, and was further treated by crystallization
 431 and hydrogen reduction of NH_4ReO_4 to rhenium metal power. Ye et al. (2020) decomposed W-Re wire

432 by a KOH-K₂CO₃ molten salt at 800 °C to form KReO₄. Subsequently, the decomposed product was
433 leached by water, and treated by crystallization to obtain high purity KReO₄ crystals which were reduced
434 by H₂ at 350 °C to produce Re powder.

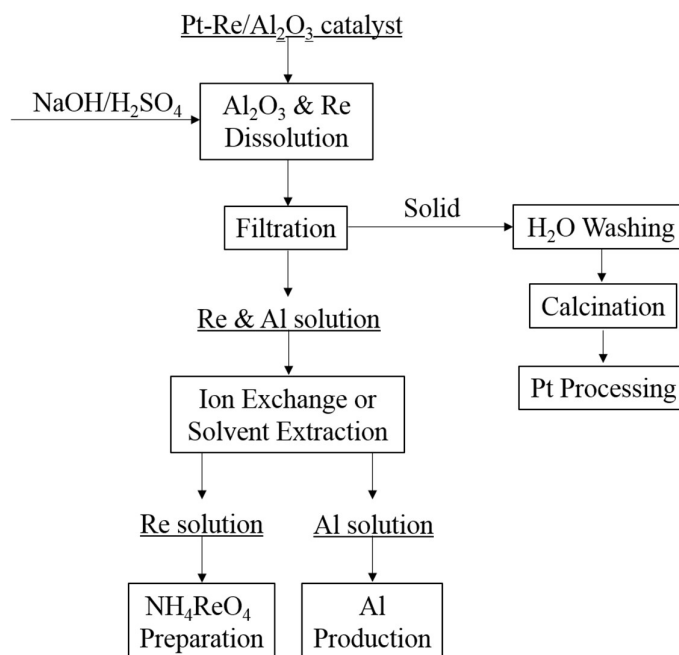
435 In addition, Levin and Levchuk (2017) proposed a flow-sheet for Re recovery from W-Re alloys.
436 W-Re alloys were firstly treated in NaOH solution with anodic dissolution, then tungsten was precipitated
437 as calcium tungstate from the electrolyte by adding Ca(OH)₂, subsequently KReO₄ precipitate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

441 **3.3 Re recycling from spent catalysts**

442 Spent rhenium-containing catalysts typically contain ~0.3 wt. % rhenium, ~0.3 wt. % platinum, and
443 alumina. These can be treated for selective recovery of rhenium and platinum. Kasikov and Petrova (2008)
444 reviewed the decomposition methods and divided them into two groups, selective extraction of rhenium
445 without the carrier material decomposition and incorporating decomposition of catalyst aluminum oxide
446 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-associated leaching, and ion exchange, to prepare high-purity NH₄ReO₄. The
454 method is similar to the pyrometallurgical-hydrometallurgical technique for recovering rhenium from
455 alloys as mentioned above. El Guindy (1997) discussed the techniques and methods for processing of
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.

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



467

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

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

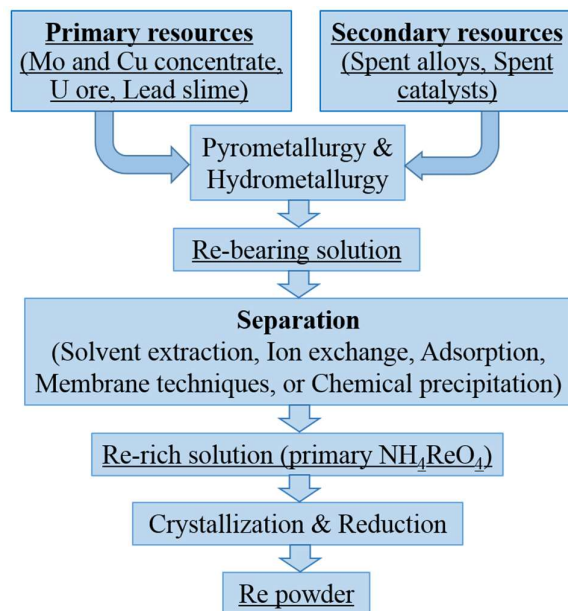
475 In total, the rhenium content present in secondary resources is much higher than that of primary
 476 resources. Recycling of rhenium from secondary resources can contribute to a sustainable, low carbon,
 477 resource efficient economy. As Heneckens et al. (2019) pointed out, recycling rhenium has 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.

493 With the science and technology development, the rhenium metallurgy industry has made great
494 progress. A flowsheet summarizing the rhenium extraction and recycling technology route is presented
495 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.

512 The challenge of rhenium extraction in molybdenum, copper, lead and uranium processing is the
513 enrichment of rhenium fractions in the production, while the recycling of spent rhenium scrap focuses
514 on the collection and classification of different spent rhenium-containing scraps. Then, a suitable and
515 efficient process flow sheet can be determined to recover rhenium from various sources with a high
516 efficiency. Additionally, extraction and recycling of rhenium should also consider the practical policy to
517 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.

521 **Acknowledgements**

522 The author (L.T. Shen) gratefully acknowledges the financially supports from The Finnish National
523 Agency for Education (EDUFI Fellowship TM-18-10745) and from Aalto CHEM Funding (Project
524 902222). This work was also partially supported by the Academy of Finland (Decision No. 311537), as
525 part of the activities of the Johan Gadolin Process Chemistry Centre at Åbo Akademi University.

526 **References**

- 527 Abisheva Z.S., Zagorodnyaya A.N., Bekturganov N.S., 2011. Review of technologies for rhenium
528 recovery from mineral raw materials in Kazakhstan. *Hydrometallurgy* 109, 1-8.
- 529 Abdollahi H., Noaparast M., Shafaei S.Z., Akcil A., Panda S., Kashi M.H., Karimi P., 2019. Prediction
530 and optimization studies for bioleaching of molybdenite concentrate using artificial neural networks
531 and genetic algorithm. *Miner. Eng.* 130, 24-35.
- 532 Agapova L.Y., Ponomareva E.I., Abisheva Z.S., 2001. Production of concentrated rhenium acid by
533 electro dialysis of rhenium salts solutions. *Hydrometallurgy* 60, 117-122.
- 534 Alamdari E.K., Darvishi D., Haghshenas D.F., Yousefi N., Sadrnezhad S.K., 2012. Separation of Re and
535 Mo from roasting-dust leach-liquor using solvent extraction technique by TBP. *Sep. Purif. Technol.*
536 86, 143-148.
- 537 Ali M.C., Suzuki T., Tachibana Y., Sasaki Y., Ikeda Y., 2012. Selective extraction of perrhenate anion in
538 nitric acid solution using 2,2'-(imino)bis(N,N0-dioctylacetamide) as an extractant. *Sep. Purif.*
539 *Technol.* 92, 77-82.
- 540 Allison J. D., Srinivasan N., Ramani S., 2003. Recovery of rhenium from a spent catalyst via sublimation.
541 U.S. Patent No. US 2003/0119658 A1.
- 542 Amer A., 2008. The Hydrometallurgical extraction of rhenium from copper industrial wastes. *JOM* 60
543 (8), 52-54.
- 544 Ammann P.R., Loose T.A., 1972. Rhenium volatilization during molybdenite roasting. *Metall. Trans.* 3,
545 1020-1022.
- 546 Anderson C.D., Taylor P.R., Anderson C.G., 2013. Extractive metallurgy of rhenium: a review. *Miner.*
547 *Metall. Process.* 30(1), 59-73.
- 548 Angelidis T.N., Rosopoulou D., Tzitzios V., 1999. Selective rhenium recovery from spent reforming
549 catalysts. *Ind. Eng. Chem. Res.* 38, 1830-1836.
- 550 Askari Zamani M.A., Hiroyoshi N., Tsunekawa M., Vaghar R., Oliazadeh M., 2005. Bioleaching of
551 Sarcheshmeh molybdenite concentrate for extraction of rhenium. *Hydrometallurgy* 80, 23-31.
- 552 Barry H.F., Hallada C.J., McConnell R.W., 1972. Liquid phase oxidation process. US Patent No. 3656888.
- 553 Beck B.K., Graedel T.E., 2012. Challenges in metal recycling. *Science* 337, 690-695.
- 554 BGS, 2011. Risk List 2011. Keyworth, UK: British Geological Survey.
- 555 BGS, 2012. Risk List 2012. Keyworth, UK: British Geological Survey.
- 556 BGS, 2015. Risk List 2015. Keyworth, UK: British Geological Survey.
- 557 Bian A.F., Miao X.X., Lei S.G., Chen S.E., Wang W.F., Struthers S., 2012. The challenges of reusing

558 mining and mineral-processing wastes. *Science* 337, 702-703.

559 Britton L.A., Markarian G.Z., 2017a. Method for platinum recovery from materials containing rhenium
560 and platinum metals. US Patent No. 9702021 B2.

561 Britton L.A., Markarian G.Z., 2017b. Method for platinum recovery from materials containing rhenium
562 and platinum metals. US Patent No. 9708690 B2.

563 Bryukvin V.A., Elemesov T.B., Levchuk O.M., Bol'shikh A.O., 2016. Reaction behavior of Ni-Re alloys
564 during direct current polarization in sulfuric acid solutions. *Russ. Metall.* 1, 12-17.

565 Cao Z.F., Hong Z., Qiu Z.H., 2009. Solvent extraction of rhenium molybdenum in alkaline solution.
566 *Hydrometallurgy* 97, 153-157.

567 Casas J.M., Sepulveda E., Bravo L., Cifuentes L., 2012. Crystallization of sodium perrhenate from
568 $\text{NaReO}_4\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ solutions at 298 K. *Hydrometallurgy* 113-114, 192-194.

569 Charewicz W.A., Wodka J., Chmielewski T., 1991. Recovery of rhenium from acidic aqueous solutions
570 by pressure reduction with gaseous reducers. *J. Chem. Tech. Biotechnol.* 52, 119-126.

571 Cheema H.A., Ilyas S., Masud S., Muhsan M.A., 2018. Selective recovery of rhenium from molybdenite
572 flue-dust leach liquor using solvent extraction with TBP. *Sep. Purif. Technol.* 191, 116-121.

573 Chekmarev A.M., Troshkina I.D., Nesterov Y.V., Maiboroda A.B., Ushanova O.N., Smirnov N.S., 2004.
574 Associated rhenium extraction in complex processing of productive solutions of underground
575 uranium leaching. *Chem. Sustainable Dev.* 12, 113-117.

576 Churchwood P.E., Rosenbaum J.B., 1963. Rhenium recovery by solvent extraction and electrodeposition.
577 *J. Met.* 648-650.

578 Cyganowski P., Cierlik A., Lesniewicz A., Pohl P., Jermakowicz-Bartkowiak D., 2019. Separation of
579 Re(VII) from Mo(VI) by anion exchange resins synthesized using microwave heat. *Hydrometallurgy*
580 185, 12-22.

581 Dasan B., Palanisamy B., Lipkin D. M., Ajdelsztajn L., Miller J. L., Sampath S., 2011. Rhenium recovery
582 from superalloys and associated methods. U.S. Patent No. US 8,038,764 B2.

583 Dresler W.H., Wadsworth M.E., Martin Fassell W., 1956. A kinetic study of the leaching of molybdenite.
584 *J. Met.* 794-800.

585 Drobot D.V., Bukin V.I., 1997. Recycling of Rhenium. In *Rhenium and Rhenium Alloys* (Bryskin B.D.
586 Edit). The Minerals, Metals & Materials Society, pp 119-127.

587 El Guindy M.I., 1997. Processing of Spent Platinum Rhenium Catalyst for Rhenium Recovery. In
588 *Rhenium and Rhenium Alloys* (Bryskin B.D. Edit). The Minerals, Metals & Materials Society, pp 89-
589 97.

590 Elutin A.V., Istrashkina M.V., Perederreeva Z.A., 1997. Rhenium Recovery from Secondary Raw
591 Materials of Various Types. In *Rhenium and Rhenium Alloys* (Bryskin B.D. Edit). The Minerals,
592 Metals & Materials Society, pp 135-139.

593 Eric J., 2017. *Rhenium: properties, uses, and occurrence*. Nova Science Publishers, Inc., New York.

594 Ferron C.G., Seeley L.E., 2015. Rhenium recovery. US Patent No. 8956582 B2.

595 Free M., 2011. Minor elements recovery and impurity control in industrial metal processing. *JOM* 68(8),
596 89.

597 Gaete J., Molina L., Alfaro I., Yanez J., Valenzuela F., Basualto C., 2019. Recovery and separation of
598 rhenium and molybdenum from aqueous solutions that simulate mine waters using magnetite
599 nanoparticles functionalized with amine-derivative groups. *Miner. Eng.* 136, 66-76.

600 Gabashi F., 1997. *Handbook of extractive metallurgy*, Volume III, Chapter 33, Rhenium. WILEY-VCH,
601 pp. 1491-1501.

602 Gaustad G., Krystofik M., Bustamante M., Badami K., 2018. Circular economy strategies for mitigating
603 critical material supply issues. *Resour., Conserv. Recycl.* 135, 24-33.

604 Gerhardt N.I., Palant A.A., Dungan S.R., 2000. Extraction of tungsten (VI), molybdenum (VI) and
605 rhenium (VII) by diisododecylamine. *Hydrometallurgy* 55, 1-15.

606 Gerhardt N.I., Palant A.A., Petrova V.A., Tagirov R.K., 2001. Solvent extraction of molybdenum (VI),
607 tungsten (VI) and rhenium (VII) by diisododecylamine from leach liquors. *Hydrometallurgy* 60, 1-5.

608 Graedel T.E., Harper E.M., Nassar N.T., Nuss P., Reck B.K., 2015. Criticality of metals and metalloids.
609 *PNAS* 112, 4257-4262.

610 Guo X.Y., Ma Z.C., Li D., Tian Q.H., Xu Z.P., 2019. Recovery of Re(VII) from aqueous solutions with
611 coated impregnated resins containing ionic liquid Aliquat 336. *Hydrometallurgy* 190, 105149.

612 Han K.N., Meng X.H., 1996. Recovery of platinum group metals and rhenium from materials using
613 halogen reagents. US Patent No. 5542957.

614 Helbig T., Gilbricht S., Lehmann F., Daus B., Kelly N., Haseneder R., Scharf C., 2018. Oxidative
615 leaching of a sulfidic flue dust of former copper shale processing with focus on rhenium. *Miner. Eng.*
616 128, 168-178.

617 Henckens M.L.C.M., Driessen P.P.J., Worrell E., 2014. Metal scarcity and sustainability, analyzing the
618 necessity to reduce the extraction of scarce metals. *Resour., Conserv. Recycl.* 93, 1-8.

619 Henckens M.L.C.M., Driessen P.P.J., Worrell E., 2019. Mineral resources governance: A call for the
620 establishment of an International Competence Center on Mineral Resources Management. *Resour.,*
621 *Conserv. Recycl.* 141, 255-263.

622 Heshmatpour B., Madonald R.E., 1982. Recovery and refining of rhenium, tungsten and molybdenum
623 from W-Re, Mo-Re and other alloy scraps. *J. Less-Common Met.* 86, 121-128.

624 Hong T., Liu M.B., Ma J., Yang G., Li L.B., Mumford K.A., Stevens G.W., 2020a. Selective recovery of
625 rhenium from industrial leach solutions by synergistic solvent extraction. *Sep. Purif. Technol.* 236,
626 116281.

627 Hong T., Zheng T., Liu M.B., Mumford K.A., Stevens G.W., 2020b. Investigation on the recovery of
628 rhenium in the high arsenite wash acid solution from the copper smelting process using reducing
629 sulfide precipitation method. *Hydrometallurgy* 195, 105402.

630 Hori H., Otsu T., Yasukawa T., Morita R., Ishii S., Asai T., 2019. Recovery of rhenium from aqueous
631 mixed metal solutions by selective precipitation: A photochemical approach. *Hydrometallurgy* 183,
632 151-158.

633 Hori H., Yoshimura Y., Otsu T., Kume K., Mitsumori Y., Kutsuna S., Koike K., 2019. Efficient
634 photochemical recovery of rhenium from aqueous solutions. *Sep. Purif. Technol.* 156, 242-248.

635 Hu H., Sun L.L., Wang T., Lv C.G., Gao Y.L., Zhang Y.F., Wu H.X., Chen X.H., 2019. Nano-ZnO
636 functionalized biochar as a superhydrophobic biosorbent for selective recovery of low-concentration
637 Re(VII) from strong acidic solutions. *Miner. Eng.* 142, 105885.

638 Hu H., Sun L., Jiang B.Q., Wu H.X., Huang Q.M., Chen X.H., 2018. Low concentration Re(VII) recovery
639 from acidic solution by Cu-biochar composite prepared from bamboo (*Acidosasa longiligula*) shoot
640 shell. *Miner. Eng.* 124, 123-136.

641 John D.A., Seal R.R. II, Polyak D.E., 2017. Rhenium, Chapter P of Critical mineral resources of the
642 United States—Economic and environmental geology and prospects for future supply (Schulz K.J.,
643 et al., Eds.). U.S. Geological Survey Professional Paper 1802, pp. P1–P49,
644 <https://doi.org/10.3133/pp1802P>.

645 John D., 2015. Rhenium-A rare metal critical to modern transportation, USGS Mineral Resources

646 Program. U.S. Department of the Interior, and U.S. Geological Survey.
647 <http://dx.doi.org/10.3133/fs20143101>.

648 Juneja J.M., Singh S., Bose D.K., 1996. Investigations on the extraction of molybdenum and rhenium
649 values from low grade molybdenite concentrate. *Hydrometallurgy* 41, 201-209.

650 Karagiozov L., Vasilev C., 1979. Separation of molybdenum and rhenium by extraction with mixtures of
651 trioctylamine and aliquat 336 followed by selective stripping. *Hydrometallurgy* 4, 51-55.

652 Kasikov L.G., Petrova A.M., 2008. Processing of deactivated platinum-rhenium catalysts.
653 *Khimicheskaya Tekhnologiya* 9(8), 376-385. *Theor. Found. Chem. Eng.* 2009, 43(4), 544-552. DOI:
654 10.1134/S0040579509040320

655 Kesieme U., Chrysanthou A., Catulli M., 2019. Assessment of supply interruption of rhenium, recycling,
656 processing sources and technologies. *Int. J. Refract. Met. Hard Mater.* 87, 150-158.

657 Ketcham V.J., Coltrinari E.L., Hazen W.W., 2000. Pressure oxidation process for the production of
658 molybdenum trioxide from molybdenite. US Patent No. 6149883.

659 Kholmogorov A.G., Kononova O.N., Kachin S.V., Ilyichev S.N., Kryuchkov V.V., Kalyakina O.P., 1999.
660 Ion exchange recovery and concentration of rhenium from salt solutions. *Hydrometallurgy* 51, 19-35.

661 Kim H.S., Park J.S., Seo S.Y., Tran T., Kim M.J., 2015. Recovery of rhenium from a molybdenite roaster
662 fume as high purity ammonium perrhenate. *Hydrometallurgy* 156, 158-164.

663 Kim M.S., Lee J.C., Park H.S., Jun M.J., Kim B.S., 2018. A multistep leaching of nickel-based superalloy
664 scrap for selective dissolution of its constituent metals in hydrochloric acid solutions.
665 *Hydrometallurgy* 176, 235-242.

666 Kuznetsova O.G., Levin A.M., Sevostyanov M.A., Bolshih A.O., 2018. The improvement of rhenium
667 recovery technology from W-Re alloys. *J. Phys.: Conf. Ser.* 1134, 012032.

668 Kuznetsova O.G., Levin A.M., Sevost'yanov M.A., Tsybin O.I., Bol'shikh A.O., Bol'shikh M.A., 2020.
669 Improved Electrodialysis Synthesis of Perrhenic Acid from the Electrolytes of Processing the Wastes
670 of Tungsten-Rhenium Alloys. *Russ. Metall.* 1, 71-76.

671 Laatikainen M., Virolainen S., Paatero E., Sainio T., 2015. Recovery of ReO_4^- by weakly basic anion
672 exchangers: Modeling of sorption equilibrium and rate. *Sep. Purif. Technol.* 153, 19-28.

673 Lan X., Liang S., Song Y., 2006. Recovery of rhenium from molybdenite calcine by a resin-in-pulp
674 process. *Hydrometallurgy* 82, 133-136.

675 Leal-Ayala D.R., Allwood J.M., Petavratzi E., Brown T.J., Gunn G., 2015. Mapping the global flow of
676 tungsten to identify key material efficiency and supply security opportunities. *Resour., Conserv.
677 Recycl.* 103, 19-28.

678 Lessard J.D., Gribbin D.G., Shekhter L.N., 2014. Recovery of rhenium from molybdenum and copper
679 concentrates during the Looping Sulfide Oxidation process. *Int. J. Refract. Met. Hard Mater.* 44, 1-6.

680 Levin A.M., Levchuk O.M., 2017. Electrochemical Recovery of Rhenium from W-Re Alloys in the Form
681 of Perrhenic Acid: I. Fundamentals of the Process. *Russ. Metall.* 1, 55-62.

682 Lou Z.N., Guo C.F., Feng X.D., Zhang S.Q., Xing Z.Q., Shan W.J., Xiong Y., 2015. Selective extraction
683 and separation of Re(VII) from Mo(VI) by TritonX-100/N235/iso-amyl alcohol/n-heptane/NaCl
684 microemulsion system. *Hydrometallurgy* 157, 199-206.

685 Lou Z.N., Cui X.R., Zhang S.Q., Feng X.D., Shan W.J., Xiong Y., 2016. Extraction of Re(VII) from
686 hydrochloric acid medium by N263/TBP/n-heptane/NaCl microemulsion. *Hydrometallurgy* 165, 329-
687 335.

688 Lou Z.N., Xing S.S., Xiao X., Shan W.J., Xiong Y., Fan Y., 2018. Selective adsorption of Re(VII) by
689 chitosan modified with imidazoliumbased ionic liquid. *Hydrometallurgy* 179, 141-148.

690 Lou Z.N., Huang M.N., Cui J.S., Wu S.Y., Xing S.S., Zhou P., Shan W.J., Xiong Y., 2019. Copolymers
691 of vinylimidazolium-based ionic liquids and divinylbenzene for adsorption of TcO_4^- or ReO_4^- .
692 Hydrometallurgy 190, 105147.

693 Luederitz E., Schlegel U.R., Halpin P.T., Schneck D.L., 2013. Method for recovering rhenium and other
694 metals from rhenium-bearing materials. US Patent Application No. 2013/0078166 A1.

695 Mamo S.K., Elie M., Baron M.G., Simons A.M., Gonzalez-Rodriguez J., 2019. Leaching kinetics,
696 separation, and recovery of rhenium and component metals from CMSX-4 superalloys using
697 hydrometallurgical processes. Sep. Purif. Technol. 212, 150-160.

698 Melaven D., Bacon J.A., 1947. Process for recovering rhenium. US Patent No. 2414965.

699 Meschke K., Daus B., Haseneder R., Repke J.U., 2017. Strategic elements from leaching solutions by
700 nanofiltration – Influence of pH on separation performance. Sep. Purif. Technol. 184, 264-274.

701 Meschke K., Hofmann R., Haseneder R., Repke J.U., 2020. Membrane treatment of leached mining waste
702 – A potential process chain for the separation of the strategic elements germanium and rhenium. Chem.
703 Eng. J. 380, 122476.

704 Millensifer A., Sinclair D., Jonasson I., Lipmann A., 2014. Rhenium. In Critical Metals Handbook, G.
705 Gunn (Ed.). doi:10.1002/9781118755341.ch14.

706 Mishra B., Anderson C.D., Taylor P.R., Anderson C.G., Apelian D., Blanpain B., 2012. CR³ update:
707 Recycling of strategic metals. JOM 64(4), 441-443.

708 Mollerstedt B.O.P., Backius K.E., 1976. Wet-chemical digestion of molybdenum sulphide containing
709 material. US Patent No. 4000244.

710 Nadler H.G., 2012. Rhenium and Rhenium Compounds, In Ullmann's Encyclopedia of Industrial
711 Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. DOI: 10.1002/14356007.a23_199

712 Nebeker N., Hiskey J.B., 2012. Recovery of rhenium from copper leach solution by ion exchange.
713 Hydrometallurgy 125-126, 64-68.

714 Olbrich A., Meese-Marktscheffel J., Jahn M., Zertani R., Stoller V., Erb M., Heine K.H., Kutzler U., 2009.
715 Recycling of superalloys with the aid of an alkali metal salt bath. US Patent Application No.
716 2009/0255372 A1.

717 Palant A.A., Levchuk O.M., Bryukvin V.A., Levin A.M., Paretskii V.M., 2011. Complex electrochemical
718 processing of the metallic wastes from a rhenium-containing nickel superalloy in sulfuric acid
719 electrolytes. Russ. Metall. 6, 589-593.

720 Palant A.A., Bryukvin V.A., Levin A.M., Levchuk O.M., 2014. Combined electrochemical processing of
721 the wastes of nickel superalloys containing rhenium, tungsten, tantalum, niobium, and other precious
722 metals. Russ. Metall. 1, 20–22.

723 Palant A.A., Levin A.M., Levchuk O.M., Bryukvin V.A., 2013. Electrochemical processing of the
724 metallic wastes of ZhS32 nickel superalloys. Russ. Metall. 7, 497–500.

725 Petrova A.M., Kasikov A.G., 2016. Rhenium(VII) solvent extraction with mixtures of tertiary amine and
726 oxygen-containing extractants from sulphate media. Hydrometallurgy 165, 270-274.

727 Quijada-Maldonado E., Allain A., Perez B., Merlet G., Cabezas R., Tapia R., Romero J., 2020. Selective
728 liquid-liquid extraction of molybdenum (VI) and rhenium (VII) from a synthetic pregnant leach
729 solution: Comparison between extractants and diluents. Miner. Eng. 145, 106060.

730 Salehi H., Tavakoli H., Aboutalebi M.R., Samim H.R., 2019. Recovery of molybdenum and rhenium in
731 scrub liquors of fumes and dusts from roasting molybdenite concentrates. Hydrometallurgy 185, 142-
732 148.

733 Sato T., Sato K., 1990. Liquid-liquid extraction of rhenium (VII) from hydrochloric acid solutions by

734 neutral organophosphorus compounds and high molecular weight amines. *Hydrometallurgy* 25, 281-
735 291.

736 Seo S.Y., Choi W.S., Yang T.J., Kim M.J., Tran T., 2012. Recovery of rhenium and molybdenum from a
737 roaster fume scrubbing liquor by adsorption using activated carbon. *Hydrometallurgy* 129-130, 145-
738 150.

739 Singh Gaur R.P., Wolfe T.A., Braymiller S.A., 2015. Recycling of rhenium-containing wire scrap. *Int. J.*
740 *Refract. Met. Hard Mater.* 50, 79-85.

741 Srivastava R.R., Kim M.S., Lee J.C., Ilyas S., 2015. Liquid-liquid extraction of rhenium(VII) from an
742 acidic chloride solution using Cyanex 923. *Hydrometallurgy* 157, 33-38.

743 Srivastava R. R., Kim M. S., Lee J. C., 2016. Novel aqueous processing of the reverted turbine-blade
744 superalloy for rhenium recovery. *Ind. Eng. Chem. Res.* 55, 8191-8199.

745 Stoller V., Olbrich A., Meese-Marktscheffel J., Mathy W., Erb M., Nietfeld G., Gille G., 2008. Process
746 for electrochemical decomposition of superalloys. US Patent Application No. 2008/0110767 A1.

747 Sun H., Yu J.J., Li G.H., Shi D.P., Luo J., Rao M.J., Peng Z.W., Jiang T., 2020. Co-volatilizing-water
748 leaching process for efficient utilization of rhenium-bearing molybdenite concentrate.
749 *Hydrometallurgy* 192, 105284.

750 Sutcliffe M.L., Johnston G.M., Welham N.J., 2012. Method of oxidative leaching of molybdenum:
751 rhenium sulfide ores and concentrates. Australian Patent No. 2011229125.

752 Tarasov A.V., Besser A.D., Gedgagov E.I., 2001. Integrated Technology for Processing Rhenium-
753 containing Molybdenite Concentrates to Recover Molybdenum and Rhenium into Commercial
754 Products. *Miner. Process. Extr. Metall. Rev.* 22, 509-517.

755 Thomas J.L., 2008. Process for recovering platinum group metals, rhenium and gold. US Patent
756 Application No. 2008/0110296 A1.

757 USGS, 2011. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2011.

758 USGS, 2012. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2012.

759 USGS, 2013. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2013.

760 USGS, 2014. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2014.

761 USGS, 2015. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2015.

762 USGS, 2016. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2016.

763 USGS, 2017. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2017.

764 USGS, 2018. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2018.

765 USGS, 2019. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2019.

766 USGS, 2020. Rhenium, U.S. Geological Survey, Mineral Commodity Summaries, January 2020.

767 Virolainen S., Laatikainen M., Sainio T., 2015. Ion exchange recovery of rhenium from industrially
768 relevant sulfate solutions: Single column separations and modeling. *Hydrometallurgy* 158,74-82.

769 Vosough M., Shahtahmasebi N., Behdani M., 2016. Recovery Rhenium from roasted dust through super
770 Para-magnetic Nano-particles. *Int. J. Refract. Met. Hard Mater.* 60, 125-130.

771 Wang Y., Wang C.Y., 2018. Recent advances of rhenium separation and enrichment in China: Industrial
772 processes and laboratory trials. *Chin. Chem. Lett.* 29, 345-352.

773 Ward L.G.L., Dillard D.P., 1997. A Database Approach to the Recycling of Rhenium. In *Rhenium and*
774 *Rhenium Alloys* (Bryskin B.D. Edit). The Minerals, Metals & Materials Society, pp 79-88.

775 Watari T., Nansai K., Nakajima K., 2020. Review of critical metal dynamics to 2050 for 48 elements.
776 *Resour., Conserv. Recycl.* 155, 104669.

777 Xiao P., Han D., Zhai M.L., Xu L., Li H.B., 2017. Comparison with adsorption of Re (VII) by two

778 different γ -radiationsynthesized silica-grafting of vinylimidazole/4-vinylpyridine adsorbents. J.
779 Hazard. Mater. 324, 711-723.

780 Xiong C.H., Yao C.P., Wu X.M., 2008. Adsorption of rhenium(VII) on 4-amino-1,2,4-triazole resin.
781 Hydrometallurgy 90, 221-226.

782 Xiong Y., Lou Z.N., Yue S., Song J.J., Shan W.J., Han G.X., 2010. Kinetics and mechanism of Re(VII)
783 extraction with mixtures of tri-alkylamine and tri-n-butylphosphate. Hydrometallurgy 100, 110-115.

784 Xiong Y., Cui X.R., Zhang P., Wang Y.J., Lou Z.N., Shan W.J., 2017. Improving Re(VII) adsorption on
785 diisobutylamine-functionalized graphene oxide. ACS Sustainable Chem. Eng. 5(1), 1010-1018.

786 Yagi R., Okabe T., 2016a. Current status and smelting technologies of rhenium. J. Japan Inst. Met. Mater.
787 80(6), 341-349.

788 Yagi R., Okabe T., 2016b. Current status of recycling of rhenium and process technologies. J. MMIJ
789 132(7), 114-122.

790 Ye L.G., Ouyang Z., Chen Y.M., Liu S.F., 2020. Recovery of rhenium from tungsten-rhenium wire by
791 alkali fusion in KOH-K₂CO₃ binary molten salt. Int. J. Refract. Met. Hard Mater. 50, 79-85.

792 Yu S.Q., Chen J.Y., 1985. Mechanism of synergistic extraction of rhenium(VII) by primary amines and
793 neutral phosphorus esters. Hydrometallurgy 14, 115-126.

794 Zagorodnyaya A.N., Abisheva Z.S., 2002. Rhenium recovery from ammonia solutions. Hydrometallurgy
795 65, 69-76.

796 Zagorodnyaya A.N., Abisheva Z.S., Sadykanova S.E., Bobrova V.V., Sharipova A.S., 2010. The
797 characterisation and origins of interphase substances (cruds) in the rhenium solvent extraction circuit
798 of a copper smelter. Hydrometallurgy 104, 308-312.

799 Zagorodnyaya A.N., Abisheva Z.S., Sharipova A.S., Sadykanova S.E., Bochevskaya Y.G., Atanova O.V.,
800 2013. Sorption of rhenium and uranium by strong base anion exchange resin from solutions with
801 different anion compositions. Hydrometallurgy 131-132, 127-132.

802 Zagorodnyaya A., Abisheva Z., Sharipova A., Sadykanova S., Akcil A., 2015. Regularities of Rhenium
803 and Uranium Sorption from Mixed Solutions with Weakly Basic Anion Exchange Resin, Miner.
804 Process. Extr. Metall. Rev. 36:6, 391-398.

805 Zhang L., Jiang X.Q., Xu T.C., Yang L.J., Zhang Y.Y., Jin H.J., 2012. Sorption characteristics and
806 separation of rhenium ions from aqueous solutions using modified Nano-Al₂O₃. Ind. Eng. Chem. Res.
807 15, 5577-5584.

808 Zhang B., Liu H.Z., Wang W., Gao Z.G., Cao Y.H., 2017. Recovery of rhenium from copper leach
809 solutions using ion exchange with weak base resins. Hydrometallurgy 173, 50-56.

810 Zhang L., Xu Z., 2018. A critical review of material flow, recycling technologies, challenges and future
811 strategy for scattered metals from minerals to wastes. J. Clean. Prod. 202, 1001-1025.

812 Zhang Q.X., Zhao Q.S., 2007. Metallurgy of Tungsten and Molybdenum. Metallurgy Industry Press,
813 Beijing.

814 Zhou T.L., Zhong X., Ma R.J., Huang Z.S., Qu M., Zhou Z.H., 1982. The amide type extractant A101
815 and its application to the separation of niobium and tantalum, and molybdenum and rhenium.
816 Hydrometallurgy 8, 379-388.