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Recovery of $Na_2SO_4 \cdot 10H_2O$ from a reverse osmosis retentate by eutectic freeze crystallisation technology

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ABSTRACT

The increasing amount of waste water and effluent from South Africa's mining industry forms a growing problem, which processing requires sustainable solutions in which both the water and the dissolved component can be re-used. Eutectic freeze crystallisation (EFC) has been identified as a key technology that is not only energy efficient, but also produces ice and salt products of high quality. Unlike reverse osmosis membrane systems, EFC can treat both dilute and concentrated systems minimising waste water volumes. In this paper it is shown that freeze and eutectic freeze crystallisation can be used for the processing of a reverse osmosis retentate stream containing 4% $NaSO_4$ and a number of impurities (F, Cl, K, Li, Mg, Ca, NO_3 and NH_4), producing both pure water and $NaSO_4 \cdot 10H_2O$ crystals. The influence of the impurities on the eutectic point and on the crystal structure of mirabilite was investigated using EFC technology investigated for a pure binary system, for a synthetic reverse osmosis retentate as well as for a concentrated NaCl system. In addition, investigations into the recovery and purity of mirabilite for these streams were conducted.

Keywords: Eutectic freeze crystallisation; Sodium sulphate decahydrate; Crystallisation; Brine

1. Introduction

The brine capacity of South Africa is increasing exponentially due to the large quantities of waste water and effluent being produced by industry. The mining industry, in particular, is under enormous pressure to recycle and re-use water in order to minimise the intake of fresh water from rivers and from water utility companies. As a result, much investigation has been carried out into identifying cost-effective methods for treatment and minimisation of this polluted water. However, low-cost treatment of large volumes of this water is not straight forward and different approaches are being followed by the various industries (Burger et al., 2003).

Salinity build-up is often a direct consequence of this drive to save water through recycling and other water saving measures. Significant progress has been made during the past few years with improved desalination technologies in industry and mining, reverse osmosis membrane technology proving the most effective. However, the recovery of water in this process is limited and is only applicable to dilute streams due to the increased potential of fouling of the permeable membrane once the treated solution reaches its mineral salt scaling limits. Although the use of anti-scalants can suppress the mineral salt precipitation to some extent (Rahardianto et al., 2007), large volumes of retentate is still being produced.

Eutectic freeze crystallisation (EFC) has been identified as a key technology in helping to overcome this limitation as EFC can treat both dilute and concentrated aqueous waste streams. The process involves the simultaneous crystallisation of both pure salt and ice from aqueous solutions at the eutectic. By exploiting the density properties of the crystals formed and the mother liquor, separation can be achieved. Ice has a much lower density (<1 g/cm^3) than the mother liquor (1–1.2 g/cm^3) which allows the ice to float to the top of the reactor for removal, and salt crystals with densities ranging from 1.2 to 1.7 g/m^3 causes the salt to sink to the bottom of the reactor to be recovered. Washing stages for both crystals ensures very high purity grades. It has been proven that this technology has shown lower energy consumption than conventional evaporative processes (van der Ham, 1999; Vaessen,

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2003; Genceli, 2008) as well as being applicable to a wide range of aqueous streams of various concentrations.

The specific focus of this paper is to investigate the feasibility of the use of EFC technology for a full recovery of water and salt from hypersaline waste streams that have been pre-treated using a reverse osmosis membrane unit for water recovery. Firstly, the scaling limits of the RO membrane separations are examined to define the composition of the retentate stream. Secondly, a preliminary study has been carried out to determine the data for the phase diagram and the eutectic points for mirabilite in a pure binary Na_2SO_4–water system and subsequently a mixed salt brine stream. Finally, an investigation to determine the effect on the eutectic and recovery and purity of mirabilite in concentrated NaCl brine is conducted.

2. Experimental

2.1. *Solution preparation*

Weighed quantities of analytical grade (>99 wt%) salts were dissolved in 10 L of ultra pure water (18 MΩ/cm) using an overhead stirrer for 30 min to obtain a homogeneous solution. The synthetic solutions (Table 1), based on an industrial brine, were subsequently transferred to the crystalliser. The main focus of these experiments was on the recovery and purity of sodium sulphate; hence the remaining ions (F, Cl, K, Li, Mg, Ca, NO_3 and NH_4) in solution were treated as impurities in the system.

2.2. *Experimental set-up and operation*

A 12 L scraped cooled wall crystalliser (SCWC) was used for conducting batch crystallisation experiments in which the scraper speed was set to 20 rpm, which was sufficient for good mixing. Cooling was achieved using a Lauda Kryomat RUK90S cooling unit. Built-in Labview^{TM} 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 reactor to record, the change in temperature of the reactant solution and temperatures of the inlet and outlet streams of the coolant. The flowrate of the coolant, Kryo 85^{TM}, was kept constant at 1500 kg/h and a recycle stream, which also served as a sampling outlet, was maintained at 72 kg/h.

The temperature of the cooling liquid was maintained at −5 °C for experiments 1 and 2. These were unseeded experiments. However, for experiment 3, the reactant 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. This system was seeded with 50 g ice seeds at various temperatures: −10 °C, −15 °C and −19 °C.

2.3. *Sampling and analysis*

20 ml filtered samples were taken at 30 min intervals and analysed using ion chromatography (±2.5% error) to measure the cations and anions in the mother liquor and the impurity content of the salt crystals produced. The salt and ice were isolated allowed to separate through gravitational separation Micrographs of the ice and salt crystals were taken using the Nikon Optiphot 200 microscope and the size was determined visually using image analysis software, Image Pro Plus 5. The hydrate content of the salt crystals was determined via thermal analysis using the Denver Instrument Company: Mark 2 Moisture Analyser to establish the hydrate number of the salt crystals produced.

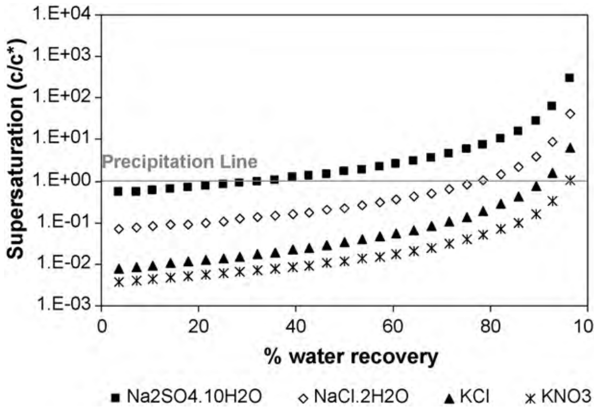

Fig. 1 – Supersaturation of various salts from the reverse osmosis retentate stream as a function of water recovery.

3. Results and discussion

3.1. *Modelling studies showing water recovery using OLI Analyser software*

As mentioned previously, the recovery of water using the reverse osmosis technology is limited by the precipitation limits of the different salts. Fig. 1 shows the potential for increased recovery of water by RO. The higher the water recovery results in higher supersaturation of the different salts. The supersaturation is defined here as the ionic activity product (IAP) divided by its solubility product. The system can be concentrated to the saturation point of Na_2SO_4 by recovering water. As can be seen from Fig. 2, a water recovery of approximately 20% can be achieved. Higher water recovery can only be achieved by further treating the reverse osmosis retentate (TDS ≈ 18,000 mg/L) using an alternative technique like eutectic freeze crystallisation, in which both salt products and the remaining water in the stream can be recovered.

3.2. *Na_2SO_4–water phase diagram*

Presented in Fig. 2 (Thomsen, 2007) is the binary phase diagram for the Na_2SO_4–water system. The diagram shows the

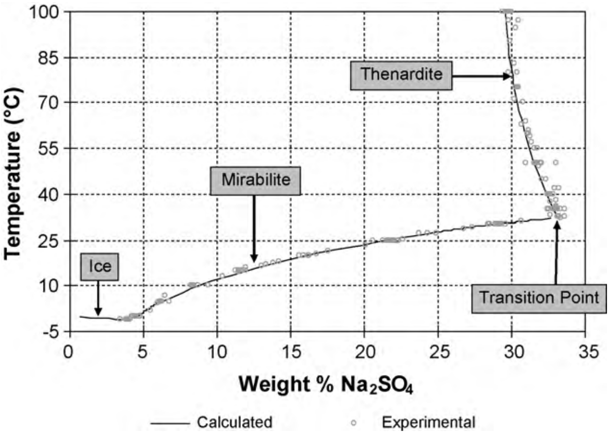

Fig. 2 – Binary phase diagram for Na_2SO_4–water showing regions of stable phases (Thomson, 2007).

Table 1 – Table showing compositions of the synthetic experimental streams investigated.

Species	Experiment		
	1 Na_2SO_4–H_2O^a (mol/kg)	2 Na_2SO_4–brine^a (mol/kg)	3 Na_2SO_4–NaCl–H_2O^a (mol/kg)
Na_2SO_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	
Remaining Cl^-		0.0062	
Remaining SO_4^{2-}		0.0120	

regions of stability for various hydrates of sodium sulphate as a function of concentration and temperature. Sodium sulphate exists in three hydrate forms: anhydrous Na_2SO_4 (thenardite), $Na_2SO_4{\cdot}7H_2O$ and $Na_2SO_4{\cdot}10H_2O$ (mirabilite) (Lide, 2006). The transition point, where the stable crystalline form of sodium sulphate changes from thenardite to mirabilite, is at a concentration of approximately 33.13 wt% and 32.27 °C (Thomsen, 2007). The focus is on the lower temperature region where mirabilite is the dominant crystalline form of the sodium sulphate.

Fig. 3 presents the temperature cooling profile of the 5 wt% Na_2SO_4–H_2O reactant solution as a function of time. The reported eutectic temperature and composition for a binary $Na_2SO_4{\cdot}10H_2O$ (mirabilite) system is −1.2 °C and 3.8 wt% (Pronk, 2007; Vaessen, 2003; van der Ham, 1999; Gmelin, 1958; Barduhn and Manudhane, 1979; Marion and Farren, 1999). The system reached supersaturation at a temperature of −0.96 °C (point A) where the first salt crystals were visibly. Upon further cooling, there was an increase in salt crystallisation, resulting in the reactant solution decreasing in concentration until point B was reached where ice began to crystallise out simultaneously with the salt product at a temperature of −2.27 °C. The release of the crystallisation enthalpy at the nucleation point B resulted in the sudden rise of the reactant temperature to −1.27 °C. After a short period of time the temperature of the system gradually began to rise to −1.24 °C where it reached a plateau and the concentration at the eutectic temperature was measured to be approximately 4 wt%. This is in good agreement with values reported above.

3.3. *Determining the eutectic for mirabilite from a 4 wt% Na_2SO_4 brine system*

In light of the above results, a synthetic reverse osmosis retentate with a 4 wt% Na_2SO_4 concentration containing the following impurities (F, Cl, K, Li, Mg, Ca, NO_3, NH_4) was investigated to determine the effect 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. 4 gives the temperature profile for the reactant solution for the above system. Point C is the point where the first mirabilite crystals were produced at 0.38 °C. This is significantly higher than the temperature of the pure binary system. The presence of 0.06 m NaCl in the brine decreased the solubility of the mirabilite ion by the common ion effect (Marliacy et al., 2000), increasing the supersaturation of the solution and hence resulting in the higher mirabilite nucleation temperature. The ice nucleation (point D) occurred at a temperature of −2.75 °C and the system reached the eutectic at −2.22 °C, which is also significantly lower than the pure binary system. This shows that the presence of impurities (F, Cl, K, Li, Mg, Ca, NO_3 and NH_4), even in low concentrations, have a clear effect on the eutectic temperature by depressing the freezing point of ice and, subsequently, the eutectic point.

Fig. 5 shows the concentration of the different components measured as a function of time for the synthetic hypersaline mixed salt brine consisting of 4 wt% Na_2SO_4. Between 60 and 150 min, a decrease in the concentration of the Na^+ and SO_4^{2-} ions was noted, corresponding to the crystallisation phase

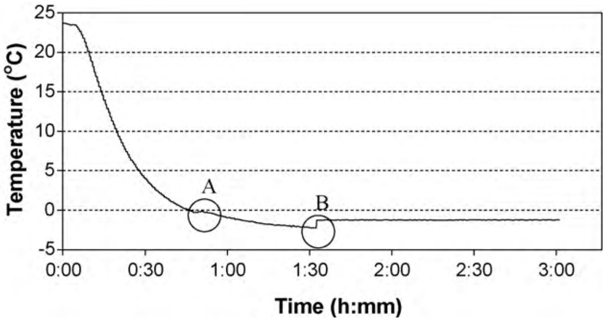

Fig. 3 – Graph showing the temperature profile for a 5 wt% Na_2SO_4–H_2O system cooled from ambient to eutectic.

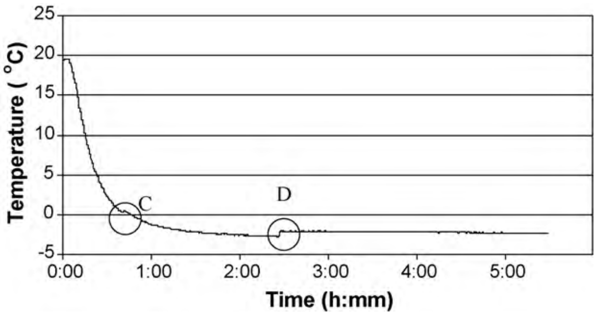

Fig. 4 – Graph showing the temperature profile for a 4 wt% Na_2SO_4–brine system cooled down from ambient to eutectic.

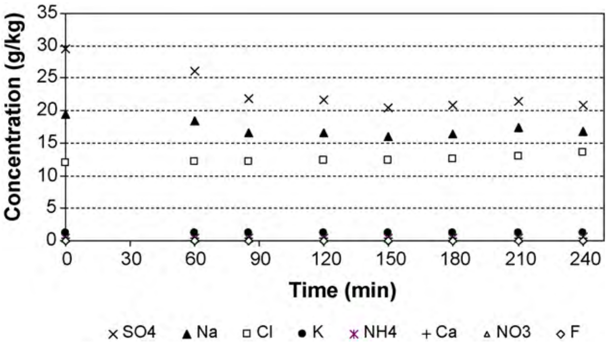

Fig. 5 – Graph showing the change in concentration of the different ions in solution for a 4 wt% Na_2SO_4–brine system cooled down from ambient to eutectic.

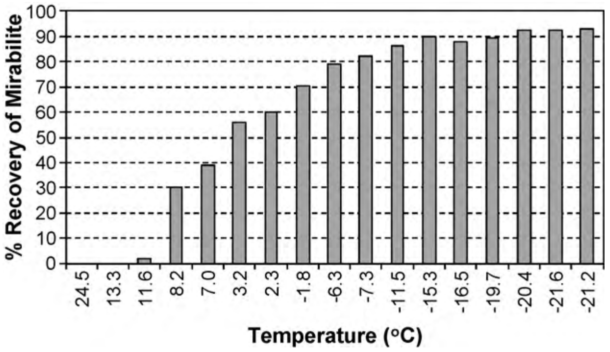

Fig. 7 – Graph showing the theoretical recovery of mirabilite with decreasing temperature.

between the temperature jump at point C and D where only $Na_2SO_4{\cdot}10H_2O$ is crystallised. After 150 min, where both ice and salt crystals are produced, the concentration of the Na^+ and SO_4^{2-} ions remained more or less constant, close to the composition of the eutectic point, while the concentration of the other remaining ions started to increase due to the removal of water from solution in the form of ice and the salt hydrate.

The mirabilite crystals presented in Fig. 6(b) do not show any imperfections that could result in impurities being incorporated into the crystal structure. The well faceted crystals are prismatic and monoclinic in shape. The size range was approximately 20–100 μm at 30 min after reaching the eutectic point. After 150 min, the crystal sizes ranged from 50 to 350 μm. The ice crystals produced ranged from 100 to 450 μm and contained an impurity content of <20 ppm after seven washing stages with super-cooled water.

The $Na_2SO_4{\cdot}10H_2O$ 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 reverse osmosis retentate stream. A thermal analysis was carried out on a small amount of washed salt product (1.5 g) to determine the hydrate number of the crystals. Mirabilite is unstable and, with a melting point of 32.1 °C (Lide, 2006), it loses the waters of crystallisation quickly. The analysis showed a loss of mass of approximately 56% which corresponds to a 10 water hydrate.

3.4. *Determining the recovery of mirabilite from a 4 wt% Na_2SO_4–20 wt% NaCl system*

Due to the high concentration of NaCl, the system reached supersaturation with regards to mirabilite crystallisation at approximately 10.45 °C. However, the temperature "jump" only occurred when the reactant solution reached 3.1 °C. It is unknown at this time why this phenomenon occurred but further investigations will be carried out.

The system was seeded with 50 g ice seeds at various temperatures: −10 °C, −15 °C and −19 °C, however, only at −19 °C was the system supersaturated for the ice seeds to create nucleation. This is an extremely significant drop in the freezing point of the water in the system. Upon further cooling, the system reached a plateau at −21.22 °C, which is in good agreement to the temperature reported by Marion and Farren (1999) as the eutectic temperature for a Na_2SO_4–NaCl system. The concentration of NaCl in this study is much lower than that reported by Marion and Farren, and therefore explains the lack of recovery of hydrohalite from the system.

Fig. 7 shows the recovery of mirabilite as a function of temperature. After 270 min after nucleation, a 90% recovery of mirabilite is seen at a temperature of −15 °C. This has great implications for sequentially removing salts from the brine.

Fig. 8 shows the trend in the concentrations of the different ions as the system is cooled to eutectic. The decrease in the concentration of SO_4^{2-} ions mimics the recovery of the mirabilite already shown in Fig. 7. The increase in concentration of Cl^- ions indicates that the system was being concentrated with respect to $NaCl{\cdot}2H_2O$, due to the crystallisation of ice and $Na_2SO_4{\cdot}10H_2O$, however, the solubility limit was never reached and no $NaCl.2H_2O$ crystals were produced. This was further confirmed by a chemical analysis of the salt

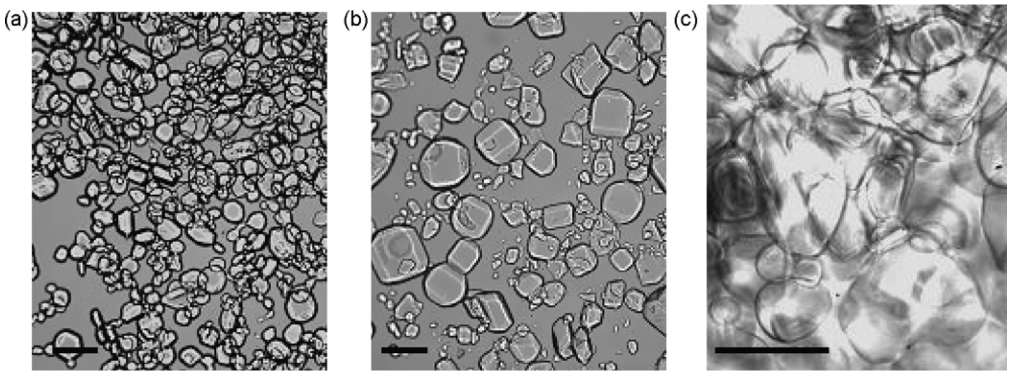

Fig. 6 – Micrographs of mirabilite crystals after 1τ (a) and after 3τ (b) {scale bar = 300 μm}. Micrograph (c) represents the ice crystal product after 3τ {scale bar = 400 μm}.

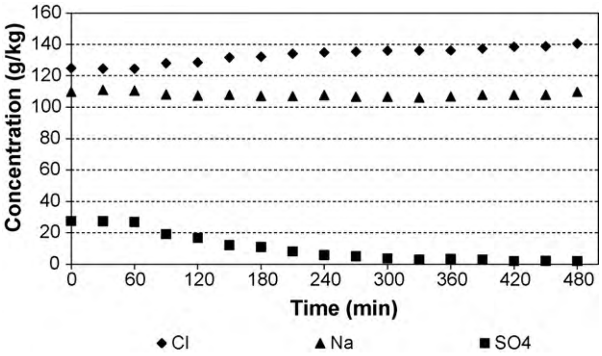

Fig. 8 – Graph showing the concentration profile of the ions in solution as a function of time.

crystals. The study revealed a recovery of >90% of sodium sulphate in the system as can be seen in Fig. 7 with mirabilite crystal sizes ranging from 50 to 400 μm.

4. Conclusions

- The eutectic temperature and concentration of the binary Na_2SO_4–water system studied was determined experimentally to be −1.24 °C and approximately 4 wt%, which is in good agreement with literature.
- The presence of low concentrations of F, Cl, K, Li, Mg, Ca, NO_3 and NH_4 impurities in a Na_2SO_4–water system depresses the eutectic point of $Na_2SO_4 \cdot 10H_2O$ crystallisation from −1.24 to −2.22 °C.
- Using EFC, pure water crystals were obtained (<20 ppm impurities) from a synthetic retentate stream after seven washing steps.
- Ice crystals produced ranged from 100 to 450 μm in size.
- Very pure mirabilite crystals, without any detectable impurities, were produced from a synthetic retentate stream as well as a sodium sulphate stream containing 20 wt% NaCl using a batch eutectic freeze process.
- Salt crystal sizes ranged from 20 to 100 μm, after 30 min of reaching the eutectic point, and 50–350 μm after 150 min for the synthetic brine stream and between 50 and 400 μm from the 20 wt% NaCl stream.
- Thermal analysis revealed that the crystals produced were mirabilite ($Na_2SO_4 \cdot 10H_2O$).
- The presence of higher concentrations of NaCl lowers the solubility of Na_2SO_4 by the common ion effect, but at the same time gives rise to a strong depression on the freezing point of water.
- A recovery of >90% pure Na_2SO_4 crystals was obtained from a concentrated NaCl stream prior to any sodium chloride crystals being produced, this has great implications for possible sequential removal of salts from a brine.

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References

Barduhn, A.J. and Manudhane, A., 1979, Temperatures required for eutectic freezing of natural waters. Desalination, 28: 233–241.

Burger, A.J., vd Merwe, I.W., Enslin, W.V., 2003, Mine water pollution and treatment methodologies.

Genceli, F.E., 2008, Scaling-up pf Eutectic Freeze Crystallisation, PhD dissertation, Delft University of Technology, The Netherlands.

Gmelin., (1958). *Gmelins Handbuch der Anorganischen Chemie, 8th edition, Deutsche Chemische Gesellschaft*. (Verlag Chemie, Weinheim).

Lide, D.R., (2006). *CRC Handbook of Chemistry and Physics: A Ready-reference Book of Chemical and Physical Data* (87th edition). (CRC Press).

Marliacy, P., Solimando, R., Bouroukba, M. and Schuffenecker, L., 2000, Thermodynamics of crystallization of sodium sulphate in H_2O-NaCl-Na_2SO_4: application to $Na_2SO_4 \cdot 10H_2O$-based latent heat storage materials. Thermochim Acta, 344: 85–94.

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. Geochim Cosmochim Acta, 63(9): 1305–1318.

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.

Rahardianto, A., Gao, J., Gabelich, C.J., Williams, M.D. and Cohen, Y., 2007, High recovery membrane desalting of low-salinity brackish water: integration of accelerated precipitation softening with membrane RO. J Membr Sci, 289: 123–137.

Thomsen, K., 2007, Aqueous electrolytes: phase diagrams and process simulation/optimization.

Vaessen, R.J.C., 2003, Development of scraped eutectic freeze crystallisers, PhD dissertation, Delft University of Technology, The Netherlands.

van der Ham, F., 1999, Eutectic freeze crystallisation, PhD dissertation, Delft University of Technology, The Netherlands.