Salts Recovery by Eutectic Freezing for Waste Brine Management: Experiments and Simulation

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1. Introduction

Desalination has become increasingly vital in alleviating water scarcity driven by rapid population growth and escalating industrial water demand. As published by the International Desalination Association (IDA) in August, 2023 [1], the global daily desalination contracted capacity desalination is 107.95M m^3 by the end of 2022. The current water recovery rate is around 35-45% [2] , with an average recovery rate of 40%, the daily generated concentrated waste brine amount is estimated to over150M m^3. The disposal of the huge increasing amount of the concentrated waste is getting more concerns as it may cause a major potential threat to the marine environment. Currently, the main disposal method is to discharge the concentrated brine back into the sea after diluted [3]. Still the rejected brine's salinity is higher than the sea salinity which raises the salinity and temperature of the seawater presenting a threaten to the marine ecosystems [4]. Notably, the brine is treated as a waste rather than a concentrated mineral source for multiple elements. A promising solution for the waste disposal with minimal effect to the environment as well as mining valuable metals from the waste brine is Zero-Liquid-Discharge (ZLD), particularly through Eutectic Freeze Crystallization (EFC), which offers higher water recovery rates and lower energy consumption compared to thermal evaporation methods [5] and membrane distillation method [6]. In EFC, the waste brine will be frozen gradually to harvest the water in the form of ice gradually and concentrate the brine to the eutectic concentration. Then the concentrated brine starts the eutectic freezing to harvest the water in the form of ice and the salt in the form of solid crystals. These techniques can efficiently handle hypersaline brine regardless of its initial concentration or ion contents, producing low-salinity ice and solid salts for resource recovery. There have been several studies on the application of EFC for recovering single salts such as sodium sulphate from binary or ternary systems [7]. In addition, Lewis et al. [8] investigated the application of EFC of RO retentate and they found that sodium can be selectively recovered as a sodium sulphate salt. The recovery of other salts by EFC from different waste brines have also been investigated. These include calcium sulphate [9], selenium impurity [10], magnesium sulphate [11], copper sulphate [12], nickel and cobalt sulphate from sulphuric acid solutions [13]. This study applies EFC method for waste brine treatment to recover water in the form of ice as well as multiple salts crystals (NaCl (78%), $MgCl_2$ (11%) and $MgSO_4$). These three salts are essential natural resources for many industries to produce chemicals like chlorine, magnesium, sodium hydroxide, medicines and fertilizers. The synthetic brine sample made from these three salts with different formulation ratio are frozen under eutectic freezing condition to explore the strategies enhancing the salt recovery at higher crystallization temperature.

Keywords: Eutectic Freezing; Zero-liquid Discharge; Freeze desalination; Salts recovery

2. Methodology

Waste brine from reverse osmosis (RO) containing high levels of chloride, sodium, sulphate and magnesium is frozen under eutectic freezing conditions to obtain salts at different temperatures. The thermodynamic modelling tool OLI Stream Analyser, developed by OLI Systems Inc (2010) [14] is applied to describe the phase behavior of the complex saline systems associated with the EFC process and will be validated by the eutectic freezing experimental work using the synthetic brine made by (NaCl, $MgCl_2$ and $MgSO_4$) as shown in Fig. 1. In particular, the specific crystallization temperatures for the individual salts are investigated and the recoveries of the salts are also predicted. The ions concentration variation in the remaining unfrozen brine will also be captured by the OLI system which helps to investigate the concentrating process of Mg^{2+} concentration. The freezing of multiple samples with different formulation ratio of the three salts is conducted experimentally and numerically to explored to promote the production of the target salts.

3. Preliminary results

The preliminary results of the simulation by OLI in Fig. 2 show that ice will crystallize first at -5 C, followed by $NaSO_4.10H_2O$ at -6C, and then NaCl-$2H_2O$ is formed at -23C. This sequential crystallization enables material recovery protocol. The EFC process has an added advantage of producing water along with salts. This modelling tool is applied to describe the phase behavior of the complex saline systems under eutectic conditions and allows the prediction of the different salts that can form, the temperature at which they will freeze out, the salt type and their yield along with ice formation.

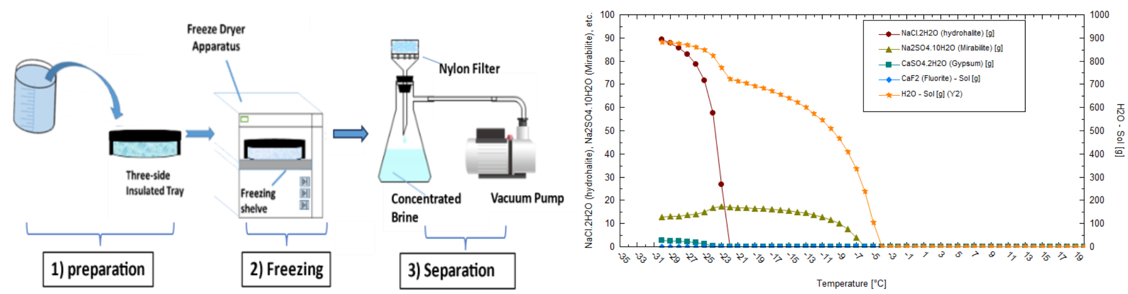

Fig. 1 : Experimental setup and procedures for the brine eutectic freezing and result of reduction on the salts and ice formation

4. Conclusion

In this work, eutectic freezing experiments of the waste brine is studied with the modeling by OLI to recover three salts NaCl, $MgCl_2$ and $MgSO_4$ from the waste brine. Based on our preliminary modeling results for the waste brine, ice will crystallize first at -5 C, followed by $NaSO_4.10H_2O$ at -6C, and then NaCl-$2H_2O$ is formed at -23C. Experimental work is under progress for the validation and more exploration for enhancing the salt production with lower energy cost. Moreover, the effect of adding acids such as HCl or H_2SO_4 is also explored.

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