INVESTIGATING FACTORS THAT AFFECT SEPARATION IN A EUTECTIC FREEZE CRYSTALLISATION PROCESS

S.T. REDDY[1], H.J.M. KRAMER[2], A.E. LEWIS[1] and J. NATHOO[1]

[1]Crystallization and Precipitation Unit, Department of Chemical Engineering,
University of Cape Town, Rondebosch, Cape Town, 7701, South Africa
E-mail: Sarashree.Reddy@uct.ac.za
[2]Process & Energy Laboratory, Leeghwaterstraat 44, Delft University of Technology
2628 CA, Delft, The Netherlands

ABSTRACT

Eutectic freeze crystallisation technology has shown great potential for the further treatment of industrial hypersaline brines. It requires less energy than a typical 3-staged evaporative crystallizer and successfully produces pure crystalline products. The process exploits the density differences of the three phases (ice, salt and mother liquor) present at the eutectic point and thus separation and recovery of the crystals is achieved. In this contribution, the effect of aggregation of ice was investigated, specifically the encapsulation of the salt crystals in the interstitial spaces of the aggregates. This not only lowers the yield of salt, but subsequently decreases the purity of the ice crystals themselves. Furthermore, key parameters such as settling/flotation time, agitation rate in the separation vessel as well as increasing the number of washing stages, is investigated to determine if the parameters reduce the effects of aggregation.

Seeded, batch experimental studies were conducted using a 5wt% binary Na_2SO_4-H_2O system where the mass solid content, i.e. mass of crystals produced in the reactor, was maintained between 8-10wt%. Investigations into the effects of increasing settling/flotation time in the separation in the absence of agitation vessel showed no appreciable effect. When the same studies were carried out with the introduction of agitation in the separation vessel, the purity of the ice and yield of $Na_2SO_4 \cdot 10H_2O$ increased considerably by approximately 75% and 53% respectively.

The effect of increasing wash cycles on the purity of the ice was also investigated. In the absence of agitation in the separation vessel, increased washing cycles were ineffective in removing the encapsulated salt crystals. The results showed that, with the addition of agitation in the separation vessel, the purity of ice could be improved by approximately 90% with by introduction of washing cycles.

From the results of the batch studies, it is recommended that the separation vessel include an agitator in the ice region to inhibit the aggregation of ice crystals, thus significantly improving the yield of $Na_2SO_4 \cdot 10H_2O$ as well as the purity of the recovered ice.

1. INTRODUCTION

Eutectic Freeze Crystallisation (EFC) dates back to the 1950's, where Nelson and Thompson attempted to determine the order of crystallisation of salts. However, using EFC as a separation technology only became apparent in the 1970's when Stepakoff et al. (1974) proposed a continuous eutectic freeze crystallisation process for the treatment of brines. This was achieved by injecting a coolant directly into the solution. However, direct contact of the coolant with the process stream caused impure crystals to be produced and the idea was abandoned.

In the 1980's, Swenne (1983) reported on the eutectic freeze crystallisation of sodium chloride. Once again, direct cooling was employed. The work showed successful recovery of pure salt crystals, however, the process never reached an industrial scale (Vaessen, 2003).

Renewed interest in the field of EFC was promoted by stricter waste water regulations and concerns on energy consumption. Much of the ground work has been laid by van der Ham (1999). The research focused on using an indirect cooling method for EFC applications as well as on technology development. The feasibility of using EFC for industrial scale application was proven with the production of potassium nitrate.

Since then, there has been various work focusing on the development of eutectic freeze crystallisers (Vaessen, 2003), characterisation and population balance modelling of scraped crystallisers (Himawan, 2005), heat exchanger surfaces (Pronk, 2006) and scale-up of the EFC equipment (Genceli, 2008). The above research focused on the isolation of a single valuable salt ($MgSO_4 \cdot 11H_20$ – Genceli, 2008; KNO_3 and HNO_3 – Vaessen, 2003; $CuSO_4 \cdot 5H_20$ and $(NH_4)_3PO_4$ – van der Ham, 1999) from an industrial stream with trace impurity content, using the eutectic freeze crystallisation technology.

This technology has shown potential to be an attractive alternative to conventional treatment of wastewaters produced from the mining industries (Reddy et al., 2008) as well as showing lower energy consumption than conventional evaporative processes (van der Ham, 1999; Vaessen, 2003; Genceli, 2008).

Nonetheless, EFC is still in its infancy and there are various parameters that require further investigation. In order to develop a viable separation process for multi-component industrial hypersaline brines, conceptual design studies are realised on the basis of a detailed thermodynamic evaluation to establish which components will be crystallised, and in what quantities, at the chosen process conditions. In EFC, separation can be achieved by exploiting the density differences between the three phases present at the eutectic point with ice having a lower density (0.9 kg/l) than the mother liquor (1-1.2 kg/l) thus floating to the top of the reactor and salt crystals having densities ranging from 1.2–1.7kg/l settling to the bottom of the reactor.

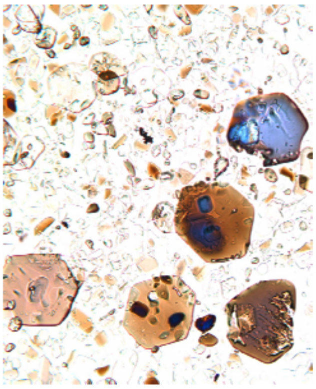


Figure 1**.** $NaCl{\cdot}2H_2O$ crystals present in the ice filter cake

However, the separation by settling or flotation is strongly affected by the solids (both ice and salt crystals) concentration in the crystalliser. Previous studies have shown that, at the lower temperatures in particular, the solids concentration in the crystalliser has a great effect on the separation of the ice and salt crystals (Lewis et al., 2008). In addition, it is known that ice crystals have a strong tendency to form loose aggregates encapsulating the smaller salt crystals (Figure 1) and thereby preventing them from settling. Large aggregates of ice are preferred if there is a negligible amount of solute or mother liquor entrained within the interstitial areas (Kobayashi and Shirai, 1996) as the impurities can be eliminated during the washing stages. However, with the inclusion of salt crystals in the interstitial spaces, the elimination of impurities proves to be far more difficult.

The specific focus of this paper is to determine to what extent the yield of salt is affected by the formation of loose aggregates of ice crystals and the consequent effect on the purity of the ice. In addition, key parameters have been identified. These include settling/flotation time, number of wash cycles as well as agitation during the settling and flotation period. It is important to determine how these parameters affect the separation of the ice and salt crystals from the mother liquor as well as from each other. This will aid in understanding how to improve the overall yield and purity of both crystalline phases.

2. EXPERIMENTAL

Solution Preparation

A 5wt% binary solution of Na_2SO_4-H_2O was used as the test case. Weighed quantities of analytical grade (> 99wt%) Na_2SO_4 were dissolved in 1kg of ultra pure water (18MΩ/cm) before being transferred to the crystalliser.

Experimental Set-Up and Operation

Batch tests were carried out in a 1L jacketed, glass reactor with baffles. Agitation was achieved using an IKA RW 20 digital overhead stirrer connected to a 4-bladed pitched-blade impeller. The agitation rate was set to 500rpm to ensure good mixing as well as to prevent scaling on the inner heat exchanger surface. Cooling was achieved using the Lauda Proline RP845 cooling unit using Wintherm Plus v2.2 software to control the thermostat temperature and the pump flowrate. A coolant, Kryo 45, was circulated at 0.155kg/s through the reactor to effect heat transfer.

Temperature and conductivity of the solution contents was measured in-line using the Handheld^{TM} AZ 86555 conductivity probe. The Handheld^{TM} data logger v2.0 software allowed for the recording and capturing of the temperature and conductivity readings every 3s with an accuracy of ±0.1˚C. The conductivity and temperature trends were used as indicators for the salt and ice crystallisation.

Table 1. Experimental Matrix

Experimental Run	Agitation Rate	Settling/Flotation Time
	rpm	minutes
1	0	1
2		5
3		10
4	50	1
5		5
6		10
7	100	1
8		5
9		10

The synthetic solution was transferred to the crystalliser and maintained at a temperature of 20˚C for 30 minutes to ensure a homogeneous solution. Thereafter, a natural cooling profile (Hojjati and Rohani, 2005) was employed which entailed setting the cooling unit temperature to -2˚C and allowing the crystalliser temperature to equilibrate. Once the crystalliser solution reached -1.8˚C, the equilibrium temperature, 0.5g salt was added. After 60 minutes, 0.5g ice seeds were added to the crystalliser. The crystals were allowed to grow for 30 minutes after nucleation, after which the crystalliser contents were placed in a cooled 1L separation vessel. Three agitation rates (0, 50 and 100rpm) were used in the separation vessel with the impeller situated in the ice region to inhibit the aggregation of the ice crystals. The solution contents were filtered and the mass of ice, salt and remaining mother liquor noted. The ice crystals were washed with deionised water and the $Na_2SO_4{\cdot}10H_2O$ crystals were washed with a saturated solution of Na_2SO_4. The washing liquors were pre-cooled to 3˚C and each wash cycle consisted of 25mL of wash liquor. Samples of the washed and unwashed ice were taken and melted in order to determine the impurity concentration. The experimental program used to generate data is presented in Table 1.

Analytical Techniques

Atomic Absorption Spectroscopy (AAS) was used to analyse the concentration of Na^+ ions in the aqueous phase. The following could be deduced from the analysis:

i. The purity of the washed and unwashed ice crystals as the concentration of Na^+ ions was used as an indicator.
ii. The yield of $Na_2SO_4{\cdot}10H_2O$ could be calculated from the mass balance. From here a fractional yield could be deduced from the ratio of the calculated yield of $Na_2SO_4{\cdot}10H_2O$ and the measured yield as shown below:

$$y_{fractional} = \frac{y_{calculated}}{y_{measured}} \qquad (1)$$

3. RESULTS AND DISCUSSION

Cooling Curve and Crystallisation Process

The 5wt% Na_2SO_4-H_2O crystalliser solution, once reaching a stable starting temperature of 20˚C, was allowed to cool naturally to -2˚C. During initial experiments 0.5g of ice and salt seeds were added simultaneously once the reactant solution reached a temperature of -1.8˚C. This resulted in very low yields of salt due to larger ice crystals being formed, compared to salt crystals. This was previously noted by Reddy et al (2008). Consequently, salt seeds were added first and given between 50-60 minutes to grow to filterable sizes. Thereafter, the ice seeds were added.

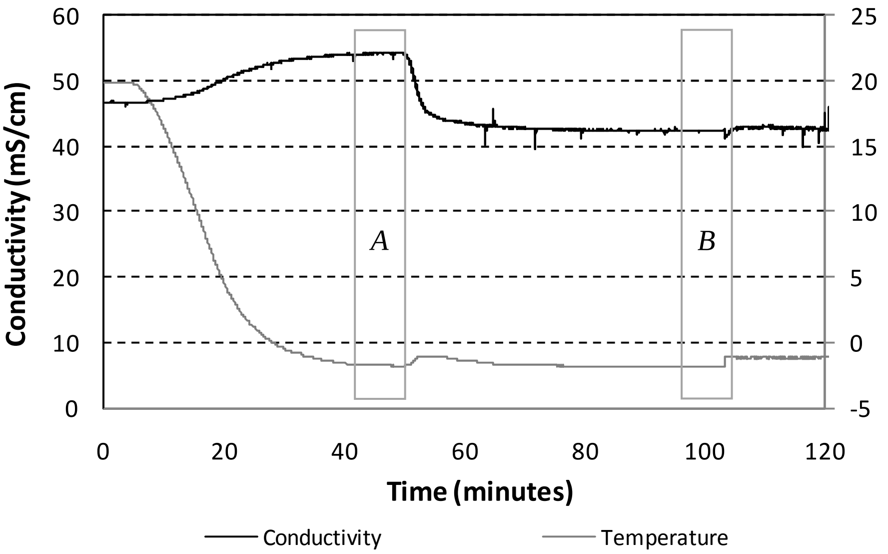


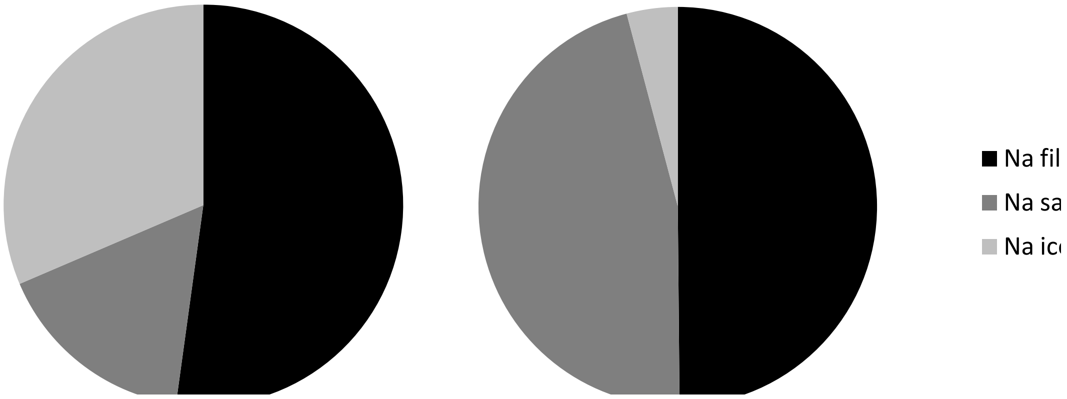
Figure 2. Change in temperature and conductivity as a function of time .
At point *A* Na_2SO_4 seeds are added and at point *B* ice seeds are added.

Figure 2 shows the change in temperature and conductivity over the duration of the experiment. In the time period between 10 and 50 minutes, the measured conductivity of the crystalliser solution increased as the solution was cooled from 20˚C to -1.8˚C. Extensive studies have been carried out by Casteel and Amis (1972) and Diego et al. (1997) trying to model the effect of temperature on the conductivity of aqueous solutions at various concentrations. The model has been fitted to over 20 different aqueous stream (excluding Na_2SO_4). However, the data has been limited to temperatures above 0˚C. Recently, Genceli et al. (2005) conducted $MgSO_4$-H_2O experiments using the measured conductivity to calculate the supersaturation of the solution at sub-zero temperatures. The data showed a linear dependence of conductivity on temperature for various concentrations. This is contradictory to the results shown here, where the conductivity of the solution increased with decreasing temperature until supersaturation was reached. Lundquist and Lewis (1975) presented data for the temperature dependence of conductivity for the Na_2SO_4-H_2O system, but this was for high temperature ranges and showed similar trends. No data could be found for the system at subzero temperatures and it is therefore unknown, at this point, whether this phenomenon is a function of this specific system. This warrants further investigation.

At point *A*, $Na_2SO_4{\cdot}10H_2O$ seeds were added to the solution and a gradual increase in the temperature of the crystalliser solution was noted as the salt nucleated from solution. The nucleation caused a significant decrease in the conductivity of the solution. $Na_2SO_4{\cdot}10H_2O$ crystals nucleated a few seconds after seeding.

The addition of the ice seeds caused the immediate crystallisation of ice crystals and an immediate increase in the crystalliser temperature which is represented by *B*. This indicates a higher degree of supersaturation with respect to the ice as compared to that of the salt at the seeding point *A*. The temperature reached an equilibrium between -1.2 and -1.3˚C corresponding to the eutectic temperature of a binary Na_2SO_4-H_2O system (Barduhn and Manudhane, 1979; Gmelin, 1952 and Marion and Farren, 1999; Reddy et al., 2007). The above trends were noted throughout all experiments.

Figure 3 illustrates the distribution of the 17g of Na^+ ions entering the EFC reactor in the feed. Approximately 50% of the Na^+ from the feed was converted to $Na_2SO_4{\cdot}10H_2O$. There was no addition of impurities to the binary system, therefore the $Na_2SO_4{\cdot}10H_2O$ crystals produced were of pure grade. The crystallised salt was split between the salt that was recovered through filtration and that quantity of salt that was encapsulated in the interstitial spaces of the ice due to aggregation of the ice.



(a) (b)

Figure 3. Pie chart showing the distribution of Na^+ ions from the feed for (a) no agitation and (b) with 100rpm agitation subsequent to 10 minutes settling/flotation time

Figure 3(a) shows that 15% of the sodium ions were recovered through filtration as $Na_2SO_4 \cdot 10H_2O$. 35% of the Na^+ that entered in the feed was present in the ice. Figure(b) shows that with the introduction of agitation, approximately 46% of the Na^+ ions were recovered as $Na_2SO_4 \cdot 10H_2O$ through filtration, with 50% in the filtrate and 4% lost to the ice. Therefore, there was a <9% loss in the yield of $Na_2SO_4 \cdot 10H_2O$. This implies that the impurities in the ice was as a result of salt encapsulation and not as a result of entrainment in the matrix of ice crystals. The main objective of Figure 3 is to illustrate that irrespective of the conversion of Na^+ in the feed to $Na_2SO_4 \cdot 10H_2O$; it is irrelevant if the separation process is ineffective and salt crystals are encapsulated in the ice due to aggregation.

Purity and Yield of $Na_2so_4 \cdot 10h_2o$ Crystals

The fractional yield of $Na_2SO_4 \cdot 10H_2O$ recovered from the experimental studies was derived by the ratio of the calculated yield obtained, from AAS analysis, and the measured yield, determined experimentally. For a system where only a single crystalline phase is present, high yields (>95% as reported by Reddy et al., 2008) are expected. However, with the addition of a second crystalline phase the fractional yield of $Na_2SO_4 \cdot 10H_2O$ crystals decreased reduced dramatically due to a quantity of the salt crystals being encapsulated by the ice crystals.

Figure 4 shows that the fractional yield of $Na_2SO_4 \cdot 10H_2O$ is approximately 0.35 irrespective of settling/flotation time. This was due to the lack of agitation in the separation vessel and implies that 65% of the salt crystallised from the reactant solution is encapsulated in the ice -crystals due to aggregation and is, essentially, lost. This directly affects the purity of the resulting ice (Figure 5).

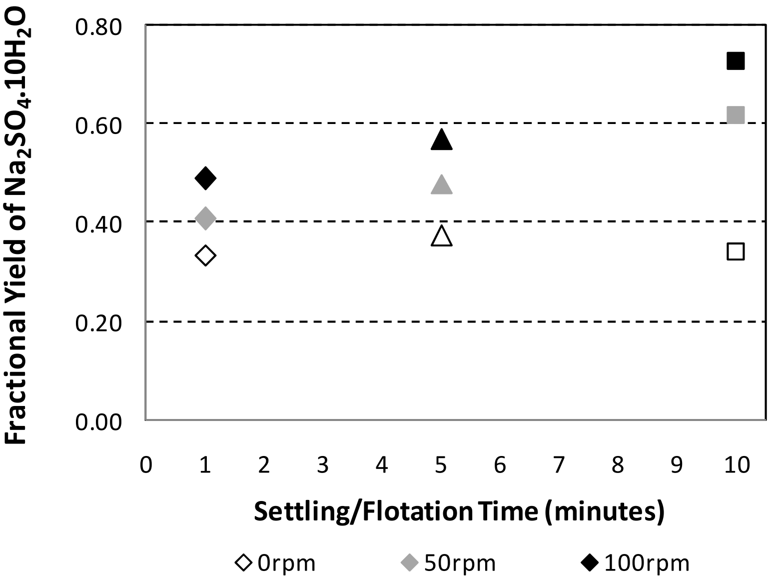


Figure 4. Fractional yield of $Na_2SO_4 \cdot 10H_2O$ as function of the settling/flotation time at various agitation rates (0, 50 and 100rpm) in the separation vessel

A second series of batch studies was conducted, where agitation (50 and 100rpm) was introduced in the ice region, at the top of the vessel. This reduced the aggregation of the ice crystals. Consequently, salt crystals were less prone to encapsulation within the interstitial spaces of the ice crystals (shown in Figure 1) and settled to the bottom of the vessel.

This increased the overall fractional yield of the $Na_2SO_4{\cdot}10H_2O$ crystals by up to 53% for the experimental run using an agitation rate of 100rpm. Therefore, it is evident that agitation in the ice region, in conjunction with increased settling/flotation time is essential for increased yield of the $Na_2SO_4{\cdot}10H_2O$ crystals.

Purity and Yield of the Ice Crystals

The yield of ice crystals is affected by the washing cycles with some ice crystals melting when the wash liquor is at a higher temperature than the ice crystals. The yield is also affected by the encapsulation of the salt. This leads to an inaccurate higher yield with respect to mass, however, the purity of the ice is severely affected.

Figure 5 shows the level of impurity (Na^+ concentration) of the washed and unwashed ice crystals for the batch study using a settling time of 5minutes in the separation vessel. In the absence of agitation, the concentration of the impurity increased exponentially from 15.5g/L to 48.9g/L when the number of washes increased from 0 to 6. Filtration is primarily a solid/liquid separation and does not remove the encapsulated solid salt crystals. A wash liquor of higher temperature (3˚C) than the ice crystals (-1.3˚C) was chosen, deliberately, to melt some of the ice thereby loosening the encapsulated salt crystals. However, the ice crystals dissolved more readily than the encapsulated salt crystals due to the low thermal stability of the ice. Therefore, the ice to salt ratio during the filtration process decreased rapidly, and resulted in the exponential increase in impurity concentration.

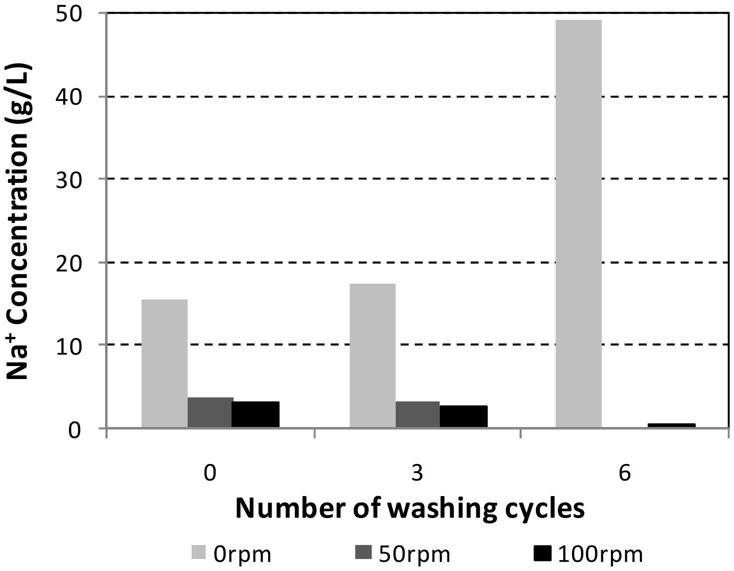


Figure 5. Concentration of Na^+ present in the ice recovered as a function of washing cycles subsequent to 5 minutes of settling/flotation time

There is an immediate decrease in impurity concentration of the ice with the introduction of agitation. In the absence of agitation (0rpm) and washing, the impurity concentration in the ice was 15.5g/L. This decreased to 3.7g/L and 3.1g/L for the 50rpm and 100rpm agitation rates used, respectively. The introduction of agitation in the separation vessel reduced the aggregation of ice and allowed the salt crystals to escape, which translated into a 75% decrease in the Na^+ concentration in the ice.

In addition, with the 50rpm agitation rate, the impurity concentration of Na^+ ions was decreased from 3.73g/L to 0.24g/L Using an agitation rate of 100rpm, a decrease from 3.13g/L to 0.42g/L is achieved. This gives an approximately 90% reduction in Na^+ impurity. This further supports the need for an agitator in the ice region of the separation vessel to reduce the ice aggregation. The mass solid content, i.e. the mass of ice and salt that crystallized, ranged between 8-10wt%. At such low mass fractions, the aggregation of the ice still had a significant effect on the purity and yield of the crystals recovered.

4. CONCLUSIONS

The experimental studies have shown that the solid mass content within the reactor, which ranged from 8-10wt% with respect to the ice, as well as the separation of the solid phases, ice and $Na_2SO_4{\cdot}10H_2O$, play a significant role in the purity and yield of both crystalline phases.

In the absence of agitation in the separation vessel, the ice crystals formed aggregates and encapsulated 65% of the salt crystals in their interstitial spaces. Consequently, a low fractional yield, 0.35, of $Na_2SO_4{\cdot}10H_2O$ was achieved. This reduced the efficiency of ice washing as it was difficult to remove the encapsulated salt crystals. This resulted in high concentrations of Na^+ ions (48.9g/L) being present in the ice after 6 washing cycles. Furthermore, increasing the settling/flotation time did not have a significant effect on the results.

The introduction of agitation in the separation vessel improved the fractional yield of $Na_2SO_4{\cdot}10H_2O$ by 53%. The impurity concentration of the ice also decreased by 75%. The washing cycles proved more efficient as well, with Na^+ concentrations decreasing to below 0.45g/L after 6 washing cycles.

From the results presented, it is evident that the yield and purity of the crystalline phases are negatively affected by the ice crystals forming loose aggregates. However, it was also shown that improvements to the yield and purity of the crystals recovered can be made by the introduction of agitation in the separation vessel, increasing settling/flotation times as well as washing the crystals.

5. ACKNOWLEDGEMENTS

The authors would like express their thanks to the NRF, Helen Divey and to Dr Rob van Hille for his input.

6. REFERENCES

Barduhn, A. J., Manudhane, A. (1979) “Temperatures required for eutectic freezing of natural waters”, *Desalination*, **28**, 233-241

Casteel, J.F. and Amis, E.S. (1972) “Specific conductance an concentrated solutions of magnesium salts in water-ethanol system”, *Journal of Chemical Engineering Data*, **17**, 55-59

De Diego, A., Madariaga, J.M. and Chapela, E. (1997) “Empirical model of general application to fit (κ, c, T) experiemtal data from concentrated aqueous electrolyte solutions”, *Electrochemica Acta*, **42**, 1449-1456

Genceli, F.E., Himawan, C., and Witkamp, G.J. (2005) “Inline determination of supersaturation and metastable zone width of $MgSO_4{\cdot}12H_2O$ with conductivity and refractive index measurement techniques”, *Journal of Crystal Growth*, **275**, 1757-1762

Gmelin, L. (1952) *Gmelins Handbuch der Anorganischen Chemie*, 8th Edition, Deutsche Chemische Gesellschaft, Weinheim: Verlag Chemie

Himawan, C (2005) *Characterisation and population balance modelling of eutectic freeze crystallisation*, PhD Thesis, TU Delft, The Netherlands

Hojjati, H. and Rohani, S. (2005) “Cooling and seeding effect on supersaturation and final crystal size distribution (CSD) of ammonium sulphate in a batch crystalliser” *Chemical Engineering and Processing*, **44**, 949-957

Kobayashi, A. and Shirai, Y. (1996) “A method for making large agglomerated ice crystals for freeze concentration”, *Journal of Food Engineering*, **27**, 1-15

Lewis, A.E., Nathoo, J., Reddy, S.T. and Randall, D. (2008) *Novel technology for the recovery of water and solid salts from hypersaline brines: Eutectic Freeze Crystallisation*, Research Project NO. K5/1727, Water Research Commission, Private bag X03, Gezina, 0031, South Africa

Lundquist, R.V. and Lewis, R.W. (1975) “Conductivity of sodium sulfate solutions containing sodium hydroxide or sulphuric acid” *Chemical and Engineering Data Series*, **2**, 69-72

Marion, G.M. and Farren, F.E. (1999) “Mineral solubilities in the Na-K-Mg-Ca-Cl-SO4-H2O system:A re-evaluation of the sulfate chemistry in the Spencer-Møller-Weare model”, *Geochimica et Cosmochimica Acta*, **63**, 1305-1318

Pronk, P. (2006) *Fluidized bed heat exchangers to prevent fouling in ice slurry systems and industrial crystallizers*, PhD Thesis, TU Delft, The Netherlands

Reddy, S.T., Lewis, A., Witkamp, G.J., Kramer, H.J.M. and van Spronsen, J., (2008) Recovery of $Na_2SO_4{\cdot}10H_2O$ from a reverse osmosis retentate using Eutectic Freeze Crystallisation technology, *17th International Symposium on Industrial Crystallization*, Maastricht, The Netherlands

Stepakoff, G.L., Siegelman, D., Johnson, R., and Gibson, W. (1974) “Development of a eutectic freezing process for brine disposal.” *Desalination,* 15, 25-38

Swenne, D.A. (1983) *The Eutectic Crystallisation of $NaCl{\cdot}2H_2O$ and Ice*, PhD Thesis, Eindhoven, The Netherlands

Vaessen, R.J.C. (2003) *Development of scraped eutectic crystallizers*, PhD Thesis, TU Delft, The Netherlands

Van der Ham, F. (1999) *Eutectic Freeze Crystallisation*, PhD Thesis, TU Delft, The Netherlands