Waste minimisation through recovery of salt and water from a hypersaline brine

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Abstract This paper focuses on applying Eutectic Freeze Crystallisation technology to a hypersaline, multi-salt brine with trace quantities of base and precious metals. The salient results show that the crystallisation process can be manipulated using seed crystals to selectively crystallise $Na_2SO_4{\cdot}10H_2O$ over ice over specific temperature regions. Both ice and $Na_2SO_4{\cdot}10H_2O$ products were recovered with low contamination by impurities. This contamination was further reduced with a washing protocol. The salt crystals showed traces of Se and HCO_3, which possibly adsorbed onto the surface of the crystal. More importantly, the results showed a 76% reduction in the mass of the hypersaline brine.

Key Words Eutectic Freeze Crystallisation, hypersaline brine treatment, $Na_2SO_4{\cdot}10H_2O$

Introduction

Eutectic Freeze Crystallisation (EFC) technology involves the simultaneous crystallisation of ice and salt products by operating at a condition near the eutectic point of the system (van der Ham 1998). Furthermore, van der Ham (1998) reported EFC technology to be more energy efficient than a 3-stage evaporative crystalliser. Reddy (2010) has shown the recovery of pure $Na_2SO_4{\cdot}10H_2O$ and ice crystals from a synthetic dilute brine; however the brine did not contain any traces of base or precious metals. The application of seeding plays a critical role in crystallisation processes as it can control the quality of the crystal products (Aamir 2010). More importantly, it can also allow for the selective recovery of one crystalline phase over another (Rousseau 1980) in a multi-salt brine where multiple peri-eutectic points exist.

The brine production is expected to increase exponentially in the next decades and novel solutions are crucial in minimising this brine. Therefore, the primary focus of this paper is to determine the feasibility of using EFC technology for the minimisation of an industrial hypersaline, multi-salt brine; with traces of base and precious metals. In addition, it will be determined to what extent the high concentration of impurities affect the peri-eutectic point of the $Na_2SO_4{\cdot}10H_2O$ and ice. This will be compared to results presented by Reddy (2010) for the pure Na_2SO_4-H_2O system and the dilute brine. Finally, an investigation into the quality of products is conducted to determine the yield and purity of the crystals using a seeding strategy.

Materials and Methods

Batch test studies were carried out in two 1L jacketed, glass crystallisers that were insulated to prevent scaling of ice on the external surfaces. One kilogram of filtered, brine solution was transferred to each crystalliser and maintained at a temperature of 20 °C for 1hr to attain uniformity. Agitation was achieved using an overhead stirrer connected to a 4-bladed pitched-blade impeller. Heat transfer was effected by circulating a coolant, Kryo 45, through the jacket of the crystallisers. The LAUDA Wintherm Plus software (v2.2) was used to control the thermostat temperature and the pump flowrate. The temperature of the brine was measured using the dataTaker DT80 Series 2 with CEM20 Channel Expansion Module connected to a temperature monitoring device, with Pt 100 thermocouples for accurate temperature measurements. A Metro-ohm conductivity meter was used to indicate salt and ice crystallisation.

The brine solution (tab.1) was cooled at a rate of 1°C/hr. A seeding protocol was implemented to selectively crystallise $Na_2SO_4{\cdot}10H_2O$ over ice and other salts in the hypersaline brine. Once the solution reached supersaturation with respect to $Na_2SO_4{\cdot}10H_2O$, 5g/L of $Na_2SO_4{\cdot}10H_2O$ seeds were added to the crystalliser. The crystalliser contents were filtered at 5 °C intervals, starting at 10 °C, to remove the built-up solids. This also allowed the monitoring of the salts that crystallised during these intervals. Once the production of ice occurred in the crystalliser, these contents were filtered more frequently to prevent the build up of ice. The experiment was run in duplicate and combined

Table 1 *Concentration of cations and anions in the hypersaline brine*

Species	mg/L	Species	mg/L	Species	mg/L
Na	75756	NO_3	2200	Pt	3
Cl	52889	NH_4	1008	Au	0.3
Ni	14	Mg	27	Rh	0.4
K	256	SO_4	72870	Ru	2
Ca	47	HCO_3	3904	Ag	0.2
Fe	0.2	Si	8	B	0.9
Cd	0.3	Se	775	As	109
Li	36	Te	2	P	8
Temperature	***20˚C***	***pH***	***9***		

to ensure a sufficient quantity of solution, at the lower temperature ranges, to produce $NaCl·2H_2O$. However, the excessive production of ice in the crystalliser reduced the quantity of solution to an impractical quantity at the very low temperature ranges (<-20 °C) and hence no $NaCl·2H_2O$ was recovered. The salt produced was washed with a saturated solution of Na_2SO_4 at approximately 4 °C. The ice crystals were washed with supercooled de-ionised water.

Results and Discussion

Figure 1 shows the change in concentration of the cations and anions in the hypersaline brine as the solution was cooled from ambient conditions to -23.4°C. Tthe graph can be divided into three distinct regions. Between 20 °C and 12 °C, only a liquid phase was present (liquid region). Between 12 °C and -7.4 °C, salt crystals were present (salt region). Between -7.4 °C and -23.4 °C, predominantly ice crystals were present (ice region).

At 12 °C, $Na_2SO_4 \cdot 10H_2O$ began to crystallise out of the solution after seeds were introduced to the crystalliser. This can be seen by the decrease in the concentration of the Na^+ and SO_4^{2-} ions until -7.4 °C. There was a decrease in the concentration of the Cl^- ions between 14 °C and -5 °C which indicated the removal of Cl^- ions. However, thermodynamically no Cl^--based salt is seen to crystallise out at this temperature and at the current conditions. Between -7.4 °C and -23.4 °C, ice crystals were present (ice region) as can be seen from the increase in the concentration of all species. The remaining ions do not show a significant change in concentration and will not be discussed in detail.

The peri-eutectic point for this system exists at -7.4 °C, as this is the point at which both ice and salt crystallise simultaneously. This temperature is significantly lower than that of a pure binary system of Na_2SO_4-H_2O, which reached its eutectic point at -1.24 °C and the peri-eutectic point of the dilute brine occurred at -2.22 °C (Reddy 2010). This highlights the effect of impurities on

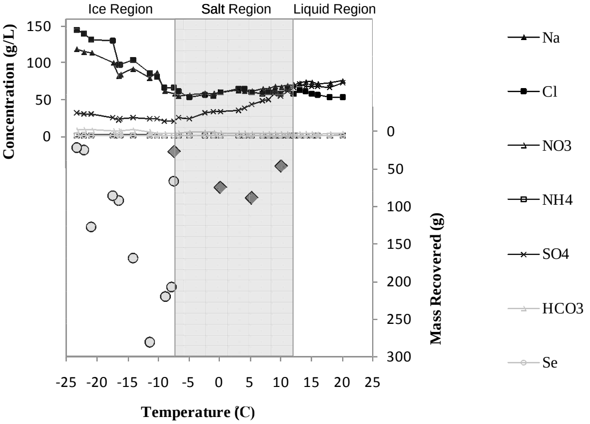

Figure 1 *Change in concentration of ionic species as well as recovery of ice (○) and $Na_2SO_4·10H_2O$ (◇) as a function of temperature*

the eutectic and peri-eutectic temperatures of a system and, therefore, it can be deduced that increasing the concentration of the impurities in a sodium sulphate rich brine leads to a greater deviation from the eutectic conditions of a pure Na_2SO_4-H_2O system.

Figure 1 also presents the mass of ice (○) and $Na_2SO_4 \cdot 10H_2O$ (◇) crystals that were recovered over the duration of the experiment. Due to the effects of seeding, a clear distinction can be made between the ice and $Na_2SO_4 \cdot 10H_2O$ regions. The 2000g hypersaline brine was reduced by more than 75% to 469g. A total of 236g of salt was produced, which when analysed, was found to be $Na_2SO_4 \cdot 10H_2O$.This translated into a 68% reduction in the concentration of SO_4^{2-} ions. A total of 1295g of crude ice was recovered.

Figure 2 (a) presents the composition of the salt recovered at 0.1 °C with no washing. The figure shows a sodium sulphate salt with a 2% contamination by impurities. The major impurities contaminating the salt were Cl^-, Se, and HCO_3^-. Similar results were seen for salt recovered at -6.5 °C and -7.4 °C. Figure 2 (b) illustrates the change in concentration of the major impurities, as a function of washes, for the salt recovered at 0.1 °C. The major impurities, Cl^-, Se, and HCO_3^-, had initial concentrations of 8.3g/kg, 2.6g/kg and 1.2g/kg respectively. After washing, the remaining impurities were present in concentrations lower than 0.1g/kg; which contributed 0.001mass%. This was assumed to be negligible and, therefore, the results for these species are not presented in this paper.

The significant decrease (92%) in the concentration of the Cl^- ions after two washes shows that the main contamination was as a result of entrained brine. Thereafter, there was minimal change in the concentration. For the Se and HCO_3^- ions, there was no significant decrease in their concentrations with washing; indicating that the contamination was not due to brine entrainment. Therefore, it can be deduced that the presence of impurities was due to adsorption onto the crystal surfaces; liquid inclusions within the crystal structure or crystallised salt particles. Thermodynamically, many of the ions do not crystallise out of solution at the experimental conditions employed. Therefore, the presences of liquid inclusions or adsorption onto the crystal surfaces are the more likely scenarios. It should be noted that if the presence of impurities is due to liquid inclusions, then the impurities should be in the same ratio as in the brine. This is not seen for the Se and HCO_3 ions as they are in higher quantities than the Cl ions indicating that these ions are due to adsorption onto the crystal surface. Furthermore, the ratio between the HCO_3 and Se ions in the salt was found to be 0.5; this is significantly lower than the ratio present in the hypersaline brine which was 5.0. This indicates that the Se ions are favoured over the HCO_3 ions during the adsorption process.

The overall contamination by the impurities was 13g/kg which was reduced to 4g/kg after five washes. This could be a saleable salt product depending on the market (Lower grade Na_2SO_4 has an impurity content of 1%, which is the equivalent of 10g/kg of impurities being present in the salt).

At approximately -7.4 °C, ice crystallised in the reactor. Figure 3 presents the concentration of impurities in the ice recovered at -11.5 °C as a function of the number of washes. The major impurities contaminating the ice were Cl^-, Na^+, SO_4^{2-} and HCO_3^-. After four washing cycles, the concentration of impurities was decreased from 76g/kg to 6/kg and, after 6 washing cycles, the concentration of impurities was decreased further to 5g/kg.

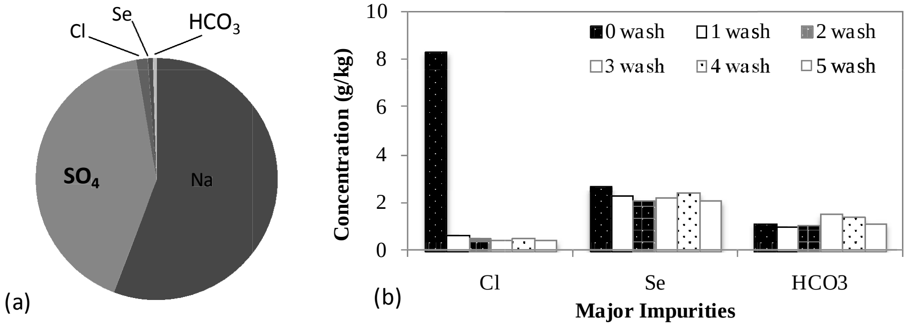

Figure 2*(a) Composition of salt recovered at 0.1°C without washing. (b) Concentration of major impurities in the salt recovered at 0.1°C as a function of washes*

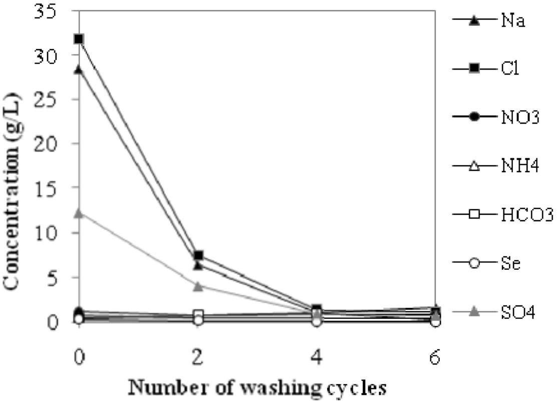

Figure 3 *Concentration of impurities in ice recovered at -11.5°C as a function of the number of washes*

The impurities present in the ice could be attributed to the following:

- Brine entrainment – this is the liquid trapped between the interstitial spaces of the ice crystals as well as the surface of the ice.
- Entrapment of the salt by the ice crystals – this is when ice crystals form loose aggregates and entrap the salt crystals. This prevents the salt crystals from settling to the bottom of the reactor and, therefore, they contaminate the ice. The entrapment is further aggravated by the high mass ratio between the ice and salt crystals in the crystalliser.
- Liquid inclusions – this is pockets of liquids that are present in the ice crystal structure.

Conclusions

The presence of high concentrations of impurities depressed the peri-eutectic point of the system to -7.4 °C. The results showed that 236g of $Na_2SO_4 \cdot 10H_2O$ and 1295g of ice was recovered from the 2000g of hypersaline brine, which was reduced by 76% to 469g. By employing a seeding protocol, the salt and ice could be isolated in different temperature regions. Both $Na_2SO_4{\cdot}10H_2O$ and ice were recovered, with low levels of contamination. The $Na_2SO_4{\cdot}10H_2O$ that was recovered had an initial concentration of impurities of 13g/kg; of which the major contributors were Cl^-, Se and HCO_3^-. After five washes, the overall concentration of impurities was reduced to 4g/kg (0.4%).It has been concluded that the Se and HCO_3 ions have been adsorbed onto the surfaces of the salt crystals. The concentration of impurities in the ice decreased from 76g/kg to 5g/kg (0.5%) after six washing cycles. The major impurities present in the ice were Cl^-, Na^+, SO_4^{2-} and HCO_3^-.

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