Lithium Recovery from Oil and Gas Produced Water: A Need for a Growing Energy Industry

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Demand for lithium (Li) is expected to continue to rise sharply with the growing worldwide deployment of electric vehicles, and prices are projected to continue to rise. Li can be sustainably recovered from oil and gas produced water by utilizing Li recovery technologies such as adsorbents, membrane-based processes, and electrolysis-based systems (Figure 1). Lithium is a valuable metal, broadly known for its current application in the energy-storage sector, in lithium-ion batteries, and for its potential use in thermonuclear fusion; lithium is also used in CO_2 adsorbents in aircrafts and submarines, glass production, medical products, and materials such as plastic and grease. In fact, the value of lithium has increased sharply in recent times due to high demands and low supply of this alkali metal, and the future of lithium price is now difficult to predict since both supply and demand of lithium is currently unstable.[1]

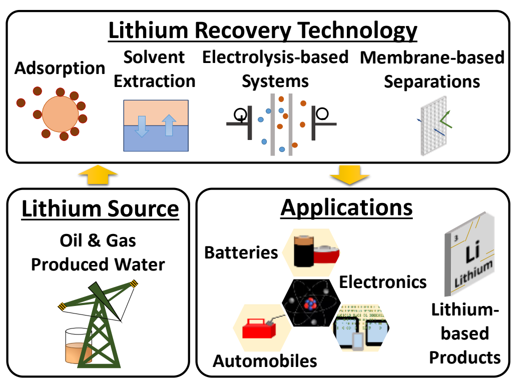


Figure 1. Lithium recovery technology platform.

While most lithium used for lithium batteries is currently produced in the lithium triangle of Argentina, Bolivia and Chile in South America[2,3], the large markets with significant demands for lithium are in North America, Europe and Asia, however. Thus, with resource-security in mind, increasing attention has been given to recovery of lithium from produced water at oilfields both in the US and globally. Various technologies that enable recovery of lithium from oilfields have been tested in order to provide the large markets with lithium from more diverse and often geographically closer sources. Although there is a plethora of reports on oilfield brines, less has been published on the use of wastewater from oilfields as a lithium resource. This paper evaluates potential for lithium resource recovery from oilfield wastewater.

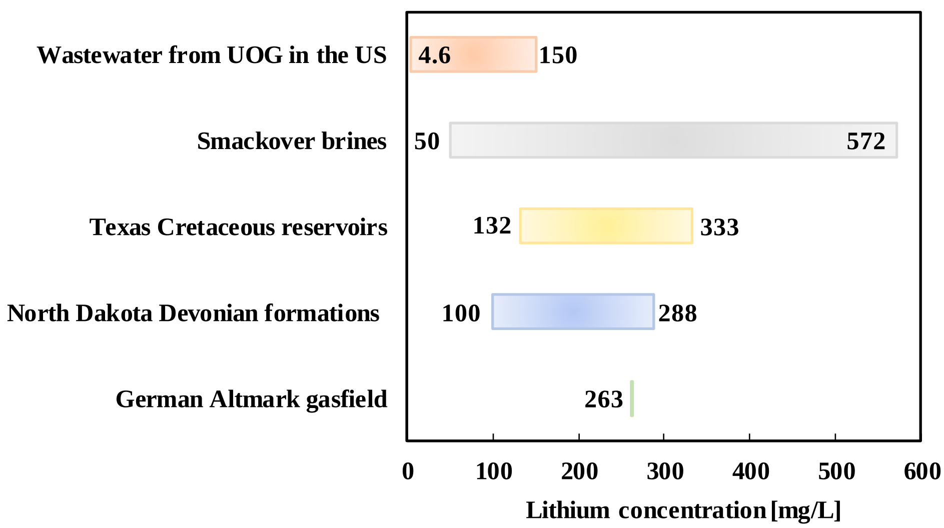


Figure 2. Lithium concentration in water from unconventional oil and gas (UOG) fields in the US[4] and some oilfield brines.[5]

Figure 2 shows that certain oilfield brines around the world contain high concentrations of lithium. For example, Smackover brines in the US have a maximum of over 500 mg/L of lithium, and some projects are moving forward to test its suitability as a lithium resource.[6,7] On the other hand, wastewater from oil and gas fields has lower concentration but nevertheless has potential as a lithium resource because there is no need to build new wells and because oil producers can benefit from the revenue stream generated by lithium recovery from the wastewater, which would otherwise, be a financial burden. Estimates of the lithium resource ranges for some US oil and gas fields are given in Figure 3. It should be noted that these estimated values are not precise, not only because some data are lacking, but also because wastewater volume and its lithium concentration are also unstable and constantly changing.

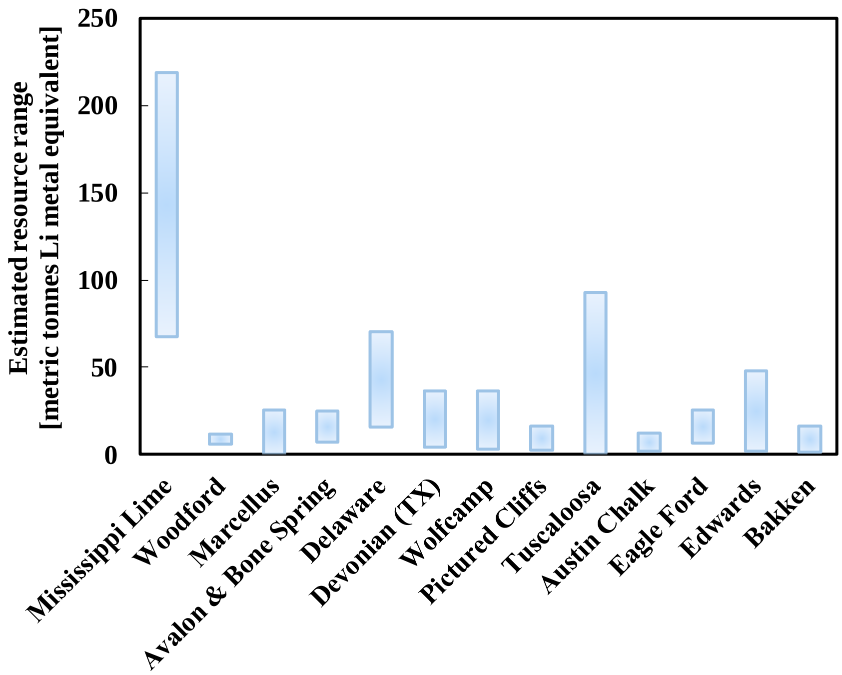
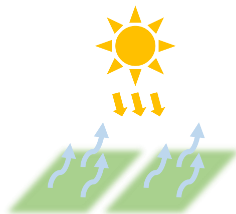
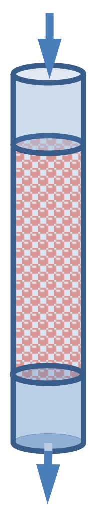
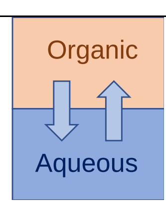


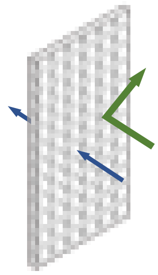
Figure 3 Estimated resource range in metric tonnes Li metal equivalent in wastewater from unconventional oil and gas formation in the US. The estimated values were calculated from a median of lithium concentration in UOG produced water from some formation (44 mg/L, calculated from 155 data points) and the volume of wastewater from each oil and gas formation (long-term produced water rates in gallons per day), both of which are reported in a EPA report.[4] The calculation assumes 100% lithium recovery and a formation lifespan of 30 years.

Figure 3 shows that wastewater from oil and gas production can contain from several dozen to several hundred tonnes of lithium. The total amount of lithium potentially available for recovery from these oil and gas production wastewaters can be comparable to that of some small lithium deposits with several thousand tonnes of lithium, such as in the Outovesi pegmatite deposits in Finland (2,000 metric tonnes Li metal equivalent)[6]. To be sure, general lithium oilfield deposits usually contain much more lithium: Fox Creek and Valleyview in Canada have 362,000 and 385,000 metric tonnes Li metal equivalent, respectively, while the Smackover Formation in the US has 750,000 metric tonnes Li metal equivalent.[6] The exploitation of lithium from oil and gas fields will enable US markets to obtain lithium domestically and avoid the potential for monopoly pricing by the South American concerns. In terms of capital cost, lithium producer can make use of existing oil and gas wells and thereby reduce their expenses for lithium recovery. For example, based on a techno-economic study on the Smackover Formation in the US, Daitch reported that since wells did not need to be drilled, the cost for lithium recovery could be reduced significantly.[7] In addition, oil and gas producers could increase profits by selling lithium obtained from their wastewater. Therefore, the exploitation of oil and gas production wastewater with its high potential as a lithium resource should be evaluated carefully, particularly in locations which frequently import lithium from other regions. This presents a potential benefit for oil and gas producers as well as the end users of lithium.

For the past several decades, a combination of solar evaporation and carbonation has been utilized to produce pure lithium compounds. Solar ponds can, however, only be applied to brine that has a relatively high concentration of lithium, roughly more than 500 mg/L. Evaporation also takes approximately one year to concentrate the lithium sufficiently to ensure effective precipitation of lithium carbonate on the addition of soda ash. Recently, other, more rapid processes to recover lower concentrations of lithium, starting at around 100 mg/L, a common concentration in oilfield brines, have been considered, as summarized in Table 1. This section reviews such technologies and discusses their applicability to oil and gas wastewater by considering some practical examples.

Table 1. Technologies for lithium extraction from brine

Technology	Mechanism	Developer
Solar evaporation	 Lithium-containing solutions in ponds are concentrated by solar heating; lithium carbonate precipitated on addition of soda ash (sodium carbonate). $2LiCl + Na_2CO_3 \rightarrow Li_2CO_3 + 2NaCl$	Conventional
Phosphate precipitation	Lithium phosphate precipitated on addition of phosphoric acid. $3LiCl + H_3PO_4 \rightarrow Li_3PO_4 + 3HCl$	POSCO[8–10]
Ion exchange resin	 Lithium ions intercalated into layers of aluminum hydroxide on ion exchange resins. $LiCl + NaCl \cdot 2Al(OH)_3 \cdot nH_2O \rightarrow NaCl + LiCl \cdot 2Al(OH)_3 \cdot nH_2O$	Dow[11–13]
Aluminum based adsorbent	Lithium ions adsorbed onto aluminum hydroxide with the almost same mechanism as ion exchange resin above.	FMC[14–16] Simbol[17,18] Eramet[19]
Manganese based adsorbent	Lithium ions adsorbed within layers of manganese oxide such as $H_{1.6}Mn_{1.6}O_4$ and λ-MnO_2.	JOGMEC[20]
Titanium based adsorbent	Lithium ions adsorbed into layers of titanium oxide such as H_2TiO_3.	Neometals[21]
Solvent extraction	 Lithium ions extracted from water phase by oil phase. $R\text{-}H_{sol} + LiCl_{aq} \rightarrow R\text{-}Li_{sol} + HCl_{aq}$	Tenova[22,23]

Nanofiltration		Lithium ions concentrated through differences in ion rejection ratios and water flow rejection by membrane	MGX[24,25]

Phosphate precipitation is a newly developed technology to replace the carbonation step in the solar evaporation process. While this method requires extra processing steps to convert lithium phosphate into the desired lithium carbonate or hydroxide[8], it has succeeded in shortening the time needed for the solar evaporation step since lithium phosphate, with solubility 0.39 g/L, can be precipitated at ambient temperature at much lower concentrations than can lithium carbonate, whose solubility is 13.3 g/L. POSCO currently has projects to recover lithium from brine or battery recycling with this method.[9,10] However, it is doubtful that phosphate precipitation can be applied to oilfield wastewater because it still partially requires solar evaporation, which can concentrate lithium only from high-concentrated brine (e.g. more than 500 mg/L) within reasonable time, as a pre-concentration step.

Adsorbents such as ion-exchange resins are typically used in packed columns for practical operations. Although is a conventional method for recovery of metal ions from solution, lithium is much more difficult than other metal ions, e.g., copper, to adsorb selectively. The reason is that, in brine, much higher concentrations of sodium, potassium, calcium and magnesium ions are present, sometimes 100-fold greater than lithium molar concentration, and these ions have better affinity for strong acidic cation exchange resins. Because of the unfavorable solution conditions for effective recovery by conventional ion exchange resins, Dow Chemical in the US developed aluminum loaded resins that can take up lithium selectively from brine[11–13], although challenges remain due to low selectivities. There have been some reports in which lithium is extracted into solvent impregnated resins. Nishihama et al., for example, used 1-phenyl-1,3-tetradecanedione (C_{11}phβDK) / tri-n-octylphosphine oxide (TOPO) impregnated resins to separate lithium from sodium and potassium ions.[26] These solvent impregnated resins are one of the most promising ways to recover lithium because of their high selectivity, but the gradual elution of solvent from the resin, which makes the resin more difficult to be reused, remains problematic especially in oil and gas wastewater which can contain some organic components.

Other adsorbents that can be packed in columns are certain metal oxides/hydroxides, which show good capacity for lithium adsorption. While they have higher selectivity for lithium than ion exchange resins, it does take longer to complete extraction than with conventional ion exchange resins because lithium needs to intercalate into the layers of the metal oxides/hydroxides. Aluminum-based adsorbents are typically $LiCl/Al(OH)_3$ compounds, which are very similar to the aluminum-loaded resin. Since the aluminum-loaded resin only has adsorption sites on the surface of the resin, and the aluminum-based adsorbent has adsorption sites along its whole surface, the latter generally has a higher capacity. Some companies, FMC, Simbol and Eramet, have their own patents for aluminum adsorbents.[14–19] A manganese-based adsorbent with high selectivity for lithium was first reported by Ooi et al.[27–29] , raising interest among many researchers. Papers published after the first report indicate that the adsorption mechanism is essentially same as that with aluminum adsorbents. The manganese-based adsorbent is now being tested with the Uyuni salt lake solutions in Bolivia by Japan Oil, Gas and Metals National Corporation (JOGMEC).[20] A titanium-based adsorbent with comparable capacity for lithium recovery has been reported by Chitrakar et al.,[30] and Neometals used a similar kind of titanium-based absorbent to successfully extract lithium directly from brine.[21] The three adsorbents are granulated for practical operation in columns, and they are currently being studied in terms of optimal binder formulation and granulation method. Despite of the potential for the effective recovery of lithium by the three adsorbents, there are few practical operations; only a small number of pilot tests have been carried out. Given the clear potential for lithium recovery from oil and gas wastewater, it is desirable to keep moving forward to improve these adsorbents.

Solvent extraction is another promising method.[22] This technology also shows higher selectivity for lithium over other monovalent ions such as sodium and potassium ions. On the other hand, divalent ions, such as magnesium and calcium, should be removed and lithium should be pre-concentrated prior to the solvent extraction step to maintain the efficiency of the process. Tenova has its own process to extract lithium by solvent extraction and electrolysis[22,23], but it does not seem to be appropriate for produced water from oilfields because the lithium concentration needs to be elevated to a certain degree, the divalent ions need to be removed before solvent extraction, and organic impurities can have a significant negative impact on the efficiency of solvent extraction.

Finally, membrane technology is expected to play an important role for lithium extraction. Somrani et al. studied nanofiltration and low pressure reverse osmosis for lithium ion separation from brine.[31] Although temperature and pressure control are required, the membrane process can be applied to low concentrations of lithium, such as found in oil and gas wastewater. Furthermore, while fouling can be a very large concern, as discussed in other membrane applications, membrane processes can be applied to a variety of brines or wastewaters when conditions are properly determined and controlled. In fact, MGX has reported success in lithium extraction from oilfield produced wastewater using membranes.[24,25]

In conclusion, various technologies can replace conventional solar evaporation to meet the lithium demand by accelerating concentration processes and adapting systems to lower lithium concentration. When it comes to lithium extraction from oil and gas wastewater, this article shows that the three reported metal oxide adsorbents and membrane technologies are the most promising. Despite this potential, few practical systems are operational. Greater efficiency is required, which can be attained both by improving the discussed methods and by developing novel methods in order to recover lithium from solutions with a range of different characteristics and conditions.

Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

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REFERENCES

(1) Martin, G.; Rentsch, L.; Höck, M.; Bertau, M. Lithium Market Research – Global Supply, Future Demand and Price Development. *Energy Storage Mater.* **2017**, *6*, 171–179. https://doi.org/10.1016/J.ENSM.2016.11.004.

(2) United States Geological Survey. *Mineral Commodity Summaries 2018*; 2018.

(3) Vikström, H.; Davidsson, S.; Höök, M. Lithium Availability and Future Production Outlooks. *Appl. Energy* **2013**, *110*, 252–266. https://doi.org/10.1016/J.APENERGY.2013.04.005.

(4) United States Environmental Protection Agency. *Technical Development Document for the Effluent Limitations Guidelines and Standards for the Oil and Gas Extraction Point Source Category*; 2016.

(5) Garrett, D. E. *Handbook of Lithium and Natural Calcium Chloride*; Academic Press: Cambridge, U.S., 2004. https://doi.org/10.1016/B978-0-12-276152-2.X5035-X.

(6) Chagnes, A.; Swiatowska, J. *Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling*; Elsevier: Amsterdam, Netherlands, 2015. https://doi.org/10.1016/B978-0-12-801417-2.00007-4.

(7) Daitch, P. J. Lithium Extraction from Oilfield Brine, PhD Thesis, The University of Texas at Austin, 2018.

(8) Chon, U.; Lee, I. C.; Kim, K. Y.; Han, G.-C.; Song, C. H.; Jung, S. R. Method for Manufacturing Lithium Hydroxide and Method Using Same for Manufacturing Lithium Carbonate. Patent US9598291B2, 2017.

(9) POSCO. POSCO Begins Lithium Production First Time in Korea http://www.posco.com/homepage/docs/eng5/jsp/prcenter/news/s91c1010025v.jsp?idx=2701&onPage=1 (accessed Nov 29, 2018).

(10) Jamasmie, C. POSCO to Buy Lithium Mining Rights in Argentina from Galaxy http://www.mining.com/posco-buy-lithium-mining-rights-argentina-galaxy/ (accessed Nov 29, 2018).

(11) Lee, J. M.; Bauman, W. C. Recovery of Lithium from Brines. Patent US4159311A, 1979.

(12) Lee, J. M.; Bauman, W. C. Recovery of Lithium from Brines. Patent US4347327A, 1982.

(13) John L. Burba, I. Method of Making Crystalline 2-Layer Lithium Aluminates in Ion Exchange Resins. Patent US4461714A, 1984.

(14) Bauman, W. C.; John L. Burba, I. Recovery of Lithium Values from Brines. Patent US5389349A, 1995.

(15) Bauman, W. C.; John L. Burba, I. Recovery of Lithium Values from Brines. Patent US5599516A, 1997.

(16) Bauman, W. C.; John L. Burba, I. Composition for the Recovery of Lithium Values from Brine and Process of Making/Using Said Composition. Patent US6280693B1, 2001.

(17) Harrison, S.; Sharma, C. V. K.; Viani, B. E.; Peykova, D. Lithium Extraction Composition and Method of Preparation Thereof. Patent US8637428B1, 2014.

(18) John L. Burba, I.; Stewart, R. F.; Viani, B. E.; Harrison, S.; Vogdes, C. E.; Lahlouh, J. G. S. Sorbent for Lithium Extraction. Patent US8753594B1, 2014.

(19) Boualleg, M.; Lafon, O.; Burdet, F. A. P.; Soulairol, R. C. J. R. Method of Preparing an Adsorbent Material Shaped in the Absence of Binder and Method of Extracting Lithium from Saline Solutions Using Said Material. Patent US20160317998A1, 2016.

(20) Chitrakar, R.; Makita, Y.; Ooi, K.; Sonoda, A. Magnesium-Doped Manganese Oxide with Lithium Ion-Sieve Property: Lithium Adsorption from Salt Lake Brine. *Bull. Chem. Soc. Jpn.* **2013**, *86* (7), 850–855. https://doi.org/10.1246/bcsj.20130019.

(21) Neometals. Successful 'Proof of Concept' testing of Direct Lithium and Potassium Extraction from Brines https://www.neometals.com.au/reports/749-DX01062017.pdf (accessed Nov 29, 2018).

(22) Cohen, L.; McCallum, T.; Tinkler, O.; Szolga, W. Technological Advances, Challenges and Opportunities in Solvent Extraction from Energy Storage Applications. In *Extraction 2018 Preceedings*; 2018; pp 2033–2045.

(23) Tenova. Lithium Processing https://www.tenova.com/product/lithium-processing/ (accessed Nov 29, 2018).

(24) Bogner, S. Successful Independent Verification of the MGX Lithium Extraction Technology https://www.rockstone-research.com/images/PDF/MGX20en.pdf (accessed Nov 29, 2018).

(25) McEachern, P. Lithium Recovery from Oilfield Produced Water Brine & Wastewater Treatment https://rockstone-research.com/images/pdfs/MGX_TechnicalReportRapidLithiumExtractionProcess.pdf (accessed Nov 29, 2018).

(26) Nishihama, S.; Onishi, K.; Yoshizuka, K. Selective Recovery Process of Lithium from Seawater Using Integrated Ion Exchange Methods. *Solvent Extr. Ion Exch.* **2011**, *29* (3), 421–431. https://doi.org/10.1080/07366299.2011.573435.

(27) Ooi, K.; Miyai, Y.; Katoh, S. Recovery of Lithium from Seawater by Manganese Oxide Adsorbent. *Sep. Sci. Technol.* **1986**, *21* (8), 755–766. https://doi.org/10.1080/01496398608056148.

(28) Miyai, Y.; Ooi, K.; Kato, S. Adsorbent for Lithium and a Method for the Preparation Thereof. Patent US4665049A, 1987.

(29) Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K. Recovery of Lithium from Seawater Using Manganese Oxide Adsorbent (H1.6Mn1.6O4) Derived from Li1.6Mn1.6O4. *Ind. Eng. Chem. Res.* **2001**, *40* (9), 2054–2058. https://doi.org/10.1021/ie000911h.

(30) Chitrakar, R.; Makita, Y.; Ooi, K.; Sonoda, A. Lithium Recovery from Salt Lake Brine by H2TiO3. *Dalt. Trans.* **2014**, *43* (23), 8933–8939. https://doi.org/10.1039/c4dt00467a.

(31) Somrani, A.; Hamzaoui, A. H.; Pontie, M. Study on Lithium Separation from Salt Lake Brines by Nanofiltration (NF) and Low Pressure Reverse Osmosis (LPRO). *Desalination* **2013**, *317*, 184–192. https://doi.org/10.1016/J.DESAL.2013.03.009.