Eutectic Freezing for Multiple Salt Recovery – A Sustainable Brine Management Approach

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The desalination industry has experienced substantial growth in recent years, driven by the increasing demand for potable water in regions with limited freshwater resources. Global contracted desalination capacity in 2021 is 7.0 million m^3/day (DesalData, 2022). Despite the benefits of desalination in meeting the increasing demand for potable water, the process generates high-concentration brine waste. The brine contains high levels of salt and other contaminants, which can have negative impacts on the marine environment and pose a threat to human health (Petersen et al., 2018). The desalination industry is facing significant challenges in disposing of the waste brine generated during the desalination process as environmental restrictions for waste brine rejection become increasingly strict. Current waste brine disposal methods include surface water discharge, deep-well injection, evaporation ponds, and land application (Panagopoulos et al., 2019), depending on the properties and volume of the brine as well as the nature of the disposal environment. In many cases, the brine waste is simply discharged back into the sea; for example, around 45% of waste brine is rejected into the ocean (Mickley, 2018). The discharge of hypersaline waste from desalination plants to the ocean raises the salinity and temperature of the seawater and affects the marine ecosystems (Bashitialshaaer et al., 2011), although the waste brine had been diluted with regular seawater or municipal wastewater before rejection (Arafat, 2017).

In addition to these methods, Zero-Liquid Discharge (ZLD) is increasingly considered a promising solution for waste brine management, as it aligns with the growing focus on sustainable and environmentally responsible practices in the desalination industry. ZLD involves treating and evaporating the waste brine until all the water has been removed, leaving behind a solid residue that can be safely disposed of. This method is considered one of the most environmentally friendly options, as it eliminates the need for liquid discharge and reduces the amount of waste that needs to be disposed of. It is expected that the global ZLD market will reach $1.76 billion by 2026 with an annual growth rate of 12.1% (Panagopoulos, 2022). However, ZLD is also the most expensive and energy-intensive method, as it requires a significant amount of energy to evaporate the brine. To make ZLD more cost-effective and energy-efficient, the desalination industry is exploring new technologies and approaches. Eutectic Freeze Crystallization (EFC) is a promising ZLD technology for managing waste brine from desalination plants. EFC uses freeze crystallization to separate salts from water. Water and salt form as ice and salt hydrates respectively when a solution cools below the eutectic point. The EFC process is known to be less energy-intensive than evaporative crystallization (Fernández-Torres et al., 2012).

EFC has successfully recovered single salts from binary or ternary systems. Copper sulfate, sodium sulfate, and magnesium sulfate have been extracted from the solutions ($CuSO_4$ (van der Ham et al., 2004), $MgSO_4$ (Genceli et al., 2005), Na_2SO_4 (Leyland et al., 2019)). However, research on separating multiple salts from multicomponent brines is limited. The group of (Randall et al., 2014) extracted Na_2SO_4 extracted Na_2SO_4 and $CaSO_4$ from RO brine with 97% water recovery by removing the salts sequentially based on their eutectic points. More salts can be recovered from seawater, such as NaCl (78%), $MgCl_2$ (11%), and $MgSO_4$ (4.74%) (*Salt - Occurrence | Britannica*, n.d.). These salts are essential natural resources for many industries to produce chemicals like chlorine, magnesium, sodium hydroxide, medicines and fertilizers. Furthermore, seawater salts are also widely used in the health and wellness industry due to their potential benefits in relaxation, skin health, and sleep quality (NAFEES et al., 2013; Polefka et al., 2012). Currently, there is no research on recovering three salts from RO waste brine, and limited studies have investigated supercoiling's effect on salt crystallization.

This paper aims to recover water and three abundant salts from waste brine using the eutectic freezing method as shown Fig.1 to conduct ZLD management of the RO waste brine. Recovered ice and salt hydrates can be separated by gravity, and the three salt hydrates can be separated based on their eutectic points. The eutectic points of $MgSO_4$, NaCl, and $MgCl_2$ are -3.9 °C, -23.3 °C, and -32.2 °C, respectively as illustrated in Fig. 2. The salt crystallization process in multiple-component seawater may differ from that in their aqueous. The first step will be to measure the eutectic points of the three salts present in seawater. The brine will be slowly cooled down until the first salt crystallizes and the salt is collected for X-ray diffraction (XRD) test to confirm its structure and composition. Once we have obtained their eutectic points in the seawater, we will then determine the optimal freezing operation parameters including temperature and time to recover high-quality salts. Then optimal freezing operation parameters and supercooling effect on salt crystallization will be investigated. This work aims to contribute to sustainable waste brine management by recovering water and multiple salts.

Fig.3 presents our preliminary findings on the freezing of NaCl aqueous solution. The temperature of the solution, measured at 1 cm away from the cooling source at the bottom, is plotted against time. At t=1723 min, the graph shows a sudden increase in temperature, and the occurrence of both salt and ice occur as shown in the picture. These results prove our current set up can reach the eutectic point of the salt and demonstrate the occurrence of supercooling prior to solution crystallization. Further research on this topic will be provided in future work.

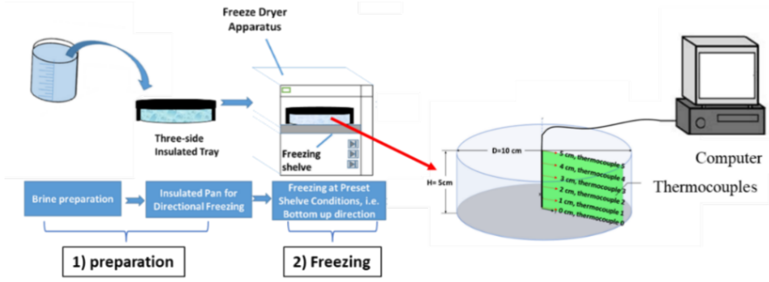

Fig. 1 Experimental setup and procedures for the brine eutectic freezing

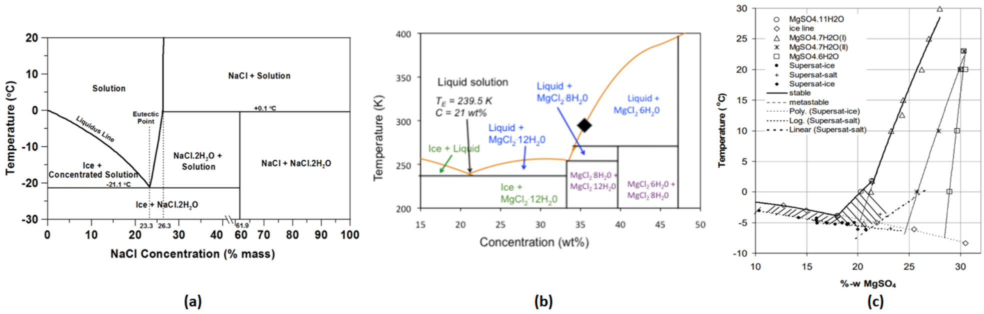

Fig. 2 Phase diagram for the salts in their binary solution (a): NaCl; (b) $MgCl_2$; (c) $MgSO_4$

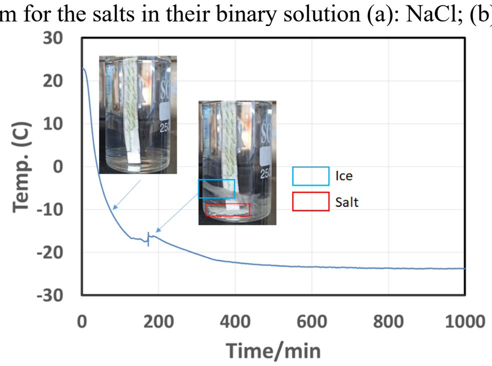

Fig. 3: Temperature and the formed crystals during the freezing of NaCl solution

References

Arafat, H. (2017). *Desalination sustainability: a technical, socioeconomic, and environmental approach*. Elsevier.

Bashitialshaaer, R. A. I., Persson, K. M., & Aljaradin, M. (2011). Estimated future salinity in the Arabian Gulf, the Mediterranean Sea and the Red Sea consequences of brine discharge from desalination. *International Journal of Academic Research*, *3*(1).

Fernández-Torres, M. J., Randall, D. G., Melamu, R., & von Blottnitz, H. (2012). A comparative life cycle assessment of eutectic freeze crystallisation and evaporative crystallisation for the treatment of saline wastewater. *Desalination*, *306*, 17–23.

Genceli, F. E., Gärtner, R., & Witkamp, G. J. (2005). Eutectic freeze crystallization in a 2nd generation cooled disk column crystallizer for MgSO4· H2O system. *Journal of Crystal Growth*, *275*(1–2), e1369–e1372.

DesalData, 2022. IDA Water Security Handbook 2021–20222. IDA and GWI DesalData

Leyland, D., Chivavava, J., & Lewis, A. E. (2019). Investigations into ice scaling during eutectic freeze crystallization of brine streams at low scraper speeds and high supersaturation. *Separation and Purification Technology*, *220*, 33–41. https://doi.org/10.1016/J.SEPPUR.2019.03.025

Mickley, M. (2018). Updated and extended survey of US municipal desalination plants. *Desalination and Water Purification Research and Development Program Report*, *27*.

NAFEES, M., KHAN, N., RUKH, S., & BASHIR, A. (2013). Analysis of rock and sea salts for various essential S and inorganic elements. *Journal of Science and Technology Univ. Peshawar*, *37*(1), 9–20.

Panagopoulos, A. (2022). Techno-economic assessment of zero liquid discharge (ZLD) systems for sustainable treatment, minimization and valorization of seawater brine. *Journal of Environmental Management*, *306*, 114488. https://doi.org/10.1016/j.jenvman.2022.114488

Panagopoulos, A., Haralambous, K. J., & Loizidou, M. (2019). Desalination brine disposal methods and treatment technologies - A review. In *Science of the Total Environment* (Vol. 693). Elsevier B.V. https://doi.org/10.1016/j.scitotenv.2019.07.351

Petersen, K. L., Paytan, A., Rahav, E., Levy, O., Silverman, J., Barzel, O., Potts, D., & Bar-Zeev, E. (2018). Impact of brine and antiscalants on reef-building corals in the Gulf of Aqaba–Potential effects from desalination plants. *Water Research*, *144*, 183–191.

Polefka, T. G., Bianchini, R. J., & Shapiro, S. (2012). Interaction of mineral salts with the skin: a literature survey. *International Journal of Cosmetic Science*, *34*(5), 416–423.

Randall, D. G., Zinn, C., & Lewis, A. E. (2014). Treatment of textile wastewaters using eutectic freeze crystallization. *Water Science and Technology*, *70*(4), 736–741.

Salt - Occurrence | Britannica. (n.d.). Retrieved February 28, 2023, from https://www.britannica.com/science/salt/Occurrence

van der Ham, F., Seckler, M. M., & Witkamp, G. J. (2004). Eutectic freeze crystallization in a new apparatus: the cooled disk column crystallizer. *Chemical Engineering and Processing: Process Intensification*, *43*(2), 161–167.