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Utilization of seawater desalination concentrate, technology and commercial potential in China

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ABSTRACT

Mining valuable minerals from desalination concentrate is a promising path to improve resource utilization efficiency and reduce the environmental impact. With the rapid expansion of the desalination industry and the improvement of extraction technology, the comprehensive utilization of desalination concentrate is approaching commercial reality. This paper summarized the development status of the desalination industry within and outside China. On this basis, the economic potential of valuable minerals mining from seawater desalination concentrate was estimated. Our results showed that when the in-operation membrane desalination projects in China run at full capacity, the discharge of seawater concentrate is about 1,696,900 m^3/d. The high commercial potential chemicals are boron, lithium, and rubidium because of their high concentration and unit price. If continuous production can be achieved, its economic value will be more than desalinated water production. In addition, this paper summarized the extraction technologies of magnesium, potassium, rubidium, boron, strontium, and lithium in desalination concentrate.

Keywords: Seawater desalination; Comprehensive utilization; Seawater concentrate

1. Introduction

Human society relies heavily on the sustainable supply of rare metals and useful minerals. With the fast development of society, the future will require increased amounts of these materials. By the end of 2050, metal and non-metallic minerals production needs to be raised by at least 50% and 100%, respectively [1]. Seawater contains a considerable amount of chemicals and minerals. It is estimated that the entire reserve of potassium, lithium, and uranium in the sea is 550 × 10^{12} t, 2400 × 10^8 t, 45 × 10^8 t, respectively, which is thousands to ten thousand times more than the land-based resources [2]. In addition, almost all of the bromine on the earth are stored in seawater [3]. Although the total amount of chemicals in seawater is huge, the concentration is much lower than that of land-based minerals and is generally not economically feasible. Currently, the extraction of chemical resources from seawater still focuses on traditional bittern, which is the residual liquid after NaCl production in the salt farm with a much higher concentration of chemicals such as K, Mg, Br, etc.

Desalination concentrate is a by-product of the desalination process. It shares the main components with seawater but doubles the concentration. The advantage of desalination brine can be summarized as follows: firstly, exploiting desalination concentrate, rather than directly using seawater, will be more energetically favorable. In addition, the parameters, such as temperature and flow rate, are more stable in desalination brine, which brings the advantage for continuous operation and can reduce the operation cost.

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Meanwhile, it can reduce the brine volume and ecological impact. Brine disposal will lead to substantial increases in salinity, temperature and the accumulation of metals in receiving waters. Experiments in the field and laboratory demonstrated the potential for acute and chronic toxicity of desalination brine [4]. Therefore, appropriate environmental-friendly brine management is essential. Chemical extraction from brine is always the most attractive option.

The expansion of seawater desalination and the improvement of extraction technologies in recent decades have brought the utilization of desalination brine one step closer to the commercial realization [5]. Recently, the EU's Horizon 2020 Sea4Value project was proposed. The project aims to recover valuable minerals and metals from seawater desalination plants brines, focusing on the critical raw material, such as boron, magnesium, lithium, scandium, vanadium, indium, and gallium, and other non-critical but still strategic elements such as molybdenum and rubidium [6].

2. Methodology

2.1. Data collection

We obtained the global desalination information from the International Desalination Association Yearbook (2018–2019). Seawater desalination plant information in China was obtained from the China seawater utilization report (2013–2021). Ministry of Natural Resources of China published this report. It contains the plant capacity, geographic location, and technology type.

2.2. Desalination concentrate production

The volume of desalination concentrate production is not reported directly in these sources, as described in 2.1 – Data collection. Therefore, we calculated the brine production based on the recovery ratio and plant capacity as:

$$V_b = \frac{V_d}{R} \times (1 - R) \quad (1)$$

where V_b is the volume of desalination concentrate produced (m^3/d); V_d is the desalination plant treatment capacity (m^3/d); and R is the recovery ratio.

We conduct a literature study to identify the values of recovery ratios for reverse osmosis (RO) plants. The plants were selected if they were in continuous operation and representative of the seawater quality. A total of 10 recovery ratios were found in literatures. The average value of these recovery ratios was used in our calculation.

3. Overview of seawater desalination technology

Fig. 1 shows the distribution of seawater desalination capacity in the world. The global desalination capacity (as of 2018) is 6.2 × 10^7 m^3/d, multi-stage flash (MSF), multi-effect distillation (MED), and RO are currently the main commercial desalination technologies, accounting for 31%, 10% and 54% of the total capacity, respectively. Half of the total capacity in the Middle East and North Africa (MENA) region is dominated by thermal desalination (MSF and MED), mainly due to high desalination demand and low energy costs. Besides this region, RO technology occupies the absolute advantage. Geographically, desalination capacity is mainly distributed in the Middle East and North Africa region, accounting for 65.24% of the total capacity, followed by East Asia and the Pacific, Western Europe, South America and the Caribbean, South Asia, Eastern Europe and Central Asia, Sub-Saharan Africa, and North America [7].

By the end of 2021, China had 144 desalination projects with a total capacity of 1.9 × 10^6 m^3/d. RO and MED accounted for 66.19% and 33.43% of the total capacity, respectively. In recent years, all the newly commissioned seawater desalination projects adopted RO technology (Fig. 2) [8].

As shown in Fig. 3, the seawater desalination plants in China are distributed in nine coastal provinces. The per

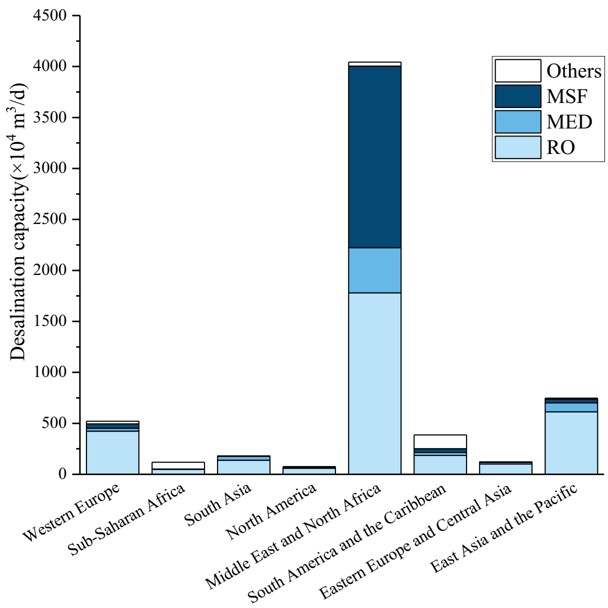

Fig. 1. Global seawater capacity distribution.

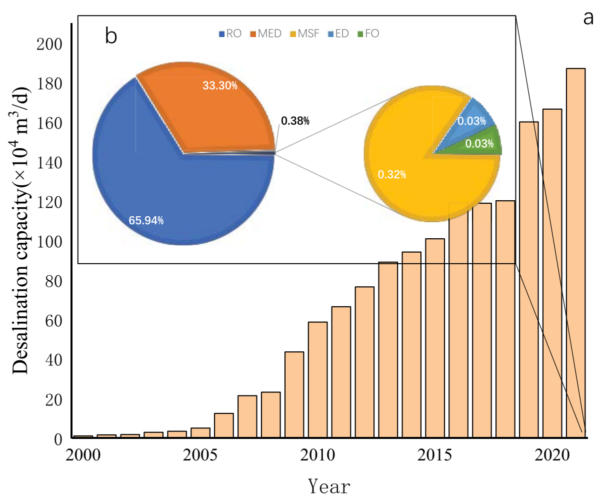

Fig. 2. China seawater desalination by (a) capacity and (b) technology in 2021.

capita water resource in most coastal regions in China is lower than the national average during the same period. The reason is that the coastal areas are the main economic engine that attract the majority of the population and factories. Therefore, with the economy's increase, the desalination industry expanded fast in the past decade. China's government has planned to almost double the seawater desalination capacity before 2025 (compared with 2020) [9].

4. Discharge scenarios

The discharge methods used for the desalination concentrate are various: mixture of discharge, enhanced diffusion discharge, direct discharge, and comprehensive utilization. A mixture of discharge is mixing desalination concentrate with the cooling water of power plants, effluent from sewage treatment plants, or other existing sewage discharged. In this way, the existing sewage with low salinity can dilute the salinity of desalination concentrate. Meanwhile, the desalination concentrate can also dilute the harmful components from power plants and sewage treatment plants, which can significantly reduce the impact of sewage discharge on the marine ecosystem. From the perspective of engineering practice, desalination plants are commonly jointly built with power plants or industrial parks. Therefore, this discharge method has potential benefits from an engineering perspective. Enhanced diffusion discharge is to install a special diffuser at the discharge outlet to enhance the mixing of desalination concentrate and receiving water to reduce the environmental impact. Direct discharge into the sea is the simplest way of desalination concentrate disposal. Small and medium-sized desalination plants usually adopt this method. The comprehensive utilization of desalination concentrate is a treatment method with the lowest environmental impact. However, this method is always barriered by cost. As technologies for seawater brine mining develop, desalination concentrate as a source of minerals becomes more economically and environmentally viable.

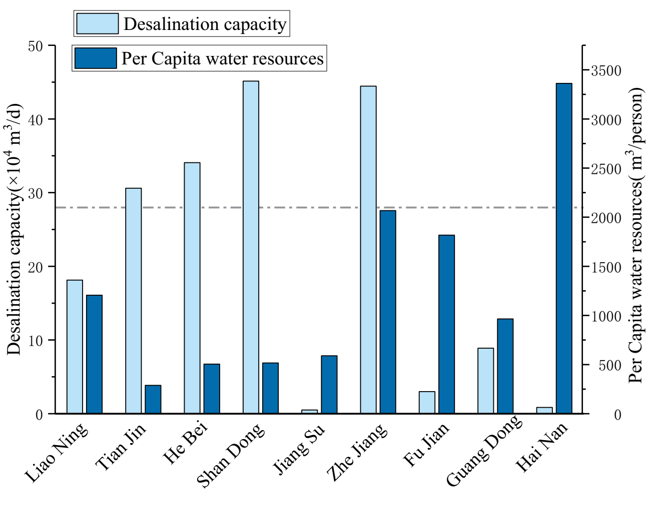

Fig. 3. Per capita of water source in 9 coastal provinces in China in 2021. *Dotted line is the average per capita water resources of China.

5. Desalination concentrate production

5.1. Mineral abundance

The concentration of minerals in the desalination concentrate is shown in Table 1. The concentration of Ca, Mg, K, and Na in seawater is the highest, but the unit price of Ca and Na products is relatively low. This is the primary reason that the extraction from seawater is not commercially attractive. However, they still have potential economic potential because of land based resource unevenly distributions and huge demand [10].

Among the trace elements, the concentration of B is the highest. B is mainly used as an additive for glass fiber, polymer, porcelain, refractory materials, etc. The second is Li, the main raw material for the lithium battery. The demand for Li continues to rise with the fast development of the new energy vehicles industry. Therefore, Li extraction has attracted much researcher's attention in recent years. Rb is mainly used in special glass. The annual consumption of Rb is only about 4 tons, which is supplied almost entirely as a by-product from hard-rock mining of the lithium-rich ores, pollucite, and lepidolite. Currently, there is no production of Rb salts outside China [11].

5.2. Commercial potential in China

The parameters of the selected seawater desalination plants in China are shown in Table 2. The recovery rate ranges from 35% to 46%. The average recovery rate of RO desalination plants is 42%. The two desalination projects with lower recovery rates are located on the island. Adopting a lower recovery rate can reduce the system's energy consumption. The recovery rate of large plants (>10,000 m^3/d) is generally above 40%. For MED desalination plant, we use the recovery rate of 25% from the literature in the calculation [12]. By 2021, RO technology has been applied in 126 projects in China, with a project capacity of 1,228,800 m^3/d; 16 projects are using MED technology, with a capacity of 620,500 m^3/d.

Table 1
Concentrations of several economic components in desalination concentrate

Type of element	Concentration
Mg, mg/L	2,019 ± 695
K, mg/L	599 ± 202
Co, ug/L	1.00
Sc, ug/L	2.55 ± 1.17
V, ug/L	12.21 ± 14.31
Ga, ug/L	3.29 ± 3.63
B, ug/L	5,809 ± 2,249
In, ug/L	1.00
Li, ug/L	199 + 95
Mo, ug/L	16.28 ± 13.29
Rb, ug/L	175.47 ± 56.95
Total dissolved solids, mg/L	60,049 ± 20,008

Data on chemical concentrations in desalination concentrate are available from the Sea4Value project website [6].

Table 2
Recovery rate of selected reverse osmosis seawater desalination project in China

No.	Province	Capacity (m^3/d)	Recovery rate (%)	In-take water salinity	Salinity of brine
1	Hebei	50,000	46	33.1	61.3
2	Hebei	20,000	45	31.3	56.9
3	Shandong	100,000	45	28.6	52.0
4	Shandong	30,000	45	31.8	57.8
5	Shandong	200,000	43	29	50.9
6	Zhejiang	75,000	45	19.9	36.2
7	Zhejiang	35,000	45	28.6	52.0
8	Zhejiang	20,000	38	28.9	46.5
9	Zhejiang	500	35	26.8	41.2
10	Hainan	1,000	35	34	52.3
Mean value			42		

When all plants are in full operation, the volume of brine from membrane desalination is about 1,696,900 m^3/d, and from MED desalination plants is 1,861,500 m^3/d.

The estimate of minerals price in desalination concentrate in China is shown in Fig. 3, where the concentrations were based primarily on the Standard Sea Water (SSW) composition from Stanford University (https://web.stanford.edu/group/Urchin/mineral.html), and the estimated price were based on current price ranges of these materials on Alibaba (as in December 2022). The chemical price is related to its purity, so we used the price of industry level in the calculation.

The economic gain obtained by extracting minerals is proportional to their concentration in the brine and the market price. The total price of Mg, Na, Br, and B is the highest if all chemicals are extracted from desalination concentrate. The main reason is that although the unit price of MgO and NaCl products is lower, the total abundance is enormous. However, Similar to most conventional chemicals, MgO and NaCl face significant market competition and high transportation costs. Therefore, extraction from brine has little commercial attraction if the consumer cannot be found near the desalination plant.

The cost is one of the major barriers to the promotion of desalination. The extraction of chemicals from brine could potentially increase the overall output of desalination plants. For example, desalinated water production in China costs 5–8 yuan/m^3. The profit of extraction boron from desalination concentrate is 2–3 times that of desalinated water production. The output value of rubidium, lithium, strontium and other compounds is also at a non-negligible level compared with desalinated water.

In addition, some recovered products, for example, the $Mg(OH)_2$, can be directly used for the post-mineralization treatment of desalinated water, will reduce the overall post-treatment cost of desalination plant.

6. Extraction technologies

6.1. Commercial status

There are rare reports of commercial plants on chemical extraction from desalination concentrate. In China, the Institute of Seawater Desalination and Multipurpose Utilization built a demonstration project of extraction $Mg(OH)_2$ from brine in 2008. In 2013, Hebei University of Technology initiated the construction of a demonstration project on desalination concentrate utilization. Br_2 and KCl were the main products in this project. Tianjin Beijiang power station seawater desalination plant, which is the largest MED desalination project in China with a capacity of 200,000 m^3/d, started commercial utilization of desalination concentrate in 2013. The Br_2, KCl, MgCl, $MgSO_4$ are the main products in the desalination concentrate utilization project. In 2019, Tianjin Changlu Hangu Saltern Co., Ltd. successfully remodeled the equipment for bromine recovery from highly concentrated seawater, enabling the construction of thousand-ton demonstration installation. As a result, energy consumption was reduced by nearly 10% and the recovery rate increased by 8% [13]. These four projects are located in Bohai Gulf, China's main base of salt chemical industry.

In Israel, Mekorot Water Company owns and operates a SWRO plant in Eilat for the production of 10,000 m^3/d of desalinated water from 1997. The brine from the SWRO plant is blended with seawater, and this stream is fed to a series of evaporation ponds and thereafter, to the salt processing factory of the salt company. As a result, the salt production in this configuration increased by 30% compared to salt production from seawater alone. The salt produced is of the highest quality within the range of the most strict standards [14].

It should be noted that both commercial plants in China and Israel cooperated with the salt company rather than producing salt alone. Eilat plant fed the brine to Israel Salt Company for further treatment. Tianjin Beijiang power station seawater desalination plant fed the brine to Changlu Salt Company.

6.2. Further concentration and Ca^{2+} removal

It is often necessary to further concentrate desalination brine before extracting minerals. Electrodialysis, evaporation pond, membrane distillation, etc., are frequently utilized in this process (Fig. 5) [15]. In some literatures, reverse electrodialysis has also been used in the brine treatment process.

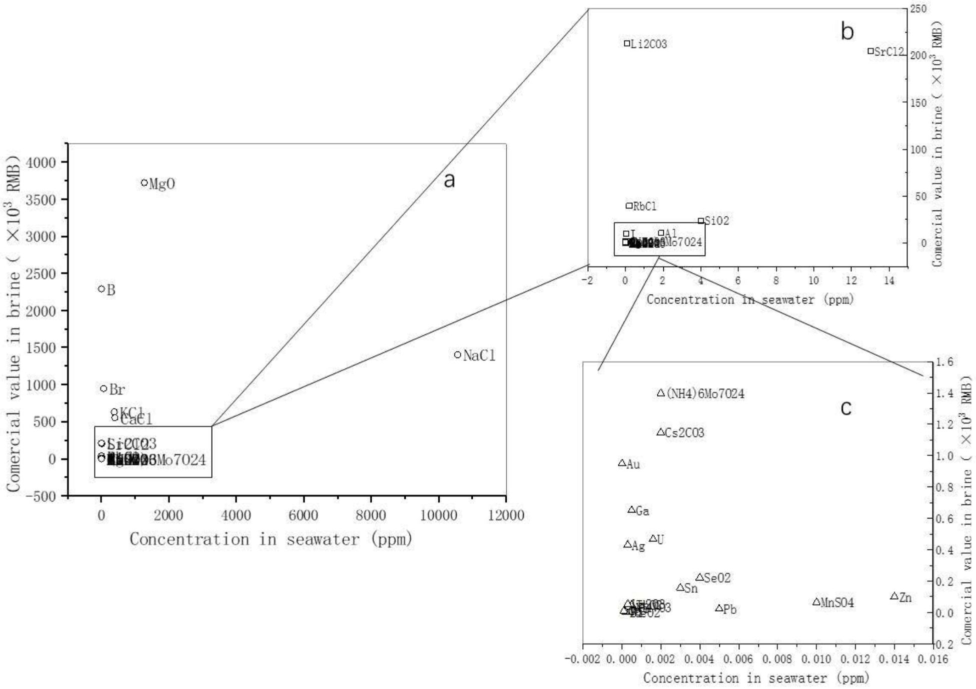

Fig. 4. Concentration of chemical species in seawater and their commercial value in China. *More information can be found in supporting information.

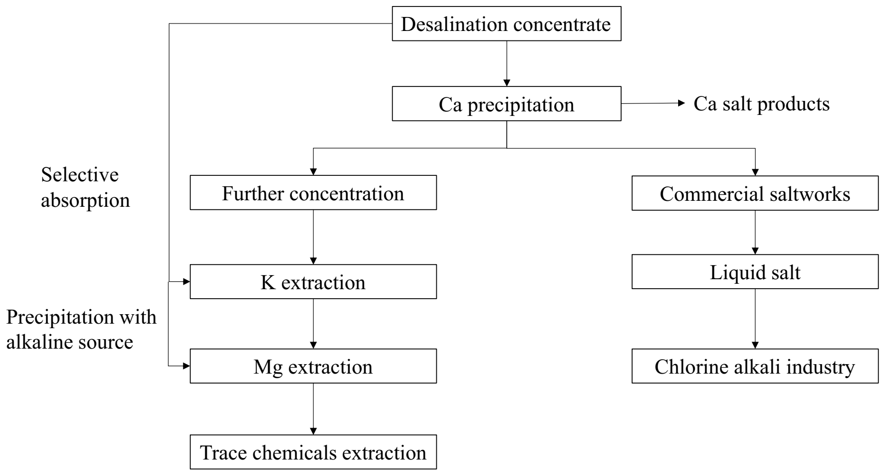

Fig. 5. Process of extraction chemicals from desalination concentrate.

Reverse electrodialysis can extract energy from desalination concentrate from the salinity difference between seawater and fresh water, thus effectively reducing the salinity of desalination concentrate and its ecological impact. However, this technology is used only in a lab or pilot stage [16]. Cui et al. [17] used desalination concentrate and river water as the feed solutions of reverse electrodialysis, and results showed that the power density could reach 0.3632 W/m^2 under optimal conditions. Du et al. [18] proposed a comprehensive system including a process flow of nanofiltration – evaporation or mechanical steam compression concentration – chemical softening – further ion exchange softening – dechlorination – membrane electrolysis to produce NaOH from desalination concentrated. The results showed that the process could reduce SWRO brine by 29%, and the NaOH and NaClO produced could be used in desalination.

Before recovering valuable elements from desalination concentrate, another necessary process is the removal/recovery of calcium to avoid scaling problems in subsequent separation processes. The hardness removal technology has been very mature. Chemical precipitation and nanofiltration membranes can effectively remove Ca^{2+}. However, Ca^{2+} and Mg^{2+} share similar chemical properties. Therefore, the traditional hardness removal process will cause the simultaneous removal of Ca^{2+} and Mg^{2+}, affecting the subsequent Mg extraction process. Mg^{2+} is considered an important mineral in seawater. Molinari et al. [19] studied the selective precipitation capacity of sodium citrate ($Na_3C_6H_5O_7$), carbonate (Na_2CO_3), and hydrogen carbonate ($NaHCO_3$) to Ca^{2+} in desalination concentrate at different pH, temperature, ionic strength and molar ratio of reagents. The results showed that at pH = 9.0 and temperature = 60°C–70°C, HCO_3^-: Ca^{2+} = 3, Ca^{2+} removal efficiency is greater than 90% and Mg loss is less than 7% [19].

6.3. Magnesium

Magnesium is widely used in different sectors. Compared with salt lakes, the concentration of magnesium in desalination concentrate is still low. It needs to be further concentrated to ensure the economy of the production process. One idea is to use a nanofiltration membrane to concentrate Mg^{2+} from brine to the concentration level of the salt lake. The subsequent process can adopt a mature extraction process for the salt lake [5].

Some researchers have also attempted to prepare magnesium salts directly from desalination concentrate. Dong et al. [20] studied the method of preparing reactive MgO from rejected brine by precipitating it with NaOH. This study selected NaOH as an alkaline source to react with Mg^{2+} in the desalination concentrate. The reaction product was $Mg(OH)_2$ and a small amount of $CaCO_3$. The $Mg(OH)_2$ was further calcined to MgO. The results showed that when adjusting NaOH/Mg^{2+} ratio to 2, $Mg(OH)_2$ is in the highest purity. Increasing the calcination temperature and time can reduce the reactivity of MgO. Although it is reported that synthesized MgO from desalination concentrate has higher reactivity and purity than commercial MgO, the production cost is 2.5 times of commercial MgO. Mohammad et al. [21] studied the method of recovering magnesium from desalination concentrate by ammonia precipitation. They evaluated the effects of brine salinity, reaction temperature, and ammonia– magnesium molar ratio on magnesium recovery. At 15°C, a salinity of 85 g/L, and an NH_3:Mg molar ratio of 4.4:1, the authors report a maximum recovery of 99% from desalination concentrate. Since the solubility of $Mg(OH)_2$ is proportional to temperature, low temperatures are recommended for the complete recovery of magnesium.

Another study reported a three-step process for recovering magnesium from rejected brine [22]. The first step is to precipitate Mg^{2+} with paper sludge ash. Then, $MgSO_4$ (production of the first step) was dissolved by sulfuric acid (H_2SO_4, 1 M). The last step is to precipitate $MgSO_4$ with ethanol (solution:ethanol = 1:1). In the optimal conditions, the reaction efficiency of the three stages is 98%, 70.8%, and 88%, respectively, and the total efficiency is 61.1%.

6.4. Potassium

Potassium is the main fertilizer component. Various electrochemical, membrane-based, and adsorption-based methods have been investigated to remove potassium from desalination concentrate. However, the price of potassium salt is usually low, and the extraction from seawater or desalination concentrate is less competitive in terms of economic profit. Efficient separation and enrichment of K^+ are the primary means to improve the economic feasibility of the extraction process. As shown in Fig. 6, Yuan et al. proposed a modified zeolite potassium ionic sieve, which shown high Na^+/K^+ selectivity and absorption ability (concentration factor = 100). They used this in a commercial K_2SO_4 production plant in China. The production cost of K_2SO_4 reported was 2,486 yuan/ton, and the K^+ extraction ratio was 85% [3,23]. Like this work, Hou et al. [24] proposed a polyamide membrane incorporating zeolite, which has high selectivity (K:Na = 4:1) and can continuously extract potassium from seawater.

Specific electrode ($Fe[Fe(CN)_6]$) has been demonstrated to keep selectively recover 69.6% of K^+ from synthetic seawater (K:Na = 140:1), with the separation factor (K^+/Na^+) of 141.7. Meanwhile, the energy consumption is about ten times lower than that of the capacitive deionization method, showing good economic feasibility [25]. Diatomite shows selective potassium adsorption and is considered a way to produce fertilizer [26]. Some researchers proposed to produce potassium salt from seawater based on an anion exchange membrane. The first step is the removal of sulfate from an anion exchange membrane with KCl solution. Then is absorption K^+ on clinoptilolite and elution with ammonium sulfate [27,28]. Maiti et al. [29] proposed a process to generate potassium sulfate from seawater through the reaction of potassium sulfate (produced by the precipitation of frozen brine), ammonia and potassium tartrate. The feasibility of this process depends on the recovery efficiency of tartaric acid.

6.5. Rubidium

Studies have shown that potassium cobalt hexacyanofer-rate [30] or potassium copper hexacyanoferrate (KCuFC) [31] can effectively adsorb Rb^+ in seawater. In addition, studies showed that high concentrations of Ca^{2+}, Na^+, and Mg^{2+} slightly affected the adsorption of Rb^+, but the presence of K^+ can significantly reduce the adsorption of Rb^+.

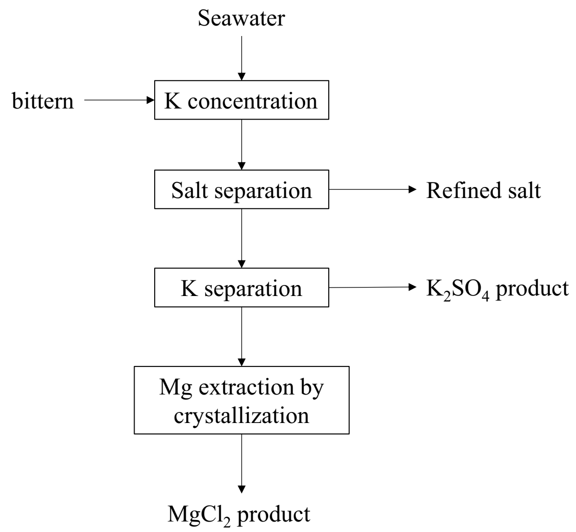

Fig. 6. Process flow of produce K_2SO_4 from seawater [23].

KCuFC adsorption column with polyacrylonitrile package is proposed to compensate for the effect of K^+. The adsorbed Rb^+ was desorbed by KCl (0.1M), and a solution of 68% pure Rb^+ was produced by passing through a resorcinol formaldehyde column and subsequently leaching with HCl, which kinetically separated the Rb^+ from the K^+ [32]. In addition, the commercially available hexacyanoferrate-based ion-exchange resin CsTreat, designed for the removal of radioactive cesium from nuclear reactor wastewater, has shown a high sorption capacity for Rb^+ from SWRO brine [33].

Naidu et al. [32] integrated the membrane distillation and Rb adsorption systems, which provided a long contact time for encapsulated adsorbent (KCuFC) to produce fresh water and Rb salt simultaneously. As a result, they successfully extracted 2.26 mg Rb^+ from 12 L desalination concentrate. The estimated annual production price will be more than $10 million (unit price $14,720 Rb^+) for a 10,000-ton/d desalination plant.

In addition, the extraction of Rb^+ into the organic phase using the selective ligands BAMBP (4-tert-butyl-2-(α-methyl benzyl) phenoxide) or dicyclohexano-18-crown-6 has been extensively investigated [34,35]. The selectivity of BAMBP for Rb^+ is about12 to 20 times than K^+, and 100 times than Cs^+ [34]. Calixarene has also been shown to be effective in the selective extraction of Rb^+ from brine [36].

6.6. Boron

In natural pH brines, boron exists in neutral form as $B(OH)_3$. Boron selective ion exchange resin is considered the best method for boron recovery. A series of commercial products can be found in the market. Figueira et al. [37] tested and compared three commercial boron selective resins, Purolite S108, DIAION CRB03, and CRB05. The results showed that DIAION CRB03 resin had a higher adsorption capacity than other resins and was the best choice for boron recovery in desalination concentrate. In addition, they selected the El Prat desalination plant in Spain as a case to perform a preliminary estimate of the costs and revenue associated with installing a boric acid production plant using brine (Table 3). The result shown that the payback period calculated was considered satisfactory, making the project attractive from an economic perspective.

Table 3
Economic evaluation in 10 y timeframe for boric acid production from the El Prat desalination plant brine [37]

Brine source	El Prat desalination plant (Spain)
Brine production	73 million·m^3/y
Boron concentration in brine	8.45 mg of B/L
Total boron in brine	617 tons of B/y
Extraction products	2,500 tons of H_3BO_3/y
CAPEX	2 million €
OPEX	0.8 million €
Selling price of H_3BO_3	680 €/t
Revenue	2 million €
Discount rate	10%
Interest rate in Spain	3%
Tax rate in Spain	25%
Payback period	4 y

6.7. Strontium

Strontium sulfate is the principal strontium ore mined, with a production of about 200,000 tons/y, mostly from China, Iran, Mexico, and Spain. Strontium salt is mainly used in drilling fluids for oil and natural gas extraction, and the oil and natural gas industry is also a significant user of seawater desalination. The overlap of the two sectors in geographical distribution allows for coupling the two processes [38].

^{90}Sr is a vital monitoring index for the safety of nuclear power plants. Therefore, studies on Sr recovery from seawater generally focus on analyzing its radioactivity [39]. The adsorption of strontium into an organic solvent or solid film by crown ether or tertiary amide can effectively separate Sr from similar ions in seawater [40,41]. However, the cost of these Sr-complexing compounds is usually high. Therefore it is necessary to find an efficient and low-cost regeneration method before being used in the commercial recovery of Sr.

Similar chemical properties of Sr^{2+} and Ca^{2+} means that conventional selective membranes or resins absorption strategies are unlikely to be successful. Hong et al. [42,43] used alginate microspheres to recover Sr from synthetic seawater. The results showed that the adsorption of Sr suffered from significant competition from other cations in seawater, and the maximum absorption of alginate microspheres was 147 mg/dm. After elution with hydrochloric acid, the concentration of Ca^{2+} in the eluent is 10 times than Sr^{2+}. Ghaeni et al. [44] found the adsorption capacity of magnetite/MnO_2/fulvic acid nanocomposite can be as high as 6.4 mg/g in natural seawater. However, the adsorption capacity of other competitive ions in seawater (such as Ca^{2+} and Mg^{2+}) has not been evaluated. The hydrothermally structured titanate nanotubes also showed high adsorption capacity (92 mg^{-1}), but its Sr^{2+} selectivity from Ca^{2+} was only about two, when applied to seawater [45].

6.8. Lithium

Although non-ocean lithium resources are widely available, the lithium in the ocean is inexhaustible, which has attracted extensive attention worldwide. Currently, the majority of lithium is from salt lakes. The mature methods for lithium extraction from salt lakes include precipitation, salt gradient solar cell, nanofiltration, electrodialysis, adsorption, etc. [46,47]. The concentration of Li^+ in salt lakes is often in the hundreds or thousands ppm rather than hundreds ppb in seawater [48]. Therefore, it is challenging to directly applied the existing extraction method for salt lakes to seawater. The methods of extracting lithium from seawater mainly include selective adsorption, selective osmosis, and electrochemical processes.

MnO_2-based ion-sieve materials are the most common strategy for the recovery of lithium from seawater. The small size of Li^+ can penetrate the spinel structure of MnO_2, so it shows strong selective adsorption capacity on MnO_2. Many strategies have been employed to improve the innate property of MnO_2, such as combining with graphene oxide [49], cellulose [50] or cellulose acetate [51] films, intercalating titanium into the MnO_2 lattice [52], and utilizing electrolytic approaches based on MnO_2 electrodes [53].

Besides the process based on MnO_2, Hoshino [54] described a membrane-based recovery process for seawater. Ion conductive glass–ceramics were selected as the Li^+ selective material film (LISM), which allows the selective transport of Li^+ ions from the negative to the positive electrode. LISM functions as a salt bridge and facilitates the transportation of Li^+ from high to low-concentration solution (from seawater to Li^+ recovery solution).

7. Discussion

The seawater desalination industry has developed rapidly in recent years in China. Most desalination plants in China adopted RO technologies. The volume of brine from SWRO plants in China is about 1,696,900 m^3/d. B, Li, and Rb in desalination concentrate are substances with high concentration and unit price. If continuous extraction can be realized, the estimated economic value could be at least three times high than that of the existing desalinated water production. It should be noted that the extraction technology of trace chemical elements from seawater is still at the pilot or laboratory stage, and it will take some time for the comprehensive utilization of desalination concentrate to be put into commercial operation, but the current work has made this possibility increasingly high.

Acknowledgements

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Supplementary information

Table S1
Concentration of chemical species in seawater and their commercial value in China

Element	Concentration in seawater (ppm)	Commercial compounds			Expectation output from reverse osmosis plants (10,000 yuan)
		Compounds	Purity	Price (yuan/kg)	
Sodium	10,561	NaCl	Industry level	0.18	1,402.51
Magnesium	1,272	MgO	Industry level	6	3,721.48
Calcium	400	$CaCl_2$	Industry level	1.72	553.54
Potassium	380	KCl	Industry level	3	632.85
Bromine	65	Br	Industry level	49.8	947.05
Strontium	13	$SrCl_2$	Industry level	30	204.86
Boron	4.6	B	–	1,700	2,287.89
Silicon	4	SiO_2	Industry level	9.5	23.82
Aluminum	1.9	Al	–	18.83	10.47
Rubidium	0.2	RbCl	Analytically pure	480	39.65
Lithium	0.1	Li_2CO_3	Industry level	760	212.82
Copper	0.09	Cu	–	67.81	1.79
Barium	0.05	$BaCl_2$	99%	3.7	0.08
Iodine	0.05	I	Medical level	678	9.92
Zinc	0.014	Zn	–	24.41	0.10
Manganese	0.01	$MnSO_4$	Industry level	8	0.06
Lead	0.005	Pb	–	15.5	0.02
Selenium	0.004	SeO_2	Industry level	135	0.22
Tin	0.003	Sn	–	179	0.16
Cesium	0.002	Cs_2CO_3	–	800	1.15
Molybdenum	0.002	$(NH_4)_6Mo_7O_{24}$	≥99%	198	1.40
Uranium	0.0016	U	Industry level	1,000	0.47
Gallium	0.0005	Ga	–	4,450	0.65
Nickel	0.0005	Ni	–	203.25	0.03
Thorium	0.0005	ThO_2	Industry level	290	0.05
Cerium	0.0004	CeO_2	Industry level	22	0.00
Vanadium	0.0003	NH_4VO_3	99.50%	170	0.03
Lanthanum	0.0003	La_2O_3	Analytically pure	260	0.05
Silver	0.0003	Ag	–	4,908	0.43
Bismuth	0.0002	Bi	–	53	0.00
Cobalt	0.0001	Co	–	338.5	0.01
Gold	0.000008	Au	–	405,800	0.95