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Extraction of strategically important elements from brines: Constraints and opportunities

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Abstract

Strategically important elements are those that are vital to advanced manufacturing, low carbon technologies and other growing industries. Ongoing depletion and supply risks to these elements are a critical concern, and thus, recovery of these elements from low-grade ores and brines has generated significant interest worldwide. Among the strategically important elements, this paper focuses on rare earth elements (REEs), the platinum-group metals and lithium due to their wide application in the advanced industrial economics. We critically review the current methods such as precipitation, ion exchange and solvent extraction for extracting these elements from low-grade ores and brines and provide insight into the technical challenges to the practical realisation of metal extraction from these low-grade sources. The challenges include the low concentration of the target elements in brines and inadequate selectivity of the existing methods. This review also critically analyzes the potential applicability of an integrated clean water production and metal extraction process based on conventional pressure-driven membrane and emerging membrane technologies (e.g., membrane distillation). Such a process can first enrich the strategically important elements in solution for their subsequent recovery along with clean water production.

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Research Highlight

- ❖ Recovery of strategically important elements from brines is reviewed.
- ❖ Challenges associated with separation processes for metal extraction are discussed
- ❖ Membrane distillation is effective to recover strategically important elements
- ❖ Critical challenge associated with membrane processes is fouling.

Extraction of strategically important elements from brines: constraints and opportunities

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Abstract

Strategically important elements are those that are vital to advanced manufacturing, low carbon technologies and other growing industries. Ongoing depletion and supply risks to these elements are a critical concern, and thus, recovery of these elements from low-grade ores and brines has generated significant interest worldwide. Among the strategically important elements, this paper focuses on rare earth elements (REEs), the platinum-group metals and lithium due to their wide application in the advanced industrial economics. We critically review the current methods such as precipitation, ion exchange and solvent extraction for extracting these elements from low-grade ores and brines and provide insight into the technical challenges to the practical realisation of metal extraction from these low-grade sources. The challenges include the low concentration of the target elements in brines and inadequate selectivity of the existing methods. This review also critically analyzes the potential applicability of an integrated clean water production and metal extraction process based on conventional pressure-driven membrane and emerging membrane technologies (e.g., membrane distillation). Such a process can first enrich the strategically important elements in solution for their subsequent recovery along with clean water production.

Keywords: Strategically important elements, challenges, low-grade ores and brines, emerging membrane process.

1. Introduction

Recent technological advances are mostly based on innovative applications of a range of rare metals and metalloids into intelligent and high-tech devices. Examples include rare earth metals (e.g., cerium, lanthanum, neodymium, dysprosium, praseodymium, scandium, erbium, europium, terbium and yttrium), precious metals (e.g., rhodium, palladium, and platinum), radioactive metals (e.g. uranium and radium) and alkaline metals (e.g., magnesium, potassium, and lithium). These elements are indispensable in the electronic and electrical industries (Alonso et al., 2012), making them some of the most valuable non-renewable resources for our modern society. For example, the production of a smartphone requires a range of rare earth metals including neodymium, gadolinium and samarium along with others metals, such as lithium, indium, palladium, tantalum, silver, gold, copper, gallium, germanium, beryllium, and zirconium (Tanskanen, 2013). However, increasing depletion of some of these elements has been revealed as a major risk to viable economic development.

To date, most metals are produced from hard-rock mining. During the last two decades, advances in water purification (e.g., desalination) and resource recovery have led to the concept of seawater and brine being perceived as important untapped sources of precious and rare earth elements (Bardi, 2010; Gibert et al., 2010; Lee et al., 2013; Saito et al., 2006). It is also notable that these elements can cause severe environmental pollution due to their toxicity. Thus, the challenge to conserve these rare metals and metalloids and to protect the environment has strategically spurred the need to extract and recover them from complex solutions.

The main technologies used for producing metals from low-grade ores and brines are based on precipitation, ion exchange and hydrometallurgical processes. The ion exchange process is

a selective process which requires a specific resin to recover valuable metals selectively. Hydrometallurgical treatments are based on the use of leaching agents in aqueous solutions such as strong acids and bases. These are often applied together with other complexing agents such as oxalic acid, cyanide, halide, acetic acid and thiosulfate (Beolchini et al., 2010). Given the techno-economic analysis, the technological challenges of the mentioned processes and the low levels of elements concentration have received attention. Hence, a cost-effective, low energy consuming and greener-recycling process needs to be developed to handle the challenges associated with next-generation metal demand and to conserve natural resources. Membrane-based technologies may provide a viable solution for efficient recovery of rare earth elements from brine as these processes can easily enrich the elements effectively.

This article critically discusses the opportunities and challenges of strategically important element recovery from low-grade ore and brine solution using conventional and emerging technologies. In terms of the strategically important elements, this paper focuses on the extraction of rare earth elements (REEs), the platinum-group metals and lithium due to their wide application in the advanced industrial economics. We conclude this article by providing an outlook of the opportunities for the separation of strategically important elements using integrated conventional and emerging membrane-based technologies. Wherever available, information on pilot or full-scale facilities in addition to lab-scale studies has been systematically presented. Information on the technology readiness level and economic feasibility is a notable gap in the literature.

2. Strategically important elements

A range of chemical elements is strategically important to modern life. Indeed, they are essential in many everyday products ranging from mobile phones to automobiles. The emerging renewable energy market also utilises many of these elements (Figure 1). Among them, three of the most notable groups are rare earth elements (REEs), the platinum-group metals, and lithium. Although the application of these elements is often not well known to the general public unfamiliar with the industrial processes, the current rate of consumption of many of these strategically important elements is not sustainable.

REEs are probably the strategically important elements of the most critical concern, given their applications in emerging technologies including fuel cells and wind turbines (Figure 1) but uncertain future supplies. Over 500 kg of REEs including neodymium, molybdenum, and dysprosium (Figure 1) are required to make the permanent magnets in a single 3.5 MW wind turbine (Constantinides, 2016). Since the growth in wind power markets is expected to continue, the demand for neodymium magnets (NdFeB) in wind turbines in 2020 is expected to be increased to approximately 13.2 kilotons, which is about 1.7 times higher compared to the NdFeB amount required in 2015 (Pavel et al., 2017). If magnet composition remains invariable, about 3.2 kilotons of neodymium, 0.8 kilotons of praseodymium and 0.93 kilotons of dysprosium would be requested by the global wind power sector in 2020. This is equivalent to 15%, 13% and 66% of the total production of neodymium, praseodymium and dysprosium, respectively in 2014 (Pavel et al., 2017). A NdFeB magnet now incorporates 29-32% neodymium/praseodymium, which might decrease to 25% by 2020 and even further to 20% by 2030 (Lacal-Aránategui, 2015). Instead of using magnets with 3-6% dysprosium, newer generator models can use permanent magnets with only about 1% dysprosium. Pathak et al. (2015) claim to have developed a new way to replace dysprosium fully and neodymium

partly (by about 20%) in the NdFeB magnet using cobalt and cerium (much cheaper and more available REE). The cerium and cobalt co-doped alloy shows excellent high-temperature magnetic properties. Terbium can replace dysprosium in a NdFeB magnet, but it is not considered a convenient substitute today. If terbium becomes cheaper than dysprosium, e.g. due to decreasing terbium demand in lighting (Pavel et al., 2016), it could be used as a substitute for some quantities of dysprosium in magnet applications.

Currently the world reserves of REEs in major countries such as China, Brazil, Vietnam, Russia and India stand at about 130 million tonnes (USGS, 2019). It is noted that the REEs reserve is not uniformly distributed globally. Most of the confirmed REE reserve is in China, which produces 85% of the global REEs output (Roskill, 2015). The current annual global production of REEs is about 120 kilotons (Izatt et al., 2016), yet the demand for REEs is expected to grow further as the renewable and electronic industries continue to expand. The annual growth rate of global REE demand is estimated to be about 5% (USGS, 2016). A similar prediction was made by Dutta et al. (2016) who noted that global REE demand is slated to grow at an annual rate of 5% by 2020. Graede (2015) indicated that there would be scarcity and supply risk for europium, dysprosium and erbium in addition to several other metals in the near future. This estimation is based on their scores in three areas, namely supply risk, environmental implications, and vulnerability to supply restrictions. Hence, the global availability of REEs appears to be at substantial risk for several reasons. These include the introduction of production quotas, export quotas and export taxes, enforced environmental legislation, and granting no new rare earth mining licenses (USGS, 2019). As a result, there has been increased interest and investigation into non-traditional REE resources, extraction, separation and purification processes.

The demand for platinum-group elements is likely to increase due to increasing demand for vehicles globally in the forthcoming decades. In 2016, the automobile industry continued to be the major consumer of platinum-group elements which accounted for approximately 84% of global rhodium consumption, 67% of palladium consumption and 46% of platinum consumption (CPM Group, 2017). Loferski (2011) noted that each year, the automobile industry alone uses 113 tons of platinum and other platinum-group metals as catalysts for air pollution control. Jollie (2017) predicts compound annual growth rates (CAGRs) of total platinum and palladium demand of 1.0 and 1.1%, respectively. An economic model by Zhang et al. (2016) shows a growth in the demand for platinum and palladium of approximately 5% and 45%, respectively over the next 15 years. This growth in demand for the platinum-group metals is driven largely by the increasing automobile sales, particularly in emerging markets such as China and India. The platinum-group metals are also essential for catalytic conversion in fuel cells. Thus, an even more significant increase in the demand for these metals is expected if fuel cell automobiles can be mass-produced in the future (Wittstock et al., 2016).

The current recoverable reserve of platinum-group metals of about 100 kilotons is geographically unevenly distributed. South Africa has about 80% of the global reserve of platinum-group metals and the remaining is in Russia (8%) and Zimbabwe (7%) (IDC, 2013). Notably, most of the world's supply of platinum-group elements comes from South Africa and Russia, which account for 56% and 24%, respectively, of the global production (USGS, 2019). The total worldwide supply in 2013 was 187.9 tons for platinum, 206.7 tons for palladium, and 22.1 tons for rhodium (Johnson, 2014). In comparison, the supply of platinum-group elements in 2000 was 153 tons for platinum, 224 tons for palladium and 20.9 tons for rhodium (Johnson, 2001). This reflects the growing worldwide use of platinum-group

elements. By contrast, Thormann et al. (2017) reported that the global platinum and palladium production decreased by 25% and 8%, respectively from 2010 to 2014. The decline observed throughout this period was mainly due to a consequence of the strikes in South Africa. According to Thormann et al. (2017), future estimates of demand, production and recycling, based on CAGRs of 0.4, 1.7 and 3.3% for primary production, recycling and demand of platinum, respectively, indicate a supply gap in the near future. The competition to obtain these elements has also led to geopolitical tension and instability.

Lithium is another notable strategically important element that is essential for rechargeable batteries (Figure 1). Due to the recent boom in the renewable energy industry and electric vehicles, lithium consumption for batteries has increased significantly in recent years. Lithium demand is expected to grow faster than supply in the coming decade. Martin et al. (2017) estimate an annual increase in lithium demand of 9% over the next 3 years.

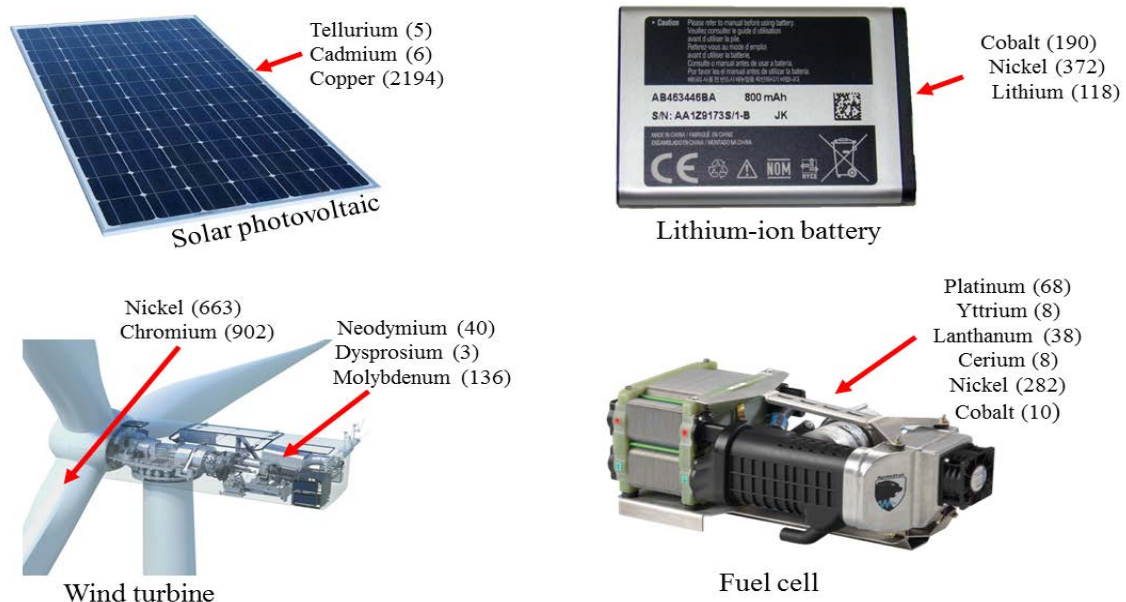


Figure 1: Examples of strategically important element demand (kg/MW) in the renewable energy industry (Moss et al., 2011; Moss et al., 2013; Teske et al., 2016).

The supply security of strategically important elements to support our modern society depends not only on their geological deposits but also the availability of separation technologies for their extraction. The latter is particularly important in the context of the future circular economy when these elements are sourced from consumer products at the end of their lifetime rather than geological deposits. As a major exporter of many minerals, Australia is a notable example of the interplay between the availability of geological deposits and separation technologies. Australia provides 8% of the global REEs production (Skirrow et al., 2013) despite having a rather modest reserve of these elements. Australia is currently the world largest lithium producer with 34% of the global production (Table 1). Yet, in terms of geological availability of lithium, Australia is only ranked fourth in the world after China, Argentina, and Chile (USGS, 2016). It is noteworthy that Australia has many salt lakes and saline groundwater deposits that contain a range of strategically important elements (Timms, 2005).

In the current hydrometallurgical industry, processes for the separation/ extraction of strategically important elements are precipitation, ion exchange and solvent extraction. A major challenge of these processes is separation selectivity (Izatt et al., 2016). Hence, a pragmatic approach is important to recover these strategically important elements from low-grade sources including salt lake brines.

1 **Table 1:** The production, resources and reserve status of some prospective elements in Australia and their application for different purposes

2 (Hoenderdaal et al., 2013; Skirrow et al., 2013; USGS, 2016)

3

Metals	Production		Resource		Reserve		Applications
	Mass (kt)	Global share (%)	Mass (kt)	Global share (%)	Mass (kt)	Global share (%)	
Cerium	7.6	8	1481	3	NA	2.8	Catalytic converters in cars, hybrid vehicles, television faceplates, silicon microprocessors.
Lanthanum	4.6	8	742	3	NA	2.8	Cracking catalysts in petroleum refining, camera lenses, battery electrodes, hydrogen storage, x-ray films.
Dysprosium	0.115	4.8	NA	NA	8	0.64	Motors or generators, wind turbines, and electrical vehicles, hard disk devices, transducers.
Yttrium	NA	NA	100	18.5	NA	NA	Microwave generators, televisions and computer screens, ceramics, superconductors.
Platinum	0.22	0.11	2.35	1.2	NA	NA	Catalytic converters, electronic application, fuel cells
Palladium	0.22	0.11	2.35	1.1	NA	NA	
Lithium	11.7	34	1006	8	1500	10.7	Electric batteries, cordless devices, ceramics, glass.

4 NA: Not available

5

6 **3. Key challenges associated with separation processes for strategically important**
7 **elements recovery**

8 Low concentration and co-occurrence with other elements of much higher concentration,
9 processing cost and environmental impacts are major challenges to the cost-effective
10 recovery of strategically important elements from low-grade ores and brines. The significance
11 of these challenges depends on the source of brine. The high amount of water and energy
12 consumed in producing these elements also makes the separation process inefficient.

13
14 Strategically important elements often occur at low concentrations in low-grade ores and
15 brines, and, thus, are difficult to recover in the presence of much higher concentrations of
16 other minerals which can interfere with the separation and enrichment process. Hu et al.
17 (2018) noted that the selective extraction of scandium was limited by the presence of other
18 REEs, aluminium and iron. Similarly Barros et al. (2019) reported that the recovery of REE
19 was affected by the competition of other base metals present in the brine solution. Callura et
20 al. (2018) noted that the presence of competing ions (calcium, magnesium, zinc, iron and
21 aluminium) could inhibit the complete recovery of REEs. The undesired elements such as
22 phosphate, iron, aluminium, nickel, chromium, manganese, zirconium, uranium and copper
23 were first separated to reduce the impurities during REEs recovery in a weak acidic medium
24 using oxalic acid (El-Awady, 2013). Safarzadeh et al. (2018) noted that nickel, copper and
25 cobalt need to be removed to achieve 99.9% purity of platinum group elements. SepraMet is a
26 metal refinery located in Houston, Texas, which features the use of molecular recognition
27 technology-hydrometallurgical processes in the selective recovery of platinum group elements
28 from low-grade ores (Izatt et al., 2015). They noted that the unwanted or deleterious elements such
29 as arsenic, iron and antimony need to be separated effectively for the target platinum group
30 elements recovery.

31

32 The level of lithium (0.06-1.21 g/L) in brine can be significantly low compared to magnesium
33 ion (3.4-113.7 g/L) (Table 2). The extraction efficiency of lithium depends on the
34 magnesium to lithium mass ratio (Table 2). A low magnesium to lithium (Mg/Li) ratio in
35 brine means that it is easier, and therefore more economical to extract lithium. Zhao et al.
36 (2013) noted that when the Mg/Li ratio is below 6, lithium can be effectively separated by
37 chemical precipitation method. However, the Mg/Li ratio of most brines is higher than 6
38 (Table 2). Therefore, the use of an appropriate treatment process (e.g., nanofiltration) for
39 avoiding their interference with the crystallisation of lithium carbonate is essential to remove
40 magnesium ion.

41

42 Purity is an important parameter that is directly related to how strategically important
43 elements can be used and their commercial value. For example, over 99.9% purity of lithium
44 carbonate is required for the production of lithium-ion batteries (Virolainen et al., 2016). On
45 the other hand, lithium carbonate with purity below 99.6% can only be used for ceramic
46 production (Virolainen et al., 2016).

47

48 Similar physiochemical properties of some strategically important elements can affect the
49 separation of the target element. Most REEs occur together in mineral deposits and therefore
50 separation of them from each other is quite difficult due to similar ionic radius and chemical
51 properties (Cardoso et al., 2019). For example, related to the aforementioned example of
52 separation of lithium from magnesium, magnesium too precipitates with lime as magnesium
53 carbonate, which prevents the formation of lithium carbonate (Kogel, 2006).

54

55

56
57

Table 2: Composition of lithium in salt lake brine around the world

Source	Status	Concentration (g/L)							Impurities	References
		Li ⁺	Mg ²⁺	Na ⁺	Ca ²⁺	K ⁺	B	SO ₄ ²⁻		
Atacama Salar Brine, Chile	Full-scale	3.02	17.6	61.9	0.41	28.2	1.72	37.9	Na ⁺ , K ⁺ , Mg ²⁺	Ogawa et al. (2014)
Uyuni Salar Brine, Bolivia		0.84	16.7	105.4	3.33	15.7	0.7	21.3	Na ⁺ , K ⁺ , B	An et al. (2012)
East Taijinar, China	Pilot-scale	0.14	5.64	117.03	0.43	3.79	-	-	Na ⁺ , K ⁺ ,	Sun et al. (2015)
West Taijinar, China		0.26	15.36	102.4	0.19	8.44	-	-	Na ⁺ , K ⁺ ,	Sun et al. (2015)
Chott Djerid Salt Lake, Tunisia		0.06	3.4	80	1.6	5.6	-	6.7	Na ⁺ , Ca ²⁺ , Mg ²⁺	Somrani et al. (2013)
Longmucuo, China		1.21	89.5	-	-	-	-	-	-	Song et al. (2017)
North Arm Salt Lake, USA	Lab-scale	0.04	9.38	100.8	0.35	5.5	0.03	19.7	Na ⁺	Bush et al. (2016)
Salt lake brine, China		0.35	113.7	-	-	-	-	-	Mg ²⁺	Xiang et al. (2016)
Salt lake brine		0.15	8.88	2.69	-	-	-	-	-	Ji et al. (2017)
Geothermal brine		0.01	-	0.11	-	0.16	0.03	-	K ⁺	Mroczek et al. (2015)
Synthetic brine		0.15	63.8	0.414	0.02	0.20	-	-	Mg ²⁺	Nie et al. (2017b)

58

59 The cost of the recovery process is an important consideration for the industry. The process
60 can be very expensive when multiple steps are required for the separation of these elements.
61 For example, lithium-losses are typically more than 10% in the multiple separation steps
62 (Virolainen et al., 2016). Solvent loss during multiple solvent extraction steps can make an
63 extraction process further uneconomical. For example, using solvent extraction for the
64 separation of niobium and tantalum, evaporation loss of the solvent (i.e., hydrofluoric acid)
65 alone was 6-7% (Wang et al., 2010). Multiple separation steps also produce large amounts of
66 secondary chemical waste resulting in high costs associated with their disposal.

67

68 Separation processes used for the recovery of strategically important elements often raise
69 environmental concerns. For example, the use of large volume of organic solvents for the
70 recovery of these elements has an adverse environmental impact. This is because organic
71 solvents are toxic, corrosive, inherently volatile and flammable (Nishihama et al., 2003).
72 Their volatility and solubility contributes to air, land and water pollution. Yang et al. (2013)
73 noted that mining and production processes in China have resulted in the creation of large
74 polluted areas, which are now attracting international attention. Every ton of rare earth metal
75 produced generates approximately 8.5 kilograms of fluorine, 13 kilograms of dust, about 75
76 cubic meters of acidic wastewater and approximately 1 ton of radioactive waste residue
77 (Hurst, 2010). Tharumarajah and Koltun (2011) conducted life cycle assessment (LCA) on
78 Bayan Obo deposit in China to determine the equivalent greenhouse gas (GHG) emissions for
79 production for rare earth oxides (REOs). Their analysis shows that the production of
80 samarium, europium and gadolinium oxides emits approximately 55 kg of CO₂ equivalent
81 per kg of oxide produced, which is significantly higher than for iron (0.02 kg of CO₂
82 equivalent) and copper (0.63 kg of CO₂ equivalent (Norgate and Haque, 2010). In a follow
83 up study, Koltun and Tharumarajah (2014) found that GHG emissions for light REOs

84 (lanthanum-, cerium-, praseodymium-oxide) were 32.29 kg CO₂ equivalent per kg of REO,
85 medium REOs (neodymium-, promethium-, samarium-oxide) were 30.29 kg CO₂ equivalent
86 per kg of REO and heavy REOs (gadolinium-, yttrium- lutetium and scandium-oxide)
87 were 34.49 kg CO₂ equivalent per kg of REO.

88

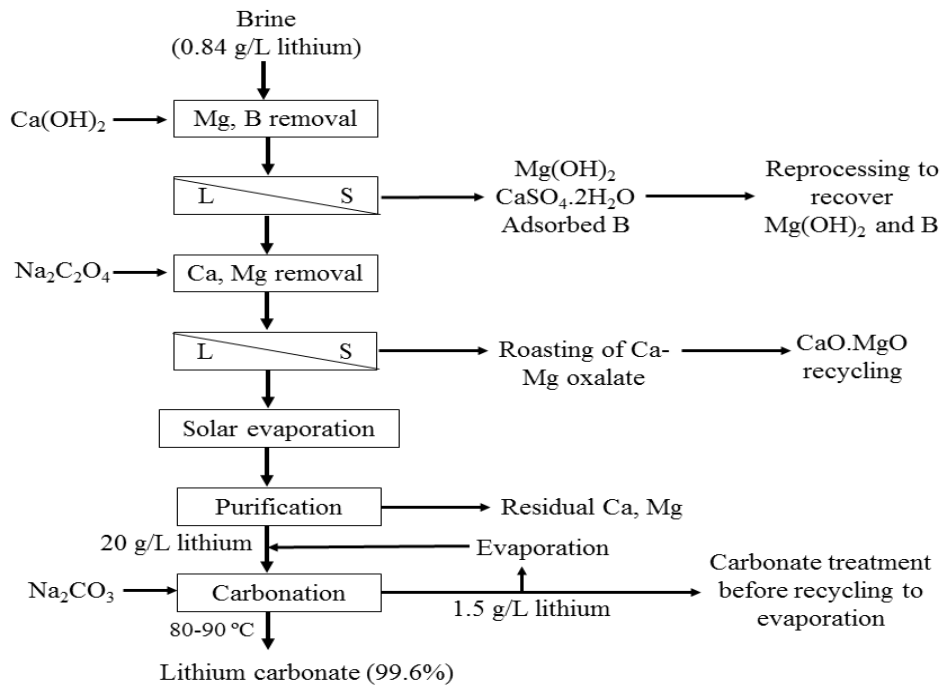
89 **4. Current separation processes for strategically important elements recovery**

90 Various separation processes have been used to extract strategically important elements from
91 low-grade ores and brines. Traditional technology to extract these elements relies on subtle
92 differences in their thermodynamic behaviors in the aqueous phase through a series of
93 precipitation and crystallization steps (Bernardis et al., 2005). The process to recover lithium
94 from the Uyuni Salar brine in Bolivia is shown in Figure 2 as an example. The Salar is a salt
95 surface crust overlying brine saturated sediment. Following the removal of calcium,
96 magnesium and boron, the concentrated brine can then be purified to remove other residual
97 impurities such as sodium, sulphate and chlorine (An et al., 2012). The lithium concentrate is
98 then subjected to carbonation for the precipitation of lithium carbonate with high purity
99 (99.6%).

100 Platinum-group metals and REEs are mainly recovered from the ore concentrate through acid
101 leaching. Target elements from the leach solution are then separated by ion exchange or
102 solvent extraction processes. For example, the ion exchange process has been used for the
103 separation of platinum-group metals from the low-grade waste stream at Impala Refineries in
104 Springs, South Africa (Figure 3). The concentrate contains about 65% platinum-group metals
105 (Crundwell, 2011). In this full-scale refinery plant, ion exchange, distillation and hydrolysis
106 have been used to separate the individual platinum-group metals from the leach solution.
107 Another industrial process for the recovery of strategically important elements is solvent
108 extraction. In the Always Plant in India, the separation of individual REEs from rare earth

109 nitrate solution is achieved by a solvent extraction process using tri-n-butyl phosphate (TBP)
 110 (Figure 4). In this process, the feed solution containing rare earth nitrate is produced during
 111 the chemical treatment of monazite ore.

112



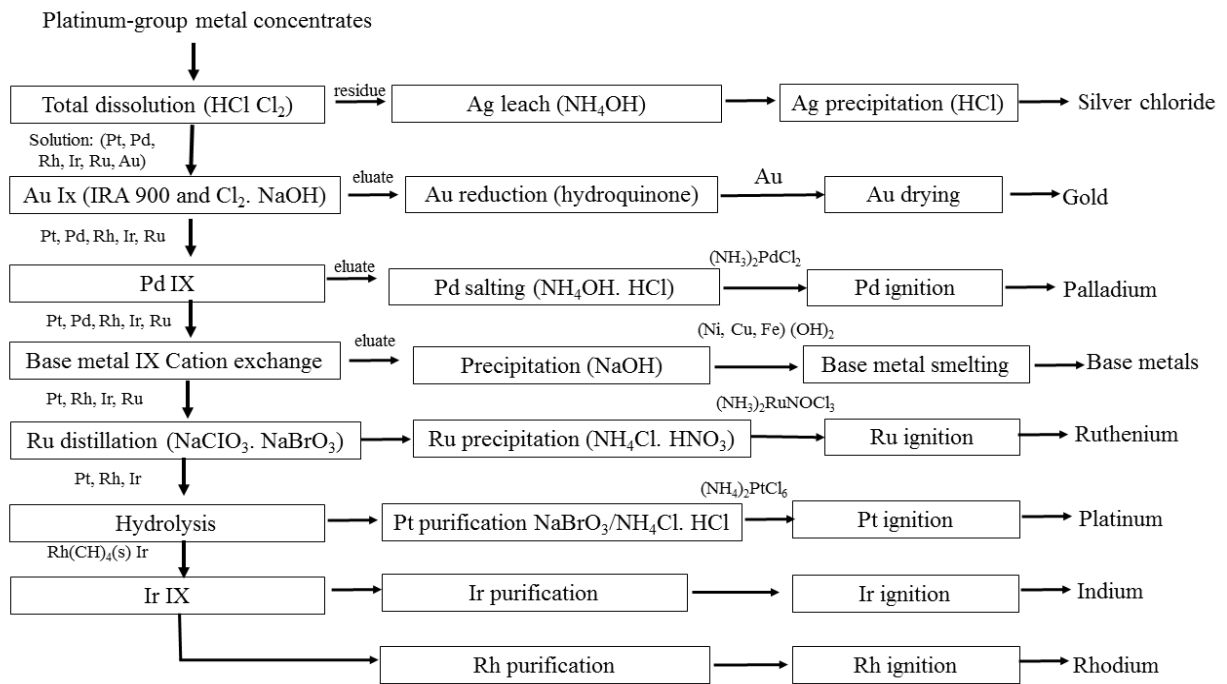
113

114 **Figure 2:** Flowsheet for the recovery of lithium as carbonate from Uyuni Salar brine, Bolivia

115

(An et al., 2012)

116

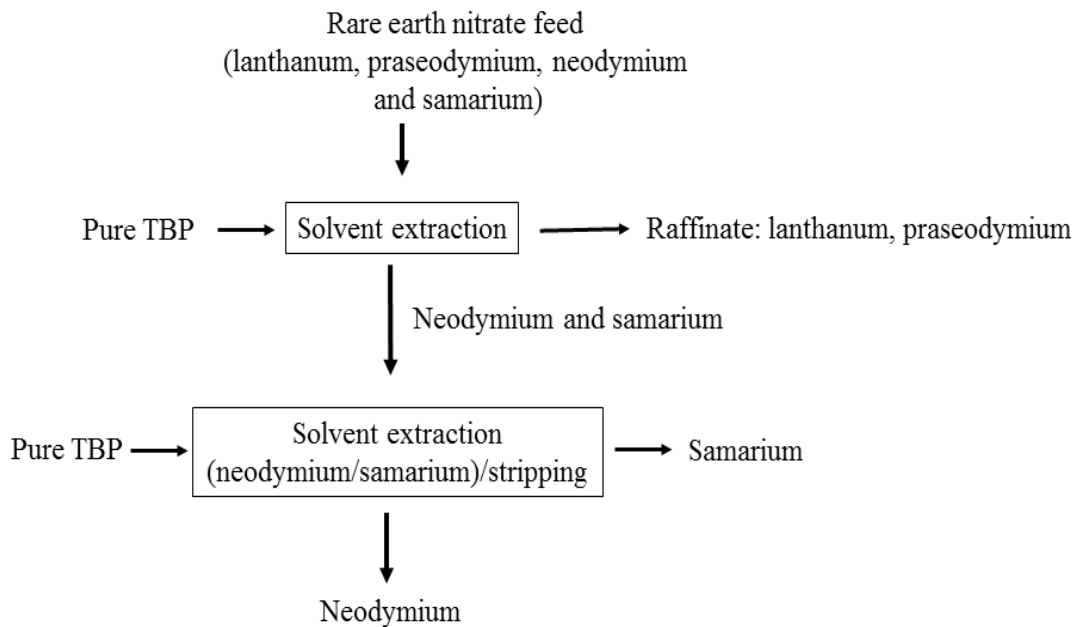


117

118

119 **Figure 3:** Platinum-group metals and other precious metal recovery using ion exchange

120 process at Springs, South Africa (Crundwell, 2011).



121

122 **Figure 4:** Flowsheet of rare earth separations by solvent extraction at Always Plant of Indian

123 Rare Earths Ltd, India (Krishnamurthy and Gupta, 2004).

124

125 **4.1. Precipitation**

126 Precipitation is commonly used to separate strategically important elements from brines. For
127 example, precipitation of lithium in the form of lithium carbonate from a concentrated lithium
128 solution has been reported previously (Nishihama et al., 2011). However, the high amount of
129 lime consumption for the precipitation of co-occurring magnesium and loss of lithium by co-
130 precipitation are major challenges for the application of precipitation process for lithium
131 recovery (Chen et al., 2017). Lithium recovery in the form of lithium aluminate from Dead
132 Sea brine and end brine (after potash production) has been reported by several researchers
133 (Epstein et al., 1981; Pelly, 1978). Pelly (1978) achieved 90% extraction efficiency of lithium
134 aluminate from both Dead Sea brine and end brine. However, they found that higher
135 temperature has an adverse effect on the extraction efficiency, and the best yield was
136 achieved at room temperature (Pelly, 1978). Another study by Epstein et al. (1981) focused
137 on lithium extraction from the Dead Sea brine by precipitation as lithium aluminate followed
138 by liquid-liquid extraction to separate the lithium from aluminium. Notably, evaporation-
139 precipitation process has been used as the industry standard commercial process for lithium
140 production from brines (Kotsupalo et al., 2013; Li, X. et al., 2015; Paranthaman et al., 2017;
141 Yang et al., 2018; Yi et al., 2018). The process has shown excellent performance for lithium-
142 precipitation and Li/Mg separation (Liu et al., 2018). However, this process is mainly suitable
143 to apply in areas with arid climate to have significant evaporation of the brine. Notably, brine
144 lakes occur at high altitudes and in areas with low rainfall, which makes an evaporation-
145 precipitation process an effective approach for lithium extraction. As an alternative attempt,
146 using concentrated sulfuric acid, leached solution containing lithium was obtained from
147 roasted Zimbabwean petalite ore concentrate, and then, lithium carbonate was precipitated by
148 adding sodium carbonate (Sitando and Crouse, 2012). However, treatment of petalite by the

149 leaching method requires highly concentrated acid (Sitando and Crouse, 2012), which raises
150 safety and environmental concerns.

151

152 REEs can also be separated using acidic and alkaline precipitation processes. For example,
153 after extraction of uranium in a pilot plant, the effluent containing sulphate solution was
154 subjected to complete precipitation for recovering REEs at pH 9.3 using ammonium
155 hydroxide (Khawassek et al., 2015). REEs can be also separated in a weak acidic medium via
156 precipitation using oxalic acid. The oxalate precipitate is free from undesired elements such
157 as phosphate, iron, aluminium, nickel, chromium, manganese, zirconium, uranium and
158 copper (El-Awady, 2013). However, precipitation with oxalic acid is an expensive process.
159 Recovering this acid along with strategically important elements would result in substantial
160 savings for the process (Krishnamurthy and Gupta, 2004).

161

162 Platinum-group metals can also be separated using precipitation process. Platinum is
163 precipitated as ammonium hexachloroplatinate with ammonium chloride from the leached
164 solution that is produced from an ore concentrate (Phetla et al., 2010). Palladium could be
165 precipitated using ascorbic acid. Palladium was reported to be precipitated selectively with an
166 increase in the ascorbic acid concentration, while the other elements such as ruthenium,
167 rhodium and iron were hardly precipitated (Lee et al., 2000). The precipitation behaviour of
168 the platinum-group metals from liquid waste in a sequential denitration process with formic
169 acid was shown by Kondo and Kubota (1992). The precipitation of ruthenium and rhodium
170 increased linearly with the increase in pH of the denitrated solution. Above 98% of ruthenium
171 and rhodium could be recovered via precipitation at $\text{pH} > 7$. However, the precipitation of base
172 metals along with platinum-group metals is a major challenge in this process.

173

174 **4.2. Ion exchange**

175 Ion exchange is an efficient and commercially mature technology for the recovery of
176 strategically important elements from low-grade sources. Some advantages of ion exchange
177 process include simple design, applicability to dilute feeds, ability to achieve a high
178 concentration factor and no loss of separation media to the environment. The shortcoming to
179 ion exchange is that the method does not work well with concentrated feeds: the kinetics is
180 usually slow, and depending on the separation agent used, selectivity can be limited.
181 Generally, the economics of ion exchange is driven mostly by the cost of resin regeneration
182 chemicals, which increases proportionally with the increase in concentration of dissolved
183 salts in the brine samples. For example, ion exchange is more cost-effective when used to
184 treat brine water with ≤ 1500 mg/L dissolved salts (Kentish and Stevens, 2001). It is also
185 noted that at lower TDS, ion exchange is extremely attractive for its low capital and
186 operational costs and high recovery (90-95%) rates (Aral et al., 2009). Ion exchange offers
187 high separation efficiency of Li from brines, but the application of this method is limited in
188 the large scale owing to the low loading capacity of resins (Al-Obaidani et al., 2008; Zhang et
189 al., 2010).

190

191 Previous studies report that ion exchange could effectively recover platinum-group metals
192 (Blokhin et al., 2009; Katsutoshi et al., 2008; Peng et al., 2009). In the metal industry,
193 Smopex®, SuperLig® and Amberlite IRA-93 materials are widely known as effective ion
194 exchange resins for the recovery of platinum-group metals (Hubicki et al., 2008; Yahorava
195 and Kotze, 2014). However, high cost and slow adsorption kinetics are the major limitations
196 of these resins. Ion exchange has been used to recover platinum group elements from brine
197 solution. Sun et al. (2012) investigated the performance of AG1-x8 resin to separate platinum
198 and Rhodium from mixed chloride solution. They found that AG1-x8 could effectively

199 separate platinum and rhodium. Nikoloski et al. (2015) used three ion exchange resins of
200 different functional groups for the simultaneous recovery of platinum and palladium present
201 in chloride solution. The tested resins included a resin with a quaternary ammonium
202 functional group (Lewatit MonoPlus MP 600), a resin with a polyamine functional group
203 (Purolite S985) and a resin with a thiouronium functional group (XUS 43600.00). They found
204 that, among the investigated resins, XUS 43600.00 was the best resin to recover platinum and
205 palladium chloride complexes. The recovery of platinum-group elements using Lewatit MP
206 600 WS and Purolite S985 anion exchangers were extensively studied by several researchers
207 (Kononova et al., 2010; Kononova et al., 2011; Mel'nikov et al., 2012). These anion
208 exchangers showed high sorption and kinetic properties for platinum-group elements
209 recovery from synthetic brine. XUS 43600.00 with thiouronium functional group showed
210 high selectivity for platinum group elements recovery (Nikoloski et al., 2015), but no data is
211 readily available about the use of thiouronium functionalised resin in the simultaneous
212 recovery of platinum, palladium and rhodium from brine solutions.

213

214 Lithium can also be recovered by ion exchange from brines. Hui (2000) reported that the
215 H_2TiO_3 ion exchange resin could recover lithium from a brine of natural gas wells. The
216 H_2TiO_3 ion exchanger has high selectivity for lithium with an exchange capacity of 25.34 mg
217 Lithium/g. In another study by Chitrakar et al. (2014), H_2TiO_3 ion exchanger achieved
218 similar lithium adsorption capacity during the treatment of salt lake brine. Nishihama et al.
219 (2011) have noted a selective recovery of lithium from seawater brine using two successive
220 processes of ion exchange. Firstly, they used $k-MnO_2$ adsorbent to concentrate lithium
221 followed by the purification of lithium from concentrated solution by a combination of acidic
222 cation exchange resin to remove divalent metal ions and b-diketone/TOPO-impregnated resin
223 to remove sodium and potassium. Finally, the recovery of lithium as precipitates of lithium

224 carbonate was achieved using a saturated solution of ammonium carbonate. By this process,
225 the lithium yield was 56% and purity was 99.9% (Nishihama et al., 2011). The recovery of
226 lithium from seawater using IX type manganese oxide adsorbent has also been reported in
227 Korea (Liu et al., 2015). They noted that manganese oxide ion sieves could be considered as
228 the most promising process for industrial application. Park et al. (2015) demonstrated that
229 HMnO could be effectively used for recovery of lithium from seawater with good selectivity.
230 Zandevakili et al. (2014) found more than 90% lithium recovery from Urmia Lake by MnO₂
231 ion-sieve. Bukowsky et al. (1991) have studied 3 different ion exchange resin (MC50, TP207,
232 Y80-N) for recovery of lithium from synthetic brine containing higher contents of CaCl₂ and
233 MgCl₂. They found that resin Y80-N at room temperature and the resin TP207 at 50 °C can
234 be feasible to recover lithium chloride. Fukuda (2019) tested thirty IX resins in lithium
235 chloride solution. They found that out of the thirty, sulfonate, iminodiacetate and
236 aminomethylphosphonate resins could achieve lithium extraction capacity with the value of
237 16.3-32.9 mg-Li/g. However, none of the resins could adsorb lithium from a real brine
238 solution effectively as a much higher concentration of sodium, potassium, calcium and
239 magnesium ions are present (sometimes 100 times as high as lithium concentration), and
240 these ions have a higher affinity to cation exchange resins (Fukuda, 2019). Thus, sodium and
241 potassium can be partially recovered via evaporation as chloride salts, and magnesium and
242 calcium can be precipitated as carbonates by soda ash before the lithium concentration gets
243 high enough to be co-precipitated as a carbonate. Despite the unfavourable conditions for ion
244 exchange resins with interfering ions, Dow Chemical (USA) introduced aluminium-loaded
245 resins which is claimed to extract lithium selectively from brine, although this approach
246 remains to be practically implemented (Fukuda, 2019).

247

248 Separation of REEs into their individual components as part of the Manhattan Project during
249 World War II was a notable achievement of the ion exchange process (Izatt et al., 2014).
250 Subsequent development of chelating resins was a significant advancement in the application
251 of the ion exchange process for the recovery of metals. Chelating ion exchange resins adsorb
252 metals through a combination of ionic and co-ordinating interactions rather than the simple
253 electrostatic interactions in conventional ion exchange processes (Harland, 1994). Chelating
254 ion exchange resins are regularly used in commercial systems to separate metal ions
255 selectively. For example, neodymium is extracted from brine using the commercially
256 available D113-III chelating resin (Xiong et al., 2011). Although this process is common for
257 metal recovery in general, the efficacy of the process is yet to be demonstrated for some
258 strategically important elements at industrial scale. Low concentration of the target elements
259 in the solution in the presence of high concentrations of other interfering elements leads to
260 slow recovery and high process cost.

261

262 **4.3. Solvent extraction**

263 The solvent extraction process has been used at commercial scale for the recovery of
264 strategically important elements. This process is economically viable when the concentration
265 of the target element is high (Kentish and Stevens, 2001). When the components of a mixture
266 have similar physico-chemical properties the separation becomes difficult. In this process,
267 separation and purification of REEs are made from the acidic/alkaline leaching solution
268 containing impurities such as calcium, iron, aluminium and lead (Jha et al., 2016). Hence, the
269 impurities affect the quality of the products formed and can be removed using precipitation
270 process. Di-(2-ethylhexyl)phosphoric acid (D2EHPA) is widely used as a solvent extraction
271 agent to recover REEs on an industrial scale (Jha et al., 2016). Studies found that D2EHPA
272 could effectively separate high-grade europium, samarium gadolinium and scandium from

273 other metals in a mixed nitrate-chloride leachate (Makanyire et al., 2016; Rabie, 2007).
274 Another study by Perez et al. (2019) shows that highest extraction rates were obtained using
275 undiluted D2EHPA, especially for light REEs lanthanum (77.1%) and cerium (94.9%), while
276 D2EHPA diluted in xylene provided the highest selectivity for terbium (heavy REE). Using a
277 three-stage cross-current extraction, terbium was first recovered from the diluted
278 methanesulfonic acid leachate with 100% selectivity and 97.5% recovery using 70% v/v
279 D2EHPA in xylene (Perez et al., 2019). Afterwards, the remaining lanthanum and cerium
280 from the diluted raffinate were recovered using three stages of extraction with undiluted
281 D2EHPA with an efficiency of 98.8% for lanthanum and 100% for cerium (Perez et al.,
282 2019). Studies have shown that neutral trialkyl phosphine oxides and tetraoctyl diglycol
283 amide have the capability of extracting cerium and europium elements effectively (Larsson et
284 al., 2012; Shimojo et al., 2008). Singh et al. (2008) reported that 2-ethylhexyl phosphoric
285 acid-2-ethylhexyl ester (EHEHPA) could recover dysprosium with 98% purity from
286 concentrated HCl leaching solution. However, this separation required several stages due to
287 the low separation factor (i.e., presence of competing ions). Wang et al. (2011) studied the
288 performance of solvent extraction using a mixture of sec-octylphenoxy acetic acid and
289 Cyanex272 for extraction of yttrium from other rare earth metals and reported high selectivity
290 of yttrium. However, the presence of iron, manganese, and aluminium are the common
291 impurities during extraction of these elements that affect the quality of products (Makanyire
292 et al., 2016). Hence, this has led to the use of other processes such as selective precipitation
293 to remove the metals competing for adsorption with the target metals. In this process, several
294 elements are produced as a co-product/by-product. For example, REEs are recovered as a by-
295 product of uranium extraction at Denison Mines, Elliot Lake in Canada (Krishnamurthy and
296 Gupta, 2004).

297

298 The solvent extraction process is also employed to recover platinum-group elements from
299 low-grade sources. Perez et al. (2019) investigated the separation of platinum and palladium
300 from chloride solution by solvent extraction using Alamine 300 as an extractant. They found
301 that platinum could be selectively extracted as the major component along with minor
302 amounts of palladium using a saturated solution of sodium chloride at pH 1.5. This process
303 could achieve a 99.9% purity of platinum. Perez et al. (2019) also found a high palladium
304 recovery (99.8%) using a two-stage countercurrent extraction process with 0.5% LIX 84I (2-
305 hydroxy-5-nonylacetophenone oxime). In their process, scrubbing using diluted HCl was
306 done to remove the co-extracted base metal and resulted in platinum of 99.7% purity. The
307 separation and recovery of palladium and platinum from chloride leach liquor was also
308 investigated by Reddy et al. (2010).

309

310 Previous studies report that solvent extraction with β -diketones and n-butanol can be used to
311 extract lithium from brines. For example, Gabra and Torma (1978) established a lab-scale
312 lithium chloride extraction process with n-butanol using synthetic solutions including
313 different quantities of lithium, sodium chloride, potassium, and calcium chloride. They found
314 that this process could recover lithium chloride with 99.6% purity (Gabra and Torma, 1978).
315 Shi et al. (2016) reported separation of lithium and magnesium from Salt Lake brine by
316 liquid-liquid extraction with tributyl phosphate. They found that under the optimum
317 conditions, the extraction efficiency of lithium was 80.64% and 99.42% by a single-stage and
318 a three-stage countercurrent extraction, respectively. Recently, Pure Energy Minerals Inc has
319 reported the results of preliminary pilot-scale tests by Tenova Advanced Technology and
320 LiSXTM technology on the Clayton Valley Project, which showed great potential for large-
321 scale application of lithium extraction from brines using novel organic reagents including
322 ketone, β -diketone, ionic liquids, and crown ethers (Energy, 2019). This process extracted

323 lithium and separated sodium and potassium after calcium and magnesium removal.
324 However, these processes are still a long way from an industrial application due to technical
325 and economic limitations. Shi et al. (2013) investigated a pilot-scale experiment for the
326 recovery of lithium using TBP in N, N-di(2-ethylhexyl)acetamide/kerosene, and they
327 observed the extraction efficiency of lithium to reach 96%. This demonstrates that TBP is an
328 effective extractant for lithium recovery from salt lake brines. However, as mentioned in
329 Section 3, the high magnesium/lithium ratio in brine found in salt lakes is a challenge for
330 large-scale lithium extraction.

331

332 The application of membrane in solvent extraction for the separation of strategically
333 important elements has been investigated in the past (Kim et al., 2015; Xing et al., 2016). In
334 this process, a membrane barrier, permeable to cations and impermeable to organic solvent, is
335 located at the interface between the organic solvent and brine, thereby selectively extracting
336 the strategically important elements. A membrane-assisted solvent extraction process for the
337 recovery of REEs from nitric acid solutions was demonstrated by Kim et al. (2015). The
338 system exhibited high selectivity for REE extraction without co-extraction of other elements.
339 Xing et al. (2016) recently tested solvent stable hydrophilic nanoporous poly (ethylene-co-
340 vinyl alcohol) membranes for lithium recovery. They observed a stable lithium extraction
341 process for approximately 45 days, indicating the potential of this process for large-scale
342 applications.

343

344 The conventional technologies have limitations in selectivity and efficiency in recovering
345 metals from low-grade sources. It is also noteworthy that often these processes consume a
346 huge amount of water during extracting metals. MacLean et al. (2009) estimated that mining
347 and processing of metals utilise 0.03% of total world water. Given the scarcity of strategically

348 important elements and clean water, a process that can concentrate metal salts for their
349 extraction and produce clean water for reuse during the extraction process is highly
350 warranted. In this context, the integration of a membrane process with conventional
351 separation techniques could be a suitable approach (Marchetti et al., 2014; Székely et al.,
352 2012). Membrane technology can provide better metal separation compared to conventional
353 techniques (Chun-Te Lin and Livingston, 2007; Geens et al., 2007; Vandezande et al., 2008)
354 and also facilitate clean water production.

355

356 **5. Membrane processes for the recovery of strategically important elements**

357 Pressure-driven membrane processes such as nanofiltration (NF) and reverse osmosis (RO)
358 have been used for the separation of lithium from brine. Lithium was separated from diluted
359 brine in the form of lithium chloride by using NF membranes (Wen et al., 2006). Separation
360 of lithium from salt lake brines by the NF90 and a low-pressure RO membrane (LPRO) was
361 investigated by Somrani et al. (2013). The NF90 membrane was found to be more efficient
362 for lithium separation compared to LPRO. This is probably due to its high hydraulic
363 permeability and separation efficiency of monovalent ions (e.g., lithium). In another study,
364 effective retention (97%) of divalent cations, namely Mg and Ca, was achieved by NF
365 membranes, while a moderate retention (70%) was observed for monovalent cations (Na and
366 Li) (Zhang et al., 2017), thus facilitating separation of lithium from the mixture. Separation
367 of lithium and magnesium from brine using NF membranes has also been reported by (Sun et
368 al., 2015) and (Pramanik et al., 2019). They found that magnesium and lithium separation
369 was highly dependent on the pH, operating pressure, and Mg/Li ratio. The competitive
370 coefficient was susceptible to the Mg/Li ratio, when the Mg/Li ratio was less than 20 (Sun et
371 al., 2015). An NF membrane with polyamide functional layer and positive charge was
372 fabricated for Li and Mg separation (Li, et al., 2015a,b). The results showed that the rejection

373 difference between magnesium chloride and lithium chloride reached 47.5% and the Mg/Li
374 ratio decreased from 20 to 7.7. Li et al. (2017) synthesized a composite NF membrane with
375 positively charged skin layer followed by modification with EDTA, which showed stable
376 separation behaviour of lithium ions.

377

378 REEs such as cerium and neodymium can also be separated using NF membranes (Murthy
379 and Choudhary, 2012). Rejection of neodymium ions from synthetic wastewater, as a
380 function of applied pressure, feed concentration and pH was investigated using a NF
381 membrane (Murthy and Choudhary, 2011). The rejection of neodymium ions increased with
382 the increase in applied pressure and decreased with the increase in feed concentration.
383 Rejection of neodymium using NF membrane was influenced by solution pH (Murthy and
384 Choudhary, 2011). This was likely due to the charged nature of the membrane which changed
385 with the variation in pH (Murthy and Choudhary, 2011).

386

387 Despite the potential of pressure-driven high retention membrane processes in the separation
388 of strategically important elements, these processes have some limitations. These processes
389 are energy-intensive and prone to severe membrane fouling, resulting in impaired membrane
390 performance and shortened membrane lifetime. Hence, combination of emerging
391 technologies such as membrane distillation (MD) and conventional processes such as
392 electrodialysis (ED) can be potentially used to recover strategically important elements from
393 brines. These processes can achieve a high concentration factor for strategically important
394 elements by pre-concentrating brines. This is due to the mass transfer properties of the
395 membranes. In addition, compared to RO/NF, these processes are expected to have lower
396 energy consumption and lower fouling propensity due to low applied hydraulic pressure
397 (Mazlan et al., 2016; McGovern, 2014).

398

399 The application of MD process could concentrate strategically important elements to
400 facilitate their recovery and it can also produce clean water (Table 3). MD has the capability
401 to concentrate salts up to the supersaturated state to allow crystallization (Ali et al., 2015).
402 Studies reported that there is ample opportunity for the recovery of lithium from seawater
403 brines using the MD-crystallization technique (Greenlee et al., 2009; Quist-Jensen, C. et al.,
404 2016; Quist-Jensen, C.A. et al., 2016). Hollins (2013) evaluated the prospects for recovering
405 minerals from desalination brines and focused on the extraction of Li from desalination
406 brines as a benchmark. They noted that 23000 tonnes of Li could be recovered from brines by
407 2030 compared to the current global production of 37000 tonnes.

408

409 ED can efficiently achieve lithium recovery from brines. This process was demonstrated to
410 recover lithium in the form of lithium bromide from a sodium-contaminated lithium bromide
411 solution (Parsa et al., 2015) and lithium hydroxide from an aqueous solution (Bunani et al.,
412 2017). After pre-concentrating and precipitating brine with sodium carbonate, 98% lithium
413 carbonate could be obtained from simulated lake brines using ED with a bipolar membrane
414 process (Jiang et al., 2014). The ED system can also be equipped with monovalent selective
415 ion exchange membrane for the recovery of lithium from salt lake brines (Ji et al., 2017). In
416 this way, the Mg/Li ratio of simulated brine was reduced from 60 to 7, which provided a
417 suitable Mg/Li condition for the extraction of lithium from the Li-enriched solution.
418 However, the concentration of co-existing ions such as sodium, potassium and sulphate,
419 differs considerably in different types of brine, which may influence the applicability of ED
420 for lithium recovery (Nie et al., 2017a). In addition, the durability of the membranes is a
421 challenge during long-term lithium recovery in this process (Jiang et al., 2014).

422

423 **Table 3:** Examples of strategically important elements separation using membrane processes.

424

Technology	Source	Concentrate (%)	Separated elements	Water recovery (%)	References
NF	Salt lake brine	NA	Lithium Lithium Lithium	NA	Wen et al. (2006) Somrani et al. (2013) Sun et al. (2015)
	Synthetic wastewater	NA	Lithium Cerium, Neodymium Neodymium	NA	Zhang et al. (2017) Murthy and Choudhary (2012) Murthy and Choudhary (2011)
RO	Salt lake brine	NA	Lithium	NA	Somrani et al. (2013)
MD	Seawater Brine	500	NA	80	Duong et al. (2015)
	Synthetic brine	NA	Lithium	NA	Quist-Jensen et al. (2016b)
	Salt lake brine	NA	Lithium	NA	Zhou (2017)
ED	Salt lake brine	NA	Lithium	NA	Liu et al. (2015) Jiang et al. (2014) Ji et al. (2017)
	Geothermal brine	NA	Lithium	NA	Mroczek et al. (2015)
	Synthetic brine	NA	Lithium	NA	Nie et al. (2017b) Bunani et al. (2017) Parsa et al. (2015)

425 NA= Data not available

426

427

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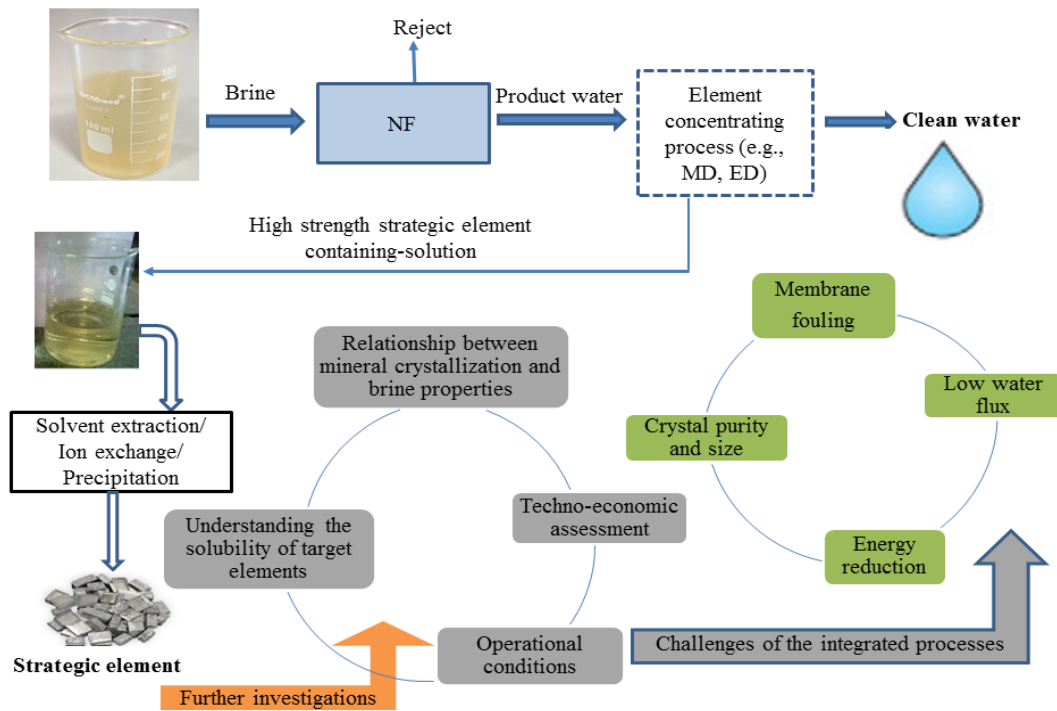
434

435 A potential integrated process for the recovery of strategically important elements along with
436 clean water production is shown in Figure 5. In this process, membranes can be used to
437 concentrate the strategically important elements as well as produce clean water. Post-
438 treatment with solvent extraction, ion exchange or precipitation process can be used to
439 retrieve the target element selectively. For example, lithium could be effectively recovered
440 from brines using integrated NF and MD processes. In a previous study, NF could only retain
441 26% of the lithium and 88% of magnesium from the seawater (Drioli et al., 2016). Thus, MD
442 can be used to treat the NF permeate, and to concentrate lithium for recovery. NF could also
443 be combined with the ED process by replacing the cation exchange membrane (Ge et al.,
444 2016). The MD process can be also integrated with renewable energy sources. Low- grade or
445 waste heat can be used to operate MD process. However, economic analysis is essential for
446 the feasibility of the MD process since a considerable amount of energy is required to
447 evaporate water to separate water from non-volatile contaminants (Kiss and Kattan Rendi,
448 2018). Recently, Deshmukh et al. (2018) examined some critical factors that affect the energy
449 efficiency of MD processes and also noted how future membrane design and process
450 development could considerably boost MD efficiency. They found that the size of the system
451 along with porosity and thickness of the membrane could significantly influence the
452 performance of the process. The cost of the MD system operation may vary from 0.26 to 130
453 $\$/\text{m}^3$ based on the optimum flow conditions and MD configurations (Deshmukh et al. (2018).
454 It was reported that by applying waste heat, the production cost of a 30,000 m^3/d MD
455 desalination plant could be reduced from 2.2 to 0.66 $\$/\text{m}^3$ (Kesieme et al., 2013). However,
456 currently limited number of studies is available on the investigation of such an integrated
457 process for the recovery of these elements along with clean water production.

458

459 The aforementioned membrane processes can concentrate strategically important elements in
460 the solution to enable their crystallisation. However, to date these lithium recovery processes
461 have been mainly tested at lab-scale. Therefore, the recovery of strategically important
462 elements along with clean water production from brines using these processes needs to be
463 further investigated. Particularly, the challenges associated with an integrated process, as
464 depicted in Figure 5, need to be addressed for the recovery of these elements and production
465 of clean water. Studies exploring application of MD on a large scale with a long-term
466 operational period reported several challenges of MD process (Van der Bruggen et al., 2008).
467 These include membrane fouling, scaling, and pore wetting which may restrict its commercial
468 application. When applied to brine treatment, inorganic fouling in the form of scaling is the
469 predominant form of fouling on the membrane surface (Van der Bruggen et al., 2008).
470 Therefore, it is necessary to fabricate novel membranes with characteristics of low resistance
471 to mass transfer, low thermal conductivity, high thermal stability and chemical resistance to
472 improve MD performance by minimising fouling and wetting phenomena, while enhancing
473 retention of target metal. In addition, there is a clear need to evaluate product purity, process
474 efficiency and life cycle costs.

475



476

477 **Figure 5.** A roadmap of an integrated membrane and metal separation process for

478 strategically important elements and clean water recovery

479

480 6. Perspective

481 The commercial viability of extracting metals is not only dependent on mineral
 482 concentration, technology implemented, recovery rates, commodity pricing and final product
 483 purity, but also market fluctuations for the minerals extracted (Shahmansouri et al., 2015;
 484 Teat, 2012). Wei (1982) followed by Brown (2016) showed the potential of mining minerals
 485 and metals from geothermal brines as a function of mineral concentration, value, demand,
 486 import dependency, strategic consideration, existing sources of supply, technology readiness
 487 level of recovery process, and resource uncertainty. They concluded that the recovery of
 488 REEs and platinum group elements (except lithium) from brine is still in its infancy stage.
 489 Both Stull (2016) and Addleman et al. (2016) show that although some of these strategic
 490 elements have a low supply risk, the recovery of REEs from geothermal brines is not
 491 economically feasible with the current market prices of fresh products. It is particularly

492 difficult for the lower grade sources. However, a study by Grosjean et al. (2012) reported that
493 the lithium production costs from mining of spodumene is estimated to be 6-8 \$/kg, which is
494 not competitive with respect to the recovery cost from salt lake brines (2-3 \$/kg). The
495 economic feasibility of mining from brine solution further improves when simultaneous
496 water, energy and mineral extractions are considered as proposed in European funded project
497 MEDINA and Global MVP project (Drioli et al., 2016; Drioli et al., 2011). Overall, there
498 might be a trade-off between energy cost and production of strategically important elements
499 along with clean water production at high water recoveries. However, a comprehensive
500 techno-economic analysis between the operating cost of the technologies and price for the
501 production of strategically important elements needs to be carried out.

502

503 **6. Conclusions**

504 Water and minerals such as metals are critical resources, and these resources are the building
505 blocks of a sustainable society and the global economy. With population-increase and
506 industrialization, the demand for these resources has increased. In this context, it is important
507 to recover strategically important elements and clean water from low-grade sources such as
508 brines as discussed in this article. This may open up an exciting gateway to reduce the overall
509 cost and environmental burden of the ore-mining processes. The recovery of strategically
510 important elements from brines compared to that from ores is still in the early stages of
511 development. These elements often occur at low concentrations in brines, and, thus, are
512 difficult to recover in presence of much higher concentrations of other minerals which can
513 interfere with the separation and enrichment process. The main technologies used for
514 producing metals from brines are based on precipitation, ion exchange and solvent extraction.
515 A major challenge of these processes is separation selectivity. An integrated membrane-based
516 process may be suitable for efficiently enriching strategically important elements for their

517 subsequent recovery, and, thus, may have a substantial role in shaping the future of this
518 industry. This may be an attractive pathway to bridge the gap between demand and supply of
519 the strategically important elements.

520

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524

525 **References**

- 526 Addleman, R.S., Chouyyok, W., Palo, D., Dunn, B.M., Brann, M., Billingsley, G., Johnson,
527 D., Nell, K.M., 2016. In support of data uploaded for GTO program on: Evaluation of
528 Advanced Sorbent Structures for Recovery of Rare Earths, Precious Metals and other
529 Critical Materials from Geothermal Waters–Preliminary Results.
- 530 Al-Obaidani, S., Curcio, E., Macedonio, F., Di Profio, G., Al-Hinai, H., Drioli, E., 2008.
531 Potential of membrane distillation in seawater desalination: thermal efficiency,
532 sensitivity study and cost estimation. *Journal of Membrane Science* 323(1), 85-98.
- 533 Ali, A., Quist-Jensen, C.A., Macedonio, F., Drioli, E., 2015. Application of Membrane
534 Crystallization for Minerals' Recovery from Produced Water. *Membranes* 5(4), 772-
535 792.
- 536 Alonso, E., Sherman, A.M., Wallington, T.J., Everson, M.P., Field, F.R., Roth, R., Kirchain,
537 R.E., 2012. Evaluating rare earth element availability: A case with revolutionary
538 demand from clean technologies. *Environmental Science & Technology* 46(6), 3406-
539 3414.
- 540 An, J.W., Kang, D.J., Tran, K.T., Kim, M.J., Lim, T., Tran, T., 2012. Recovery of lithium
541 from Uyuni salar brine. *Hydrometallurgy* 117, 64-70.

542 Aral, H., Vo, B.S., McCallum, D., Barton, T., Norgate, T., 2009. High efficiency ion
543 exchangewater recoveryfor mineral industry. CSIRO Minerals, 2009,DMR-3569

544 Bardi, U., 2010. Extracting minerals from seawater: an energy analysis. Sustainability 2(4),
545 980-992.

546 Barros, Ó., Costa, L., Costa, F., Lago, A., Rocha, V., Vipotnik, Z., Silva, B., Tavares, T.,
547 2019. Recovery of Rare Earth Elements from Wastewater Towards a Circular
548 Economy. Molecules 24(6), 1005.

549 Beolchini, F., Fonti, V., Ferella, F., Veglio, F., 2010. Metal recovery from spent refinery
550 catalysts by means of biotechnological strategies. Journal of Hazardous Materials
551 178(1), 529-534.

552 Bernardis, F.L., Grant, R.A., Sherrington, D.C., 2005. A review of methods of separation of
553 the platinum-group metals through their chloro-complexes. Reactive and Functional
554 Polymers 65(3), 205-217.

555 Blokhin, A., Abovskiy, N., Murashkin, Y., Mikhaylenko, M., 2009. Sorption recovery of
556 platinum and palladium from spent affinage solutions with their low contents,
557 Proceeding of the 1st Int. Congress on Non-Ferrous Metals of Siberia, Krasnoyarsk,
558 587-592.

559 Brown, D.P., 2016. A Preliminary Feasibility Study of Geothermal and Mineral Extraction
560 Applications of Hydrocarbon Wells.

561 Bukowsky, H., Uhlemann, E., Steinborn, D., 1991. The recovery of pure lithium chloride
562 from “brines” containing higher contents of calcium chloride and magnesium
563 chloride. Hydrometallurgy 27(3), 317-325.

564 Bunani, S., Arda, M., Kabay, N., Yoshizuka, K., Nishihama, S., 2017. Effect of process
565 conditions on recovery of lithium and boron from water using bipolar membrane
566 electro dialysis (BMED). Desalination 416, 10-15.

567 Bush, J.A., Vanneste, J., Cath, T.Y., 2016. Membrane distillation for concentration of
568 hypersaline brines from the Great Salt Lake: Effects of scaling and fouling on
569 performance, efficiency, and salt rejection. *Separation and Purification Technology*
570 170, 78-91.

571 Callura, J.C., Perkins, K.M., Noack, C.W., Washburn, N.R., Dzombak, D.A., Karamalidis,
572 A.K., 2018. Selective adsorption of rare earth elements onto functionalized silica
573 particles. *Green chemistry* 20(7), 1515-1526.

574 Cardoso, C.E., Almeida, J.C., Lopes, C.B., Trindade, T., Vale, C., Pereira, E., 2019.
575 Recovery of Rare Earth Elements by Carbon-Based Nanomaterials—A Review.
576 *Nanomaterials* 9(6), 814.

577 Chen, P., Tang, S., Yue, H., Liu, C., Li, C., Liang, B., 2017. Lithium enrichment of high
578 Mg/Li ratio brine by precipitation of magnesium via combined CO₂ mineralization
579 and solvent extraction. *Industrial and Engineering Chemistry Research* 56(19), 5668-
580 5678.

581 Chitrakar, R., Makita, Y., Ooi, K., Sonoda, A., 2014. Lithium recovery from salt lake brine
582 by H₂TiO₃. *Dalton Transactions* 43(23), 8933-8939.

583 Chun-Te Lin, J., Livingston, A.G., 2007. Nanofiltration membrane cascade for continuous
584 solvent exchange. *Chemical Engineering Science* 62(10), 2728-2736.

585 Constantinides, S., 2016. Permanent magnets in a changing world market, Arnold Magnetic
586 Technologies.

587 CPM Group, 2017. The CPM platinum group metals yearbook 2017: New York, NY, CPM
588 Group, 235 p. (Accessed February 26, 2018, at [http://cpmgroup.com/
589 files/The%20CPM%20PGM%20Yearbook%202017%20EBook.pdf](http://cpmgroup.com/files/The%20CPM%20PGM%20Yearbook%202017%20EBook.pdf)).

590 Crundwell, F.K., 2011. Extractive metallurgy of nickel, cobalt and platinum group metals.
591 Elsevier.

592 Deshmukh, A., Boo, C., Karanikola, V., Lin, S., Straub, A., P, Tong, T., Warsinger, D.M.,
593 Elimelech, M., 2018. Membrane distillation at the water-energy nexus: limits,
594 opportunities, and challenges. *Energy and Environmental Science* 11(5), 1177-1196.

595 Drioli, E., Ali, A., Quist-Jensen, C.A., Macedonio, F., 2016. Water, energy and minerals from
596 the sea, 2016 World Congress on Advances in Civil, Environmental and Materials
597 Research. Republic of Korea.

598 Drioli, E., Criscuoli, A., Macedonio, F., 2011. Membrane based desalination: an integrated
599 approach, IWA Publishing.

600 Dutta, T., Kim, K.-H., Uchimiya, M., Kwon, E.E., Jeon, B.-H., Deep, A., Yun, S.-T., 2016.
601 Global demand for rare earth resources and strategies for green mining.
602 *Environmental Research* 150, 182-190.

603 El-Awady, E.M., 2013. Recovery of rare earth elements as by-product from GATTAR (V)
604 mineralization MSc Thesis, Benha University, Egypt.

605 Energy, M.P., 2019. <http://www.pureenergyminerals.com/>.

606 Epstein, J., Feist, E., Zmora, J., Marcus, Y., 1981. Extraction of lithium from the dead sea.
607 *Hydrometallurgy* 6(3-4), 269-275.

608 Fukuda, H., 2019. Lithium extraction from brine with ion exchange resin and ferric
609 phosphate. University of British Columbia.

610 Gabra, G., Torma, A., 1978. Lithium chloride extraction by n-butanol. *Hydrometallurgy* 3(1),
611 23-33.

612 Ge, L., Wu, B., Li, Q., Wang, Y., Yu, D., Wu, L., Pan, J., Miao, J., Xu, T., 2016.
613 Electrodialysis with nanofiltration membrane (EDNF) for high-efficiency cations
614 fractionation. *Journal of Membrane Science* 498, 192-200.

615 Geens, J., De Witte, B., Van der Bruggen, B., 2007. Removal of API's (active pharmaceutical
616 ingredients) from organic solvents by nanofiltration. *Separation Science and*
617 *Technology* 42(11), 2435-2449.

618 Gibert, O., Valderrama, C., Peterkova, M., Cortina, J.L., 2010. Evaluation of selective
619 sorbents for the extraction of valuable metal ions (Cs, Rb, Li, U) from reverse
620 osmosis rejected brine. *Solvent Extraction and Ion Exchange* 28(4), 543-562.

621 Graede, T., 2015. Metals used in high-tech products face future supply risks. . PNAS,
622 <https://phys.org/print346672145.html> .

623 Greenlee, L.F., Lawler, D.F., Freeman, B.D., Marrot, B., Moulin, P., 2009. Reverse osmosis
624 desalination: water sources, technology, and today's challenges. *Water Research*
625 43(9), 2317-2348.

626 Grosjean, C., Miranda, P.H., Perrin, M., Poggi, P., 2012. Assessment of world lithium
627 resources and consequences of their geographic distribution on the expected
628 development of the electric vehicle industry. *Renewable and Sustainable Energy*
629 *Reviews* 16(3), 1735-1744.

630 Harland, C.E., 1994. *Ion exchange: theory and practice*. Royal Society of Chemistry.
631 ISBN 978-0-85186-484-6.

632 Hoenderdaal, S., Espinoza, L.T., Marscheider-Weidemann, F., Graus, W., 2013. Can a
633 dysprosium shortage threaten green energy technologies? *Energy* 49, 344-355.

634 Hollins, O., 2013. *Seawater mining: Mining desalination brine residues*.

635 Hu, Y., Florek, J., Larivière, D., Fontaine, F.G., Kleitz, F., 2018. Recent advances in the
636 separation of rare earth elements using mesoporous hybrid materials. *The Chemical*
637 *Record* 18(7-8), 1261-1276.

638 Hubicki, Z., Wawrzekiewicz, M., Wołowicz, A., 2008. Application of ion exchange methods
639 in recovery of Pd (II) ions—a review. *Chem. Anal.(Warsaw)* 53, 759-784.

640 Hui, Z., 2000. Property of H₂TiO₃ type ion-exchangers and extraction of lithium from brine
641 of natural gas wells. *Chinese Journal of Applied Chemistry* 17(3), 307-309.

642 Hurst, C., 2010. China's rare earth elements industry: What can the west learn? Institute for
643 the Analysis of Global Security Washington DC.

644 IDC, 2013. Opportunities for downstream value addition in the platinum group metals value
645 chain: fuel cells. South Africa Department of Research and Information.

646 Izatt, R.M., Izatt, S.R., Bruening, R.L., Izatt, N.E., Moyer, B.A., 2014. Challenges to
647 achievement of metal sustainability in our high-tech society. *Chemical Society*
648 *Reviews* 43(8), 2451-2475.

649 Izatt, R.M., Izatt, S.R., Izatt, N.E., Krakowiak, K.E., Bruening, R.L., Navarro, L., 2015.
650 Industrial applications of molecular recognition technology to separations of platinum
651 group metals and selective removal of metal impurities from process streams. *Green*
652 *Chemistry* 17(4), 2236-2245.

653 Izatt, S.R., McKenzie, J.S., Izatt, N.E., Bruening, R.L., Krakowiak, K.E., and , R.M., I., 2016.
654 Molecular recognition technology: a green chemistry process for separation of
655 individual rare earth metals. *White Paper on Separation of Rare Earth Elements*,
656 February, 1-13.

657 Jha, M.K., Kumari, A., Panda, R., Kumar, J.R., Yoo, K., Lee, J.Y., 2016. Review on
658 hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* 165, 2-26.

659 Ji, Z.-Y., Chen, Q.-B., Yuan, J.-S., Liu, J., Zhao, Y.-Y., Feng, W.-X., 2017. Preliminary study
660 on recovering lithium from high Mg²⁺/Li⁺ ratio brines by electrodialysis. *Separation*
661 *and Purification Technology* 172, 168-177.

662 Jiang, C., Wang, Y., Wang, Q., Feng, H., Xu, T., 2014. Production of lithium hydroxide from
663 lake brines through electro-electrodialysis with bipolar membranes (EEDBM).
664 *Industrial and Engineering Chemistry Research* 53(14), 6103-6112.

665 Johnson, M., 2001. Platinum 2001: Interim Review. Johnson Matthey Public Limited
666 Company, London, UK (32 pp.).

667 Johnson, M., 2014. PGM Market Report November 2014. Forecast of Platinum. Supply &
668 Demand in 2014. Johnson Matthey Public Limited Company, London, UK (32 pp.).

669 Jollie, D., 2017. Overview of PGM Markets. Available online:
670 [http://www.angloamerican.com/~media/Files/A/Anglo-American-PLC-](http://www.angloamerican.com/~media/Files/A/Anglo-American-PLC-V2/documents/platinum-marketing-david-jollie-241116.pdf)
671 [V2/documents/platinum-marketing-david-jollie-241116.pdf](http://www.angloamerican.com/~media/Files/A/Anglo-American-PLC-V2/documents/platinum-marketing-david-jollie-241116.pdf) (accessed on 10 May
672 2017).

673 Katsutoshi, I., Durga, P., Kanjana, K., 2008. Adsorption of precious metals on some
674 lignophenol compounds. Vladivostok, Russia: Institute of Chemistry, Far East Branch
675 of Russian Academy of Sciences (FEB RAS), 220-226.

676 Kentish, S., Stevens, G., 2001. Innovations in separations technology for the recycling and re-
677 use of liquid waste streams. *Chemical Engineering Journal* 84(2), 149-159.

678 Kesieme, U.K., Milne, N., Aral, H., Cheng, C.Y., Duke, M., 2013. Economic analysis of
679 desalination technologies in the context of carbon pricing, and opportunities for
680 membrane distillation. *Desalination* 323, 66-74.

681 Khawassek, Y., Eliwa, A., Gawad, E., Abdo, S., 2015. Recovery of rare earth elements from
682 El-Sela effluent solutions. *Journal of Radiation Research and Applied Sciences* 8(4),
683 583-589.

684 Kim, D., Powell, L.E., Delmau, L.H., Peterson, E.S., Herchenroeder, J., Bhave, R.R., 2015.
685 Selective extraction of rare earth elements from permanent magnet scraps with
686 membrane solvent extraction. *Environmental Science and Technology* 49(16), 9452-
687 9459.

688 Kiss, A.A., Kattan Readi, O.M., 2018. An industrial perspective on membrane distillation
689 processes. *Journal of Chemical Technology and Biotechnology* 93(8), 2047-2055.

690 Kogel, J.E., 2006. Industrial minerals & rocks: commodities, markets, and uses. SME.

691 Koltun, P., Tharumarajah, A., 2014. Life cycle impact of rare earth elements. ISRN
692 Metallurgy 2014.

693 Kondo, Y., Kubota, M., 1992. Precipitation behavior of platinum group metals from
694 simulated high level liquid waste in sequential denitration process. Journal of Nuclear
695 Science and Technology 29(2), 140-148.

696 Kononova, O., Leyman, T., Melnikov, A., Kashirin, D., Tselukovskaya, M., 2010. Ion
697 exchange recovery of platinum from chloride solutions. Hydrometallurgy 100(3-4),
698 161-167.

699 Kononova, O., Melnikov, A., Borisova, T., Krylov, A., 2011. Simultaneous ion exchange
700 recovery of platinum and rhodium from chloride solutions. Hydrometallurgy 105(3-
701 4), 341-349.

702 Kotsupalo, N., Ryabtsev, A., Poroshina, I., Kurakov, A., Mamylova, E., Menzheres, L.,
703 Korchagin, M., 2013. Effect of structure on the sorption properties of chlorine-
704 containing form of double aluminum lithium hydroxide. Russian Journal of Applied
705 Chemistry 86(4), 482-487.

706 Krishnamurthy, N., Gupta, C.K., 2004. Extractive metallurgy of rare earths. CRC press.

707 Lacal-Arántegui, R., Serrano-González, J., 2015. 2014 JRC wind status report; Joint
708 Research Centre (JRC). Publications Office of the European Union. EUR 27254 EN.
709 <http://dx.doi.org/10.2790/676580>.

710 Larsson, K., Ekberg, C., Ødegaard-Jensen, A., 2012. Using Cyanex 923 for selective
711 extraction in a high concentration chloride medium on nickel metal hydride battery
712 waste. Hydrometallurgy 129, 35-42.

713 Lee, J., Yu, S.-H., Kim, C., Sung, Y.-E., Yoon, J., 2013. Highly selective lithium recovery
714 from brine using a λ -MnO₂-Ag battery. *Physical Chemistry Chemical Physics*
715 15(20), 7690-7695.

716 Lee, S.H., Jung, C.H., Shon, J.S., Chung, H., 2000. Separation of palladium from a simulated
717 radioactive liquid waste by precipitation using ascorbic acid. *Separation Science and*
718 *Technology* 35(3), 411-420.

719 Li, W., Shi, C., Zhou, A., He, X., Sun, Y., Zhang, J., 2017. A positively charged composite
720 nanofiltration membrane modified by EDTA for LiCl/MgCl. *Separation and*
721 *Purification Technology* 186, 233-242.

722 Li, X., Zhang, C., Zhang, S., Li, J., He, B., Cui, Z., 2015a. Preparation and characterization of
723 positively charged polyamide composite nanofiltration hollow fiber membrane for
724 lithium and magnesium separation. *Desalination* 369, 26-36.

725 Li, Y., Zhao, Z., Liu, X., Chen, X., Zhong, M., 2015b. Extraction of lithium from salt lake
726 brine by aluminum-based alloys. *Transactions of Nonferrous Metals Society of China*
727 25(10), 3484-3489.

728 Liu, Zhang, H., Zhang, Y., Cao, D., Zhao, X., 2015. Lithium extraction from seawater by
729 manganese oxide ion sieve MnO₂·0.5 H₂O. *Colloids Surfaces A: Physicochemical*
730 *Engineering Aspects* 468, 280-284.

731 Liu, X., Zhong, M., Chen, X., Zhao, Z., 2018. Separating lithium and magnesium in brine by
732 aluminum-based materials. *Hydrometallurgy* 176, 73-77.

733 Loferski, P.J., 2011. 2010 minerals yearbook: Platinum-group metals. US Department of the
734 Interior, US Geological Survey.

735 MacLean, H., Duchin, F., Hagelücken, C., Halada, K., Kesler, S., Moriguchi, Y., Mueller, D.,
736 Norgate, T., Reuter, M., Van der Voet, E., 2009. Stocks, flows, and prospects of
737 mineral resources. *Linkages of sustainability*.

738 Makanyire, T., Sanchez-Segado, S., Jha, A., 2016. Separation and recovery of critical metal
739 ions using ionic liquids. *Advances in Manufacturing* 4(1), 33-46.

740 Marchetti, P., Jimenez Solomon, M.F., Szekely, G., Livingston, A.G., 2014. Molecular
741 separation with organic solvent nanofiltration: a critical review. *Chemical reviews*
742 114(21), 10735-10806.

743 Martin, G., Rentsch, L., Höck, M., Bertau, M., 2017. Lithium market research—global supply,
744 future demand and price development. *Energy Storage Materials* 6, 171-179.

745 Mazlan, N.M., Peshev, D., Livingston, A.G., 2016. Energy consumption for desalination—A
746 comparison of forward osmosis with reverse osmosis, and the potential for perfect
747 membranes. *Desalination* 377, 138-151.

748 McGovern, R.K., 2014. On the potential of forward osmosis to energetically outperform
749 reverse osmosis desalination. *Journal of Membrane Science* 469, 245-250.

750 Mel'nikov, A., Kononova, O., Ozerova, T., Luk'yanenko, A., 2012. Sorption recovery of
751 platinum (II, IV) from chloride and sulfate-chloride solutions. *Russian Journal of*
752 *Applied Chemistry* 85(10), 1560-1566.

753 Moss, R., Tzimas, E., Kara, H., Willis, P., Kooroshy, J., 2011. Critical metals in strategic
754 energy technologies. JRC-scientific and strategic reports, European Commission Joint
755 Research Centre Institute for Energy and Transport.

756 Moss, R., Tzimas, E., Willis, P., Arendorf, J., Thompson, P., Chapman, A., Morley, N., Sims,
757 E., Bryson, R., Peason, J., 2013. Critical metals in the path towards the
758 decarbonisation of the EU energy sector. Assessing rare metals as supply-chain
759 bottlenecks in low-carbon energy technologies. JRC Report EUR 25994.

760 Mroczek, E., Dedual, G., Graham, D., Bacon, L., 2015. Lithium extraction from Wairakei
761 geothermal fluid using electrodialysis, *Proceedings World Geothermal Congress*. p.
762 2015.

763 Murthy, Z., Choudhary, A., 2011. Application of nanofiltration to treat rare earth element
764 (neodymium) containing water. *Journal of rare earths* 29(10), 974-978.

765 Murthy, Z.V.P., Choudhary, A., 2012. Separation and estimation of nanofiltration membrane
766 transport parameters for cerium and neodymium. *Rare Metals* 31(5), 500.

767 Nie, X.-Y., Sun, S.-Y., Song, X., Yu, J.-G., 2017a. Further investigation into lithium recovery
768 from salt lake brines with different feed characteristics by electrodialysis. *Journal of*
769 *Membrane Science* 530, 185-191.

770 Nie, X.-Y., Sun, S.-Y., Sun, Z., Song, X., Yu, J.-G., 2017b. Ion-fractionation of lithium ions
771 from magnesium ions by electrodialysis using monovalent selective ion-exchange
772 membranes. *Desalination* 403, 128-135.

773 Nikoloski, A.N., Ang, K.-L., Li, D., 2015. Recovery of platinum, palladium and rhodium
774 from acidic chloride leach solution using ion exchange resins. *Hydrometallurgy* 152,
775 20-32.

776 Nishihama, S., Hirai, T., Komasaawa, I., 2003. Advanced liquid–liquid extraction systems for
777 the separation of rare earth ions by combination of conversion of the metal species
778 with chemical reaction. *Journal of Solid State Chemistry* 171(1), 101-108.

779 Nishihama, S., Onishi, K., Yoshizuka, K., 2011. Selective recovery process of lithium from
780 seawater using integrated ion exchange methods. *Solvent Extraction and Ion*
781 *Exchange* 29(3), 421-431.

782 Norgate, T., Haque, N., 2010. Energy and greenhouse gas impacts of mining and mineral
783 processing operations. *Journal of Cleaner Production* 18(3), 266-274.

784 Ogawa, Y., Koibuchi, H., Suto, K., Inoue, C., 2014. Effects of the chemical compositions of
785 Salars de Uyuni and Atacama brines on lithium concentration during evaporation.
786 *Resource Geology* 64(2), 91-101.

787 Paranthaman, M.P., Li, L., Luo, J., Hoke, T., Ucar, H., Moyer, B.A., Harrison, S., 2017.
788 Recovery of lithium from geothermal brine with lithium–aluminum layered double
789 hydroxide chloride sorbents. *Environmental Science and Technology* 51(22), 13481-
790 13486.

791 Park, H., Singhal, N., Jho, E.H., 2015. Lithium sorption properties of HMnO in seawater and
792 wastewater. *Water Research* 87, 320-327.

793 Parsa, N., Moheb, A., Mehrabani-Zeinabad, A., Masigol, M.A., 2015. Recovery of lithium
794 ions from sodium-contaminated lithium bromide solution by using electro dialysis
795 process. *Chemical Engineering Research and Design* 98, 81-88.

796 Pathak, A.K., Khan, M., Gschneidner Jr, K.A., McCallum, R.W., Zhou, L., Sun, K., Dennis,
797 K.W., Zhou, C., Pinkerton, F.E., Kramer, M.J., 2015. Cerium: an unlikely
798 replacement of dysprosium in high performance Nd–Fe–B permanent magnets.
799 *Advanced Materials* 27(16), 2663-2667.

800 Pavel, C.C., Lacal-Arántegui, R., Marmier, A., Schöler, D., Tzimas, E., Buchert, M., Jenseit,
801 W., Blagoeva, D., 2017. Substitution strategies for reducing the use of rare earths in
802 wind turbines. *Resources Policy* 52, 349-357.

803 Pavel, C.C., Marmier, A., Tzimas, E., Schleicher, T., Schöler, D., Buchert, M., Blagoeva, D.,
804 2016. Critical raw materials in lighting applications: Substitution opportunities and
805 implication on their demand. *Physica Status Solidi* 213(11), 2937-2946.

806 Pelly, I., 1978. Recovery of lithium from Dead Sea brines. *Journal of Applied Chemistry and*
807 *Biotechnology* 28(7), 469-474.

808 Peng, L., Liu, G.-F., Chen, D.-L., Cheng, S.-Y., Ning, T., 2009. Adsorption properties of Ag
809 (I), Au (III), Pd (II) and Pt (IV) ions on commercial 717 anion-exchange resin.
810 *Transactions of Nonferrous Metals Society of China* 19(6), 1509-1513.

811 Perez, J.P.H., Folens, K., Leus, K., Vanhaecke, F., Van Der Voort, P., Du Laing, G., 2019.
812 Progress in hydrometallurgical technologies to recover critical raw materials and
813 precious metals from low-concentrated streams. *Resources, Conservation and*
814 *Recycling* 142, 177-188.

815 Phetla, T., Muzenda, E., Belaid, M., 2010. A Study of the Variables in the Optimisation of a
816 Platinum Precipitation Process. *World Academy of Science, Engineering and*
817 *Technology* 45, 248-254.

818 Pramanik, B.K., Asif, M.B., Kentish, S., Nghiem, L.D., Hai, F.I., 2019. Lithium enrichment
819 from a simulated salt lake brine using an integrated nanofiltration-membrane
820 distillation process. *Journal of Environmental Chemical Engineering*, 103395.

821 Quist-Jensen, C., Macedonio, F., Drioli, E., 2016. Membrane crystallization for salts recovery
822 from brine-an experimental and theoretical analysis. *Desalination and Water*
823 *Treatment* 57(16), 7593-7603.

824 Quist-Jensen, C.A., Macedonio, F., Drioli, E., 2016. Integrated Membrane Desalination
825 Systems with Membrane Crystallization Units for Resource Recovery: A New
826 Approach for Mining from the Sea. *Crystals* 6(4), 36.

827 Rabie, K., 2007. A group separation and purification of Sm, Eu and Gd from Egyptian beach
828 monazite mineral using solvent extraction. *Hydrometallurgy* 85(2), 81-86.

829 Reddy, B.R., Raju, B., Lee, J.Y., Park, H.K., 2010. Process for the separation and recovery of
830 palladium and platinum from spent automobile catalyst leach liquor using LIX 84I
831 and Alamine 336. *Journal of Hazardous Materials* 180(1-3), 253-258.

832 Roskill, 2015. *Rare earths: market outlook to 2020*, 15th Edition ed, Roskill, London.

833 Safarzadeh, M.S., Horton, M., Van Rythoven, A.D., 2018. Review of recovery of platinum
834 group metals from copper leach residues and other resources. *Mineral Processing and*
835 *Extractive Metallurgy Review* 39(1), 1-17.

836 Saito, T., Sato, H., Motegi, T., 2006. Recovery of rare earths from sludges containing rare-
837 earth elements. *Journal of Alloys and Compounds* 425(1), 145-147.

838 Shahmansouri, A., Min, J., Jin, L., Bellona, C., 2015. Feasibility of extracting valuable
839 minerals from desalination concentrate: a comprehensive literature review. *Journal of*
840 *Cleaner Production* 100, 4-16.

841 Shi, C., Jing, Y., Jia, Y., 2016. Solvent extraction of lithium ions by tri-n-butyl phosphate
842 using a room temperature ionic liquid. *Journal of Molecular Liquids* 215, 640-646.

843 Shi, D., Li, J., Zhang, B., Nie, F., Zeng, Z., Li, L., 2013. Process study on N523-TBP-
844 sulfonated kerosene extraction system for extraction of lithium from brine saturated
845 by magnesium chloride. *Journal of Salt Lake Research* 21(2), 52-57.

846 Shimojo, K., Kurahashi, K., Naganawa, H., 2008. Extraction behavior of lanthanides using a
847 diglycolamide derivative TODGA in ionic liquids. *Dalton Transactions*(37), 5083-
848 5088.

849 Singh, D., Kotekar, M., Singh, H., 2008. Development of a solvent extraction process for
850 production of nuclear grade dysprosium oxide from a crude concentrate. *Desalination*
851 232(1), 49-58.

852 Sitando, O., Crouse, P.L., 2012. Processing of a Zimbabwean petalite to obtain lithium
853 carbonate. *International Journal of Mineral Processing* 102, 45-50.

854 Skirrow, R.G., Huston, D.L., Mernagh, T.P., Thorne, J.P., Dulfer, H., Senior, A., 2013.
855 Critical commodities for a high-tech world: Australia's potential to supply global
856 demand. *Geoscience Australia*, Canberra.

857 Somrani, A., Hamzaoui, A., Pontie, M., 2013. Study on lithium separation from salt lake
858 brines by nanofiltration (NF) and low pressure reverse osmosis (LPRO). *Desalination*
859 317, 184-192.

860 Song, J.F., Nghiem, L.D., Li, X.-M., He, T., 2017. Lithium extraction from Chinese salt-lake
861 brines: opportunities, challenges, and future outlook. *Environmental Science: Water*
862 *Research and Technology*.

863 Stull, D.P., 2016. Environmentally friendly economical sequestration of rare earth metals
864 from geothermal waters. Tusaar Corp., Lafayette, CO (United States).

865 Sun, P., Lee, J., Lee, M., 2012. Separation of platinum (IV) and rhodium (III) from acidic
866 chloride solution by ion exchange with anion resins. *Hydrometallurgy* 113, 200-204.

867 Sun, S.-Y., Cai, L.-J., Nie, X.-Y., Song, X., Yu, J.-G., 2015. Separation of magnesium and
868 lithium from brine using a Desal nanofiltration membrane. *Journal of Water Process*
869 *Engineering* 7, 210-217.

870 Székely, G., Bandarra, J., Heggie, W., Sellergren, B., Ferreira, F.C., 2012. A hybrid approach
871 to reach stringent low genotoxic impurity contents in active pharmaceutical
872 ingredients: Combining molecularly imprinted polymers and organic solvent
873 nanofiltration for removal of 1, 3-diisopropylurea. *Separation and Purification*
874 *Technology* 86, 79-87.

875 Tanskanen, P., 2013. Management and recycling of electronic waste. *Acta Materialia* 61(3),
876 1001-1011.

877 Teat, S., 2012. *Industrial Symbiosis Kawerau – Minerals Background Study*, 1-6.

878 Teske, S., Florin, N., Dominish, E., Giurco, D., 2016. Renewable energy and deep sea
879 mining: supply, demand and scenarios. Report prepared by ISF for JM Kaplan Fund,
880 *Oceans* 5.

881 Tharumarajah, R., Koltun, P., 2011. Cradle to gate assessment of environmental impact of
882 rare earth metals, *Proceedings of the 7th Australian Conference on Life Cycle*
883 *Assessment*, Melbourne, Australia. pp. 9-10.

884 Thormann, L., Buchspies, B., Mbohwa, C., Kaltschmitt, M., 2017. PGE production in
885 Southern Africa, part I: Production and market trends. *Minerals* 7(11), 224.

886 Timms, B.V., 2005. Salt lakes in Australia: present problems and prognosis for the future.
887 *Hydrobiologia* 552(1), 1-15.

888 USGS, 2016. Mineral Commodity Summaries 2016, in: Survey, U.S.G. (Ed.). Government
889 Printing Office.

890 USGS, 2019. Mineral Commodity Summaries , United State Geological Survey, Government
891 Printing Office.

892 Van der Bruggen, B., Mänttari, M., Nyström, M., 2008. Drawbacks of applying nanofiltration
893 and how to avoid them: a review. *Separation and Purification Technology* 63(2), 251-
894 263.

895 Vandezande, P., Gevers, L.E., Vankelecom, I.F., 2008. Solvent resistant nanofiltration:
896 separating on a molecular level. *Chemical Society Reviews* 37(2), 365-405.

897 Virolainen, S., Fini, M.F., Miettinen, V., Laitinen, A., Haapalainen, M., Sainio, T., 2016.
898 Removal of calcium and magnesium from lithium brine concentrate via continuous
899 counter-current solvent extraction. *Hydrometallurgy* 162, 9-15.

900 Wang, X.-H., Zheng, S.-L., Xu, H.-B., Zhang, Y., 2010. Dissolution behaviors of Ta₂O₅,
901 Nb₂O₅ and their mixture in KOH and H₂O system. *Transactions of Nonferrous
902 Metals Society of China* 20(10), 2006-2011.

903 Wang, Y., Liao, W., Li, D., 2011. A solvent extraction process with mixture of CA12 and
904 Cyanex272 for the preparation of high purity yttrium oxide from rare earth ores.
905 *Separation and Purification Technology* 82, 197-201.

906 Wei, M.S.J.I.T.G.R.S., 1982. Potential for recovery of by-products from spent geothermal
907 fluids. 6.

908 Wen, X., Ma, P., Zhu, C., He, Q., Deng, X., 2006. Preliminary study on recovering lithium
909 chloride from lithium-containing waters by nanofiltration. *Separation and Purification*
910 *Technology* 49(3), 230-236.

911 Wittstock, R., Pehlken, A., Wark, M., 2016. Challenges in Automotive Fuel Cells Recycling.
912 *Recycling* 1(3), 343-364.

913 Xiang, W., Liang, S., Zhou, Z., Qin, W., Fei, W., 2016. Extraction of lithium from salt lake
914 brine containing borate anion and high concentration of magnesium. *Hydrometallurgy*
915 166, 9-15.

916 Xing, L., Song, J., Li, Z., Liu, J., Huang, T., Dou, P., Chen, Y., Li, X.-M., He, T., 2016.
917 Solvent stable nanoporous poly (ethylene-co-vinyl alcohol) barrier membranes for
918 liquid-liquid extraction of lithium from a salt lake brine. *Journal of Membrane*
919 *Science* 520, 596-606.

920 Xiong, C., Xinyi, C., Caiping, Y., 2011. Enhanced adsorption behavior of Nd (III) onto
921 D113-III resin from aqueous solution. *Journal of Rare Earths* 29(10), 979-985.

922 Yahorava, V., Kotze, M., 2014. Ion exchange technology for the efficient recovery of
923 precious metals from waste and low-grade streams. *Journal of the Southern African*
924 *Institute of Mining and Metallurgy* 114(2), 173-181.

925 Yang, F., Chen, S., Shi, C., Xue, F., Zhang, X., Ju, S., Xing, W., 2018. A facile synthesis of
926 hexagonal spinel λ -MnO₂ ion-sieves for highly selective Li⁺ adsorption. *Processes*
927 6(5), 59.

928 Yang, X.J., Lin, A., Li, X.-L., Wu, Y., Zhou, W., Chen, Z., 2013. China's ion-adsorption rare
929 earth resources, mining consequences and preservation. *Environmental Development*
930 8, 131-136.

931 Yi, D., Xiao, L., Wang, B., Tian, Z., Zhu, B., Yu, H., 2018. Method for quickly extracting
932 lithium carbonate from saline lake water. Google Patents.

933 Zandevakili, S., Ranjbar, M., Ehteshamzadeh, M., 2014. Recovery of lithium from Urmia
934 Lake by a nanostructure MnO₂ ion sieve. *Hydrometallurgy* 149, 148-152.

935 Zhang, H.-Z., Xu, Z.-L., Ding, H., Tang, Y.-J., 2017. Positively charged capillary
936 nanofiltration membrane with high rejection for Mg²⁺ and Ca²⁺ and good separation
937 for Mg²⁺ and Li⁺. *Desalination* 420, 158-166.

938 Zhang, J., Dow, N., Duke, M., Ostarcevic, E., Gray, S., 2010. Identification of material and
939 physical features of membrane distillation membranes for high performance
940 desalination. *Journal of Membrane Science* 349(1-2), 295-303.

941 Zhang, J., Everson, M.P., Wallington, T.J., Field III, F.R., Roth, R., Kirchain, R.E., 2016.
942 Assessing economic modulation of future critical materials use: the case of
943 automotive-related platinum group metals. *Environmental Science and Technology*
944 50(14), 7687-7695.

945 Zhao, Z., Si, X., Liu, X., He, L., Liang, X., 2013. Li extraction from high Mg/Li ratio brine
946 with LiFePO₄/FePO₄ as electrode materials. *Hydrometallurgy* 133, 75-83.

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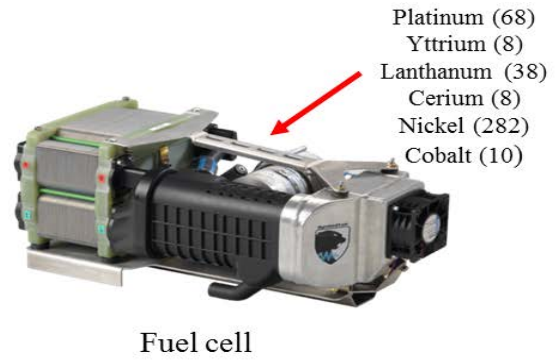
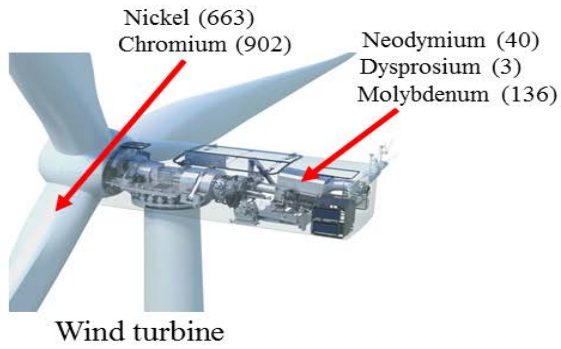
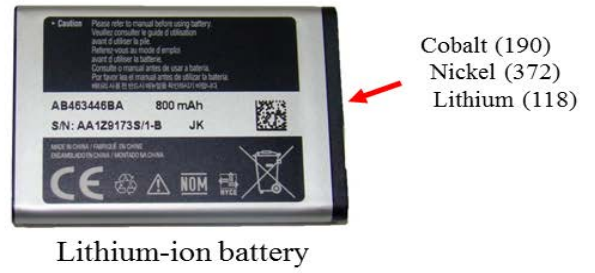
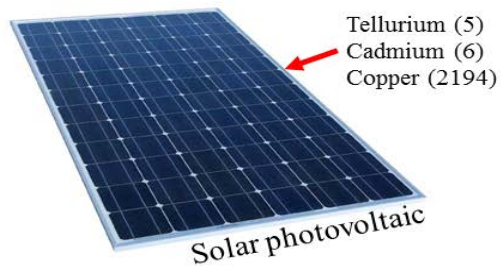


Figure 1: Examples of strategically important element demand (kg/MW) in the renewable energy industry (Moss et al., 2011; Moss et al., 2013; Teske et al., 2016).

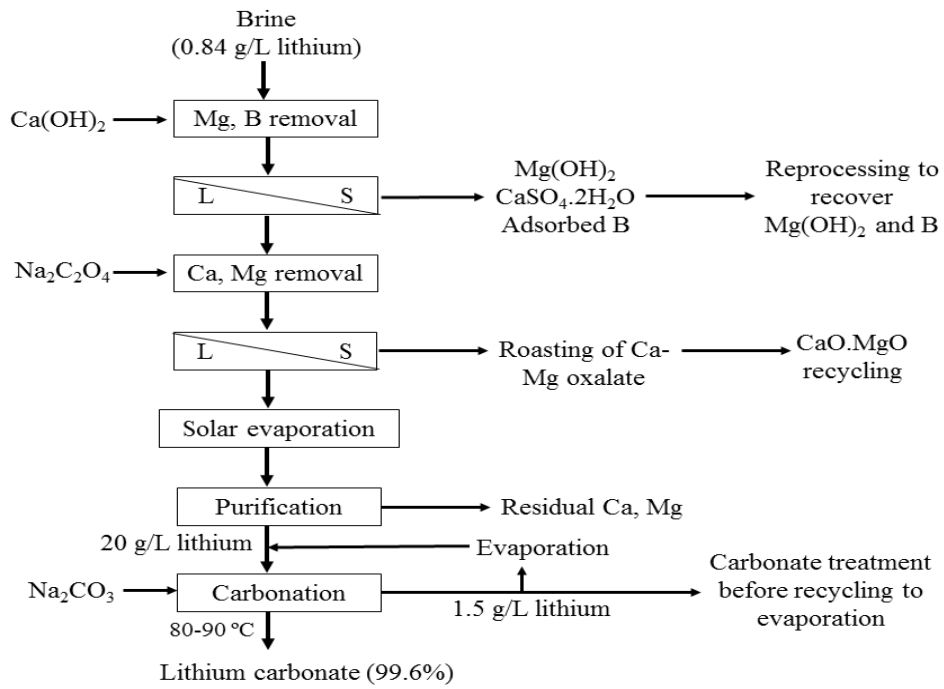


Figure 2: Flowsheet for the recovery of lithium as carbonate from Uyuni Salar brine, Bolivia

(An et al., 2012)

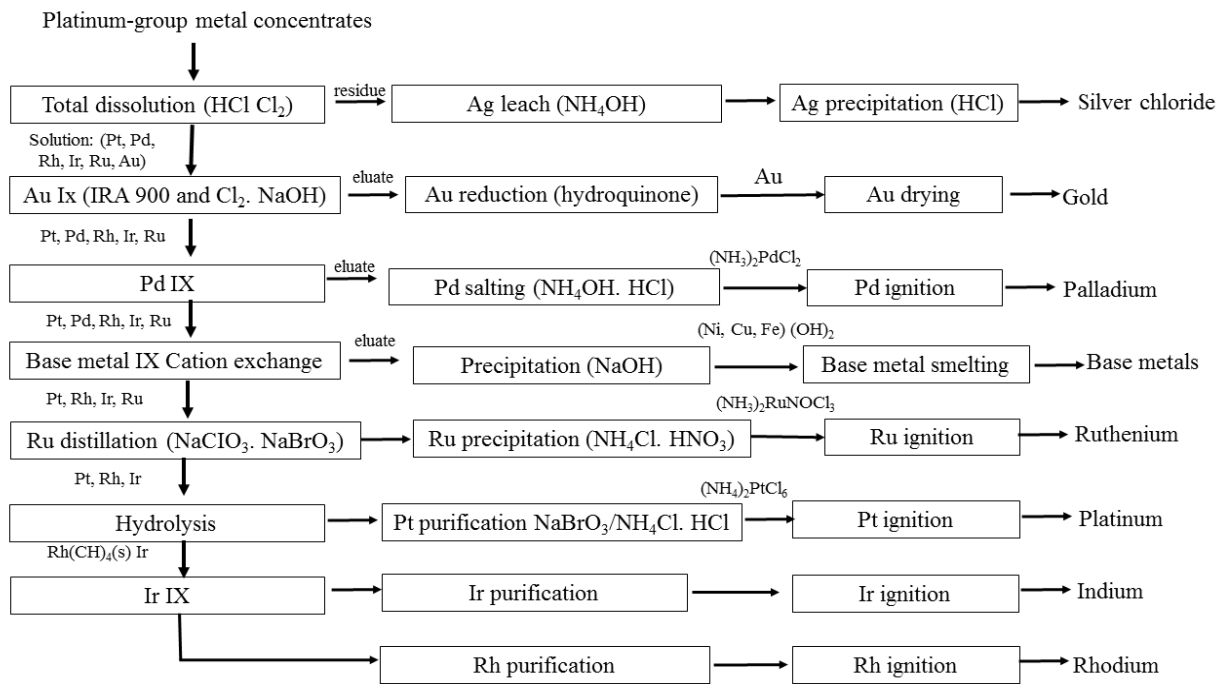


Figure 3: Platinum-group metals and other precious metal recovery using ion exchange process at Springs, South Africa (Crundwell, 2011).

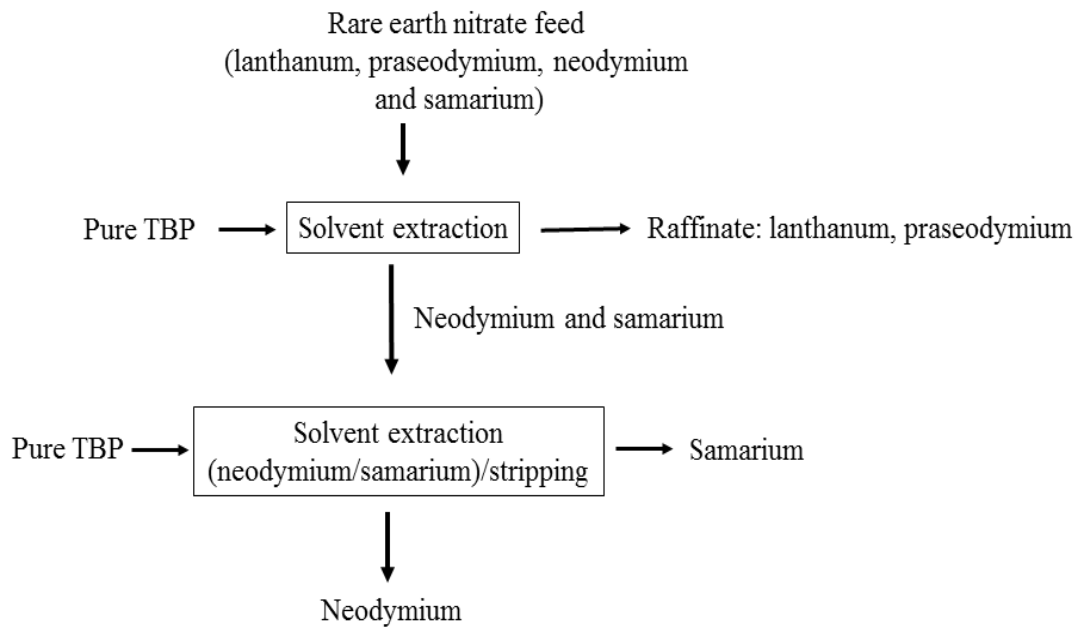


Figure 4: Flowsheet of rare earth separations by solvent extraction at Alwaye Plant of Indian Rare Earths Ltd, India (Krishnamurthy & Gupta, 2004).

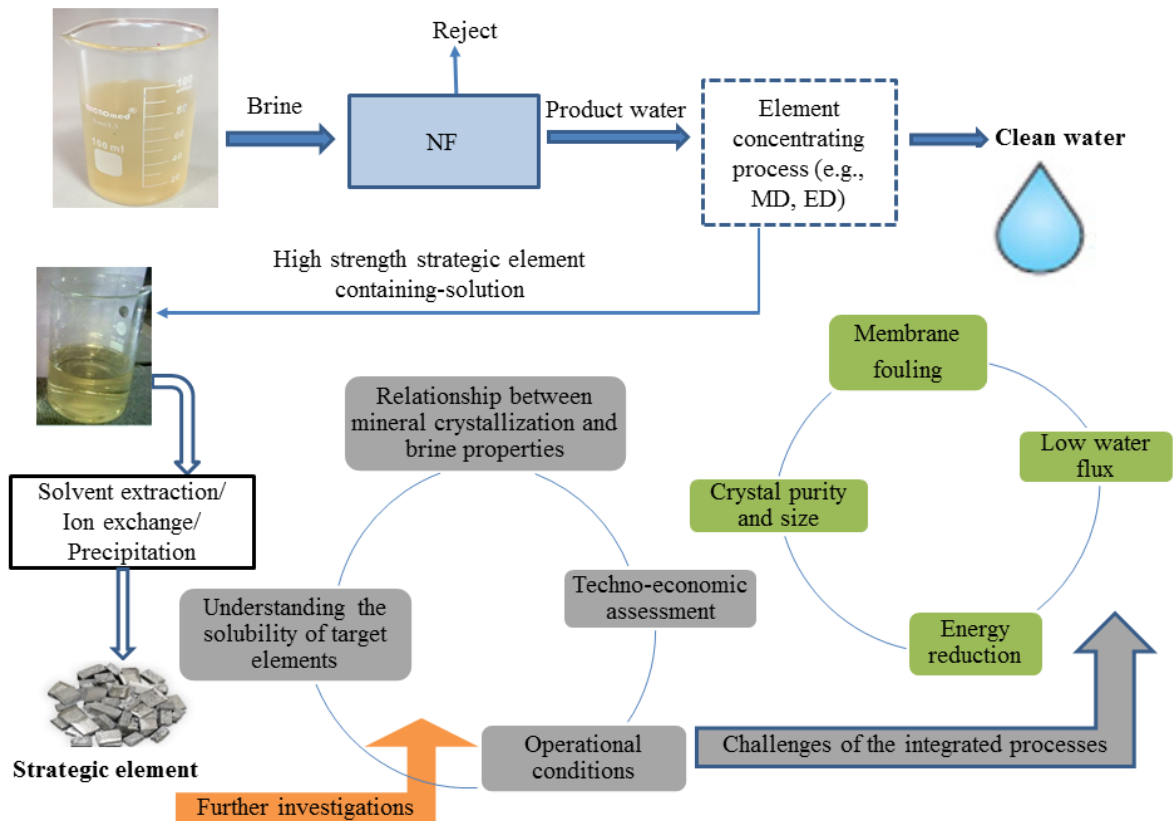


Figure 5. A roadmap of an integrated membrane and metal separation process for strategically important elements and clean water recovery

Table 1: The production, resources and reserve status of some prospective elements in Australia and their application for different purposes (Hoenderdaal et al., 2013; Skirrow et al., 2013; USGS, 2016)

Metals	Production		Resource		Reserve		Applications
	Mass (kt)	Global share (%)	Mass (kt)	Global share (%)	Mass (kt)	Global share (%)	
Cerium	7.6	8	1481	3	NA	2.8	Catalytic converters in cars, hybrid vehicles, television faceplates, silicon microprocessors.
Lanthanum	4.6	8	742	3	NA	2.8	Cracking catalysts in petroleum refining, camera lenses, battery electrodes, hydrogen storage, x-ray films.
Dysprosium	0.115	4.8	NA	NA	8	0.64	Motors or generators, wind turbines, and electrical vehicles, hard disk devices, transducers.
Yttrium	NA	NA	100	18.5	NA	NA	Microwave generators, televisions and computer screens, ceramics, superconductors.
Platinum	0.22	0.11	2.35	1.2	NA	NA	Catalytic converters, electronic application, fuel cells
Palladium	0.22	0.11	2.35	1.1	NA	NA	
Lithium	11.7	34	1006	8	1500	10.7	Electric batteries, cordless devices, ceramics, glass.

NA: Not available

Table 2: Composition of lithium in salt lake brine around the world

Source	Status	Concentration (g/L)							Impurities	References
		Li ⁺	Mg ²⁺	Na ⁺	Ca ²⁺	K ⁺	B	SO ₄ ²⁻		
Atacama Salar Brine, Chile	Full-scale	3.02	17.6	61.9	0.41	28.2	1.72	37.9	Na ⁺ , K ⁺ , Mg ²⁺	Ogawa et al. (2014)
Uyuni Salar Brine, Bolivia		0.84	16.7	105.4	3.33	15.7	0.7	21.3	Na ⁺ , K ⁺ , B	An et al. (2012)
East Taijinar, China	Pilot-scale	0.14	5.64	117.03	0.43	3.79	-	-	Na ⁺ , K ⁺ ,	Sun et al. (2015)
West Taijinar, China		0.26	15.36	102.4	0.19	8.44	-	-	Na ⁺ , K ⁺ ,	Sun et al. (2015)
Chott Djerid Salt Lake, Tunisia		0.06	3.4	80	1.6	5.6	-	6.7	Na ⁺ , Ca ²⁺ , Mg ²⁺	Somrani et al. (2013)
Longmucuo, China		1.21	89.5	-	-	-	-	-	-	Song et al. (2017)
North Arm Salt Lake, USA	Lab-scale	0.04	9.38	100.8	0.35	5.5	0.03	19.7	Na ⁺	Bush et al. (2016)
Salt lake brine, China		0.35	113.7	-	-	-	-	-	Mg ²⁺	Xiang et al. (2016)
Salt lake brine		0.15	8.88	2.69	-	-	-	-	-	Ji et al. (2017)
Geothermal brine		0.01	-	0.11	-	0.16	0.03	-	K ⁺	Mroczek et al. (2015)
Synthetic brine		0.15	63.8	0.414	0.02	0.20	-	-	Mg ²⁺	Nie et al. (2017b)

Table 3: Examples of strategically important elements separation using membrane processes.

Technology	Source	Concentrate (%)	Separated elements	Water recovery (%)	References
NF	Salt lake brine	NA	Lithium Lithium Lithium	NA	Wen et al. (2006) Somrani et al. (2013) Sun et al. (2015)
	Synthetic wastewater	NA	Lithium Cerium, Neodymium Neodymium	NA	Zhang et al. (2017) Murthy and Choudhary (2012) Murthy and Choudhary (2011)
RO	Salt lake brine	NA	Lithium	NA	Somrani et al. (2013)
MD	Seawater Brine	500	NA	80	Duong et al. (2015)
	Synthetic brine	NA	Lithium	NA	Quist-Jensen et al. (2016b)
	Salt lake brine	NA	Lithium	NA	Zhou (2017)
ED	Salt lake brine	NA	Lithium	NA	Liu et al. (2015) Jiang et al. (2014) Ji et al. (2017)
	Geothermal brine	NA	Lithium	NA	Mroczek et al. (2015)
	Synthetic brine	NA	Lithium	NA	Nie et al. (2017b) Bunani et al. (2017) Parsa et al. (2015)

NA= Data not available