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

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Introduction

Overview:

Eutectic freeze crystallization (EFC) is a novel method for the recovery of pure salt and water from hypersaline waste brines and a promising technology for the treatment of industrial waste water[1]. The recovery of salts during freeze desalination plays a crucial role in brine management by the waste volume reduction, the efficient use of resources, environmental impact mitigation and cost efficiency improvement[2-4]. This work investigates the attempt of recovery of three salts: Sodium chloride (NaCl), magnesium chloride ($MgCl_2$) and magnesium sulphate ($MgSO_4$); during the freezing of a reverse osmosis (RO) waste brine stream taken from an industrial plant **(see table 1)** using EFC. These three salts are essential resources for many industries to produce chemicals like chlorine, magnesium, sodium hydroxide, medicines and fertilizers.

Objective:

1. To apply EFC method for a RO waste brine containing high levels of chloride, sodium, sulphate and magnesium for the simultaneous production of salt and ice.
2. To recover water in the form of ice and multiple salt crystals or hydrate in attempt in reaching to their eutectic temperatures during the freezing process.

The overarching goal is to use freeze crystallization to enable successive material recovery under decreasing temperature conditions

Methodology:

1. Prepare & use synthetic RO brine by ignoring small ion contents (Table 1).
2. Subject the RO brine to both freeze [20 until -30 °C] crystallizations via:
   a) Experimental freezing 20 until -30 (see fig. 1)
   - Collect 8 samples: 4 samples for ice, and 4 samples for unfrozen brine.
   - Carry out ion analysis via the Ion Chromatography System (ICS) (Fig. 3).
   b) Thermodynamic modeling using OLI Stream Analyzer, developed by OLI Systems Inc (2010)[5] (see results Fig. 2).

a) Preparing synthetic brine based on industrial RO with ions distribution using ICS

Table 1: Ion's compositions of the industrial RO waste brine stream and the synthesized one on the basis of g/L

Detected Ion Via ICS	Na^+	Mg^{2+}	Ca^{2+}	K^+	Cl^-	Br^-	NO^{3-}	SO_4^{2-}	HCO^{3-}	Sr^{2+}	Total
Industrial RO	22.12	3.49	0.95	1.05	43.34	0.08	0.015	5.10	0.23	0.02	76.39
Synthetic RO	22.98	3.50	N/A	N/A	43.47	N/A	N/A	5.10	N/A	N/A	75.05

Table 2: Synthetic brine preparation for 1 L

Salt/Compound	Amount
NaCl	60.84 g
$MgCl_2$	8.66 g
$MgSO_4$	6.39 g

b) Carry out freeze crystallization aiming at reaching eutectic conditions using freeze dryer and separation setup of multiple successive samples

Fig. 1: Experimental setup & procedures for the waste brine freezing and ice samples, brine samples collection

c) Carry out thermodynamic modeling to assess experimental results and conditions using OLI multiple-stream equilibria separation analyzer

Table 3: Different collected samples & their conditions

Temperature (°C)	Designated ICE & Brine Samples	
-6	1. Ice 1	5. UFB 1
-8	2. Ice 2	6. UFB 2
-12	3. Ice 3	7. UFB 3
-21	4. Ice 4	8. UFB 4

Results & Discussion

a) Experimental crystallization measurements (g/L)

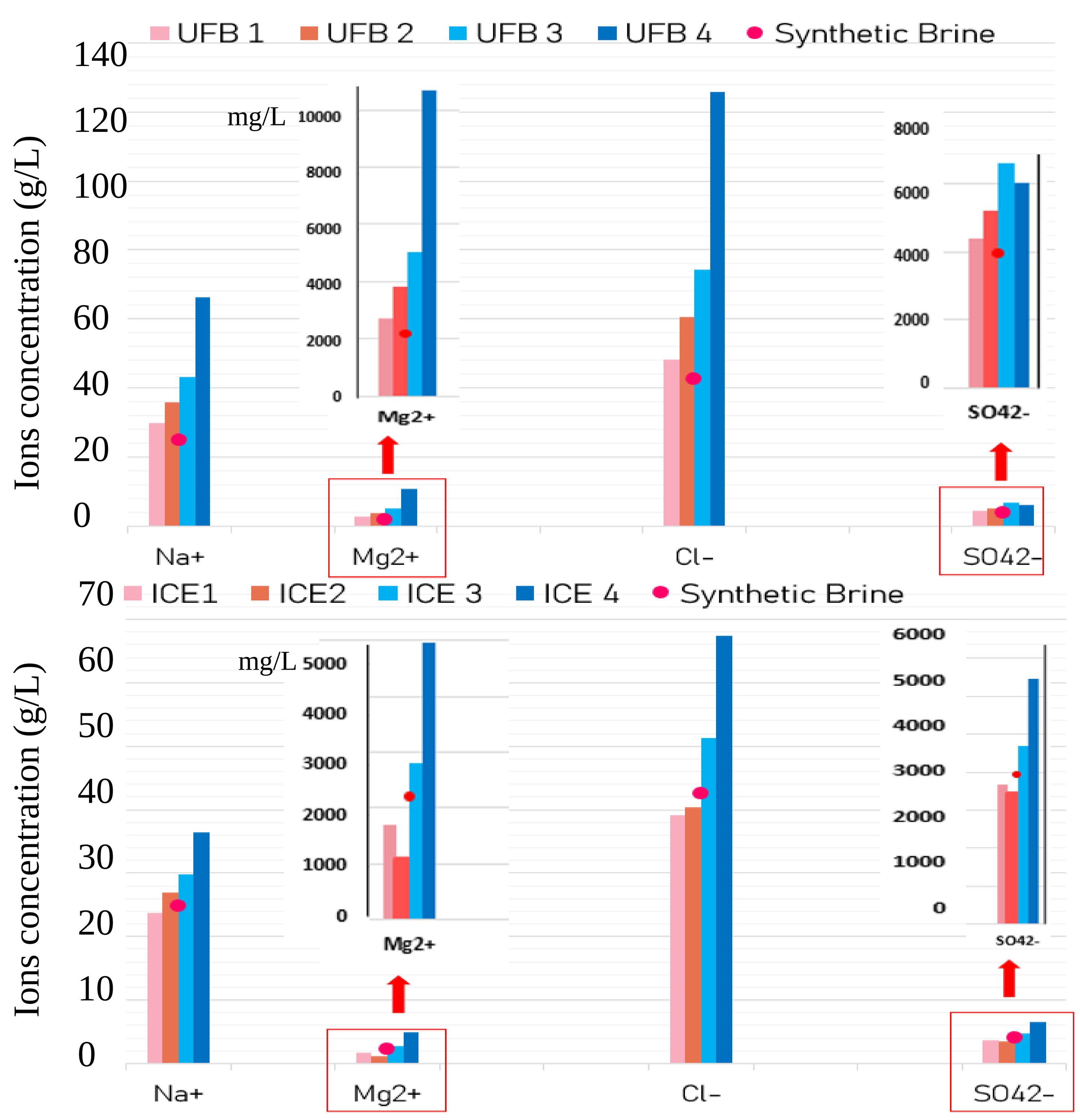

Fig. 2: Ion chromatography system (ICS) results for a) Ice samples, b) unfrozen brine samples

b) Thermodynamic OLI crystallization modelling (g/L)

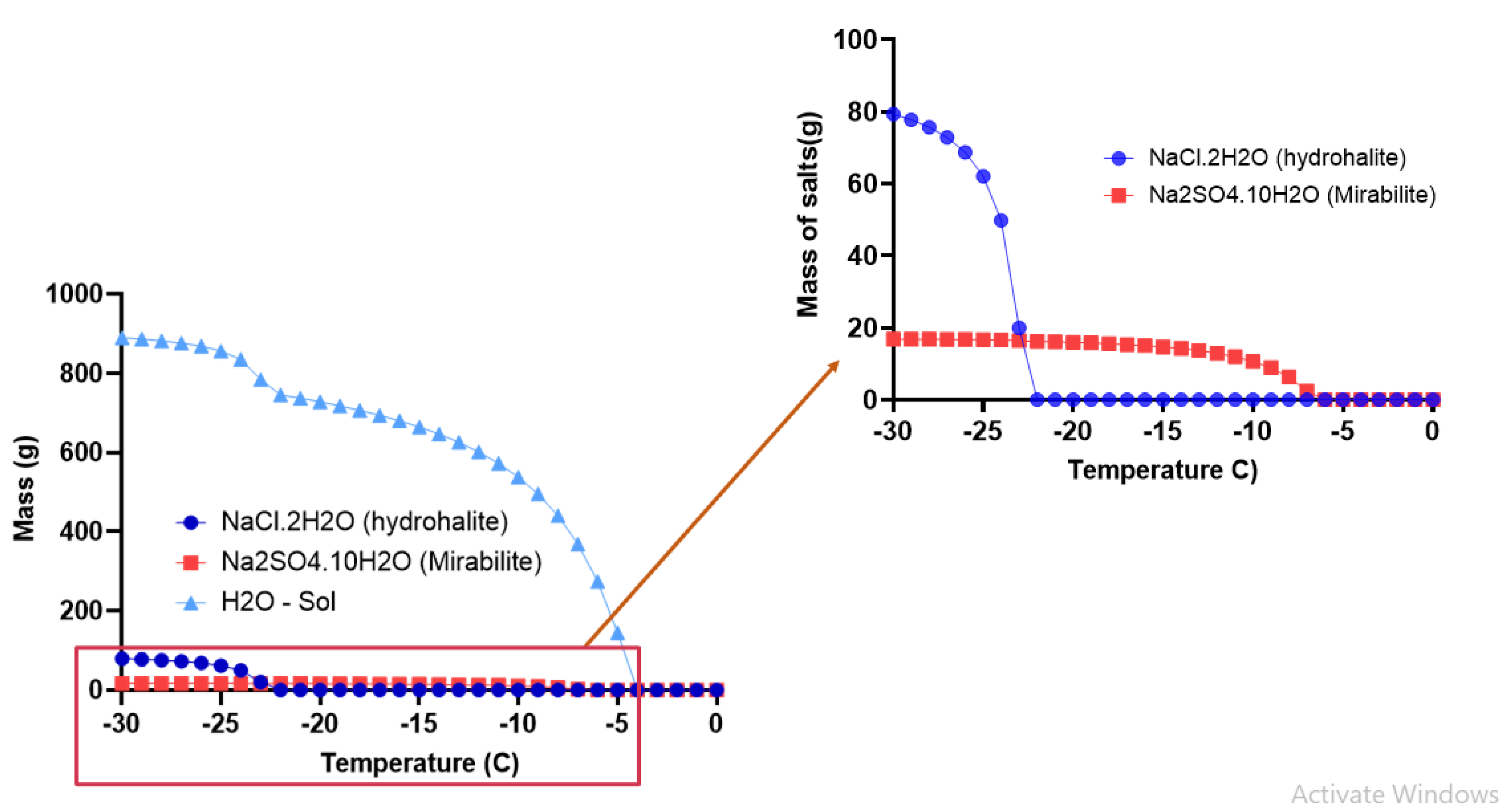

Fig. 3: Impact of temperature reduction on ice and salts formation starting from zero until -30 °C

- The formation of the salts increase gradually as the temperature is decreased
- The onset of ice crystallization incur at -5 °C
- The first solid salt to appear is $NaSO_4.10H_2O$ (mirabilite) when temperature reaches -8 °C
- The second solid to appear is $NaCl.2H_2O$ (hydro-halite) when temperature reaches -24 °C
- Modeling suggest no formation of the anticipated 3 salts in the form of pure crystals but rather as another hydrated salts
- Another discrepancy between molding and experimental observations the model shows presence of liquid brine beyond -25 °C whereas experimentally no liquid cease to exist beyond -21 °C

Experimental Results- Tables

Table 4: Ions increasing ratio in the unfrozen brine samples during the freezing

Samples	Na+	Ratio	Mg2+	Ratio	Cl-	Ratio	SO4 2-	Ratio
Synthetic Brine	24756.8	0%	2176.5	0%	42457.4	0%	3939.4	0%
UFB 1 (-6 ℃)	29887.6	21%	2693.7	24%	48085	13%	4413.1	12%
UFB 2 (-8 ℃)	35815.9	45%	3845.7	77%	60471.2	42%	5222.4	33%
UFB 3 (-12 ℃)	43155.2	74%	5017	131%	74208.4	75%	6641.7	69%
UFB 4 (-21℃)	66283.3	168%	10678.5	391%	125800.7	196%	6035.3	53%

Table 5: Ions increasing ratio in the ICE samples during the freezing

Samples	Na+	Ratio	Mg+2	Ratio	Cl-	Ratio	SO42-	Ratio
Synthetic Brine	24756.8	0%	2176.5	0%	42457.4	0%	3939.4	0%
ICE 1 (-6 ℃)	23726.5	-4%	1693.9	-22%	39127.6	-8%	3681.6	-7%
ICE 2 (-8 ℃)	26992.2	9%	1058.7	-51%	40421.8	-5%	3420.5	-13%
ICE 3 (-12 ℃)	29881.8	21%	2810.4	29%	51212	21%	4685.7	19%
ICE 4 (-21 ℃)	36497.5	47%	4960	128%	67397.8	59%	6458.6	64%

Conclusions & Perspective

- Model results of RO brine freezing shows ice formed at -5 ◦C before 1st salt $NaSO_4.10H_2O$ (mirabilite) starts to crystallization at -8 ◦C.
- Continuous cooling until -24◦C resulted in further formation of the 2nd salt $NaCl{\cdot}2H_2O$ hydrate
- Experimentally ice salinity in the initial freezing stage (ICE1/UFB1) is lower than the initial salinity of the synthetic brine.
- The salinity of unfrozen brine samples (UFB) continues increasing with decreasing temperature.
- In ICE2 sample, an increase of Na^+ ion is observed which assists the formation of $Na_2SO_4.10H_2O$ at -8 ℃. This is also in accordance with OLI simulation results in figure 2.
- The increasing concentrations of Mg^{2+} and Cl^- (at lower temperatures) indicate the presence of $MgCl_2$ in the unfrozen brine.
- Lower cooling temperature should be explored in future work to verify the formation of $NaCl.2H_2O$.

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