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Design of a Eutectic Freeze Crystallization process for multicomponent waste water stream

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ABSTRACT

Complex, hypersaline brines originating from the mining and extractive metallurgical industries have the potential to be treated using Eutectic Freeze Crystallization (EFC). Although EFC has been shown to be effective in separating a single salt and water, it has yet to be applied to the complex hypersaline brines that are typical of reverse osmosis retentates in South Africa. This paper focuses on the application of EFC for the purification of a typical brine containing high levels of sodium, chlorine, sulphate and ammonia that cannot be achieved with other separation techniques. The presence of ammonia prevents the application of membrane technology to treat the brine, leaving only cooling or evaporation as other possible options. Evaporation produces a mixed salt that requires further treatment. Modelling tools were applied to describe the phase behaviour of the complex saline systems under different process conditions and were experimentally validated. The results showed that Eutectic Freeze Crystallization could be used to selectively recover the sodium as a sodium sulphate salt. The simulation tools were especially useful in the design and optimisation of the process.

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Keywords: Crystallization; Waste water; Eutectic; Phase diagram

1. Introduction

Two major problems currently facing industrial water users are the declining availability of sufficient quantities of water and the deterioration of the quality of the available water (Buckley, 2005). However, with the increasing use of water recycling, the result has been an increased generation of inorganic brines and concentrates. Eutectic Freeze Crystallization (EFC) offers a novel method of treating brines and concentrates in order to recover pure water and salt (van der Ham, 1999). Because the heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol), the energy required to separate the water as ice is significantly less than that required to separate it by evaporation, although the cost of energy for freezing is more expensive than that for heating.

The principle of the process is as follows: when a solution containing dissolved contaminants is slowly frozen, ice crystals form and rise to the surface, while the contaminants become concentrated in the remaining solution and eventually crystallize out at the eutectic temperature (Gartner et al., 2005). The ice crystals can be separated from the mother liquor, washed and melted to yield a nearly pure water stream. Theoretically, a 100% yield can be obtained in a binary system, which is one of the advantages of EFC technology. The level of accumulation of impurities can be controlled by means of purge streams (Vaessen, 2003a,b). The energy consumption for a Eutectic Freeze Crystallization process was compared to that of a three-stage evaporative crystallizer and found to be 65% less for a copper sulphate system and 30% less for a sodium nitrate system (van der Ham et al., 1998).

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Although EFC has been shown to be effective in separating a single salt and water, it has yet to be applied to the complex hypersaline brines that are typical of reverse osmosis retentates in the mining and extractive metallurgical industries. Thus, the aim of this research has been to investigate the applicability of EFC to a particular hypersaline brine containing high levels of sodium, chlorine, sulphate and ammonia. The presence of ammonia prevents the application of membrane technology to treat the brine due to damage of the membranes, leaving only cooling or evaporation. Evaporative crystallization results in a mixed salt contaminated with ammonia, which means that the salt cannot be treated in a chlor-alkali plant to recover sodium and chlorine. Thus, if it was possible to separate out an ammonia-free salt using Eutectic Freeze Crystallization, then this would be an extremely attractive process from both an economic and environmental point of view.

2. Background

2.1. Phase diagrams

In order to design, simulate and optimize a Eutectic Freeze Crystallization process, a detailed knowledge of the phase equilibria is required. Since solubility data available in the open literature is very limited and the quality of the data is often questionable, phase diagrams based on experimental solubility data alone are therefore of limited scope. In this work, two models were used and compared: that developed by Thomsen (1997), in which the extended UNIQUAC activity coefficient model was used to calculate the two- and three-salt saturation points directly, and that developed by OLI (OLI Systems Inc., 2005), which uses the revised Helgeson–Kirkham–Flowers (HKF) model for the calculation of standard thermodynamic properties of aqueous species and the frameworks of Bromley, Zemaitis, Pitzer, Debye–Huckel, and others for the excess terms. Each solid in equilibrium with the aqueous phase is considered to be an independent phase, with the condition for physical equilibrium between phases being that the total Gibbs Free Energy is equal for the phases in equilibrium. The Gibbs Free Energy for individual solids is calculated separately using:

$$G_S = G_S^{Tr} + S_S^{Tr}(T - Tr) + \int C_p dT + \int V dP$$

The extended UNIQUAC model (Thomsen, 1997) was used to develop phase diagrams for the system of interest. These are important in order to provide information on which salt(s) can be encountered in a given electrolyte system as a function of temperature, the theoretical yields of the salts, as well as the process paths for fractional crystallization processes. For design of Eutectic Freeze Crystallization processes for sequential removal of salts and ice, the ability to develop accurate phase diagrams is essential.

The OLI Stream Analyser (OLI Systems Inc., 2005) was used as a direct tool to simulate the effect of temperature reductions on the brine system. The temperature at which the salts and ice are formed, as well as the recoveries and yields of all solids, can be predicted using this simulation tool.

2.2. Composition of the hypersaline brine

The typical brine to be investigated in this work has the composition given in Table 1.

Table 1 – Typical brine composition.

Element	Brine composition (mol)
Cl [−]	1.2
Na ⁺	1.18
SO ₄ ^{2−}	0.18
NH ₃	0.23
NO ₃ [−]	0.04
Water	11
Temperature	20 °C

This suggests that, if the phase diagram is to take into account the major components of the brine, then it should incorporate the five major species: Na⁺, NH₃, NO₃[−], Cl[−] and SO₄^{2−}. However, for systems with more than four ions, the use of phase diagrams becomes impractical. Thus, at this point, OLI thermodynamic modelling software, OLI Stream Analyser (OLI Systems Inc., 2005) was a more suitable simulation tool to investigate how the phase behaviour of the brine changed with decreasing temperature.

For comparison purposes, the binary Na₂SO₄–water phase diagram is given in Fig. 1 calculated with the extended UNIQUAC model. The diagram shows the regions of stability for various hydrates of sodium sulphate as a function of concentration and temperature. Sodium sulphate theoretically exists in three hydrated forms: anhydrous Na₂SO₄ (thenardite), Na₂SO₄·7H₂O (not a stable form) and Na₂SO₄·10H₂O (mirabilite) (Lide, 2006). The transition point, where the stable crystalline form of sodium sulphate changes from Na₂SO₄ to Na₂SO₄·10H₂O, is at a concentration of approximately 33.13 wt% and 32.27 °C. Thus, in this work, the focus is on the lower temperature region where Na₂SO₄·10H₂O is the dominant crystalline form of sodium sulphate.

The composition in Table 1 was used to compose a charge-neutral brine stream, with the charge imbalance being made up using the dominant ion method, which meant that 0.420 mol of Na⁺ was added to the stream as Na⁺ was the dominant cation. The calculated pH of this stream (11.5) corresponded to the measured pH of the brine (10–12), so the charge-neutral brine stream was accepted as a satisfactory starting point for the thermodynamic modelling using OLI Stream Analyser. The thermodynamic model was used to investigate the effect of decreasing temperature on water and salt recovery.

Fig. 2 shows the recovery of water and the two salts as the temperature of the brine is decreased. The water recovery is

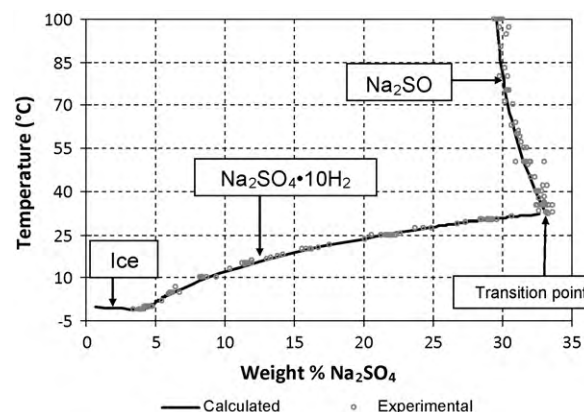


Fig. 1 – Binary phase diagram for Na₂SO₄–water showing regions of stable phases.

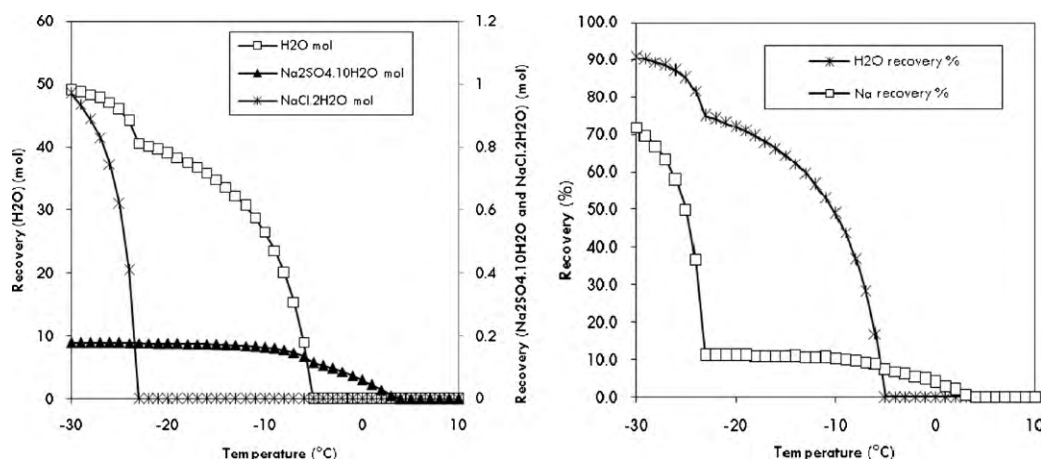


Fig. 2 – Effect of temperature reduction on salt and water recovery for the brine stream.

plotted on the primary Y axis, and the salt recovery on the secondary Y axis. The model predicts that the first solid phase to crystallize out will be $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, at $+3.5^\circ\text{C}$, followed by ice at -5.25°C . Finally, at -23.25°C , $\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystallizes out. In terms of recovery, the Na recovery is less than 12% while the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallizes out, between $+3.5^\circ\text{C}$ and -23.25°C , although most of it crystallizes out between $+4^\circ\text{C}$ and -9°C and 72% at -30°C . In terms of water recovery, ice begins to

crystallise out at -5°C , and reaches a peak of 75% recovery at -23.25°C , with another peak of 91% recovery at -30°C .

As a consequence of these findings, the phase diagram can be simplified to exclude the nitrate ion, since it is clear that it does not crystallize out as a solid phase in the region considered. The phase diagram was thus constructed considering the ions Na^+ , NH_4^+ , SO_4^{2-} and Cl^- using the extended UNIQUAC model. The diagram in Fig. 3 shows the Jänecke projection of

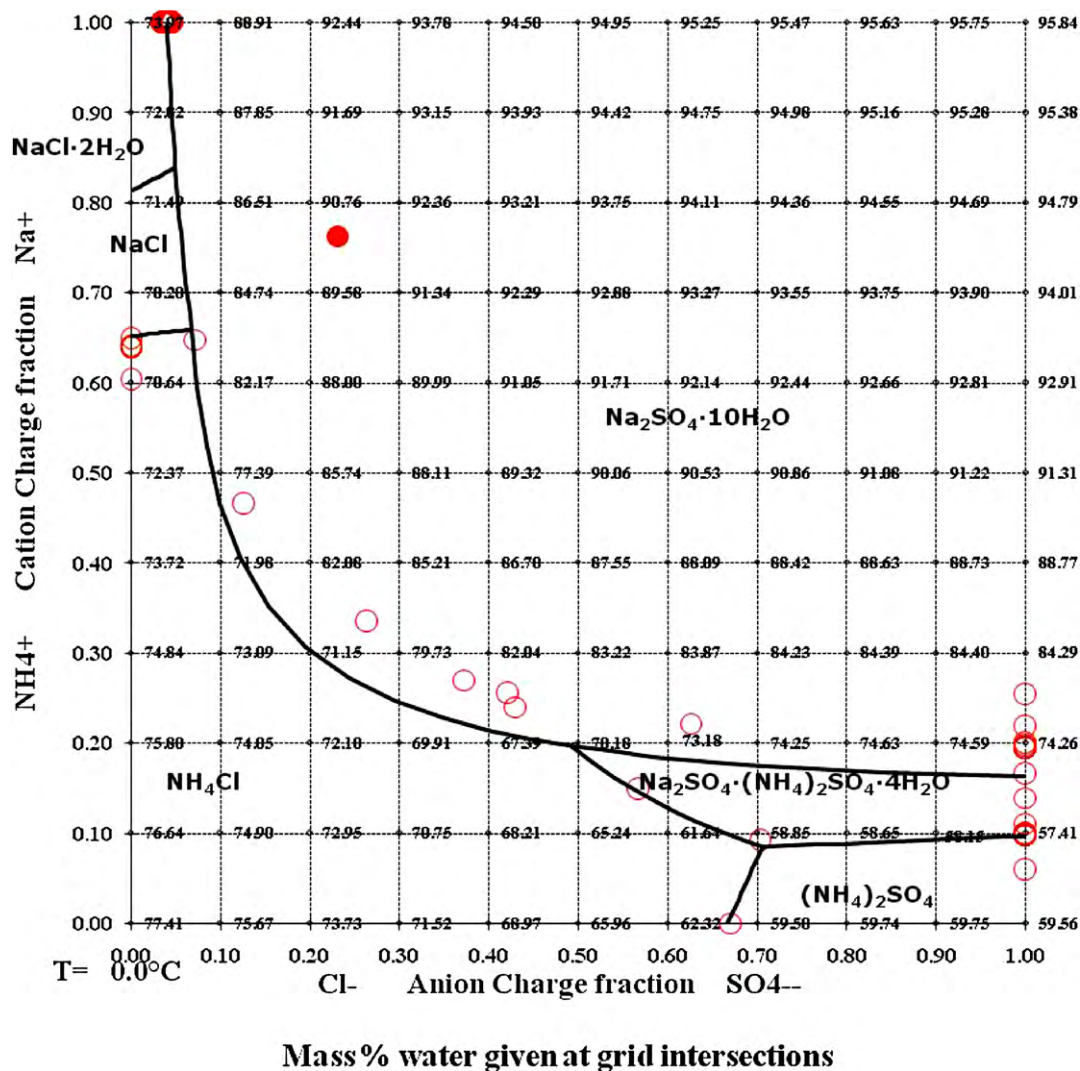


Fig. 3 – Jänecke projection of the $\text{Na}:\text{NH}_4^+:\text{Cl}^-:\text{SO}_4^{2-}$ system at $T = 0^\circ\text{C}$. Experimental data from various sources are marked with circles.

Table 2 – Brine composition for the Jänecke projection.

Element	Brine composition (mol)	Brine composition (wt%)
Cl ⁻	1.2	3.9
Na ⁺	1.18	2.5
SO ₄ ²⁻	0.18	1.6
NH ₃	0.23	0.4
NO ₃ ⁻	0	
Water	11	91.6

the Na: NH₄⁺:Cl⁻:SO₄²⁻ system with the water content given as a weight percent on the grid line intersections.

Table 2 gives the composition of the brine without nitrate and expressed as mass percentages. These are calculated in order to be able to identify the brine composition on the Jänecke projection. The starting brine composition is found at the co-ordinates (0.231; 0.762), signified by the dot. At this point, the mass percentage of water corresponding to the intersection with the surface is approximately 90%. In fact, for the brine with the composition given in Table 2, the Na₂SO₄·10H₂O is already supersaturated, and the solid already crystallized out at 5 °C.

The phase diagram enables the process to be designed with the knowledge of all possible phases that can occur as the concentrations of the species are varied and as the temperature changes.

3. Experimental validation

A series of experiments was carried out to investigate the potential for recovery of Na₂SO₄·10H₂O from the mixed brine.

The matrix of experiments is illustrated in Table 3 with the compositions of the synthetic experimental streams being given in Table 4.

3.1. Experimental set-up and operation

A 12L scraped cooled wall crystallizer (SCWC) was used for conducting batch crystallization experiments in which the scraper speed was set to 20 rpm, sufficient for good mixing. Cooling was achieved using a Lauda Kryomat RUK90S cooling unit. Built-in Labview™ software allowed for the recording and capturing of temperature readings every 10 s using the ASL F250 precision thermometer connected to a PT-100 temperature sensor with an accuracy of ±0.01 °C. The sensors were placed at various points in the crystallizer to record, the change in temperature of the crystallizer solution and temperatures of the inlet and outlet streams of the coolant. The flowrate of the coolant, Kryo 85™, was kept constant at 1500 kg/h and a recycle stream, which also served as a sampling outlet, was maintained at 1.2 kg/min.

3.2. Solution preparation

Weighed quantities of analytical grade (>99 wt%) salts were dissolved in 10 l of ultra-pure water (18 mΩ) using an overhead stirrer for 30 min to obtain a homogeneous solution. The synthetic solutions were subsequently transferred to the crystallizer. The ions (F⁻, Cl⁻, K⁺, Li⁺, Mg²⁺, Ca²⁺, NO₃⁻ and NH₄⁺) in solution were treated as impurities in the system.

3.3. Sampling and analysis

20 ml filtered samples were taken at 30 min intervals and analysed using ion chromatography (±2.5% error) to measure the

Table 3 – Matrix of experimental work for Na₂SO₄·10H₂O system.

Experiment number	Aim	Solution concentration	Conditions
E1	Determine the eutectic composition and temperature of a binary Na ₂ SO ₄ –water system and compare this to data obtained in literature	5 wt% Na ₂ SO ₄ in water	<ul style="list-style-type: none"> • Batch operated • Cooled naturally to –5 °C • No seeds added
E2	Investigate the eutectic conditions of Na ₂ SO ₄ from the concentrated brine; determine the shape, size and purity of the salt and ice crystals produced	4 wt% Na ₂ SO ₄ and trace concentrations of other elements in water	<ul style="list-style-type: none"> • Batch operated • Cooled naturally to –5 °C • No seeds added
E3	Determine the recovery of Na ₂ SO ₄ ·10H ₂ O from a concentrated NaCl stream; determine the size, shape and purity of the salt crystals formed from this stream	4 wt% Na ₂ SO ₄ 20 wt% NaCl in water	<ul style="list-style-type: none"> • Batch operated • Crystallizer solution was cooled at a rate of 5 °C/h for 6 h, thereafter the coolant liquid temperature was maintained at a constant temperature of –25 °C until the system reached eutectic conditions • Seeded with 50 g ice seeds at various temperatures: –10 °C, –15 °C and –19 °C

Table 4 – Compositions of the synthetic experimental streams investigated.

Species	Concentration (mol/kg)		
Experiment	E1: Na ₂ SO ₄ –water system	E2: Na ₂ SO ₄ –brine system	E3: Na ₂ SO ₄ –NaCl system
Na ₂ SO ₄	0.352	0.287	0.296
NaCl		0.0594	2.05
NH ₄ ⁺		0.0014	
Li ⁺		0.0007	
K ⁺		0.0004	
Mg ²⁺		0.0001	
Ca ²⁺		0.0116	
F [−]		0.0004	
NO ₃ [−]		0.0004	
Additional Cl [−]		0.0062	
Additional SO ₄ ^{2−}		0.0120	

anions in the mother liquor and the impurity content of the salt crystals produced. The ice crystals were washed using super-cooled deionised water. Micrographs of the ice and salt crystals were taken using a Nikon Optiphot 200 microscope and the size was determined visually using image analysis software, Image Pro Plus 5. The moisture content of the salt crystals was determined via thermal analysis to 80 °C using the Denver Instrument Company: Mark 2 Moisture Analyser to establish the hydrate number of the salt crystals produced.

4. Results and discussion

4.1. The binary Na₂SO₄–water system

Fig. 4 presents the temperature of the 5 wt% Na₂SO₄ crystallizer solution as a function of time. The reported eutectic temperature and composition for a binary Na₂SO₄·10H₂O system is −1.2 °C and 3.8 wt% (Pronk, 2007; Vaessen, 2003a,b). The system reached supersaturation at a temperature of −0.96 °C (point A) where the first salt crystals were visible. As the system was further cooled, the salt crystallization continued, which resulted in the crystallizer solution decreasing in salt concentration until point B was reached where ice also began to crystallize out (simultaneously with the salt product) at a temperature of −2.27 °C. The release of the crystallization enthalpy at the nucleation point resulted in the sudden rise of the solution temperature to −1.27 °C. After this, the temperature of the system gradually reached a plateau at −1.24 °C. The concentration at the eutectic temperature was measured to be approximately 3.98 wt%. This is in good agreement with eutectic temperature and composition values reported in the literature above (Reddy et al., 2008).

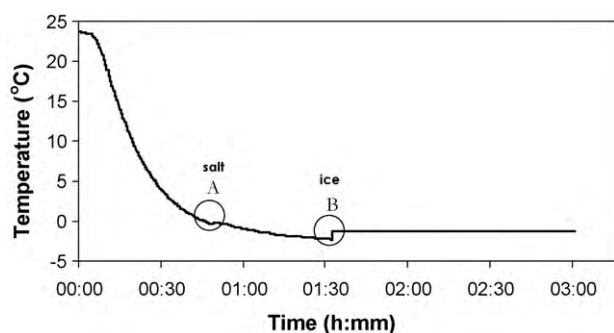


Fig. 4 – Temperature profile for a 5 wt% Na₂SO₄–H₂O system cooled naturally from ambient temperature to eutectic conditions.

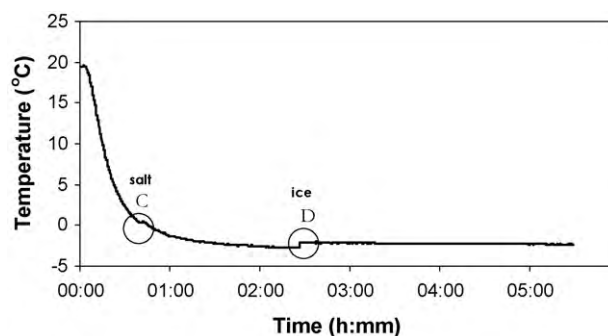


Fig. 5 – Temperature profile for a 4 wt% Na₂SO₄–brine system cooled naturally from ambient temperature to eutectic conditions.

4.2. The Na₂SO₄–brine system

Since the eutectic composition in the first experiment had been established as 3.98 wt% Na₂SO₄, a synthetic brine containing 4 wt% Na₂SO₄ and the impurities F[−], Cl[−], K⁺, Li⁺, Mg²⁺, Ca²⁺, NO₃[−] and NH₄⁺ were formulated. This was to determine the effect of impurities on the eutectic point of the system as well as to monitor crystal size and purity. The coolant temperature was maintained at −5 °C. Fig. 5 gives the temperature profile for the crystallizer solution as it was cooled from ambient temperature to the eutectic point. Point C is the point where the first Na₂SO₄·10H₂O crystals were produced at a temperature of 0.38 °C. This is significantly higher than the temperature of the pure binary system. This is due to the presence of 0.059m NaCl in the brine, which decreased the solubility of the Na₂SO₄·10H₂O salt due to the common ion effect, resulting in the higher Na₂SO₄·10H₂O nucleation temperature. The ice nucleation (point D) occurred at a temperature of −2.75 °C. With the ice crystallization and release of the heat of fusion, the temperature of the overall system increased until equilibrium was reached at the eutectic point of −2.22 °C, which is significantly lower than the eutectic temperature of the pure binary system. This indicates that the presence of impurities (F, Cl, K, Li, Mg, Ca, NO₃ and NH₄), even in low concentrations, have a clear effect on the eutectic temperature by depressing the freezing point of ice and, subsequently, the eutectic point of the system (Reddy et al., 2008).

For this system, because salt concentrations exceeded those at the eutectic composition, the Na₂SO₄·10H₂O salt crystallized before the ice. As the temperature was lowered, the system continued to produce salt crystals, decreasing

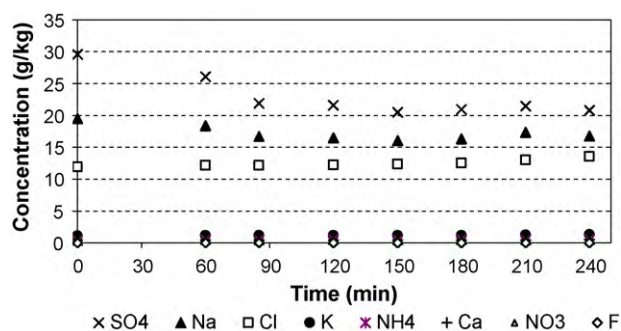


Fig. 6 – Change in concentration of the ions in solution for a 4 wt% Na_2SO_4 -brine system cooled down from ambient temperature to eutectic.

the overall concentration of salt in solution until the system reached the depressed, freezing point of ice. According to the phase diagram, the ice should have crystallized out at the eutectic point. However, due to the fact that the system was unseeded, the eutectic point was exceeded and the first ice crystals were formed at a temperature lower than the eutectic. With the release of the heat of fusion due to the ice crystallization, the energy released caused the temperature of the overall system to gradually increase until an “equilibrium” eutectic point was reached between the heat removal by the cooling liquid and the heat production by the crystallization of the ice and the salt crystals.

Fig. 6 shows the concentration of the species in solution measured as a function of time. Between 60 min and 150 min, a decrease in the concentration of the Na^+ and SO_4^{2-} ions was noted, corresponding to the crystallization phase between points C and D in Fig. 5, where only $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallized. After 150 min, where both ice and salt crystals were produced, the concentration of the Na^+ and SO_4^{2-} ions remained approximately constant, close to the composition of the eutectic point, while the concentration of the remaining ions started to increase due to the removal of water from solution in the form of ice (Reddy et al., 2008).

The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals presented in Fig. 7 exhibit well formed, faceted crystals, with a lack of the necessary imperfections to allow impurity incorporation into the crystal structure. The well faceted crystals are prismatic and monoclinic in shape. The size range was approximately 20–100 μm at one residence time after reaching the eutectic point ($\tau = 30$ min). After 3 residence times, the crystal sizes ranged from 50 μm to 350 μm . The ice crystals produced

ranged from 100 μm to 450 μm and contained an impurity content of <20 ppm after seven washing stages with supercooled water.

The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals were washed initially with a saturated solution of sodium sulphate and then with ethanol to remove any impurities. The crystals were analysed to determine if there were any traces of impurities within the crystal structure. The analysis showed that 100% pure crystals were produced from the synthetic brine stream. A thermal analysis to 80 °C was carried out on a small amount of washed salt product (1.5 g) to determine the hydrate number of the crystals. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is unstable and, with a melting point of 32.1 °C (Lide, 2006), it loses the waters of crystallization quickly. The analysis showed a loss of mass of approximately 56% which corresponds to ten waters of hydration ((Reddy et al., 2008).

4.3. The 4 wt% Na_2SO_4 –20 wt% NaCl system

For this system, the high concentration of NaCl caused the common ion effect to reduce the solubility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and the system reached the metastable point with regards to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallization at approximately 11.64 °C and 10.45 °C in two different experiments. This point was observed visually. According to the extended UNIQUAC model, the thermodynamic saturation point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in this system is reached at 13 °C.

The system was seeded with 50 g ice seeds at various temperatures: –10 °C, –15 °C and –19 °C but only at –19 °C was the system sufficiently supersaturated for the ice seeds to survive and induce ice production. As the system was cooled further, a plateau was reached at –21.22 °C, which is in good agreement with the eutectic temperature for a H_2O – Na_2SO_4 –NaCl system of –21.34 °C, calculated by Marion and Farren (1999).

Fig. 8 shows the theoretical recovery of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as a function of time. The recovery was calculated from the chemical analysis of the ions remaining in solution as filtering the entire contents of the crystallizer was not feasible. It was assumed that the depletion of sulphate ions from the solution was entirely due to the formation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. At 270 min after nucleation, a 90% recovery of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was measured, at a temperature of –15 °C.

Fig. 9 shows the concentrations of the different ions as the system was cooled to the eutectic point. The decrease in the concentration of SO_4^{2-} ions reflects the recovery of the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ already shown in Fig. 9. The increase in concentration of Cl^- ions indicates that the system became more

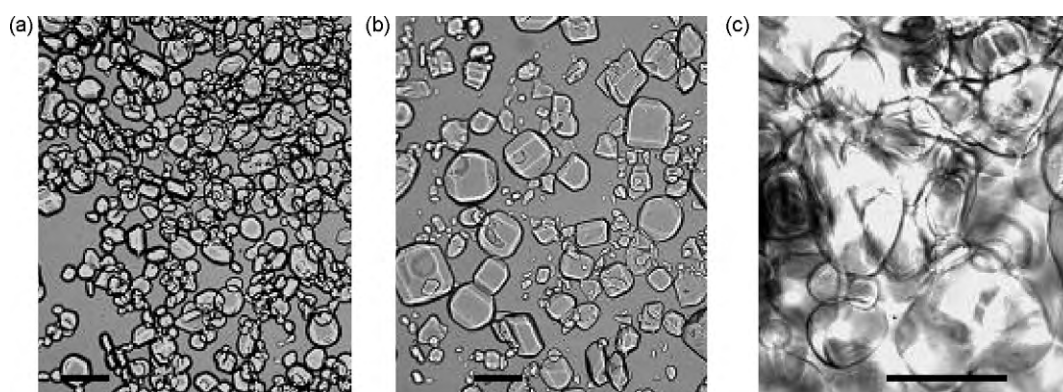


Fig. 7 – Micrographs of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals after 1 τ (a) and after 3 τ (b) {scale bar = 300 μm }. Micrograph (c) represents the ice crystal product after 3 τ {scale bar = 400 μm }.

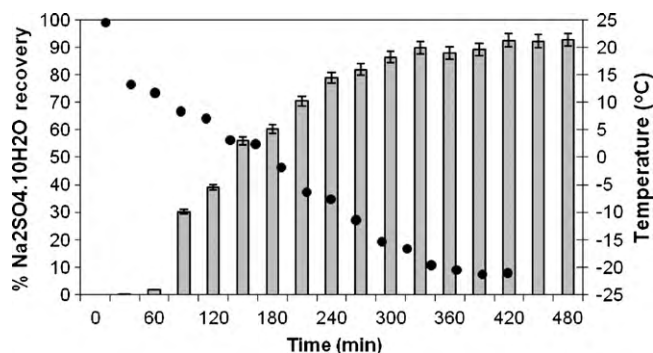


Fig. 8 – Theoretical recovery of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (bars) from a concentrated NaCl solution at with decreasing temperature (dots) over time.

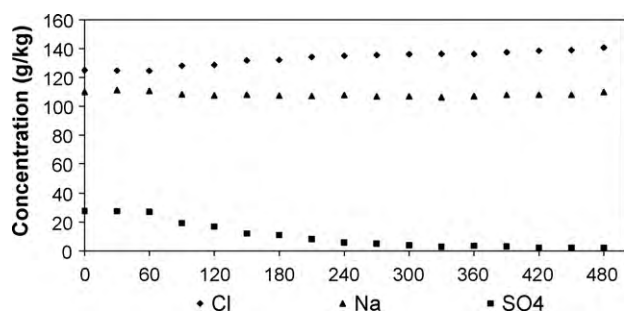


Fig. 9 – Concentration of the ions in solution as a function of time.

concentrated with respect to $\text{NaCl} \cdot 2\text{H}_2\text{O}$, due to the crystallization of ice and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. However, the solubility limit for NaCl was never reached in the temperature range investigated and no $\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystals were produced. This was further confirmed by a chemical analysis of the salt crystals. The study revealed a recovery of >90% of sodium sulphate with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystal sizes ranging from 50 μm to 400 μm (Reddy et al., 2008).

5. Conclusions

- The thermodynamic modelling predicted, for a complex brine containing Na^+ , NH_3 , NO_3^- , Cl^- and SO_4^{2-} , that the first solid phase to crystallize out will be $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, at 3.5 °C, followed by ice at −5.25 °C. Finally, at −23.25 °C, $\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystallizes out. In terms of recovery, the Na recovery is less than 12% while $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallizes out, between 3.5 °C and −23.25 °C, but begins to increase once the $\text{NaCl} \cdot 2\text{H}_2\text{O}$ starts to crystallize out and reaches 72% at −30 °C. In terms of water recovery, ice begins to crystallise out at −5 °C, and reaches a peak of 75% recovery at −23.25 °C, with another peak of 91% recovery at −30 °C.
- For the simple binary Na_2SO_4 –water system, the eutectic temperature and concentration were determined experimentally to be −1.24 °C and 3.98 wt%, which is in good agreement with literature.
- For the Na_2SO_4 –brine system, the presence of low concentrations of F^- , Cl^- , K^+ , Li^+ , Mg^{2+} , Ca^{2+} , NO_3^- and NH_4^+ impurities depressed the eutectic point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallization from −1.24 °C to −2.22 °C.
 - In this system, pure ice crystals were obtained (<20 ppm impurities) ranging in size from 100 μm to 450 μm after seven washing steps.

- Very pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals, without any detectable impurities, were also produced. The salt crystal sizes ranged from 20 μm to 100 μm after 1 τ to 50–350 μm after 3 τ . Thermal analysis identified the crystals as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. In this case, $\tau = 30$ min.
- For the 4 wt% Na_2SO_4 –20 wt% NaCl system, the solubility of Na_2SO_4 was lowered due to the common ion effect. The metastable point with respect to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals was reached at 11.64 °C and 10.45 °C in two different experiments. At the same time, there was a strong depression of the freezing point of water to −19 °C. The eutectic point for the 4 wt% Na_2SO_4 –20 wt% NaCl system was found to be −21.22 °C.
- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals without any traces of impurities were produced from this system. The salt crystal sizes ranged from 50 μm to 400 μm .
- A recovery of >90% pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals with sizes ranging from 50 μm to 400 μm was obtained, but only at temperatures <−20 °C.
- No solid phases of NaCl were produced in the temperature range investigated.

References

- Buckley, C., 2005, Research into the treatment of inorganic brines and concentrates, Water Research Commission Project No. 201, Revision 1.021, May 2005.
- Gartner, R.S., Genceli, F.E., Trambitas, D.O., Witkamp, G.J., 2005, Impurity gradients in solution-grown ice and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ crystals measured by cryo-laser ablation and high-resolution-induced-coupled plasma mass spectrograph, in Proceedings of the 14th International Conference on Crystal Growth and the 12th International Conference on Vapor Growth and Epitaxy, *Journal of Crystal Growth* 275 (1–2), 15 February 2005, pp. 1773–1778.
- Lide, D.R., (2006). *CRC Handbook of Chemistry and Physics: A Ready-reference Book of Chemical and Physical Data* (87th edition). (CRC Press).
- Marion, G.M. and Farren, F.E., 1999, Mineral solubilities in the Na–K–Mg–Ca–Cl– SO_4 – H_2O system: a re-evaluation of the sulfate chemistry in the Spencer–Møller–Weare model. *Geochimica et Cosmochimica Acta*, 63(9): 1305–1318.
- OLI Systems Inc., 2008, OLI Stream Analyser, Version 2.0.57, Morris Plains (New Jersey, USA).
- Pronk, P., 2007, Fluidised bed heat exchangers to prevent fouling in ice slurry systems and industrial crystallisers, PhD Dissertation (Delft University of Technology, The Netherlands).
- Reddy, S.T., Lewis, A., Witkamp, G.J., Kramer, H.J.M. and van Spronsen, J., 2008, Recovery of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ from a reverse osmosis retentate using Eutectic Freeze Crystallisation technology, In *17th International Symposium on Industrial Crystallization* Maastricht, The Netherlands.
- Thomsen, K., 1997, Aqueous electrolytes: model parameters and process simulation, PhD Thesis (Department of Chemical Engineering, Technical University of Denmark, Denmark).
- Vaessen, R.J.C., 2003a, Development of scraped eutectic freeze crystallisers, PhD Dissertation (Delft University of Technology, The Netherlands).
- Vaessen, R.J.C., 2003b, Development of scraped eutectic crystallizers, PhD Thesis (TU Delft, Netherlands).
- van der Ham, F., 1999, Eutectic Freeze Crystallization, PhD Thesis (TUDelft, Netherlands).
- van der Ham, F., Witkamp, G.J., de Graauw, J. and van Rosmalen, G.M., 1998, Eutectic freeze crystallization: application to process streams and waste water purification. *Chemical Engineering and Processing*, 37(March (2)): 207–213.