

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**

3 Leiting Shen<sup>a,c\*</sup>, Fiseha Tesfaye<sup>b</sup>, Xiaobin Li<sup>a,\*\*\*</sup>, Daniel Lindberg<sup>c</sup>, Pekka Taskinen<sup>c</sup>

<sup>a</sup> Central South University, School of Metallurgy and Environment, Changsha 410083, China

<sup>5</sup> Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Turku FI-20500, Finland

<sup>6</sup> <sup>c</sup> Aalto University, School of Chemical Engineering, Metallurgical Thermodynamics and Modelling,  
<sup>7</sup> Espoo FI-00076, Finland

<sup>8</sup> \*Corresponding author: shenleiting@csu.edu.cn

<sup>9</sup> \*\*Corresponding author: x.b.li@csu.edu.cn

10 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

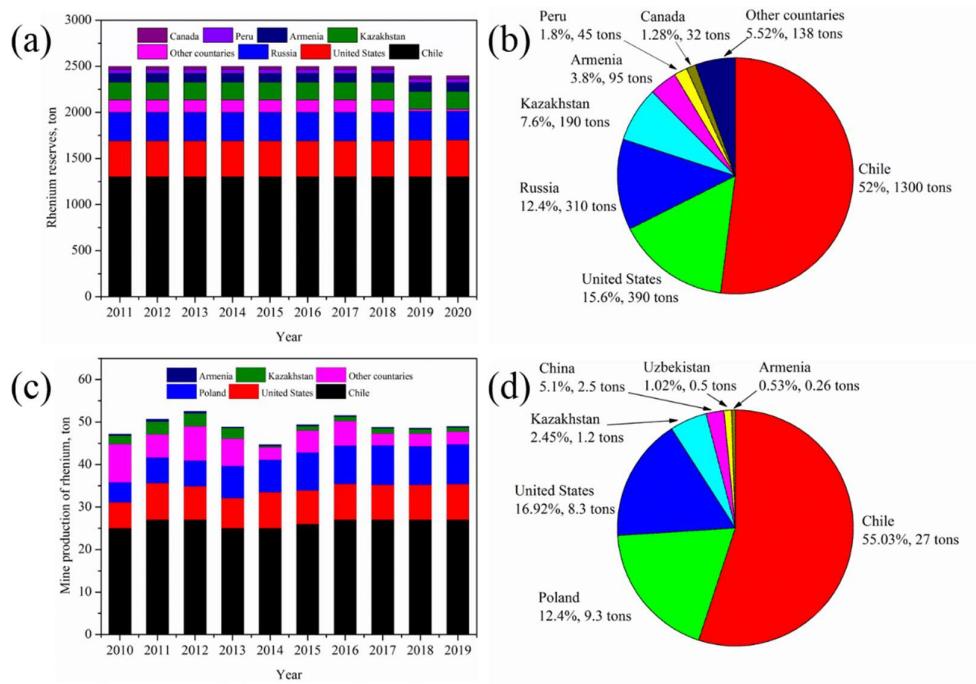
29 1. Introduction

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).

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).



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 ( $\text{ReS}_2$ , 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.

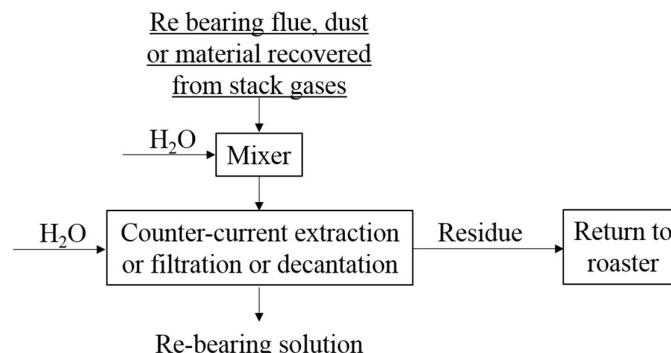
118 **Table 1** The process, technology and existing form of rhenium extracted from primary resources.

| Production process | Resource type                 | Extraction technology  | Re existing form   |
|--------------------|-------------------------------|--|--|
| Mo production      | Re-containing Mo concentrates | Oxidation roasting-hydrometallurgical leaching<br>Hydrometallurgical methods | Re <sub>2</sub> O <sub>7</sub> in roasting fume and dust;<br>Residue<br>In solution together with Mo |
| Cu production      | Re-containing Mo concentrates | Pyrometallurgy-hydrometallurgical leaching<br>Hydrometallurgical methods     | Smelting fume and dust; Slime<br>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*

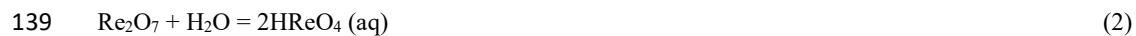
120 Pyrometallurgy is the traditional method to extract by-product rhenium from concentrates, still  
121 employed in commercial production. It includes molybdenum roasting at about 600-650 °C, copper  
122 smelting process at ~1200-1300 °C and lead (galena) roasting process at ~900-1000 °C. The early  
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

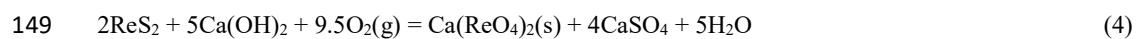
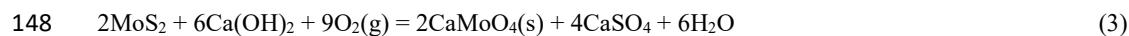


127  
128 **Fig. 2.** Conceptual flowsheet for rhenium extraction from pyrometallurgical wastes of Re-containing  
129 concentrates in accordance with the literature (Anderson et al., 2013; Yagi and Okabe, 2016a).

130 In pyrometallurgical processes, rhenium existing in concentrates is oxidized to rhenium heptoxide  
131 ( $\text{Re}_2\text{O}_7$ ) according to Eq. (1). Due to the high volatility property of  $\text{Re}_2\text{O}_7$  ( $P_{\text{vap}} = 0.936 \text{ atm}$  at  $360^\circ\text{C}$ ),  
132 nearly all  $\text{Re}_2\text{O}_7$  volatilize at the pyrometallurgical temperatures for molybdenum, copper and lead  
133 production (Ammann and Loose, 1972). The volatile  $\text{Re}_2\text{O}_7$  in the furnace flue gas is subsequently  
134 scrubbed with water and recovered as soluble perrhenic acid ( $\text{HReO}_4$ ), 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.



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  $\sim 50 \text{ g/L H}_2\text{SO}_4$  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.

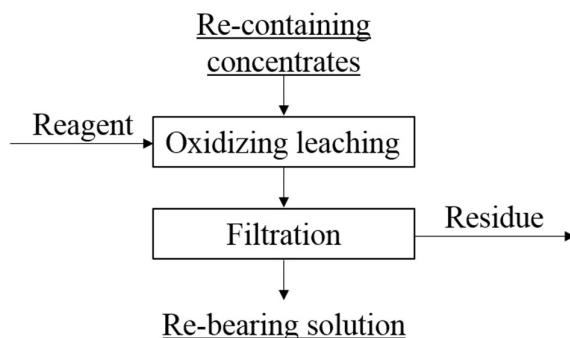


150 Juneja et al. (1996) investigated molybdenum and rhenium extraction from a low grade molybdenite  
151 concentrate by roasting in the presence of lime and soda ash. The molybdenum and rhenium reacted  
152 according to reactions (3) and (4), respectively. 74% of rhenium was extracted from the lime-roasted  
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  $\text{Re}_2\text{O}_7$  produced during  
158 pyrometallurgical processing of molybdenum and copper concentrate was directly reduced to rhenium  
159 metal by  $\text{S}_2$ . 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  $\text{HCl}$  and  $\text{CaCl}_2$ , then co-volatilized of 99.9% Re and  
161 90.4% of Mo at  $1050^\circ\text{C}$ , subsequently the volatile molybdenum oxide was condensed above  $500^\circ\text{C}$  to  
162 obtain highly pure  $\text{MoO}_3$  (99.9%) with almost no rhenium while high-content  $\text{Re}_2\text{O}_7$  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.

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 ( $\text{ReO}_4^-$ )  
 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  $>150$  °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  $<90$  °C, particle size  $\leq 23$  µm 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  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2/\text{O}_3$  system is the most efficient lixiviant to extract these  
 197 metals.

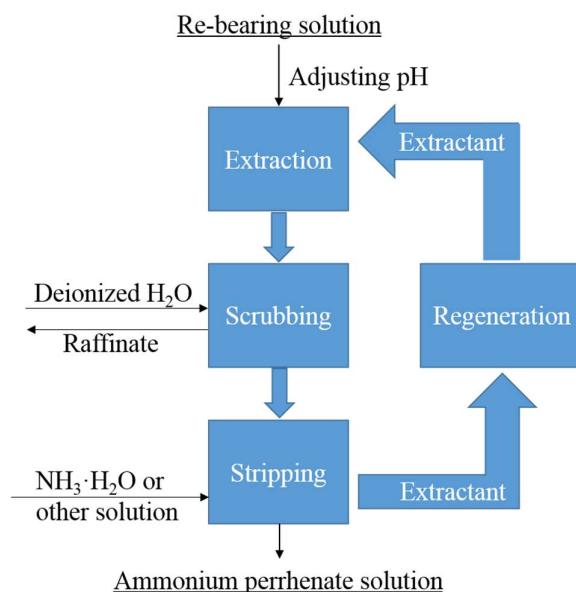
198       Additionally, Askari Zamani et al. (2005) tested the bioleaching of a molybdenite concentrate to  
 199 extract rhenium, with a low rhenium yield of only 7.3 %. Abdollahi et al. (2019) optimized the operational  
 200 parameters of dissolving Cu, Mo and Re from molybdenite concentrate through 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

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

**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 solutouns                | 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              | Diocetylamine DOA  | Aqueous ammonium solution | 99.5                   | -                      | Gerhardt et al., 2000; 2001  |
| Re-Mo               | Alkaline solution                 | A mixture of tributyl phosphate and trioctylamine  | 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               | Molybdenu m oxide leaching liquor | Tri-butyl phosphate (TBP)  | Ammonia solution          | 98%                    | 450                    | Alamdari et al., 2012        |
| Re                  | Nitric acid solution              | 2,20-(imino)bis(N,N-diocylacetamide)   | -                         | -                      | -                      | Ali et al., 2012             |

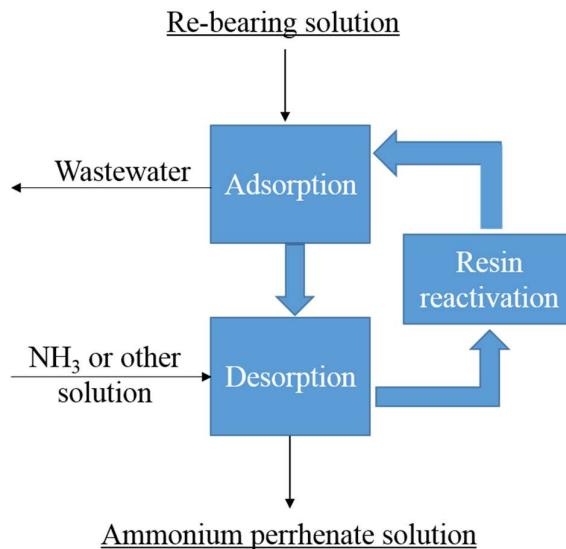
|             |  |  |   |             |           |                                |
|-------------|--|--|---|-------------|-----------|--------------------------------|
| Re          | A scrub liquor of molybdenite roaster fume                               | A 10 v/v.% tertiary amine, 10 v/v.% Isodecanol 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 <sup>-1</sup> NH <sub>4</sub> 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 <sub>4</sub> 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 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 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 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*

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<sub>4</sub><sup>-</sup>  
 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 <sub>4</sub> OH solutions | >99.5%  | Kholmogorov et al., 1999       |
| Molybdenite calcine leaching solution   | Re-Mo               | Resin D216 and gel type resin 201X7                                   | HNO <sub>3</sub> 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 <sup>-1</sup> HCl solution    | Separation coefficient $\beta_{Re/Mo}=17.3$         | 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 Re 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 <sub>4</sub> 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 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               |

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 Fe<sub>3</sub>O<sub>4</sub> 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 NH<sub>4</sub>HCO<sub>3</sub>-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 ReO<sub>2</sub> and ReO<sub>3</sub> 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(NH<sub>3</sub>)<sub>4</sub>](ReO<sub>4</sub>)<sub>2</sub>, 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 KReO<sub>4</sub> 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 electrodialysis 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 <sub>3</sub> 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 <sub>2</sub> O <sub>2</sub>                                    | 2008                   |
| Olbrich et al., 2009                 | Rhenium-containing superalloys                                    | Digesting in a salt melt containing 60-95 wt.% NaOH and 5-40 wt.% Na <sub>2</sub> SO <sub>4</sub>   | 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 <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub> +HCl/HNO <sub>3</sub> electrolytes                             | 2011;<br>2013;<br>2014 |
| Bryukvin et al., 2016                | Rhenium containing materials alloy residue and cermet catalysts   | Solubilization in HCl solution or a mixture of HCl and HNO <sub>3</sub>   | 2016                   |
| Luederitz et al., 2013*              | Alloys, super-alloys  | Using an oxidizing acid solution or a mixture of HCl and HNO <sub>3</sub>   | 2013                   |
| Ferron and Seeley, 2015*             | Tungsten-rhenium wire   | Roasting at 900 °C in the presence of air   | 2015                   |
| Singh Gaur et al., 2015              | Reverted Turbine-Blade Superalloy                                 | A two-step HCl leaching process followed by the liquid-liquid separation  | 2016                   |
| Srivastava et al., 2016              | Particularly superalloys  | Digestion with 50-1000 g/L H <sub>2</sub> SO <sub>4</sub> and a halide-free oxidant; further digesting in an oxidizing and complexing milieu                | 2017                   |
| Britton and Markarian, 2017a; 2017b* | Nickel-based superalloy   | Pyrometallurgical pretreatment with Al powder-selective two-step HCl leaching   | 2017                   |
| Kim et al., 2018                     | 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 <sub>4</sub> | 2018;                  |
| Levin and Levchuk, 2017              | Nickel-based superalloy   | Leaching with aqua-regia  | 2017                   |
| Kuznetsova et al., 2018; 2020        | Tungsten-rhenium wire   | Decomposition by KOH-K <sub>2</sub> CO <sub>3</sub> molten salt at 800 °C   | 2020                   |
| Ye et al., 2020                      |   |   |                        |

\*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.

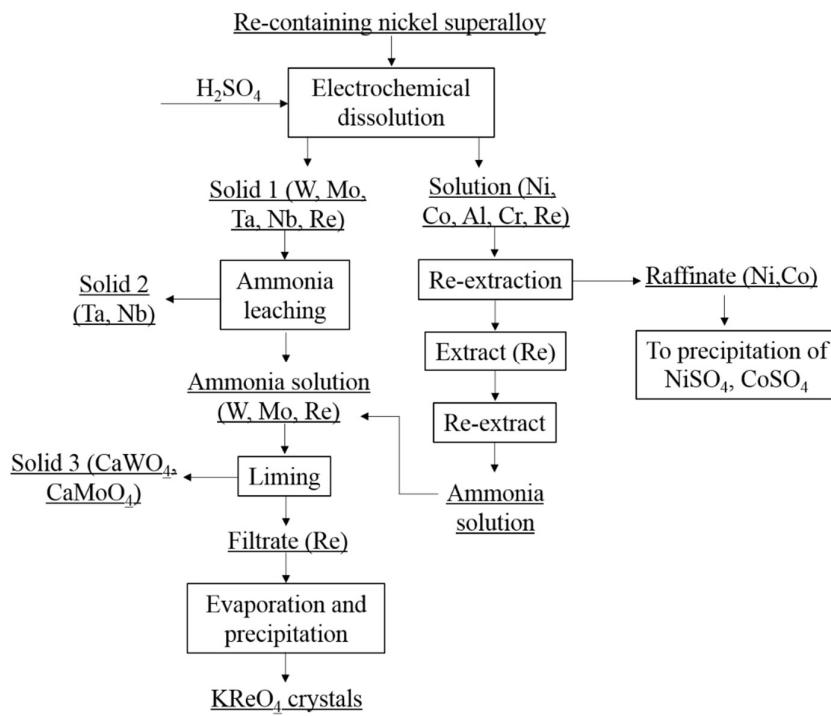
Technological developments have been covered in many publications and patents reported recently. The recycling technologies included e.g. digestion in molten salts, selective leaching with a

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. % Na<sub>2</sub>SO<sub>4</sub> (preferably 70–80 wt. % NaOH and 20–30 wt. %  
 356 Na<sub>2</sub>SO<sub>4</sub>) at temperatures between 800–1200 °C, preferably at 900–1050 °C. The addition of 5–8 wt. %  
 357 Na<sub>2</sub>CO<sub>3</sub> and some oxidizing agent including NaNO<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and Na<sub>2</sub>O 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 H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>+HCl, or HNO<sub>3</sub> 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, KReO<sub>4</sub> 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<sub>3</sub> to form their corresponding aqueous salts. Rhenium is then selectively  
378 precipitated as Re<sub>2</sub>S<sub>7</sub>, which is later oxidized and sublimed as Re<sub>2</sub>O<sub>7</sub>. 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<sub>3</sub> 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<sub>2</sub>S<sub>7</sub>, absorption on activated carbon or an absorbent resin, or by solvent extraction. Finally, the solid  
387 intermediate NH<sub>4</sub>ReO<sub>4</sub> 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 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 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<sub>4</sub>ReO<sub>4</sub> 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 50-1000 g/L H<sub>2</sub>SO<sub>4</sub>  
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.

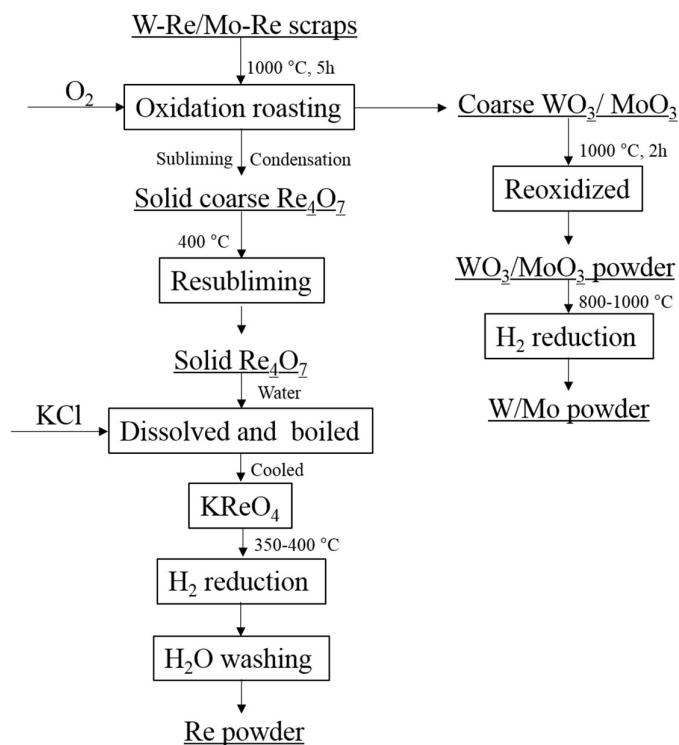
401 Kim et al. (2018) investigated a selective two-step leaching process for nickel and rhenium from  
402 nickel-based superalloy scrap in hydrochloric acid solutions. Superalloy scrap with particle size < 150  
403 µm was pyrometallurgically pretreated with aluminum granule at 1500 °C to form Al<sub>3</sub>Ni 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 MacDonald (1982) developed a prototype method for recovering rhenium  
 415 from W-Re and Mo-Re alloy scraps based on the different volatilization properties of  $\text{Re}_4\text{O}_7$  referred to  
 416  $\text{WO}_3$  and  $\text{MoO}_3$  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 MacDonald (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 volatized oxide.

428 Singh Gaur et al. (2015) used a similar roasting method to Heshmatpour and MacDonald (1982) to  
 429 recovery of rhenium from tungsten-rhenium wire scrap at 900 °C in the presence of air. Then the  
 430 volatilized  $\text{Re}_2\text{O}_7$  solid was recovered as a  $\text{NH}_4\text{ReO}_4$  solution, and was further treated by crystallization  
 431 and hydrogen reduction of  $\text{NH}_4\text{ReO}_4$  to rhenium metal power. Ye et al. (2020) decomposed W-Re wire

432 by a KOH-K<sub>2</sub>CO<sub>3</sub> molten salt at 800 °C to form KReO<sub>4</sub>. Subsequently, the decomposed product was  
433 leached by water, and treated by crystallization to obtain high purity KReO<sub>4</sub> crystals which were reduced  
434 by H<sub>2</sub> at 350 °C to produce Re powder.

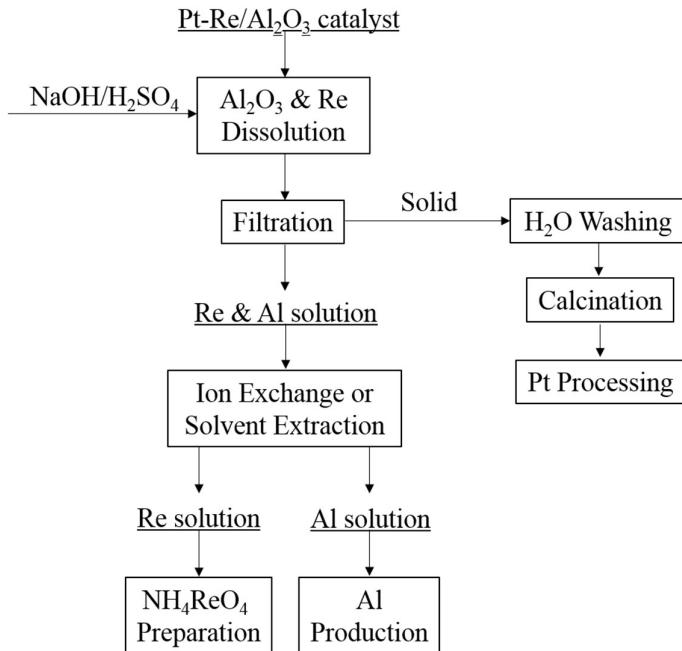
435 In addition, Levin and Levchuk (2017) proposed a flow-sheet for Re recovery from W-Re alloys.  
436 W-Re alloys were firstly treated in NaOH solution with anodic dissolution, then tungsten was precipitated  
437 as calcium tungstate from the electrolyte by adding Ca(OH)<sub>2</sub>, subsequently KReO<sub>4</sub> precipitate was  
438 obtained by adding KOH to the NaReO<sub>4</sub> solution. This was further treated by electrodialysis to produce  
439 perrhenic acid. Kuznetsova et al. (2018; 2020) simplified this scheme to directly produce perrhenic acid  
440 by electrodialysis of neutralized NaReO<sub>4</sub> 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-assosiated leaching, and ion exchange, to prepare high-purity NH<sub>4</sub>ReO<sub>4</sub>. 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 H<sub>2</sub>SO<sub>4</sub> 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 NaHCO<sub>3</sub> 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 NaHCO<sub>3</sub> dissolution were recovered by H<sub>2</sub>SO<sub>4</sub> 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.

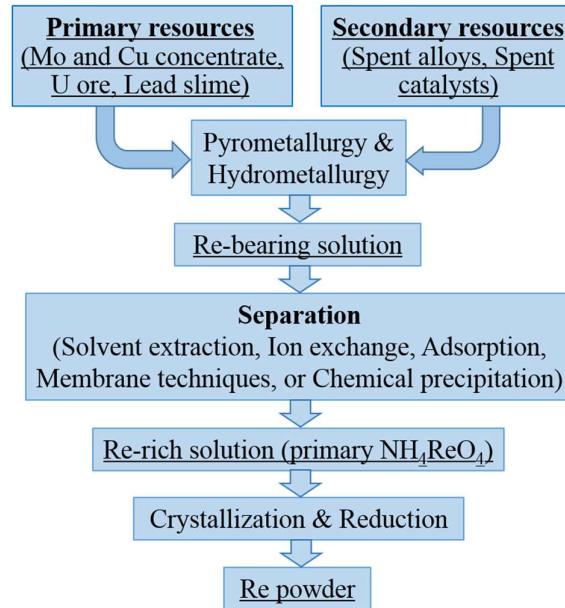
475 In total, the rhenium content present in secondary resources is much higher than that of primary  
 476 resources. Recycling of rhenium from secondary resources can contribute to a sustainable, low carbon,  
 477 resource efficient economy. As Heneckens et al. (2019) pointed out, recycling rhenium 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., Bekturbanov 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 electrodialysis of rhenium salts solutions. *Hydrometallurgy* 60, 117-122.  
534 Alamdari E.K., Darvishi D., Haghshenas D.F., Yousefi N., Sadrnezhaad 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-diethylacetamide) 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 NaReO<sub>4</sub>-H<sub>2</sub>O-C<sub>2</sub>H<sub>5</sub>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 Dresher 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  $\text{ReO}_4^-$  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  $\text{TaO}_4^-$  or  $\text{ReO}_4^-$ .  
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. CR<sup>3</sup> 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-Markscheffel 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  $\gamma$ -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-K<sub>2</sub>CO<sub>3</sub> 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., Sadyanova 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., Sadyanova 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., Sadyanova 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-Al<sub>2</sub>O<sub>3</sub>. 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.