Public

# ZERO LIQUID DISCHARGE SYSTEM WITH INTERNAL REUSE OF BRINE MINERALS

**Author/Presenter:** Christopher Paul East[1],

[1]*Water Innovation Center, ENOWA, NEOM, Laboratory Manager, Saudi Arabia, christopher.east@neom.com*

**Co-Authors:** Hyuk Soo Son[1], Noura Ahmed Chehab[2], Ahmed Saleh Al-Amoudi[3], Nikolay Voutchkov [4]

[1]*Water Innovation Center, ENOWA, NEOM, Innovation and Research Project Lead, Saudi Arabia, hyuksoo.son@neom.com*

[2]*Water Innovation Center, ENOWA, NEOM, Water Research and Innovation Manager, Saudi Arabia, noura.chehab@neom.com*

[3]*Water Innovation Center, ENOWA, NEOM, Director of Desalination & Brine Innovation Solutions, Saudi Arabia, ahmed.alamoudi@neom.com*

[4] *Water Innovation Center, ENOWA, NEOM, Executive Director Water Innovation Center, Saudi Arabia, nikolay.voutchkov@neom.com*

## EXTENDED ABSTRACT

The effects of desalination brine on the environment have been a point of discussion for a number of years. As a consequence, the zero liquid discharge (ZLD) has been researched by many groups around the globe. Despite the ongoing research there are still many technical challenges remain, the chief of which is preparing minerals of acceptable quality for sale into global markets. If the proceeding minerals can not be sold, then the accumulation of salts on land will create a far larger environmental problem than discharge of brine back to the ocean. This paper proposes a scheme for zero liquid discharge that takes approximately 25% of the sodium chloride in the seawater and uses it for the production of other minerals and chemicals in the process including recycling where possible.

**Keywords:** Zero liquid discharge, ocean brine mining



Public

Public

## I. INTRODUCTION

The provision of water for human activity is essential. In the areas with significant water stress one viable option is desalination of either seawater of brackish water. The question of the environmental impact of seawater desalination brine discharge on the environment is a concern for many countries with brine potentially forming plumes that concentrate on the sea floor among other issues [1-5]. One year's worth of brine from a 100 megaliter a day desalination plant contains between two and three million tons of salts which are returned to the ocean at approximately twice the concentration of which they were taken. Although the water cycle is short, with most of the water returning to the ocean within 2 weeks, questions remain about the local effects of brine on marine life.

Zero liquid discharge (ZLD) has been used in small scale operations at inland locations where it is not possible to discharge brine to natural bodies of water. These systems aim to significantly reduce to volume of liquid waste, which is then trucked offsite. Zero liquid discharge systems have yet to be applied to seawater desalination brine due to the volumes and complexity of seawater desalination brine, which is a mixture of salts. Given the amount of brine generated the only viable route is to make salt from the brine and unless that salt can be sold, the amount of salt that would need to be stored on land would create an unmitigable environmental disaster on a scale that dwarfs the debate on the environmental impact of discharging the brine back to the ocean.

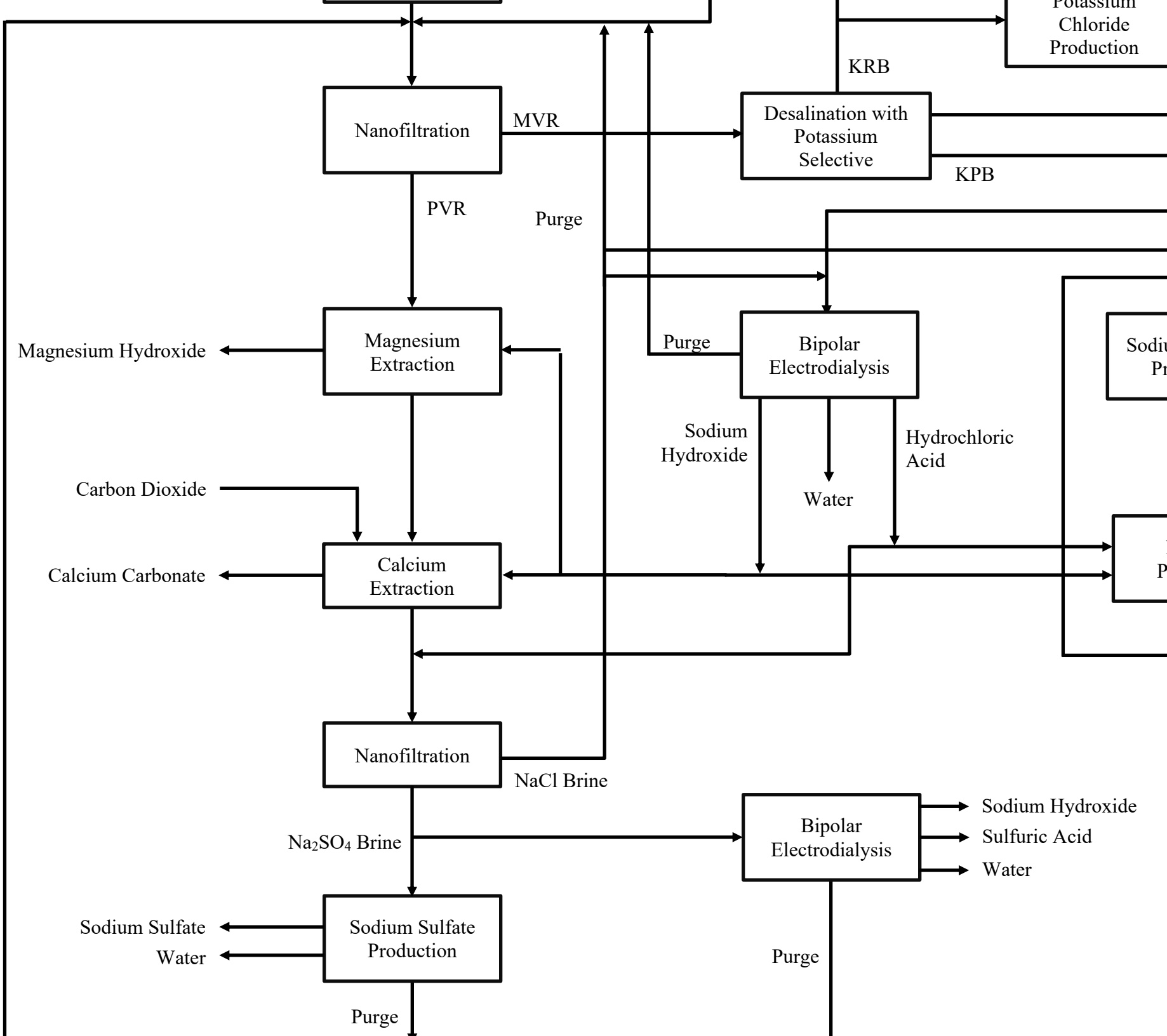
In regions where ZLD is mandated for seawater desalination, such as NEOM in Saudi Arabia, the development of a viable ZLD scheme for the economical extraction of salable slats from the desalination brine is critical. Others have looked at this problem in a modular way before, proposing different seawater desalination brine mining schemes for: sodium chloride, bromine, magnesium sulfate, magnesium [6-14] but a viable system for complete treatment of the brine is yet to emerge. In case of NEOM, such a system also needs to adhere to NEOM's land use policy, making the use of large-scale evaporation ponds to reduce energy consumption impossible, but still be able to handle the large the brine volume coming from the 500 million liter per day desalination plant to be built at Oxagon in NEOM.

## II. ZERO LIQUID DISCHARGE SCHEME

Taking into account the previous work already mentioned, ongoing research and the regulations and needs of NEOM, the ENOWA Water Innovation team has developed the following scheme for the ZLD of seawater desalination brine for the extraction of salable products, Figure 1.



Public


Potassium Chloride Production
KRB
Nanofiltration
MVR
Desalination with Potassium Selective
KPB
PVR
Purge
Magnesium Hydroxide
Magnesium Extraction
Purge
Bipolar Electrodialysis
Sodium Hydroxide
Hydrochloric Acid
Water
Carbon Dioxide
Calcium Carbonate
Calcium Extraction
Nanofiltration
NaCl Brine
Bipolar Electrodialysis
Sodium Hydroxide
Sulfuric Acid
Water
$Na_2SO_4$ Brine
Sodium Sulfate
Water
Sodium Sulfate Production
Purge
Purge

Taking seawater and putting it though standard reverse osmosis pretreatment and nanofiltration has now become an accepted first step method in the mining of seawater for various minerals, allowing the seawater to be split into a monovalent rich brine (MVR) and polyvalent rich brine (PVR). The MVR brine is passed to a reverse osmosis system which has a modified configuration to include a potassium selective membrane, currently under development by PWS and ENOWA. The configuration includes a selective membrane, which passes water, potassium and chloride followed by brackish reverse osmosis, producing a potassium rich brine (KRB), potassium poor brine (KPB) and potable water (after post treatment).

The KRB is sent in two further processes. Firstly, for potassium chloride crystallization which will include a concentration step and then crystallization by conventional method. The concentration and subsequent crystallization are expected to produce water, which may need further treatment before being supplied as potable water. Secondly, to a bipolar electrodialysis (BPED) for production of hydrochloric acid and potassium hydroxide. Both of these minerals are of high value.

The KPB will be sent to two different processes. The first process is BPED to produce sodium hydroxide and hydrochloric acid, which will supply a number of other processes in the brine mining complex. Due to the nature of the facility the purity of the sodium hydroxide coming out of this process is not of major concern. The second process is concentration, by osmotically assisted reverse osmosis (OARO), and then crystallization of sodium chloride, as reported previously [7]. It is expected that more than one purity of sodium chloride will be produced and upfront separation of the potassium from the sodium will allow for more of the high purity grade sodium chloride to be produced as potassium will be one of the main impurities. The purge from the crystallizers will be rich in bromide and sent for bromine extraction via the air blowing alkali absorption process. The bromine extraction process requires chlorine, acid (either sulfuric or hydrochloric) and sodium hydroxide. Hydrochloric acid and sodium hydroxide are produced on site and when used in the bromine extraction they will recombine to make sodium chloride again, which can be sent back to the sodium chloride crystallizers for recovery or recycled through the whole plant again if required.

The PVR brine from the NF system will contain the majority of the calcium, magnesium and sulfate ions but also measurable amounts of sodium and chloride ions. Separation of magnesium ions from calcium ions can be achieved by the precipitation of magnesium hydroxide using the sodium hydroxide generated in the BPED system feed by the KPB, which is essentially a sodium chloride stream. Controlling the pH of the precipitation will yield minimal magnesium losses in the clarifier overflow and calcium contamination in the magnesium hydroxide.

Using the magnesium hydroxide clarifier overflow calcium carbonate can then be precipitated with the addition of some carbonate source, either sodium carbonate, sodium bicarbonate or carbon dioxide. In the case of carbon dioxide, the pH will need to be further increased for which the sodium hydroxide generated in the PBED system will be used. Following this method also allows the carbon dioxide to be captured, making the process greener.

The overflow of the calcium carbonate clarifier is largely a mixture of sodium chloride and sodium sulfate. After pH adjustment by hydrochloric acid (produced by the BPED system) this stream is fed to another NF system to separate the sulfate and chloride ions. The permeate from this NF system should be of a much higher purity than the MVR brine from the first system and even the KPB from the potassium selective reverse osmosis system. This makes it extremely suited for high purity sodium chloride production and for a feed solution to the BPED system for the production of more sodium hydroxide which is used in the precipitation of magnesium hydroxide.

When looking at the composition of seawater, Table 1, we can see that the mole ratio of sodium

to magnesium is approximately 9 to 1. If the hydroxide demands of making magnesium hydroxide, calcium carbonate and bromine were met by the conversion of sodium chloride to sodium hydroxide then approximately 25% of the sodium chloride in seawater would need to be converted to supply those processes. This would provide an internal off taker for the sodium chloride, reducing the need to find local and international off takers for the 8 – 10 million dry tons of annual sodium chloride production for a zero liquid facility that needs to process brine from a 500,000 m3 per day desalination plant.

**Table 1: Average composition of Red Sea water at Duba, Kingdom of Saudi Arabia, 2023-24**

| Parameter | mg/L | StDev (mg/L) |
|---|---|---|
| Sodium, $Na^+$ | 12700 | 700 |
| Potassium, $K^+$ | 604 | 59 |
| Calcium, $Ca^{2+}$ | 501 | 30 |
| Magnesium, $Mg^{2+}$ | 1500 | 96 |
| Strontium, $Sr^{2+}$ | 9.3 | 1.0 |
| Rubidium, $Rb^+$ | 0.15 | 0.01 |
| Lithium, $Li^+$ | 0.19 | 0.04 |
| Boron*, B | 5.2 | 0.38 |
| Chloride, $Cl^-$ | 22900 | 660 |
| Bromide, $Br^-$ | 76 | 2.8 |
| Sulfate, $SO_4^{2-}$ | 3230 | 110 |
| Bicarbonate, $HCO_3^-$ | 146 | 4.0 |
| TDS (Total Dissolved Solids) (measured) | 41300 | 770 |

*Boron is measured elementally not as $BO_3^{3-}$

The sodium sulfate stream can be used in two processes, crystallized to make sodium sulfate and water and feed to another BPED system to produce sodium hydroxide and sulfuric acid. Both streams are expected to have purges.

Since it is impossible to recycle brine without the buildup of impurities and the overall goal of the scheme is zero liquid discharge, all streams have two purge options. The first is to send the purge streams back to the front end into the treated seawater and have the minerals reprocessed through the NF system or, where appropriate to directly to the main reverse osmosis system. The second option is to have a small series of evaporation ponds where the water in the brine can evaporate to solid state/crystals. The solids would then be discarded or sold as low purity sodium chloride. The evaporation pond also serves as an emergency outfall if needed.

Any of the water streams that are produced by various crystallization processes may need treatment by a brackish reverse osmosis system to provide extra water, effectively increasing the capacity of the desalination plant.

Currently, the core components of this schematic are being tested at the Enowa Water Innovation Center (WIC) ZLD Duba desalination plant in the Kingdom of Saudi Arabia.

Public

## III. VARIATIONS

It is acknowledged that this scheme relies on technology still under development but could be modified for existing technologies. The potassium can be extracted after the sodium chloride and bromine using, for example, the floatation method. Also, the final purge from the MVR brine is expected to contain a number or other valuable minerals, like rubidium chloride, and further processing can be added to the system as the technology develops to extract these minerals.

## IV. CONCLUSION

Many technical challenges remain for complete zero liquid discharge of desalination brine. Although the proposed scheme is still in development promising results are being produced during testing. The proposed scheme offers some flexibility in the minerals produced from the potassium chloride, sodium chloride and sodium sulfate streams, giving access to different markets for the minerals. The internal recycling loop of sodium chloride, sodium hydroxide and hydrochloric acid provides logistical advantages because of the elimination of lime, calcium hydroxide, which would need to be trucked in large quantities.
The different minerals and chemicals produced from the proposed scheme are: potassium chloride, potassium hydroxide, hydrochloric acid, sodium chloride, sodium sulfate, sodium hydroxide, sulfuric acid, magnesium hydroxide and calcium carbonate. Should a scheme like this be implemented, the water production capacity should be increased by 30% to 50% over the standard reverse osmosis desalination plant, leading to smaller intakes, pretreatment, and reverse osmosis facilities for the equivalent water supply.

## V. REFERENCES

1. Sola, I., Zarzo, D., Carratalá, A., Fernández-Torquemada, Y., de-la-Ossa-Carretero, J. A., Del-Pilar-Ruso, Y., & Sánchez-Lizaso, J. L. (2020). Review of the management of brine discharges in Spain. Ocean & Coastal Management, 196, 105301.

2. Campos, E.J., Vieira, F., Cavalcante, G., Kjerfve, B., Abouleish, M., Shahriar, S., Mohamed, R. and Gordon, A.L. (2020). Impacts of brine disposal from water desalination plants on the physical environment in the Persian/Arabian Gulf. Environmental Research Communications, 2(12), p.125003.

3. Soliman, M. N., Guen, F. Z., Ahmed, S. A., Saleem, H., Khalil, M. J., & Zaidi, S. J. (2021). Energy consumption and environmental impact assessment of desalination plants and brine disposal strategies. Process Safety and Environmental Protection, 147, 589-608.

4. Panagopoulos, A., & Haralambous, K. J. (2020). Environmental impacts of desalination and brine treatment-Challenges and mitigation measures. Marine Pollution Bulletin, 161, 111773.

5. Sola, I., Fernández-Torquemada, Y., Forcada, A., Valle, C., del Pilar-Ruso, Y., González-Correa, J. M., & Sánchez-Lizaso, J. L. (2020). Sustainable desalination: Long-term



Public

Public

monitoring of brine discharge in the marine environment. Marine Pollution Bulletin, 161, 111813.

6. Athanasoulia, I. G., Kyriazi, M., Katsiolis, S., Novakovic, J., & Malamis, D. (2023). Nanofiltration and selective crystallisation as technologies for the recovery of chemicals from seawater desalination brine to be used as ingredients for Bio-based fertilisers. Technical Annals, 1(4).

7. Sharkh, B.A., Al-Amoudi, A.A., Farooque, M., Fellows, C.M., Ihm, S., Lee, S., Li, S. and Voutchkov, N. (2022). Seawater desalination concentrate—a new frontier for sustainable mining of valuable minerals. NPJ Clean Water, 5(1), p.9.

8. Bi, J., Chen, T., Xie, Y., Shen, R., Li, B., Sun, M., Guo, X. and Zhao, Y. (2024). Bipolar membrane electrodialysis integrated with in-situ CO2 absorption for simulated seawater concentrate utilization, carbon storage and production of sodium carbonate. Journal of Environmental Sciences, 142, pp.21-32.

9. Randazzo, S., Vicari, F., López, J., Salem, M., Brutto, R.L., Azzouz, S., Chamam, S., Cataldo, S., Muratore, N., de Labastida, M.F. and Vallès, V. (2024). Unlocking hidden mineral resources: Characterization and potential of bitterns as alternative sources of critical raw materials. Journal of Cleaner Production, 436, p.140412.

10. Rivero-Falcón, Á., Peñate Suárez, B., & Melián-Martel, N. (2023). SWRO Brine Characterisation and Critical Analysis of Its Industrial Valorisation: A Case Study in the Canary Islands (Spain). Water, 15(8), 1600.

11. Al-Amoudi, A. S., Ihm, S., Farooque, A. M., Al-Waznani, E. S., & Voutchkov, N. (2023). Dual brine concentration for the beneficial use of two concentrate streams from desalination plant-Concept proposal and pilot plant demonstration. Desalination, 116789.

12. Ihm, S., Al-Amoudi, A.S., Yoo, Y., Fellows, C.M., Farooque, A.M., Al-Waznani, E.S., Al-Jehani, Y., Al-Shaikh, K., Al-Biladi, A.O., Al-Senani, A.N. and Voutchkov, N. (2024). Multistage nanofiltration system for supplementing Shoaiba Ph. 4 product water with magnesium extracted from seawater. Desalination, p.117414.

13. Molinari, R., Avci, A. H., Argurio, P., Curcio, E., Meca, S., Plà-Castellana, M., & Cortina, J. L. (2021). Selective precipitation of calcium ion from seawater desalination reverse osmosis brine. Journal of Cleaner Production, 328, 129645.

14. Figueira, M., Reig, M., de Labastida, M. F., Cortina, J. L., & Valderrama, C. (2022). Boron recovery from desalination seawater brines by selective ion exchange resins. Journal of environmental management, 314, 114984.



Public