

Mining valuable minerals from seawater: a critical review

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Water impact

Methods of extracting valuable minerals from seawater and seawater brines generated in desalination plants are critically reviewed in this paper. Also, ways are suggested to overcome the limitations and challenges associated with the extraction methods.

Abstract

Seawater contains large quantities of valuable minerals, some of which are very scarce and expensive in their land-based form. However, only a few minerals, the ones in high concentrations, are currently mined from the sea. Due to recent problems associated with land-based mining industries as a result of depletion of high-grade ores, sustainable water and energy demand and environmental issues, seawater mining is becoming an attractive option. This paper presents a comprehensive and critical review of the current methods of extracting valuable minerals from seawater and seawater brines generated in desalination plants, and suggests ways to overcome some of the limitations and challenges associated with the extraction process. The extraction methods discussed are solar evaporation, electrodialysis (ED), membrane distillation crystallisation (MDC), and adsorption/desorption.

28 **1. Introduction**

29 Oceans and seas cover nearly three-quarters of the earth's surface¹ and contain about 1.3×10^{18}
30 tonnes of water.² They are composed of 96.7% water and 3.3% dissolved salts.^{3,4} This
31 concentration of salts works out to be approximately 5×10^{16} tonnes of salts which constitutes
32 much more than most minerals that are available as land-based reserves and annually mined
33 from lands (**Fig. 1**).⁵ Almost all elements in the periodic table can be found in seawater although
34 many are at very low concentrations.⁴⁻⁷ The main ions which make up 99.9% of the salts in
35 seawater in decreasing order are: $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$, $\text{K}^+ > \text{Sr}^{2+}$ (for cations) and $\text{Cl}^- > \text{SO}_4^{2-} >$
36 $\text{HCO}_3^- > \text{Br}^- > \text{BO}_3^{2-} > \text{F}^-$ (for anions).⁶

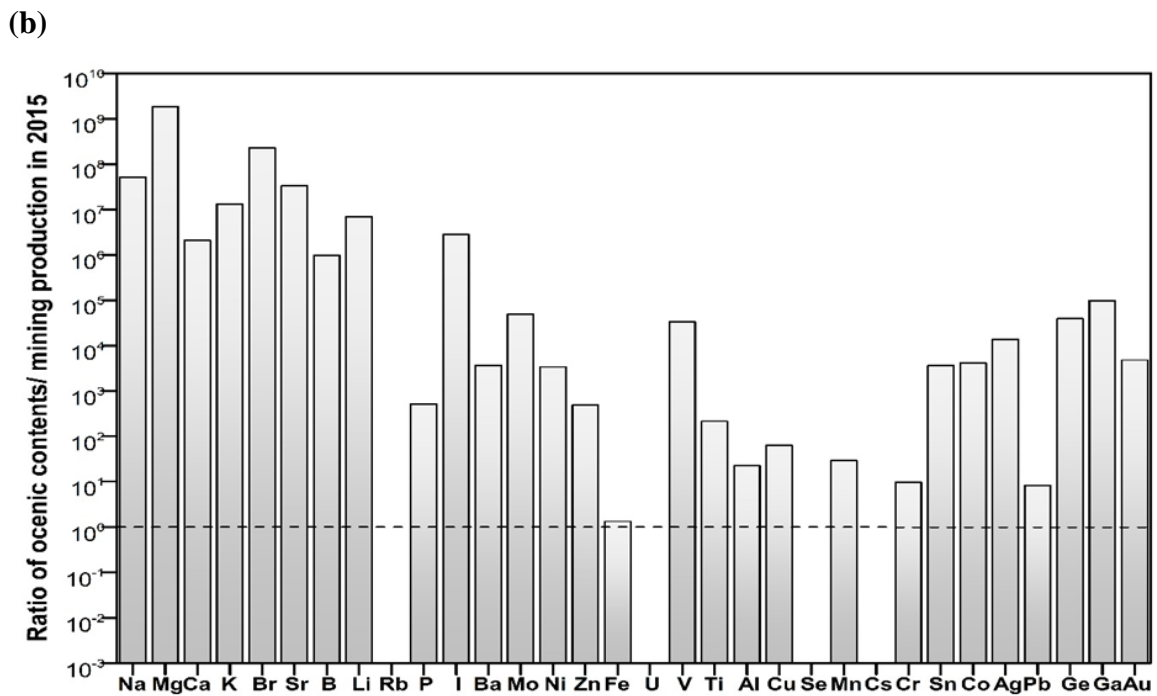
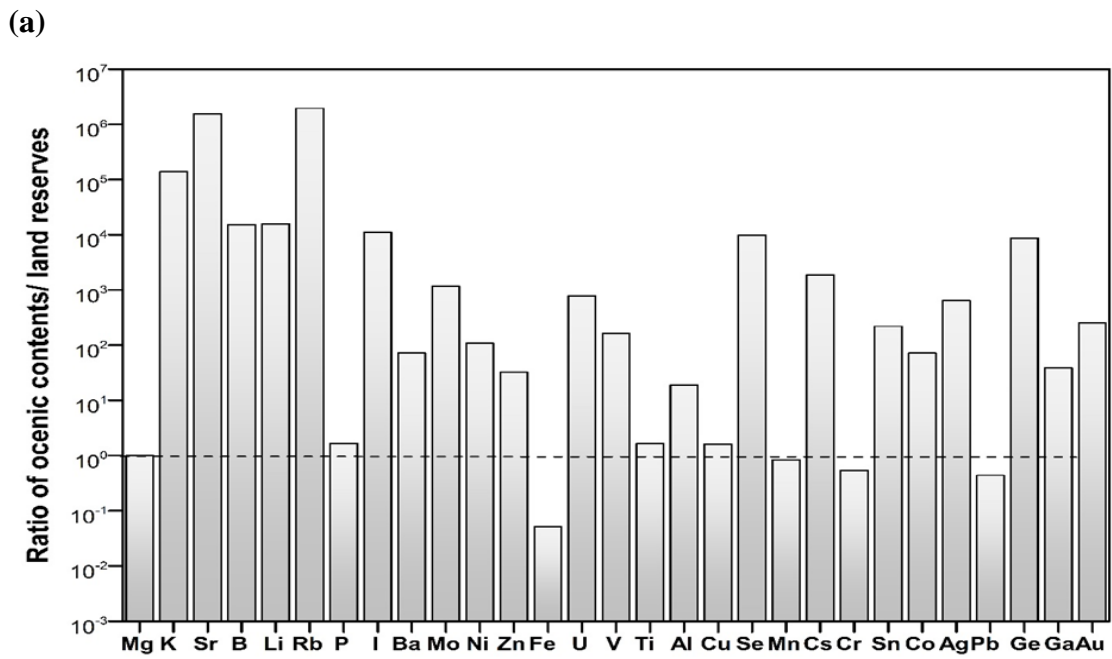
37 Minerals have been mined from seawater since ancient times. It has been recorded that
38 common salt (NaCl) was extracted even before 2000 BC in China and also in the Old Testament
39 period.^{1,3} Currently the four most concentrated metals - Na, Mg, Ca and K - are commercially
40 extracted in the form of Cl^- , SO_4^{2-} , and CO_3^{2-} .² Mg is also extracted as MgO.^{1,7} Mineral elements
41 with low concentrations have not been recovered from seawater because their market values
42 are much lower than the capital and operational costs of extraction.

43 However, this situation has changed in recent times with the presence of many seawater
44 desalination plants. Rapid population growth and industrialisation have drastically increased
45 the demand for fresh water. Although abundance of seawater is available, the dissolved salts
46 concentration of 33-37 g/L in seawater is too high for drinking, industry or agriculture and for
47 this reason the water needs to be desalinated. This has resulted in the emergence of desalination
48 plants in many parts of the world to produce fresh water mainly using seawater reverse osmosis
49 (RO) technology.⁸

50 During the seawater extraction process, many minerals occur as by-products in the
51 exhausted brine. If these minerals are economically recovered, not only would the water
52 production cost decline, but also the pollution problems associated with the brine disposal
53 would to some appreciable extent abate. For example, it was estimated that the market value
54 of Na, Ca, Mg, and K, if they are successfully extracted from the rejected brine of a desalination
55 plant in Saudi Arabia, would be approximately \$US18 billion per year.⁹

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59 **Fig. 1** Estimated ratio of the amounts of minerals in oceans to (a) the land reserves of minerals⁵
 60 and (b) amounts of minerals mined in 2015⁵. Oceanic abundance is calculated assuming a total
 61 ocean volume of $1.3 \times 10^9 \text{ km}^3$ ($1.3 \times 10^{18} \text{ tons}$)² and ocean mineral concentrations taken from
 62 *Anthoni*.⁶

63

64 Overall, many situations in present times have arisen that favour the commercial mining
65 of minerals from the sea. They are: ^{2,3,7,10}

- 66 1. Increased demand for clean water in many countries has necessitated cost reductions in
67 desalination. The cost of desalination can fall further if additional income is able to be
68 generated from the recovery of valuable minerals in the brine concentrate by-product
69 of desalination.
- 70 2. Developing nations can obtain affordably priced fertilisers containing plant nutrients
71 (K, Mg, Ca, S, and B) from seawater compared to commercial fertilisers available on
72 the market.
- 73 3. The availability of high grade mineral ore deposits located on lands that can be easily
74 mined is depleting steadily, leaving more of the low grade ores found deeper in the
75 lands and socio-economically sensitive areas. This has increased the cost of mining. As
76 the ore grade degrades, the production costs (water and energy costs) increase. Some
77 countries have restricted the mining industry's operations to protect their scarce water
78 resources. The advantage of seawater mining of minerals is that seawater is
79 homogeneous and there is no mineral grade difference as there is in the land. Energy
80 intensive processes of extraction and beneficiation are not required for mining minerals
81 from seawater.
- 82 4. Land-based mining results in environmental problems that are a consequence of wastes
83 generated and pose health hazards to miners. Strict environmental regulations that may
84 be imposed by governments in the future can restrict land mining.
- 85 5. New advances in extraction methods can be applied to mining of valuable minerals
86 from seawater.

87

88 Although methods of mining valuable minerals from seawater and seawater
89 desalination brine have been reported in the literature on an individual mineral basis, to our
90 knowledge, in recent times, only the study by *Shahmansouri et al.* reviewed the extraction
91 methods of a large number of minerals in a single paper.¹¹ However, the emphasis in their paper
92 was mainly on cost-benefit analysis for individual minerals and not between different methods
93 of mineral extraction. Another review of mining minerals from seawater by *Bardi* considered
94 the feasibility of extraction of minerals on the basis of the energy needed and concluded that
95 the amounts of minerals in the sea were much more than those in the land reserves.²

96 Nevertheless, with reference to most minerals, especially those which occur at low
97 concentrations, the energy requirement for their extraction was reported to be very high. This
98 was based on the reasoning that: firstly, the total volume of water that needed to be processed
99 to meet the annual requirement of minerals in relation to the total volume of water desalinated
100 at that time (2007) (1.6×10^{10} tonnes/year) was high; and secondly, it involved enormous
101 amounts of energy which was expensive. However, the desalination capacity in the world has
102 rapidly increased in the last decade because of the increase in clean water demand and a marked
103 reduction in desalination cost due to significant advances in the reverse osmosis technology.¹²
104 The cost of desalinated water has fallen below US \$ 0.50/m³ for a large-scale seawater
105 desalination plant in 2010 compared to nearly US \$10/m³ 50 years ago.¹² It was estimated that,
106 by 2030, the world production of desalinated water would grow to reach levels up to 345×10^6
107 tonnes/day or 1.2×10^{11} tonnes/year and continue to grow thereafter.^{13,14} Therefore, extraction
108 of some minerals that were not economical in the past would become economical in the near
109 future. Also, while the process is energy intensive and expensive for extracting minerals from
110 seawater, it might be economically feasible to extract minerals from nanofiltration (NF) and
111 RO brines where the minerals concentrations are roughly twice that of seawater and in doing
112 so the waste stream from NF and RO can be transformed into resources.

113 The objective of this paper is to highlight the mining of potentially profitable minerals
114 from seawater and seawater brine and critically review the current status of the methods of
115 mining potentially valuable minerals from seawater and seawater brine. The paper compares
116 the methods of extraction of the minerals in terms of the chemical feasibility of extraction by
117 grouping the minerals under each method. Strategies are suggested here to overcome some of
118 the limitations and challenges associated with the extraction process.

119

120 **2. Potentially profitable minerals from seawater and seawater brine**

121 The economic gains obtained by extracting minerals depend mainly on the concentration of
122 minerals in seawater and the market price of these minerals. It rises with an increase in the
123 concentration and the market price of minerals (**Fig. 2**). In this respect, Na, Ca, Mg, K, Li, Sr,
124 Br, B and U are potentially attractive for extraction, provided suitable methods of extraction
125 can be found that are more economical than mining them from lands. A very similar list of
126 minerals was reported by *Shahmansouri et al.* as being potentially profitable for mining from
127 desalination concentrate.¹¹ The minerals that can be profitably extracted from seawater or

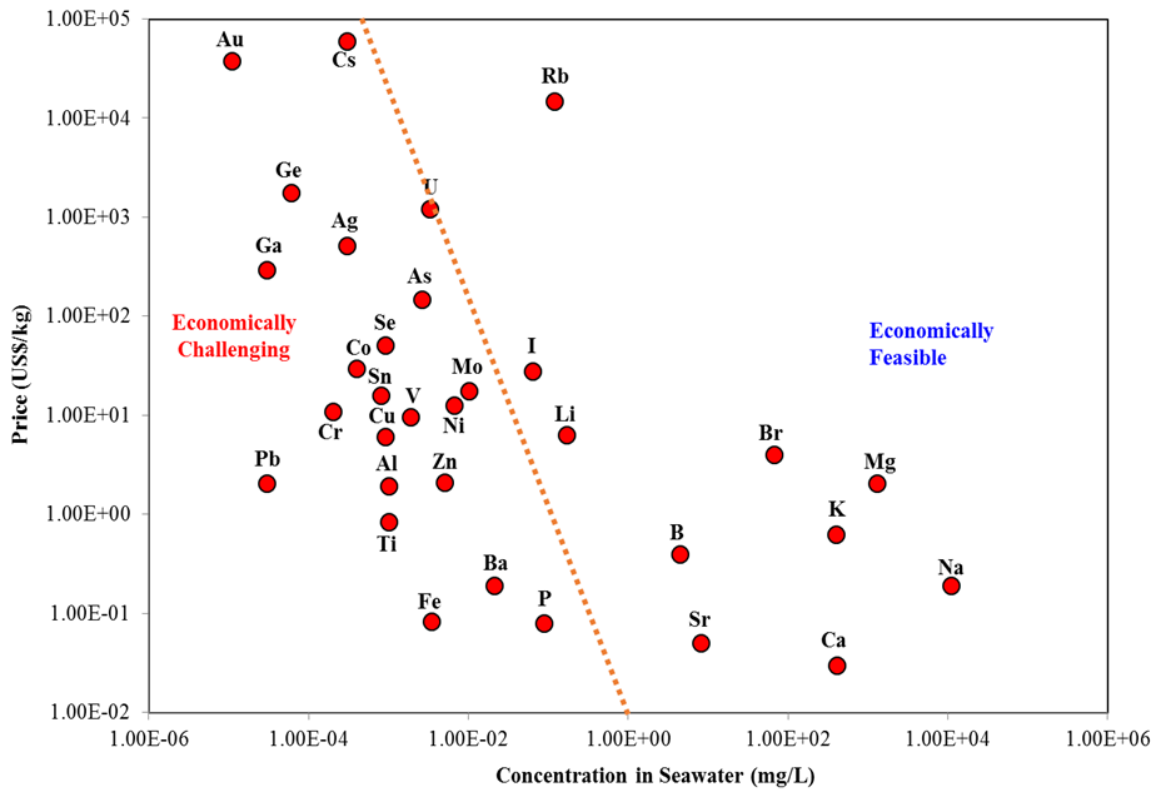
128 seawater brine have a great demand for using them in agriculture, industry, environmental
129 remediation and medicine (**Table 1**).

130 **Table 2** presents a list of methods of mining valuable minerals on an individual mineral
131 basis such as solar evaporation ponds, lime softening treatment, electro dialysis (ED),
132 membrane distillation (MD)/membrane distillation crystallisation (MDC), as well as
133 adsorption/desorption/crystallisation. Details of these methods will be discussed in the next
134 section of this paper.

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140 **Fig. 2** Screening of minerals that can be economically extracted from seawater based on current
 141 market prices and seawater concentrations of the minerals. All mineral price values are based
 142 on 2015 USGS mineral commodity summaries⁵ except for U where the price was taken from
 143 *Sodaye et al.*¹⁵ Mineral concentrations in seawater was taken from *Anthoni*⁶

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147 **Table 1** Major uses of valuable minerals that can be economically mined from seawater and
148 seawater brines.^{3,16}

Mineral	Major uses
Na (NaCl, Na ₂ CO ₃ , Na ₂ SO ₄)	Food, glass, soap, detergent, textiles, pulp and paper industries, road de-icing
Mg (Mg, MgSO ₄ , MgCO ₃)	Al, steel, chemical and construction industries, fertiliser
Ca (CaCO ₃ , CaSO ₄)	Soil amendment, construction industries, fertiliser
K (KCl, K ₂ SO ₄)	Fertiliser
Br	Fire retardant, agriculture, well-drilling fluids, petroleum additives
B	Glass products, soap and detergents, fire retardants, fertiliser
Sr ¹⁷	Ceramics, glass and pyrotechnics industries, ceramic ferrite magnets, fireworks, phosphorescent pigments, fluorescent lights, Oil and gas industry as drilling mud
Li	Batteries, glass manufacturing, lubricants and greases, pharmaceutical products,
Rb	Fibre optics, lamps, night vision devices, laser technology
U	Nuclear fuel in nuclear power reactor

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151 **Table 2.** Selected references on mining of minerals from seawater and seawater desalination
 152 brines.

Mineral	Source/type of study	Mining method	Ref.
NaCl	Seawater		
	Seawater RO brine (field study)	Solar evaporative ponds	18, 19
	Simulated synthetic RO concentrate (laboratory study)	MD/MDC	7, 20
	Artificial NF retentate solution (laboratory study)	MD/MDC	21
	NF/RO retentate brine (laboratory study)	MD/MDC	22
	Seawater RO brine (laboratory study)	ED /evaporation/crystallisation	23
	Seawater (field study)	ED (17-25 pairs of unit cells) after sand filtration/evaporation	24
	Artificial RO brine (laboratory study)	ED (5 pairs of unit cells) /evaporation/crystallisation in vacuum evaporator	25
	Sea water RO concentrate (pilot plant study)	EDs. Scaling avoided by adding HCl. NaCl concentrate of 280 g/L reached	26
MgSO ₄	Simulated synthetic RO concentrate (laboratory study)	MD/MDC	7, 20
	Artificial NF retentate solution (laboratory study)	MD/MDC	21

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Mineral	Source/type of study	Mining method	Ref.
	NF/RO retentate brine (laboratory study)	MD/MDC	22
MgCO ₃ . 3H ₂ O	Seawater (pilot plant study)	Adsorption on carboxylic cation exchange resin. Desorption of Mg by eluting with Na ₂ CO ₃ , NaHCO ₃ . MgCO ₃ crystals in eluate	27
Mg(OH) ₂	Seawater (field study)	Adding lime or dolomite to seawater after softening the seawater by precipitating carbonates	28, 29
	Seawater (field study)	Adding milk of lime (Ca(OH) ₂) manufactured by calcining oyster shells to seawater	1
	Seawater RO brine (laboratory study)	ED diluate Mg concentrate 5 times higher than seawater Mg. Mg(OH) ₂ precipitated by adding NaOH to diluate	23
MgO	Seawater and brine (laboratory study)	Cofloatation of Ca and Mg as oleates using Na oleate, precipitation of Ca as CaSO ₄ and refloatation to recover Mg oleate which was heated to produce MgO	30
K	Synthetic seawater (laboratory study)	Solution flow through a jacket pipe containing a K ionic sieve membrane reactor made-up of K-selective synthetic zeolite. K was selectively adsorbed in the presence of Na, Ca, Mg.	31, 32
	Seawater (laboratory study)	Batch adsorption by a modified synthetic zeolite W. Selective rapid K adsorption. Very high K/Na selectivity	33
HBr	Seawater (model simulation)	Blowout process: Cl ₂ added to acidified seawater liberates Br ₂ . Air pumped in and SO ₂ added to Br ₂ enriched air to produce HBr liquid	34
Br	Sea water (field study)	Blowout process: Cl ₂ added to acidified seawater liberates Br ₂ . Soda ash (Na ₂ CO ₃) added to bromine to produce Na bromide and bromate which was reacted with acid to produce Br ₂	29, 35
	Seawater RO brine (laboratory study)	ED concentrate was treated with chlorine gas to produce bromine gas.	23
Li	Seawater (laboratory study)	Batch adsorption capacity of a manganese oxide adsorbent was found to be higher than that of several other adsorbents reported in literature	36
	Seawater (laboratory study)	Membrane-type Mn oxide adsorbent to remove Li. Li desorbed by HCl	37

Mineral	Source/type of study	Mining method	Ref.
	Seawater (benchmark-scale plant)	Adsorption on λ -MnO ₂ /desorption separation/vacuum evaporation and precipitation as carbonate	38
	Nylon mesh bags containing adsorbent placed at different depths in the sea for different durations (Field study)	Adsorption on granulated manganese oxide. Bags containing adsorbent placed for different number of days	39
	Seawater and seawater RO retentate (laboratory study)	Adsorption on mixed matrix nanofiber membrane/Mn oxide adsorber in batch, and continuous flow-through membrane permeate system. Regenerated using 0.5 M HCl. Enriched LiCl solution.	40
Rb, Cs	Seawater RO concentrate spiked with metals (laboratory study)	Batch adsorption on <u>Cstreat</u> (potassium cobalt hexacyanoferrate ; no desorption, recovery)	16
	Seawater RO concentrate spiked with 20 mg/L metals (laboratory study)	Column adsorption on <u>Cstreat</u> (potassium cobalt hexacyanoferrate)	41
Rb	Artificial seawater RO concentrate (laboratory study)	Column adsorption and desorption with KCl using organic polymer encapsulated potassium copper hexacyanoferrate, followed by Rb recovery by adsorption on resorcinol formaldehyde ion exchange resin and desorption using HCl	42
Sr	Simulated seawater (laboratory study)	Batch and inflow adsorption on macroporous LTA (synthetic zeolite) monolith. Rapid adsorption with very high adsorption capacity. Desorption not reported	43
	Seawater spiked with Sr (laboratory study)	Batch adsorption on titanate nanotubes after removing Ca as Ca(OH) ₂ because Ca competed with Sr adsorption. Sr desorbed by HCl addition	44
	Seawater spiked with Sr (laboratory study)	Batch adsorption on alginate microsphere. Na, Ca, Mg competed with Sr adsorption. Sr desorption by CaCl ₂	45
U	Adsorbent in nylon mesh bags at different depths in the sea (field study)	Adsorption onto an amidoxime grafted non-woven polyethylene fabric. Bags containing adsorbent placed for different number of days	39

Mineral	Source/type of study	Mining method	Ref.
	Seawater RO concentrate spiked with 20 mg U/L (Laboratory study)	Column adsorption on amidoxime-functionalised Purolite S910 resin	41
	Seawater (field study)	Column adsorption in series and parallel on amidoxime-based polymeric adsorbent. After adsorption for 8 weeks the adsorbent digested with aqua regia to measure adsorbed U. Maximum adsorption capacity 3.3 mg U/g adsorbent	46
	Simulated seawater (laboratory study)	Batch adsorption on polyacrylonitrile/polygorskite composite chemically modified with amidoxime groups. U desorbed by HCl. Regenerated adsorbent fully for 5 cycles. Maximum adsorption at pH 5. Ionic strength had little effect	47
	U spiked synthetic seawater and actual seawater (laboratory study)	Batch adsorption on porous polymer with amidoxime pendant group. Optimum adsorption at pH 6. Adsorbent regenerated fully during 3 cycles. Regenerated adsorbent with Na ₂ CO ₃	48
	Seawater spiked with U (laboratory study)	Batch adsorption on high affinity ligands (diphosphonic acid, phosphonic acid, hydroxypyridinone) installed on high surface area nanostructured materials. Adsorbent fully regenerated in 4 cycles using Na ₂ CO ₃	49
	Seawater (laboratory study: synthetic seawater; field study: natural seawater)	Batch (laboratory) and column (56 days, field) adsorption on high surface area polyethylene fibre adsorbent grafted with amidoxime groups. Effects of grafted group molar ratio, presence of V, Fe, Ca, and Mg studied	50
	U spiked simulated seawater (laboratory study)	Adsorption on electrospun nanofibrous amidoxime-based adsorbent. Desorption with 0.5 M HCl.	51
	U spiked simulated seawater (laboratory study)	Adsorbent with Zr metal-organic framework with orthogonal phosphorylurea groups had Langmuir adsorption capacity at pH 2.5 of 188 mg U/g but capacity at the seawater U concentration is needed	52
B	Seawater (laboratory study)	Adsorption on a B selective resin CRB05 containing N-methyl glucamine functional group and desorption using HCl or H ₂ SO ₄	53

160**Table 2** (continued)

Mineral	Source/type of study	Mining method	Ref.
	Seawater (laboratory study)	Adsorption on a chitosan/ferric hydroxide composite adsorbent. Continuous column experiment with 5 cycles of adsorption/desorption (using 0.01 M NaOH) removed 10.7 mmol B/mol Fe(OH) ₃ from seawater with B concentration of 4.2 mg/L	54

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162

163 **3. Methods of mining**

164 Several methods have been used to mine minerals from seawater as listed in **Table 2**.
165 Recent technology advancements on these methods have led to more promising potential of
166 mining minerals. A detail examination is carried out on the mechanisms, advancements and
167 limitation on four main mining methods of (1) solar or vacuum evaporation, (2) ED, (3)
168 MD/MDC, and (4) adsorption/desorption/crystallisation. In all these methods the mineral
169 concentrations are increased to the level of supersaturation to enable their crystallisation. The
170 first three methods have proven to be suitable only for the recovery of minerals having high
171 concentrations in seawater where the ionic product of the constituent ions of the salt can be
172 easily manipulated to exceed the solubility product of the salt. Minerals which are commonly
173 mined using these methods are NaCl, MgSO₄, Mg(OH)₂, CaCO₃, and Br (**Table 2**). The fourth
174 method is used for minerals which can be selectively adsorbed by specific adsorbents in the
175 presence of other minerals and the adsorbed minerals are quantitatively desorbed and
176 crystallised. Examples of minerals which can be mined by this method are Li, Sr, Rb and U
177 (**Table 2**).

178 The minerals are mined directly from seawater or from the concentrated brine produced
179 as a by-product in the desalination process using ED, RO, NF, and membrane filtration (MF).
180 The brine can be further concentrated by membrane distillation (MD) and salts can be
181 crystallised by an integrated MDC process when the concentrations of the minerals reach the
182 saturation point of crystallisation.^{10,20,22,55} The minerals' concentrations in the brine are 2.5
183 times higher than in the sea water which favours their crystallisation before or after adsorption
184 for further concentration.²⁵ However, the competition from other minerals in the brine for
185 adsorption will also trigger a high reduction in adsorption.

186

187 **3.1 Solar evaporation**

188 **3.1.1 Basic mechanism**

189 This method of recovering minerals from seawater and seawater desalination brine involves
190 natural evaporation of water using the sun's energy and leaving a concentrated salt solution. In
191 turn this leads to salt crystallisation when the saturation points of the salts are reached. This
192 method has been employed for thousands of years to produce common salt from seawater in
193 many parts of the world.^{1,3} It is a simple and effective method that is suitable for arid regions

194 with high evaporative rates and where land is available at low cost and there is no risk of natural
195 underground water contamination from the leakage of minerals. Large land area is required
196 because the evaporation ponds need to be shallow.

197

198 **3.1.2. Extraction of salt from seawater brine**

199 Traditional salt farming in Goa, India has been practiced as a village industry for nearly
200 1500 years by using salterns consisting of three distinct pans (**Fig. 3**).⁵⁶ The first pan called the
201 reservoir pan is used for receiving seawater during tidal influxes and is connected to many
202 evaporator pans (i.e. second set of pans). The third pan known as the crystalliser pan is fed by
203 the evaporator pans. The waters in the respective pans are released from one pan to the other
204 when the salinity level reaches particular values. CaCO_3 starts to precipitate in the reservoir
205 pan and completes its precipitation in the first evaporator pan. In the second evaporator pan,
206 CaSO_4 crystallises in the form of gypsum. NaCl crystallises in the crystalliser pan at the highest
207 salinity. This order of precipitation is the same as that predicted by thermodynamic modelling
208 which showed that the saturation index decreases in this order.⁵⁷

209 The salt works at Trapani in Sicily had a similar pond arrangement as those in Goa. In
210 this salt works, the salt density grows from the initial seawater value of 3.7% to the saturation
211 point of NaCl (25.7%) by evaporation of the water using the sun's energy.⁵⁸ There were four
212 sets of ponds arranged in order of increasing salt concentration (**Fig. 3**). The first set of ponds
213 was called 'cold ponds' with 3.5 Bé (specific gravity, $\text{SG} = 1.45 / (1.45 - ^\circ\text{Bé}) = 1.02$) to 5-6 Bé
214 ($\text{SG} = 1.04$), the second set known as 'driving ponds' having 5-6 Bé ($\text{SG} = 1.04$) to 10-12 Bé,
215 ($\text{SG} = 1.07 - 1.09$) the third set of ponds referred to as 'hot ponds' followed by the last set of
216 ponds where the water reached the saturation point of NaCl (25.7 Bé ($\text{SG} = 1.22$)). The last set
217 of ponds were shallower than the others and where NaCl crystallised out. The resulting NaCl
218 content of the produced salt was 97-98.5%. Laboratory experiments conducted by *Cipollina et al.*
219 on the exhausted brines discharged from the salt works showed that high-purity $\text{Mg}(\text{OH})_2$
220 with extremely high precipitation efficiency could be produced by adding NaOH to the brine.⁵⁸

221 3.1.3. Limitation

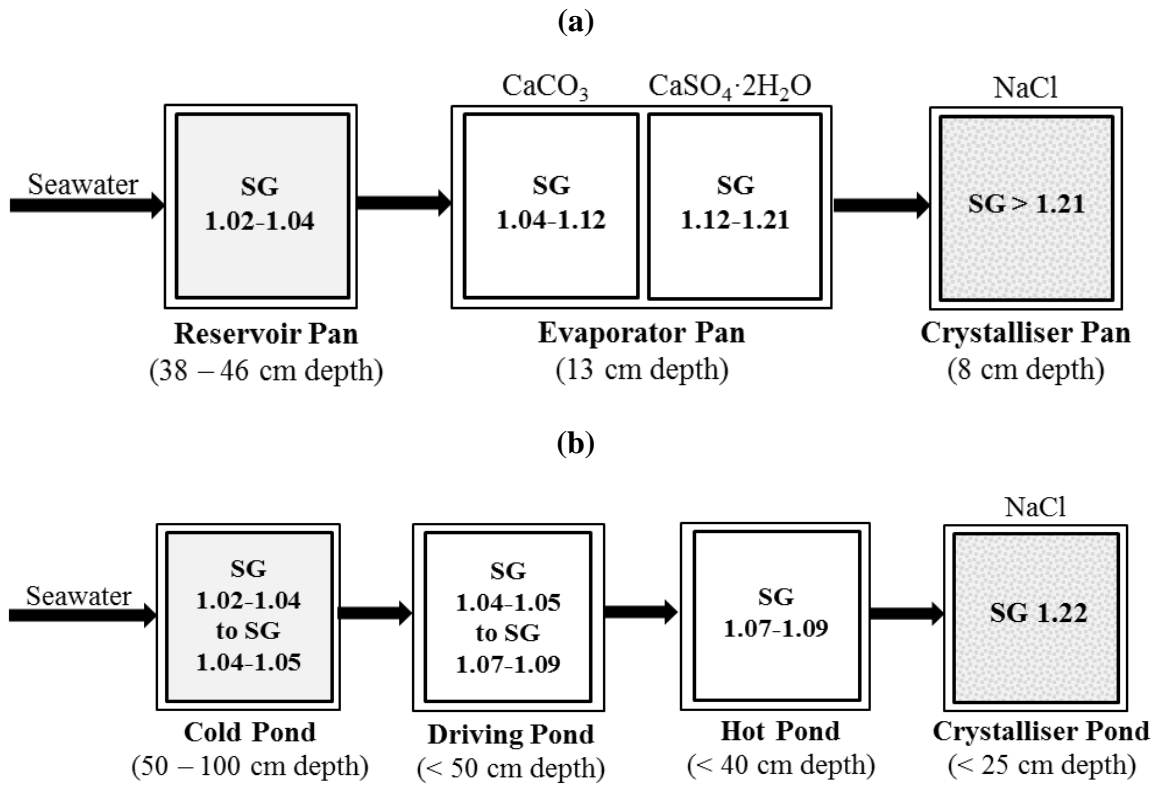
222 Although evaporation ponds are relatively easy to construct, require low maintenance
223 and a minimum amount of mechanical equipment, they do need a large land area (large
224 footprint), lengthy time and is susceptible to land pollution.⁵⁸ To prevent groundwater
225 pollution, the ponds need to be lined with clay, polyvinyl, polyethylene materials^{59,60} or
226 constructed with galvanised iron.⁹ Evaporation ponds are constructed along a basic pattern of
227 a series of shallow concentrating ponds followed by crystallisation ponds.⁵⁹ The ponds need to
228 be small in size because large size ponds tend to have excessive depths along one side and the
229 control of wave action becomes a problem.⁵⁹

230

231 3.1.4. Recent enhancements

232 *Abdulsalam et al.* fabricated solar ponds using galvanised iron and evaporation ponds
233 employing stainless steel and utilised a heat exchanger to transfer the heat from the solar pond
234 to the evaporator pond.⁹ This process thereby enhanced the evaporation rate. Insulation of the
235 ponds was provided by high-quality black paint which has the ability to absorb the maximum
236 amount of heat. The authors suggested that the desalination brine can be concentrated to
237 produce minerals in a shorter time span compared to conventional techniques without the heat
238 exchanger.

239 Improving the evaporation process can also be achieved by using wind energy. *Gilron*
240 *et al.* developed a method using wind energy to evaporate water from surfaces wetted with
241 brine.⁶¹ The evaporation surfaces consisted of different types of hydrophilic fabrics that were
242 vertically packed in high density per footprint largely mounted parallel to the wind direction.
243 This type of evaporation was called Wind-Aided Intensification of eVaporation (WAIV). By
244 deploying such an arrangement of surfaces with large lateral dimensions and significant height
245 with minimal depths, the wind can be exploited while it is still less than saturated with vapour
246 and the driving force is maintained. WAIV technology requires less land compared to
247 traditional evaporation ponds.⁶² A pilot plant experiment conducted by *Gilron et al.* indicated
248 that the WAIV unit evaporated water at a rate that was more than 10 times the daily rate for a
249 control evaporation pond with the same area as the footprint of the WAIV array.⁶¹ They
250 cautioned that in devising the WAIV unit, an optimum must be found in the hydrophilic nature
251 of the surface. It should in fact be hydrophilic enough to allow the water to spread but not so
252 hydrophilic as to reduce the effective vapour pressure.



254 **Fig. 3.** Schematic illustration of salt production in (a) Goa, India⁵⁶ and (b) Maristella saltworks
 255 at Western Sicilian Coast⁵⁸. (SG represents specific gravity calculated from °Bé using the
 256 formula $SG=1.45/(1.45- °Bé)$).

258 **3.2. Electrodialysis (ED)**

259 **3.2.1. Basic mechanism**

260 ED is an electromembrane process for extracting or concentrating ions in solutions by
261 migration of ions, under the influence of an electric field, through anon-selective and cation-
262 selective semipermeable membranes.⁶³ In this process, an alternative anion- and cation-
263 permeable membrane are placed perpendicularly to a mono-directional electric field. The
264 anion-selective membrane permits only the anions to pass through, and the cation-selective
265 membrane allows only the cations to pass through. In a typical ED cell, a series of anion- and
266 cation-exchange membranes are arranged in an alternating fashion between an anode and a
267 cathode to form individual cells.⁶⁴ A cell consists of a volume with two adjacent membranes.
268 The migration of anions and cations through the respective selective membranes causes ion
269 depletion in one cell and in ion concentration in the adjacent cell. This results in a desalting
270 and salt concentration in ED.

271

272 **3.2.2. Extraction of salt from seawater brine**

273 The conventional ion exchange membranes, though selective between cations and
274 anions, are ineffective in separating ions of the same charge. In the application of ED to extract
275 minerals from seawater or seawater brines, it is important to have membranes which are
276 selective to monovalent ions to separate them from the divalent ions. Developments of such
277 membranes began in the 1960s with the production of salts from seawater in Japan.^{64,65} Using
278 selective monovalent cation and anion permeable membranes in ED made it possible to
279 separate the monovalent ions, Na^+ and Cl^- from the divalent ions, Ca^{2+} , Mg^{2+} and SO_4^{2-} (**Fig.**
280 **4**), producing concentrated solutions of NaCl which was crystallised by evaporation.^{26,65} The
281 common monovalent selective membranes used in ED belongs to the Neosepta group
282 developed in Japan.^{23,26,65}

283

284 **3.2.3. Extraction of other minerals from seawater brine**

285 To date only a few studies have reported the use of ED in producing minerals other than
286 NaCl from seawater or seawater desalination brine. The *University of South Carolina Research*
287 *Foundation* conducted a laboratory study on the production of NaCl, $\text{Mg}(\text{OH})_2$ and Br_2 from
288 seawater RO brine using ED (**Fig. 5**).²³ The study used monovalent selective Neosepta
289 membranes to allow Na^+ , Cl^- , and Br^- to pass through the membranes and reject the divalent
290 ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . The relative transport numbers for the ions were 1, 1, 3.8, 0.8, 0.5,

291 0.11, 0.05, and 0.03 for Na⁺, Cl⁻, Br⁻, K⁺, HCO₃⁻, Ca²⁺, Mg²⁺, and SO₄²⁻, respectively. NaCl in
292 the ED brine was recovered by crystallisation after concentration by evaporation. Because of
293 the greater rejection of divalent ions, the purity of NaCl produced was higher than that produced
294 by solar evaporation.

295 The bromide-rich bittern that remained after NaCl recovery was treated with Cl₂ gas to
296 oxidise bromide to Br₂ gas (**Fig. 5**). NaBr is more soluble than NaCl and therefore the latter
297 precipitated first leaving bromide in solution for later conversion to Br₂. The NaCl depleted
298 ED diluate had a Mg²⁺ concentration 5 times greater than that in seawater. This allowed Mg²⁺
299 to be precipitated as Mg(OH)₂ when NaOH was added (**Fig. 5**). The study also reported that
300 Ca would interfere with the Mg precipitation but this was avoided by pretreating the RO brine
301 with Na₂CO₃ to remove Ca. This produced a Mg(OH)₂ having greater than 99% purity.
302 Removal of Ca by pretreatment would also help in preventing precipitation of CaSO₄ which
303 commonly forms a scale on the membrane and compromises ED performance.

304

305 **3.2.4. Limitation**

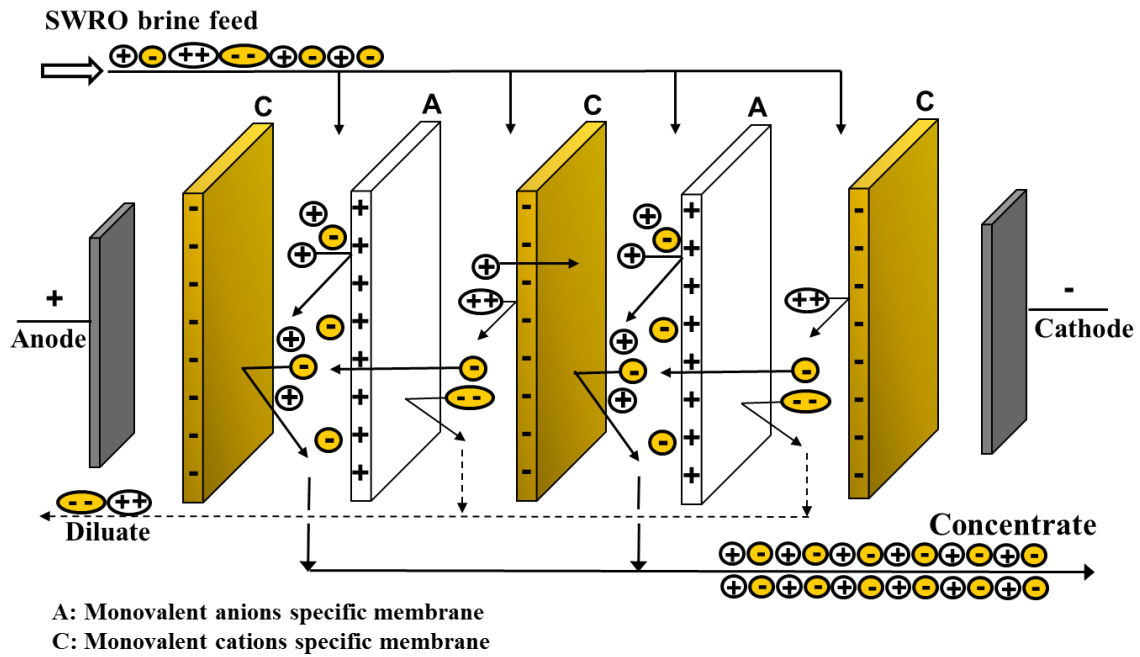
306 Membrane scaling due to carbonate and sulphate precipitation on the membranes is a major
307 problem with the ED process of concentration of salts.⁶⁰ Therefore, prior to ED, pretreatment
308 of the feed is required to prevent calcium carbonate formation such as acidification and
309 removing gypsum to reduce ED membrane scaling.²⁶ Effective methods for scaling reduction
310 of the ED membranes is important for its progress. At the same time more research is needed
311 to improve the ions' selective permeability to advance ED applications.

312

313 **3.2.5 Recent enhancements**

314 Recently, monovalent cation selective and monovalent anion selective membranes with
315 antifouling properties have been developed but not extensively tested in minerals recovery.^{66,67}
316 Further, Hoshino developed a Li permeable membrane as a Li ionic superconductor through
317 which Li passes but not the other cations in seawater.⁶⁸ More research needs to be conducted
318 to test this membrane in recovering Li salts from seawater or seawater brine.

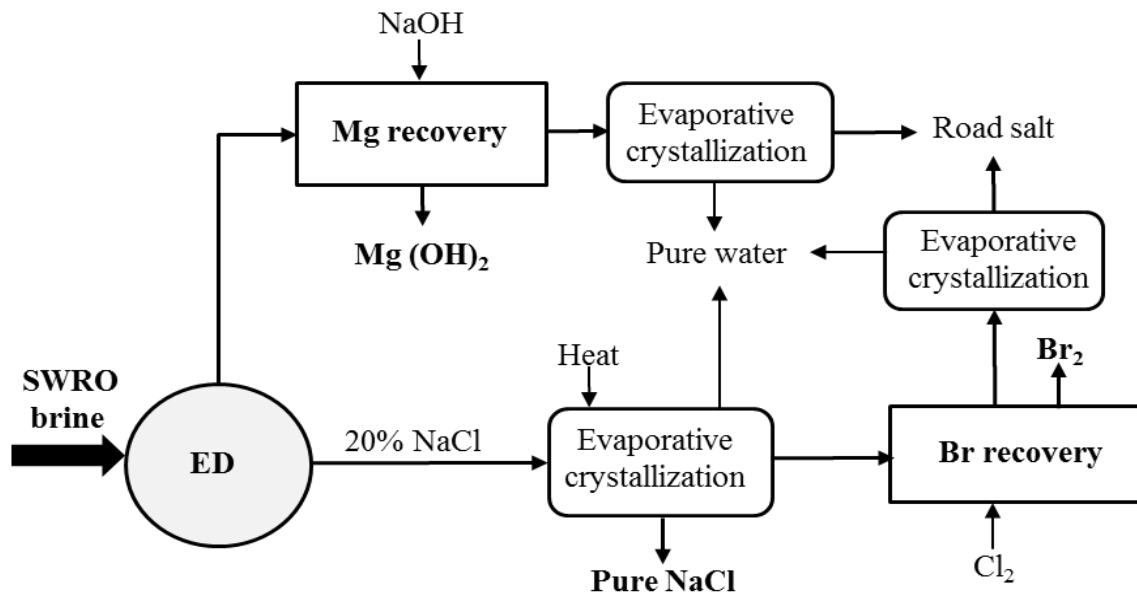
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320

321 **Fig. 4.** Schematic illustration of electrodesialysis process used to concentrate SWRO brine
322 prior to salt production by evaporation.

323

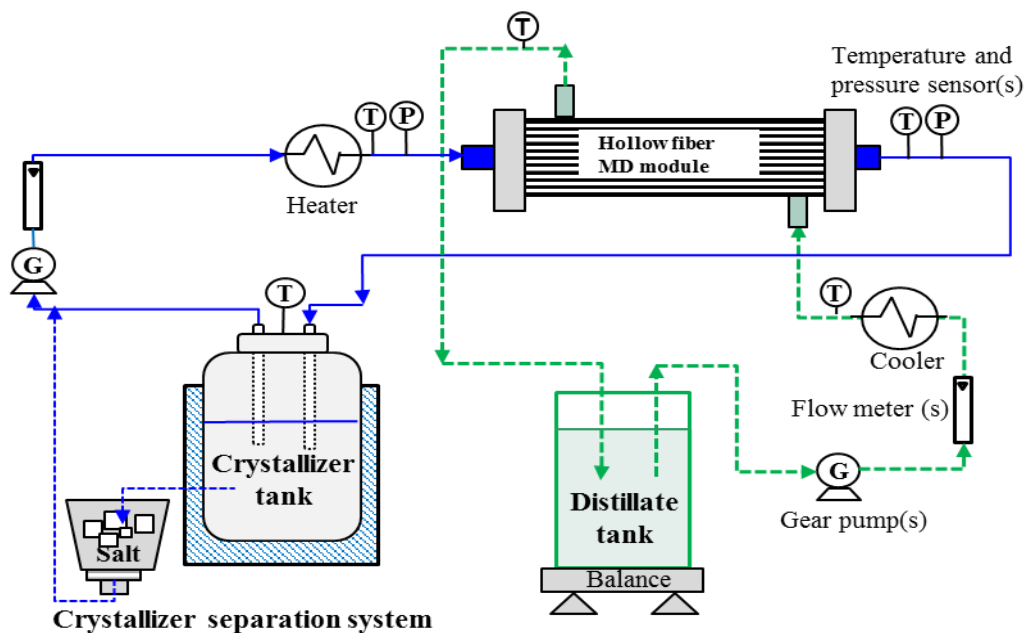


324 **Fig. 5.** Schematic illustration of SWRO brine treatment with ED and recovery of NaCl, Br₂
325 and Mg(OH)₂.²³

326 **3.3. Membrane distillation crystallisation (MDC)**

327 **3.3.1. Basic mechanism**

328 MDC is an innovative process of recovering minerals from seawater brines. MD which acts as
329 a precursor of membrane crystallisation, is a thermally driven operation where a hydrophobic
330 microporous membrane separates pure water produced as distillate from the brine solution. The
331 hydrophobic nature of the polymeric membrane prevents the penetration of water into the
332 pores, thus creating a vapour/liquid interface at each pore entrance. The water evaporates at the
333 membrane interface on the warm side (retentate), diffuses through the pores and condenses in
334 the opposite cold side (distillate). In MDC, a hydrophobic porous hollow fibre membrane
335 module serves to maintain a tight control of supersaturation of the salts while crystallisation
336 takes place in a circulating crystalliser and recovered in a crystals recovery system, thus
337 avoiding their deposition and/or accumulation inside the MDC plant (**Fig. 6**).^{22,55} The process
338 induces supersaturation in solution and creates a metastable state in which crystal nucleation
339 and growth occur.^{21,69} MDC is an attractive method for concentrating brines because of its
340 optimal control of the supersaturation level. Furthermore, it can produce higher quality crystals
341 compared to other solid separation techniques such as cooling or evaporative crystallisation.⁷⁰



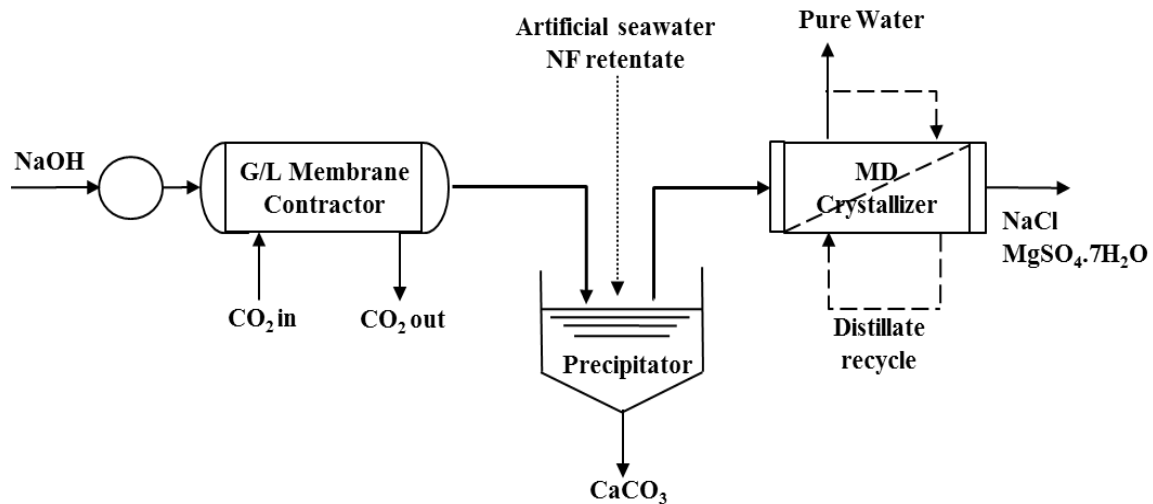
342

343 **Fig. 6.** Schematic flow sheet of a typical MDC (redrawn from *Curcio et al.*⁷¹).

344 3.3.2. Extraction of minerals

345 In laboratory studies, using MDC, high purity NaCl and MgSO₄ · 7H₂O (epsom salt) have been
346 produced from RO and NF brines.^{7,22,69} (Fig. 7). The quality of the recovered mineral product
347 is usually assessed by its structure (polymorphism) and morphologies (size, size distribution,
348 shape, habit). *Macedonio et al.* produced NaCl crystals from artificial seawater RO brine which
349 were characterised by low crystal diameter coefficients of variation (CV) compared to the
350 values generally obtained in conventional crystallisers (approximately 50%).⁵⁷ The low CVs
351 are characteristic of narrow crystal-size distributions and, therefore, the crystals constitute a
352 qualitatively better product. This was attributed to the fact that a membrane crystalliser,
353 compared to conventional crystallisers, is characterised by an axial flux of the crystallising
354 solution through the membrane fibres. The solution is expected to reduce mechanical stress,
355 improve the homogeneity of the crystallising solution and promote an oriented organisation of
356 the crystallising molecules. Consequently, crystals of good structural properties, narrow size
357 distribution and low CVs are generally produced. Similarly, *Quist-Jensen et al.* found low CVs
358 (31-41%) for the MgSO₄ crystals produced by MDC from sea water RO brine compared to
359 approximately 50% for the conventional crystallizer.⁷ Based on these results, it was concluded
360 that MDC was able to produce superior quality crystals.

361 Apart from NaCl and MgSO₄, no other compounds have been produced from seawater
362 brines using MDC. Even these compounds were produced only in laboratory scale experiments
363 and not on an industrial scale. Recently, based on theoretical considerations, *Quist-Jensen et*
364 *al.* have proposed that there is potential for the recovery of minerals such as Ba, Sr, Li, Cu, and
365 Ni from NF and RO seawater brines using MDC if water recovery of > 99% is achieved.^{7,10}
366 *Quist-Jensen et al.* suggested that Ba, Sr and Mg are more easily recovered from NF retentate
367 while Li only from RO brine, but Ni from both NF retentate and RO brine.¹⁰ These proposals
368 need to be experimentally tested.



369

370 **Fig. 7.** Schematic flow sheet of a process of mining CaCO_3 , NaCl and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from
 371 artificial seawater NF retentate using MDC (redrawn from *Drioli et al.*²¹).

372

373 3.3.3. Limitations

374 Although the capacity to produce high quality crystals with MDC was established, this is
 375 limited to major salts present at high concentration in seawater and brines. It has been implied
 376 that the capacity of MDC to selectively fractionalize valuable minerals present at low
 377 concentrations in saline seawater and brine may only be achieved at high water recovery rates.
 378 At such conditions, the supersaturated brines may result in scaling formation specifically
 379 gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which has an inverse solubility in thermal conditions.⁷² This tends to
 380 disrupt the MDC's operation. For instance, prior to the recovery of NaCl and MgSO_4 through
 381 MDC, Ca was removed as CaCO_3 by adding Na_2CO_3 to prevent gypsum scaling on the
 382 membrane's surface.²² *Drioli et al.* produced $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ by reacting CO_2 with NaOH .²¹
 383 This operation was carried out in a membrane contactor device. The crystallising solution pH
 384 was adjusted to 5 by adding HCl to prevent $\text{Mg}(\text{OH})_2$ precipitation that impedes the formation
 385 of MgSO_4 . Further, at high water recovery, significant effect of polarization and increase
 386 resistance to vapour transport within the membrane pores would limit the performance of MD
 387 and MDC.⁷²

388

389 3.3.4. Advantages

390 MDC provides the opportunity to simultaneously produce high quality fresh water while
391 concentrating and producing salts/minerals compared to ED and evaporation method. This
392 approach would enable to achieve a sustainable near zero liquid discharge for desalination
393 process with a small footprint. In line with this, *Drioli et al.* compared the economics of water
394 desalination using NF/RO and NF/RO/MDC.⁶⁹ They reported that the higher thermal energy
395 demand of the latter system can be offset by the 100% water recovery, elimination of the brine
396 disposal problem, and recovery of valuable pure crystals product. Further, the low thermal
397 requirement of MDC (less than 60 °C) can be met by alternative energy sources such as
398 industrial waste heat or solar. *Al Bazedi et al.* compared the economics of salt recovery schemes
399 from NF and RO of brines based on evaporation ponds, brine evaporator and MDC.⁷³ Their
400 analysis showed that the water cost was more competitive when salts (NaCl and MgSO₄) were
401 recovered from brines produced from NF and RO systems. They concluded that including
402 MDC in the process improved the performance, and hence, the economics of seawater
403 desalination processes through higher water recovery and obtaining valuable mineral products.

404

405 4. Adsorption/desorption process

406 Minerals that occur at low concentrations in seawater are difficult to recover because: firstly,
407 it is hard to selectively separate them from other minerals; and secondly, they are not easy to
408 precipitate and crystallise using the techniques described so far. However, special adsorbents
409 having high capacity to selectively adsorb these minerals have been developed and successfully
410 tested recently to recover many of them using the adsorption/desorption process. This process
411 of mineral recovery has been mostly achieved only in laboratory studies (**Table 2**).

412

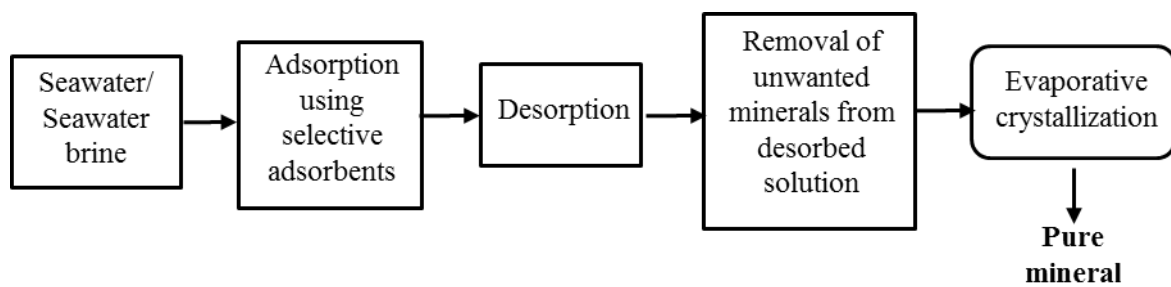
413 4.1. Basic mechanism

414 For the practical extraction of minerals utilising this process the adsorbent needs to have high
415 adsorption capacity and selectivity towards the mineral of interest in the presence of other
416 minerals present in seawater and brines, particularly those present at high concentrations.
417 Following the adsorption of the mineral, it has to be quantitatively desorbed using minimum
418 volume and concentration of desorbent and precipitated to crystallise the mineral (**Fig. 9**). If
419 other minerals are present in the desorbed solution, they should be removed by using adsorbents

420 selective to them³⁸ or by precipitation⁴⁴ to prevent their interference with crystallisation.
421 Extraction of minerals from seawater brines might be easier than from seawater because the
422 minerals in brines are nearly two to three times concentrated. However, the competition for
423 adsorption from other minerals would also be higher because of their higher concentrations.

424 The adsorbents used for removing minerals can be inorganic compounds, organic
425 polymeric ion exchange resins or chelating resins and nanomaterials.^{14, 16, 39, 41, 74} Selective
426 adsorption of minerals is governed by ligand exchange, inner-sphere complexation or specific
427 adsorption (including mineral elements exchanging with elements within the crystal lattices of
428 the adsorbents⁴²) opposed to electrostatic attraction, outer-sphere complexation or non-specific
429 adsorption.^{75,76} These mechanisms of adsorption, where relevant are discussed under each
430 mineral below.

431



432

433 **Fig. 9.** Schematic illustration of the adsorption/desorption process to recover minerals from
434 seawater and seawater brines.

435

436 **4.2. Extraction of minerals**

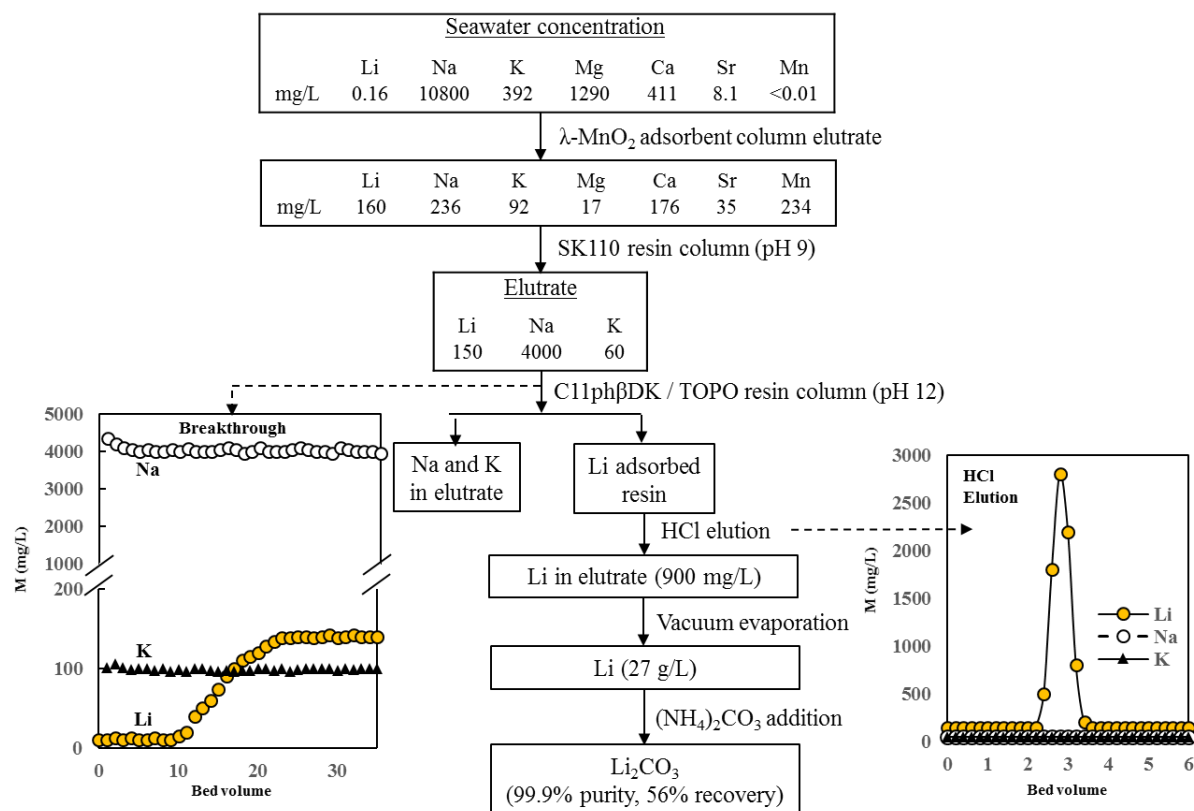
437 The four minerals which have been extensively studied using the adsorption/desorption process
438 of recovery from seawater or seawater brine are Li, U, Sr, and Rb. The steps used in the process
439 are basically the same as in **Fig. 9** but in most cases the studies have not proceeded beyond the
440 desorption step. The studies vary from those conducted in batch and column experiments in
441 the laboratory to those in sea. The studies in the laboratory generally used synthetic seawater
442 or actual seawater where the mineral was spiked to provide a higher concentration. Doing so
443 enabled the researcher to easily measure the concentrations within the detection limits of the
444 analytical instruments.

445 4.2.1. Lithium

446 The adsorbents used were those having high adsorption capacities. For Li, the main
447 adsorbent used was a MnO₂-based adsorbent converted into a H-form³⁶ or λ-MnO₂.^{38, 39}
448 *Chitrakar et al.* showed that the H-form of MnO₂ had the highest adsorption capacity for Li
449 from seawater among 12 inorganic adsorbents.³⁶ The ratio of metal ion uptake (mg/g) to metal
450 ion in seawater (mg/L) for Li on the H-MnO₂ was 2.0-2.4 x 10⁵ compared to 0.2-9.5 for Na, K,
451 Mg, and Ca. The maximum adsorption capacity of Li was 34-40 mg/g compared to <10 mg/g
452 for the other ions. Li had higher selectivity of adsorption on MnO₂ because of its very small
453 size which helps it to penetrate into the spinal structured MnO₂ and occupy the vacant
454 tetrahedral sites inside the structure whereas the other monovalent cations with higher ionic
455 radii cannot do this.⁷⁷

456 Using λ-MnO₂ adsorbent, Nishihama et al. were able to concentrate Li from seawater
457 by passing seawater through a column packed with λ-MnO₂ for 150 days followed by eluting
458 the adsorbed-Li using HCl (**Fig. 10**).³⁸ This process concentrated Li but diluted the highly
459 concentrated major cations in the seawater. The divalent cations - Mg, Ca, Sr, and Mn were
460 separated from the monovalent cations Li, Na and K by passing the HCl eluate through a
461 fixed-column containing a divalent cation-specific ion exchange resin. The eluate from this
462 column contained Li, Na, and K. Li was separated from Na and K using another column
463 adsorption process to produce a highly concentrated Li solution from which high purity
464 (99.9%) Li₂CO₃ was recovered.

465 Li was also recovered from the sea using MnO₂ adsorbent packed in nylon mesh bags
466 and placed at different depths in the sea for 58 days.³⁹ The recovery of Li was 14-15 mg/g
467 adsorbent.



468

469

470 **Fig. 10.** Selective recovery and purification of Li from seawater (redrawn from *Nishihama et*
 471 *al.*)³⁸

472

473 4.2.2. Uranium

474 Research on U recovery from seawater has been conducted for over six decades.⁷⁴ Most
 475 of the research focussed on U adsorption on inorganic materials, chelating polymers and
 476 nanomaterials in the laboratory using synthetic seawater or U-spiked seawater (**Table 2**). Only
 477 recently have a few studies been done in fields adjoining the sea.^{46,50,74} Of the numerous
 478 adsorbents used to recover U, adsorbents grafted with amidoxima functional group indicated
 479 the highest adsorption capacity (up to 3.9 mg/g) and stronger preference for U adsorption than
 480 alkali and alkaline earth metal ions⁷⁸. However, a highly porous and stable metal-organic
 481 framework containing an orthogonal phosphorylurea group (750-3730 m²/g BET surface area)
 482 had a saturation capacity of 188 mg U/g in simulated seawater at pH 2.5 compared to 54 mg/g
 483 for amidoxima resin.⁵² The high adsorption capacities were reported to be due to monodentate

484 binding of one uranyl ion with two phosphorylurea ligands (specific adsorption). The bonding
485 was considered to be covalent and ionic in character.

486 In marine tests in Japan, using various types of fibrous amidoxime adsorbent beds such
487 as plastic nets fibre sheets and cages anchored at 2-15 m depths in the sea, up to 1.5 mg U/g
488 adsorbent were recovered after 30-40 days.⁷⁴ The lower reported adsorption capacities
489 compared to the laboratory tests were explained as due to matrix complexity, mass-transfer
490 limitations, and natural movement forces (waves/currents). In a similar experiment as that used
491 in Li recovery from the sea, Nakazawa et al. reported an adsorption capacity for U of 1 mg/g
492 amidoxima adsorbent submerged in the sea for 58 days.³⁹

493 The adsorption mechanism for U is complex and varies with the U species in solution
494 and the functional group in the adsorbent. For example, *Gibert et al.* using chemical speciation
495 methods reported that the predominant U species in artificial seawater brine around neutral pH
496 was $\text{UO}_2(\text{CO}_3)$.^{4,41} They suggested that the main mechanism of U adsorption by amidoxima
497 group based adsorbents involved decomposition of $\text{UO}_2(\text{CO}_3)^{4-}$ to UO_2^{2+} followed by
498 complexation of UO_2^{2+} with four amidoxime groups ($\text{RC}(=\text{NOH})\text{NH}_2$). However, in another
499 study on U adsorption by a cation exchange resin having phosphonic acid and sulphonic acid
500 functional groups the adsorption capacity was reported to be higher for this resin (22.8 mg/g)
501 compared to that in an amidoxime-based resin (5 mg/g).¹⁶ The higher adsorption capacity of
502 the cation exchange resin was explained as due to the strong affinity of the negatively charged
503 bifunctional phosphonic/sulphonic acid group towards the positively charged U cations.

504

505 **4.2.3. Strontium**

506 Recently, Sr recovery from synthetic seawater was studied using Ca form of alginate
507 microspheres and hydrothermally structured titanate nanotubes.^{44,45} These adsorbents were
508 found to have high adsorption capacities for Sr (110 mg/g for alginate and 92 mg/g for titanate
509 nanotubes) in pure Sr solutions. However, the adsorption capacities decreased in synthetic
510 seawater solution due to competition from Ca, Na, and Mg for adsorption.

511 Adsorption of Sr on alginate microspheres is due to cross-linking of alginic acid and
512 Sr, a behaviour similar to that of Ca and Mg.⁴⁵ The cross-linking of the metals is with the
513 carboxylate (-COO) and hydroxyl (-OH) groups in the alginate. The reduction in the adsorption
514 capacity of Sr in the presence of Ca and Mg is due to the competition for adsorption of the

515 latter metals with the former. Sodium at the concentration found in seawater also competed
516 with Sr.⁴⁵ This was explained as due to the extremely high ionic strength caused by the Na
517 concentration and not due to competition in cross-linking as Na is a monovalent ion.

518 It was suggested that by increasing the dosage of the adsorbent or using Ca-removed
519 seawater the competition of Ca with Sr can be reduced.⁴⁴ By removing Ca by precipitation as
520 Ca(OH)₂ using NaOH the adsorption capacity of titanate nanotubes for Sr was improved. The
521 mechanism of adsorption was explained using FTIR and Raman spectra as due to Sr
522 exchanging with Na located in the interlayer of titanium oxide octahedrans. As Ca has similar
523 chemical behaviour as Sr, it reduced Sr adsorption the most compared to Na, K, and Mg.

524

525 **4.2.4. Rubidium**

526 Rb recovery from synthetic seawater was studied using many adsorbents and potassium
527 cobalt hexacyanoferrate (KCoFC) was found to have the highest Rb adsorption capacity.¹³ The
528 Langmuir adsorption maximum for this adsorbent was 47 mg/g in a batch study and an
529 adsorption capacity of 238 mg/g in a column study.^{16,41} *Naidu et al.* also reported high
530 Langmuir adsorption capacities for the adsorption of Rb on laboratory prepared and
531 commercial samples of KCoFC (96 and 100 mg/g).⁷⁹ Sorption capacity of alkali metals and
532 alkaline earth metal Ca on the KCoFC followed the decreasing order Rb > Cs > Li, Na, Ca.
533 They gave two explanations for the higher adsorption capacity of Rb compared to the other
534 metals. Firstly, Rb had greater surface sorption on the KCoFC as a result of its lower hydrated
535 ionic radii. This was supported by the zeta potential data. Secondly, Rb was reported to have
536 made a greater penetration into the crystal lattice to replace structural K in the body centre of
537 KCoFC than other metals. Rb released the largest amount of K, due to Rb and K having similar
538 unhydrated ionic radius.

539 In a subsequent study, *Naidu et al.* compared the adsorption capacities of Cu, Ni, Co
540 and Zn metal form of the potassium hexacyanoferrate and reported that the Cu form (KCuFC)
541 had the highest Rb adsorption capacity.⁴² Presence of high concentrations of Na, Ca, and Mg
542 reduced Rb adsorption slightly, but K reduced Rb sorption markedly. As a result of the
543 superiority of KCuFC adsorbent in removing Rb, an organic polymer encapsulated KCuFC
544 was prepared and column adsorptive removal of Rb was studied. The adsorbed Rb was
545 desorbed using 0.1 M KCl. It emerged that 95% of the Rb was desorbed. Adsorbing K and Rb

546 in the desorbed solution in a resorcinol formaldehyde column and subsequently leaching them
547 with HCl kinetically separated the Rb from the K producing a solution with 68% pure Rb.

548

549 **4.3. Advantages**

550 The adsorption process is a simple, low-cost and an established process used in water treatment
551 plants in many parts of the world for the purification of contaminated water. By using a
552 selective adsorbent, the mineral of interest can be concentrated on the adsorbent for easy
553 recovery. Desorption is also an established process used in water treatment plants to regenerate
554 the adsorbent for multiple reuse⁷⁶. Adsorption/desorption process can concentrate minerals
555 present at low concentrations in seawater to levels suitable for evaporative crystallisation.
556 Adsorbents can be placed inside the sea in plastic nets, stacks of fibre sheets, and fibre cages
557 for continuously recover minerals that occur at low concentration over many weeks.^{39,74} Many
558 of these minerals are difficult or impossible to crystallise using the other processes described
559 previously because of their low concentrations.

560

561 **4.4. Limitations**

562 Though new adsorbents with high adsorption capacities are being continuously developed for
563 different minerals, complete selectivity of adsorption/desorption of the minerals have not been
564 established for recovering minerals from seawater and brines because of the presence of much
565 higher concentration of other minerals which compete for adsorption. This has led to secondary
566 treatments after adsorption/desorption of the mineral of interest by removing the competing
567 minerals by precipitation or using other adsorbents.^{38,44} *Ryu et al.* also suggested using a larger
568 dosage of the adsorbent to overcome the hindering effects of the competing mineral.⁴⁴
569 However, a larger dose would also adsorb more of the competing mineral which would
570 interfere with the crystallisation of the mineral. Minerals in the desorbing agent can also
571 interfere with the mineral's crystallisation.⁴²

572

573 **5. Economic analysis**

574 The profitability of mining minerals from sea or seawater brine depends on the capital cost,
575 operation and maintenance cost, sale revenues of water and minerals, and geological
576 location.¹¹ The major capital costs are those of equipment, buildings, construction of plants,
577 and land. Operational and maintenance costs include cost of energy (e.g. electric power),
578 chemicals and other consumables, labour, equipment replacements, and maintenance.

579

580 **5.1. Solar evaporation**

581 For solar evaporation ponds, the major cost is the price of the large area of land required for
582 the pond which depends largely on the geographical location. Additional capital cost is
583 linings that need to be put below and around the pond to prevent leakage of minerals that may
584 contaminate underground water. The cost of construction and maintenance of the pond are
585 relatively cheap. Only minerals having high concentrations (e.g. NaCl) can be economically
586 recovered by this process. For WAIV, land cost is less. However, capital cost in plant
587 construction is high.

588

589 **5.2. Electrodialysis (ED)**

590 ED process uses only electricity as the energy source and therefore electrical energy is the
591 main operational cost. The suspended solids in seawater need to be removed using
592 pretreatment using sand filter and sometimes a secondary filtration is also necessary before
593 ED.²⁴ Pretreatment to avoid scaling of the membranes is also required. These pretreatments
594 add to the operational cost.

595 The University of South Carolina Research Foundation²³ conducted a preliminary
596 economic analysis on the results of the ED study described earlier in the paper for three
597 scenarios of recovering potable water, NaCl, Br₂, and Mg(OH)₂ from RO concentrate. The
598 scenarios were: (1) sand filtration prior to RO and ED, (2) partial softening by adding
599 Na₂CO₃ to selectively precipitate Ca, and (3) evaporation of all the water in the discharge
600 stream to make road salt. The volume of RO concentrate treated was 11,230 m³/day. A
601 mathematical model was used to predict the economics of the process. For the first scenario,
602 the capital cost was \$2,400,000 and annual operating cost was \$8,600,000. Annual value of

603 products (potable water, NaCl, Br₂, and Mg(OH)₂) was \$19,000,000. This was expected to
604 give a profit of \$8,000,000 per year. Scenarios 2 and 3 were also expected to give a profit of
605 80% and 50% of this value, respectively. The predictions showed that NaCl, Br₂, and
606 Mg(OH)₂ can be economically produced by the ED process in addition to the clean water
607 production.

608 Japanese manufacturing companies have been economically producing salt from
609 seawater using ED since 1970s at a production rate of 360,000 tonnes/year during 1970-1980.
610 ²⁴ The economics of production was reported to be improved by constructing an integrated
611 complex for salt and chlor-alkali production. Salt was produced from seawater by the ED
612 process and it was further processed into caustic soda and chlorine by an ion-exchange
613 membrane electrolytic process.

614

615 **5.3. Membrane distillation crystallisation (MDC)**

616 The MDC process can simultaneously produce clean water and minerals with low heat
617 energy input. The water recovery percentage generally increases to 88% by MDC operating
618 on the RO retentate while RO unit alone produces a recovery of only 40%.⁶⁹ *Drioli et al.*
619 compared the economics of producing water and salt in a laboratory study using a
620 conventional NF/RO system and an integrated NF/RO/MDC system.⁶⁹ They reported that the
621 capital cost (mainly from membrane) was nearly the same for both the systems. The
622 operational cost (mainly from energy) was \$1.04 for the integrated system compared to \$0.55
623 for the NF/RO system. However, the water recovery was 100% for the integrated system
624 compared to 50% for the other system. Increased water recovery and production of salt and
625 elimination of brine disposal problem was considered to produce a higher profitability when
626 MDC was integrated to the NF/RO system.

627 *Quist-Jensen et al.* conducted an economic analysis on LiCl production by MDC
628 using a single salt aqueous LiCl feed solution.¹⁰ A calculation was performed considering a 1
629 m³/h plant equipment with a pre-filtration treatment of the feed. The economical evaluation
630 showed that the capital costs were \$12,886/year and annual operating costs were
631 \$10,509/year. The unit LiCl cost was determined to be \$2.18/kg which was competitive with
632 the Li production cost from salt lake brines (around \$2/kg). However, the crystal quality was
633 better for the MDC product.

634 *Al Bazedi et al.* compared the economics of minerals and water recoveries from NF
635 and RO brines based on evaporation ponds, brine evaporator and MDC.⁷³ They used
636 computer software programmes to calculate the total capital cost, total annual cost and annual
637 revenues from sale of minerals (NaCl, MgSO₄ · 7H₂O, CaCO₃) and water. The results
638 indicated that the scheme involving MDC gave the highest revenues and profits and
639 therefore, the highest simple rate of return (net profits/capital costs).

640

641 **5.4. Adsorption/desorption process**

642 This process has the advantage over the other methods in extracting minerals that occur at
643 low concentrations in seawater or seawater brines. The capital and operational costs are also
644 lower than the other processes. However, unlike the other processes, this process cannot
645 produce desalinated clean water and, thus need to be combined with MDC or RO. The
646 revenue obtained comes only from the extracted minerals. The process is profitable only for
647 the extraction of high values minerals.

648

649 **6. Conclusions**

650 There are much more minerals in the sea compared to those in land-based reserves. Given the
651 difficulties facing land-based mining industries such as sustainable energy and water demands,
652 depletion of easily available high-grade ores and environmental issues related to waste disposal
653 and miners' health, mining minerals from the sea is becoming more attractive. Increasing
654 demand for clean water has led to the installation more desalination plants worldwide. This
655 process generates enormous amounts of brine. The brine contains all the minerals present in
656 the sea at nearly twice the concentration as in seawater. Mining minerals from these brines can
657 offset part of the desalination cost as well as solve the brine disposal problem.

658 The main methods of recovery of minerals are solar evaporation, ED, MDC, and
659 adsorption/desorption. Of these, the first three can recover only minerals which are found at
660 high concentrations (Na, Mg, Ca). The centuries-old solar evaporation method is limited in its
661 use, in that it is mainly employed in arid regions requiring high solar evaporation and where
662 land is available at low cost. The new WAIV is a promising method that may overcome these
663 limitations. The application of ED for mineral recovery have increased with the developments

664 of monovalent cationic and anionic permeable membranes to separate Na, Cl, and Br from Ca,
665 Mg and SO₄. Further, new research is in progress to develop membranes permeable to specific
666 individual metals such as Li. MDC is a relatively new method which has been shown to recover
667 NaCl and MgSO₄ in laboratory studies. New membrane developments with anti-scaling and
668 other beneficial properties and pre-treatment of the feed water are expected to increase the
669 applicability of this method to other minerals recoveries. Studies have shown that using MDC
670 has the potential to recover Li, Sr, Ba, and Ni.

671 Unlike the other methods, the adsorption/desorption method can concentrate minerals
672 that exist at low concentrations by selectively adsorbing a mineral and quantitatively desorbing
673 it for evaporative crystallisation. Though adsorbents with high adsorption capacities have been
674 developed (MnO₂-based materials for Li, potassium metal hexacyanoferrate for Rb, and
675 amidoxima-based materials for U), they are not completely selective to the mineral of interest.
676 This has led to the use of several other adsorbents to specifically remove the minerals
677 competing for adsorption with the mineral of interest and removal of the competing mineral by
678 selective precipitation. Only Li appears to have been recovered in pure crystalline form using
679 the adsorption/desorption method.

680 The technology advancements of each method show promising potential for its
681 application in mining minerals from seawater brine. Nevertheless, it is still a challenge to use
682 a single method to selectively extract valuable minerals from complex brine matrices. An
683 integrated approach of combining a number of methods may be necessary to extract a specific
684 valuable mineral of seawater brine. A similar observation was made by *Jepessen et al.* and
685 *Dirach et al.* on the potential of mineral extraction from seawater brine and nuclear desalination
686 brine.^{80,81} In this regards, MDC appear to show promising potential in its capacity to
687 simultaneously produce fresh water while recovering major salts from the brine. In an
688 integrated approach, selective valuable minerals, even those present at very low concentrations
689 in seawater, could be extracted from concentrated MDC brine with a post treatment of
690 adsorption/desorption method.

691

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