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Potential of desalination for lithium production in the Kingdom of Saudi Arabia

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ABSTRACT

The fact that the ocean contains an essentially inexhaustible store of lithium has exerted a hypnotic effect on scientists and funding agencies. However, there is a negligible chance that exploitation of the ocean for lithium will ever be broadly economically competitive with non-oceanic sources. While research into improving lithium extraction from brines is of interest from the point of view of fundamental science, the low concentration of lithium in seawater and desalination brines make them inherently uncompetitive compared to more concentrated terrestrial brines and terrestrial ore bodies. There are likely to be hard-rock deposits and/or natural brines associated with geothermal formations which will be more attractive sources of lithium in the Kingdom of Saudi Arabia for the foreseeable future.

Keywords: Seawater concentrate; Valorization; Lithium; Techno-economic analysis

1. Introduction

Lithium extraction from seawater has attracted a great deal of research attention in recent years, due to the rapidly increasing market for Li-containing batteries for consumer electronics and electric cars [1–13]. Production of lithium salts (in terms of amount of elemental lithium) has increased from 30,000 to 80,000–100,000 metric tons since 2010 [14,15]. Prices of lithium salts have also surged recently with increasing demand, spiking to almost seven times their average price in 2010–2015 (Fig. 1).

2. Existing sources of lithium

Until recently, lithium was commercially extracted largely from brines, which today still account for about 40% of production. These are primarily underground brines formed under unusual geological condition, largely located beneath dry lakes in the Andes mountains and the high plateaux of western China, which have concentrations thousands of times greater than that found in seawater – 350–2,000 ppm rather than 180 ppb [16]. Existing brine treatment technologies rely on precipitating Li as Li_2CO_3 by addition of sodium carbonate [17]. This method cannot be directly applied to seawater or desalination brines because of their much reduced concentration [18]. There are also lake brines (e.g., Great Salt Lake, Utah, ~40 ppm Li), geothermal brines (e.g., Salton Sea, California, ~200 ppm Li) and underground brines associated with oil and gas formations (e.g., Smackover formation, Arkansas, ~350 ppm Li) with concentrations of lithium orders of magnitude greater than seawater [19]. For comparison, our analyses of lithium in desalination brines from the Red Sea and Arabian Gulf have found lithium concentrations between 210 and 310 ppb.

Rising demand for lithium has led to an increase in recent years in hard-rock mining of high-grade lithium-rich ore associated with granitic pegmatites, which currently account for about 60% of world production. The most important

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of these minerals are spodumene ($LiAlSi_2O_6$) and petalite ($LiAlH_4Si_4O_{10}$). Typical commercial ore bodies of these minerals contain 0.5%–1.4% lithium [19]. Significant deposits of these minerals exist in many places in the world, but current production is highest in Australia and China. While in the first decades of the 21st century mining of brines was considered to be less capital-intensive than mining of high-quality hard-rock deposits, this situation has more recently been reversed [20,21].

More recently still, there has been interest in commercial exploitation of lower-grade lithium deposits. These include clays (200–4,000 ppm Li) – a major project is proposed to mine lithium-rich clay in northern Mexico [22] – and micas (e.g., lepidolite, $KLi_{1.5-2}Al_{2.5-1}Si_{3-4}O_{10}(F,OH)_2$) [23]. Typical lepidolite-bearing ores have concentrations of about 0.5%, although the Yichun mine in Jiangxi produces lithium commercially from a lepidolite ore reported to contain 2% lithium [19]; a project is planned to produce lithium from lepidolite in Namibia [24]. Significantly, lepidolite also contains rubidium and cesium in appreciable amounts [25], and the business models for recent lepidolite mining projects include production of salts of these alkali metals in addition to lithium [15].

3. Extraction of lithium from low-quality brines

In order to extract lithium from seawater and other low quality brines, some form of selective concentration is required. Research in this area has been driven primarily by the desire to exploit salt lake brines in Qinghai and Tibet with a much higher Mg:Li ratio than South American brines, where the traditional process of precipitating Li_2CO_3 using sodium carbonate is ineffective [21]. Attempts to achieve selective absorption [26], selective permeation [1], and/or exploit the electrochemical behavior [3] of lithium have been the main strategies investigated for extraction of Li from dilute aqueous solutions. Manganese dioxide-based ion-sieve materials have been the most extensively investigated strategy for separation of lithium from complex aqueous solutions [27]. The small size of the Li^+ ion allows it to penetrate the spinel structure of MnO_2 and thus exhibit a higher selective adsorption on MnO_2 [28]. Various strategies have been employed to improve the selectivity and efficiency of this innate property of manganese dioxide, including combining it with graphene oxide [29], cellulose [30], or cellulose acetate [4] membranes, intercalating titanium into the MnO_2 lattice [31], and using electrolytic approaches based on MnO_2 electrodes [32,33]. Other materials that have been shown promise for selective lithium absorption are polydopamine [5], polymeric 1,3-diketones [6], and ruthenium complexes embedded in a poly(methacrylic acid) resin [7]. Methods based on selective complexation of lithium followed by liquid–liquid extraction [9,10], transport through a liquid membrane [34], or transport through a solid membrane [11] have also attracted research interest.

Some recent studies have achieved very high Li^+:Na^+ selectivities in seawater treatment [8,12,33]. An electrochemically driven intercalation process using titania coated iron (III) phosphate electrodes has achieved a Li^+:Na^+ selectivity of 18,000 and near quantitative removal of Li from a 300 mL sample of salt water over ten cycles of extraction [8]. On a larger scale, gram quantities of Li_3PO_4 have been obtained by precipitation of a solution in which Li was concentrated 43,000 times by iterative electrically-driven membrane sieving [12]. A 'pilot scale' process treating desalination brine by absorption to MnO_2 electrodes has reported an increase in the Li^+:Na^+ ratio by a factor of 430,000 [33]. While these studies are exciting from the proof-of-concept view, the energy involved in simply moving the large volumes of water required to obtain viable amounts of lithium by either of these process makes them uncompetitive.

It has been suggested that sufficiently-selective technology relying on passive uptake of Li^+ to a material submerged in the ocean would be the only economically viable way to recover Li from seawater [35–37]. The Korean steelmaker POSCO and the Korea Institute of Geoscience and

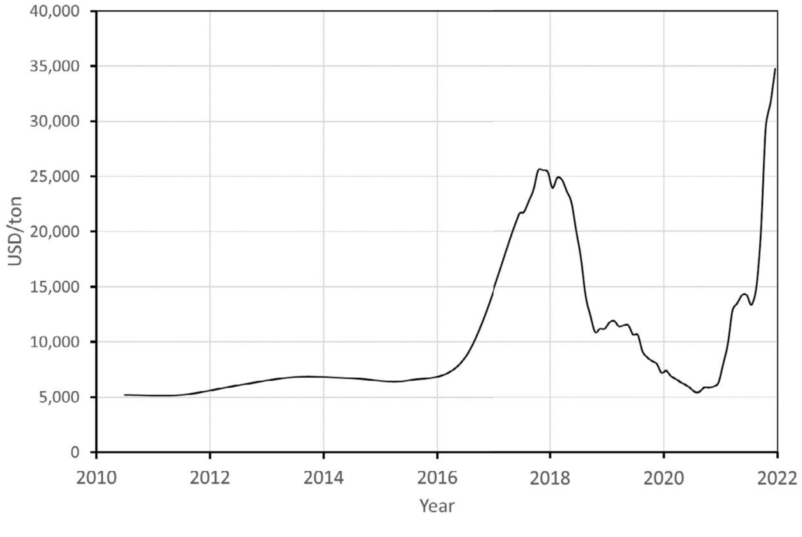

Fig. 1. Lithium carbonate (battery grade) price, 2010–2021. Data from: statista.com/statistics/606350/battery-grade-lithium-carbonate-price/ and tradingeconomics.com/commodity/lithium.

Mineral Resources invested seriously in research into such a facility, but it proved to be uneconomic and the pilot was closed in 2018 [38].

If Li is collected not directly from seawater or brine, but from the more concentrated solution remaining after the principal solid components of desalination brine are removed ('bittern' or 'purge'), the hundredfold increase in Li concentration will make many of the approaches currently being investigated much more practicable [39].

4. Techno-economic comparison

Two recent studies comparing the expenditure of lithium production utilizing brines and hard-rock mining were consulted [20,21]. These gave the range of OPEX and CAPEX (amortized over 25 y) per ton of lithium carbonate by these two processes for commercially viable projects (Table 1). The average breakdown of OPEX and CAPEX for both types of project were calculated by Johnston [20] as: OPEX of production of lithium carbonate from brine was estimated to be 53% reagents, 16% salt harvesting, 10% labor, 8% energy, 6% maintenance and 6% other; corresponding CAPEX was 51% evaporation ponds, 22% plant, 13% infrastructure, 10% utilities and 4% brine extraction wells. Costs of a scale-up of the recent process proposed by Li et al. [12] applied to seawater, desalination brine of TDS = 65,000 ppm, and to a concentrated seawater derived purge stream were then calculated. The process of concentration was considered as an additional step required to obtain a brine for treatment, which was then added to a fraction of the OPEX required to produce lithium from pre-existing brine. It was considered that approximately the same quantity of reagents would be required by stoichiometry, and that probable reduced labor costs would be balanced by increased maintenance costs for the more complex plant; thus, only the '16% salt harvesting' item was removed from the OPEX, giving a 0.84× multiplier. For comparing CAPEX, it was considered that while the large expense of evaporation ponds and brine wells would no longer be required, the significantly greater complexity of the plant required – especially if it is required to co-produce hydrogen and chlorine, as suggested by Li et al. – could easily double its cost, giving an overall 0.67× multiplier.

Li et al. [12] quote 76.34 kWh per kg of lithium obtained for the electrolytic process for concentration of lithium. This figure does not include the significant energy required for moving the large amounts of seawater needed – at a seawater concentration of 180 ppm and 90% recovery, 6,172 tons to obtain one kg of lithium. Estimating a pump head of 20 m and 80% pump efficiency and a recovery of 90%, a pumping cost of 421 kWh per kg of lithium can be calculated. (This can be compared to the energy cost of seawater intake alone for producing one m^3 of product water by the Reverse Osmosis process (involving handling of about 2.5 m^3 of seawater) of 0.335 kWh calculated by Gude [40], which would give an estimated 800 kWh per kg of lithium).

Lai et al. report production of 31.12 kg Cl_2 and 0.87 kg H_2 for every kg of lithium produced by their process, and suggest that the market price of these commodities could fully offset the energy cost of electrolysis. The effect of selling these commodities at USD 1.25/kg for hydrogen and USD 0.175/kg for chlorine is also shown in Table 1. It can be seen that it has little overall impact on the profitability of the process, with production costs of in excess of USD 5.40/kg for Li_2CO_3, compared to a maximum estimated production cost of USD 3.73/kg for conventional brines and USD 1.88/kg from conventional hard-rock mining.

If bitterns or purge remaining after extraction of sodium chloride is considered, the concentration will be increased by approximately 30 times, and thus the amount of liquid that must be moved to obtain the same amount of lithium will be reduced by the same factor. This drastic reduction in volume reduces the OPEX considerably. However, this may come at the cost of a significant loss in economy of scale. The numbers of Johnston [20] were calculated on the basis of a plant producing 20,000 TPA of Li_2CO_3. What is the largest credible amount of Li_2CO_3 that could be produced from a concentrated bittern or purge stream? The largest SWCC plants can produce 1 million m^3 of water per day, treating about 800 million m^3 of seawater per year. If coupled to a facility for production of industrial sodium chloride, such a plant could produce 30 million TPA of NaCl. While considerably in excess of the total demand in the GCC countries, it is not entirely inconceivable that markets could be found for such production. Approximately 900 TPA of Li_2CO_3 could be obtained from this enormous quantity of seawater, which is a relatively

Table 1
Major chemical components of seawater

Source	Brine		Hard rock mining		Seawater (0.18 ppm Li)		Desalination brine (0.3 ppm Li)		Purge (5.4 ppm Li)	
(USD/kg Li_2CO_3)	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
OPEX	0.18	0.40	0.28	0.42	5.49	5.67	3.68	3.87	1.12	1.31
CAPEX	1.25 [20]	3.33 [20]	0.83 [20]	1.46 [20]	0.84	2.23	0.84	2.23	0.56	0.98
CAPEX	0.58 [21]	1.58 [21]	0.67 [21]	1.00 [21]						
Total	0.76–1.43	1.98–3.73	0.95–1.11	1.42–1.88	6.33	7.91	4.52	6.10	1.68	2.28
Cl_2	N/A		N/A		(0.90)		(0.46)		(0.17)	
H_2	N/A		N/A		(0.25)		(0.13)		(0.05)	
Total	0.76–1.43	1.98–3.73	0.95–1.11	1.42–1.88	5.40	6.98	4.04	5.62	1.51	2.11

small production for a lithium mine. The largest facility currently planned to produce sodium chloride from desalination brine in the Kingdom of Saudi Arabia would have a potential production of only 60 TPA Li_2CO_3 and would incur significant diseconomies of scale.

Any technology for enhancing the viability of production of lithium from seawater will, a fortiori, enhance the production of production of lithium from the numerous other brines where lithium occurs at a higher concentration. Such technologies can be expected to enhance the competitiveness of brines with lithium concentrations <200 ppm for lithium production, vastly increasing the range of salt lake brines, geothermal brines, and mineral wastewater streams that can be counted towards world lithium reserves.

5. Prospects for lithium production in the kingdom of Saudi Arabia

As lithium is an increasingly important strategic product, there are motives of national interest in establishing a lithium production capacity in the Kingdom of Saudi Arabia. How might this best be achieved? The following possibilities may be considered, in order of commercial viability:

- Lithium-rich granites with average lithium concentration in excess of 200 ppm are associated with the Arabian Shield [41] and spodumene deposits are known from the Nubian Shield which is part of the same geological formation [42]. It is probable that there are commercially viable hard-rock deposits of lithium ores in the western half of the Kingdom of Saudi Arabia which are yet to be identified. Currently, hard-rock mining is the most economically viable process for producing lithium and thus minerals exploration to identify potential projects for hard-rock mining should be the first priority.
- The Red Sea is a tectonically-active area with the potential for geothermal brines that could fall into the lithium concentration range either currently viable, or potentially viable in the future with the application of technology such as that developed by Li et al. Currently such a source would typically be less commercially attractive than a hard-rock deposit. So as not to create a waste problem, the exhausted brines from a geothermal source would need to be returned underground after use. Because of this, and because of the possibility of powering such a project with geothermal energy, lithium produced in such a manner could be considered 'green lithium' and may command a premium in certain markets [43,44]. Identifying potential geothermal brines for lithium extraction should be a second-priority for lithium self-sufficiency. However, it is less likely that suitable sources will be found in the Kingdom than that hard-rock deposits will be identified.
- Brines have been identified beneath dry lakes in the Rub al Khali with a significantly higher Li:Na ratio than seawater, approximately 10 times greater [45]. While the overall concentrations of lithium in these brines are low (210–310 ppb), it is probable that further exploration would find more concentrated brines with a similar L:Na ratio.
- If neither hard-rock deposits nor suitable natural brines can be found in the Kingdom of Saudi Arabia, then there may be a strategic interest in extracting lithium from the relatively small amount of purge/bittern produced by commercial salt-making operations to meet vital national needs. This would allow production on the order of a few hundred TPA of Li_2CO_3, at a price potentially competitive with current lithium production from underground brines (Table 1).
- Production of lithium by treating desalination concentrate, utilizing all the desalination brines currently produced in the Kingdom would give of order 10,000 TPA of Li_2CO_3, at a cost significantly above current world costs of production.
- Some Saudi Arabian oilfield produce brines have been found to have approximately ten times the lithium concentration as desalination brines [46]. Although there is a lower overall volume of these brines and they are more geographically dispersed, they could potentially produce a similar amount of Li_2CO_3.
- Production of lithium directly from seawater is a yet less efficient process and should be considered a last resort.

As lithium prices have been historically volatile, if no relatively high-grade sources of lithium can be identified within the Kingdom of Saudi Arabia, it will be more cost-effective to establish a strategic stockpile at the next low point in the price cycle than to seek to produce lithium from very low-grade sources.

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