

SEEDING FOR SELECTIVE SALT RECOVERY DURING EUTECTIC FREEZE CRYSTALLIZATION

D.G. RANDALL, J. NATHOO and A.E. LEWIS

Crystallization and Precipitation Research Unit, Department of Chemical Engineering, University of Cape Town, Cape Town, South Africa; E-mail: D.Randall@uct.ac.za

ABSTRACT

Eutectic Freeze Crystallization (EFC) is a novel separation technique that can recover salt and ice by operating the crystallizer at eutectic conditions. It has the potential to treat South African hypersaline brines and produce a number of pure salts and pure ice. However, a significant problem arises when two salts crystallize at the same temperature. This problem can be solved by adding seed crystals so that only the crystallization of the desired product is promoted.

In this paper, selective crystallization using salt and ice seeding in a binary sodium sulphate system as well as salt seeding in a ternary $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ system is investigated. Salt and ice seeding in the binary system resulted in reproducible experimental results while unseeded experiments were irreproducible in this binary system. Salt seeding with $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ crystals in the ternary $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ system resulted in a high salt purity of 95% $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ after two washes but a low yield of 57%. The low yield could be attributed to the fact that the saturated washing solution was prepared at 22°C and the crystals thus dissolved. However, if the saturated solution was prepared at a lower temperature (14°C), this problem could be avoided. Salt seeding with $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ in the ternary system resulted in a low salt purity of 66% $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ and a low yield of 16%.

The results from this study seem to indicate that sodium sulphate seeding promotes the selective crystallization of sodium sulphate while magnesium sulphate seeding does not promote the crystallization of magnesium sulphate. Thus sodium sulphate should be the first component to be removed by seeding with $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ followed by the removal of magnesium sulphate at a lower temperature from a then predominately binary magnesium sulphate system.

1. INTRODUCTION

One of the most important environmental issues in the mining industry of South Africa is hypersaline brine production. Major methods aiming to reduce these brine volumes consist of either brine disposal in evaporation ponds or brine treatment using evaporative crystallization. Brine disposal merely stores the problem and does not treat it. Evaporative crystallization is costly because of the high amounts of energy required and the product that is formed is usually an unsalable mixed salt. Both these methods can reduce the volume of brine but they fail to produce pure salts. These current methods of brine disposal and treatment only offer short-term solutions but have not been shown to be sustainable in the long-term.

A novel technology known as Eutectic Freeze Crystallization (EFC) has the potential to treat these hypersaline brines. Operation at eutectic conditions will separate the aqueous solution (brine) into a number of pure salts as well as pure ice. Thus, the problem of salt contamination is avoided by the fact that each salt has its own unique eutectic temperature, therefore providing the possibility of crystallizing out pure individual salts from a brine. Also, the energy requirement for EFC operation is significantly lower when compared to a three-stage evaporative crystallization process. In some instances energy savings of up to 65% have been reported (van der Ham et al., 1999). EFC has been successfully used to separate a single salt and water from a binary magnesium sulphate stream (Genceli et al., 2005) but it has yet to be applied to hypersaline brines.

However, a significant problem arises if there is more than one salt crystallizing at the same temperature since the one salt will contaminate the other. The system can in theory be manipulated into only crystallizing one salt by merely adding seed crystals of the desired salt product. If this approach is successful it would make EFC a very attractive process for hypersaline brine treatment because it would then allow for the production of a number of pure salts as well as pure, potable water from an otherwise unusable and environmentally harmful waste stream.

2. BACKGROUND

Phase Diagrams and Thermodynamic Modelling

A binary sodium sulphate solution has different solid phase hydrates at different temperatures. Figure 1 is a binary phase diagram for sodium sulphate and it is based solely on the thermodynamics for this system. It shows that the hydrate formed around the eutectic point is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and that the thermodynamic eutectic point is at 4.19wt% Na_2SO_4 and -1.27°C . Figure 2 shows the theoretical yield for a 20wt% Na_2SO_4 solution cooled from 30°C to -5°C (line ABCD in Figure 1). The yield of crystalline material increases as the temperature decreases. Also, a maximum yield (100%) of salt is only achieved below the eutectic temperature. The ice yield is limited to 68% because the remaining 32% is used to form 10 moles of water for each mole of hydrate salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). The yield at a fixed seeding temperature can be determined from Figure 2.

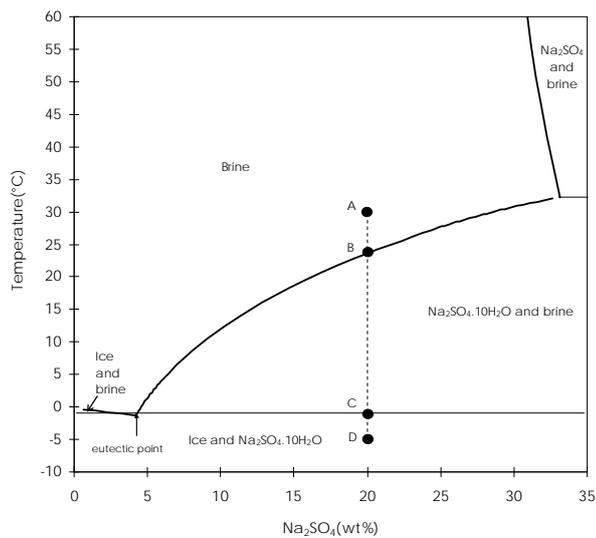


Figure 1. Binary phase diagram (Thomsen, 2008).

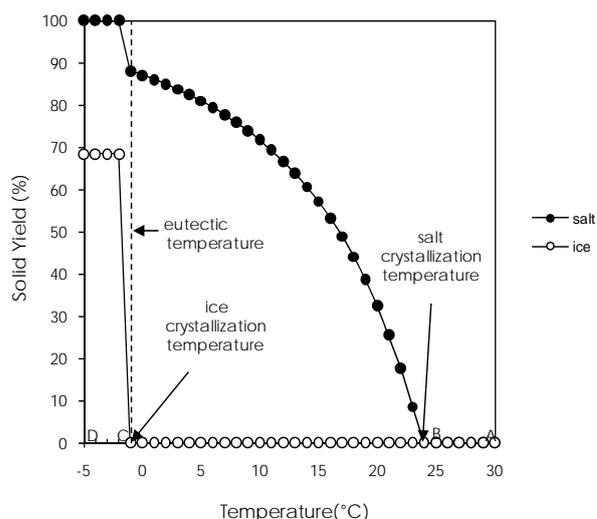


Figure 2. Theoretical yield for a 20wt% sodium sulphate solution.

Kinetics

A phase diagram illustrates the properties of a system based on the thermodynamics. In reality, the cooling rate, reactor configuration and heat transfer all play a significant role in the crystallization process. These aspects relate to the kinetics of the system.

A solution, for example, will only begin to crystallize once the solute concentration has exceeded the thermodynamic or equilibrium concentration. A solution is termed supersaturated when it is more concentrated than the thermodynamic concentration (Myerson, 2002). Supersaturation is thus the thermodynamic driving force for crystallization; and the rate of nucleation and growth of crystals is driven by the existing supersaturation in the solution (Loffelmann and Mersmann, 2002).

Figure 3 shows the different nucleation regions of a solution. The region below the solubility line is a supersaturated region where nucleation can occur.

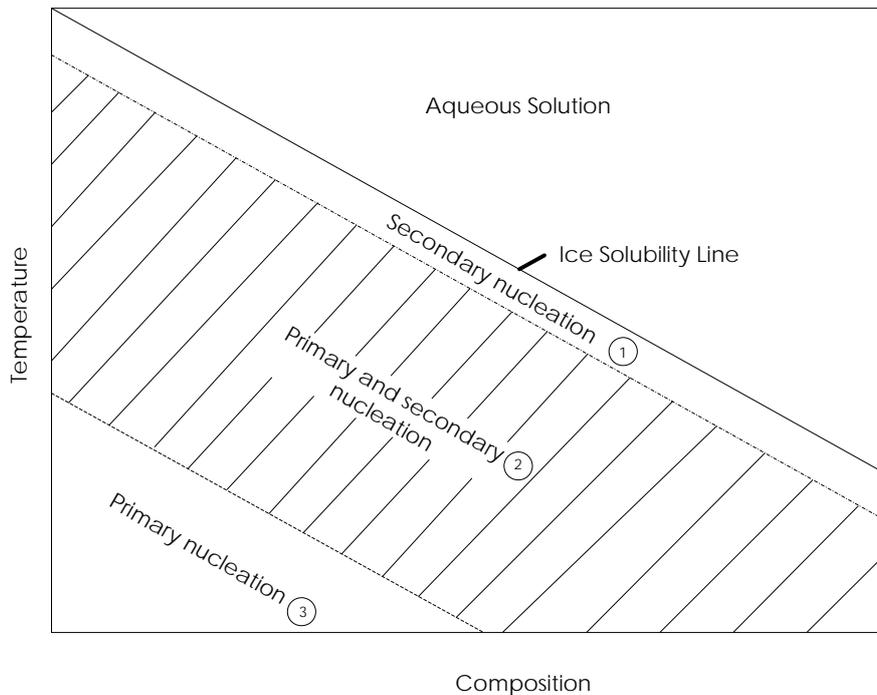


Figure 3. Nucleation regions in a supersaturated solution.

Secondary nucleation is the process of nucleation onto a parent material such as a seed while the process of nucleation in systems with no parent material is termed primary nucleation. The primary nucleation process can be further subdivided into homogenous and heterogeneous nucleation. Homogenous nucleation involves the spontaneous formation of crystals in the bulk solution while heterogeneous nucleation occurs on a solid surface typically because of impurities in the system (Mullin, 2001).

The secondary nucleation region (1) is a region where no nucleation will occur in the absence of seed material. If seed material is added within this region, spontaneous nucleation will occur.

The primary and secondary nucleation region (2) is a region where spontaneous nucleation will occur but because of the stochastic nature of nucleation, the nucleation temperature will be different for repeat experiments at exactly the same conditions. The stochastic theory of nucleation explains that nuclei, which promote spontaneous nucleation, are formed in a random process when two or more particles of the solute approaching one another forming nuclei (Nyvlt, et al., 1970). The probability that nucleation will occur, at a fixed concentration, will be low at higher temperatures and will increase as the temperature is decreased further. This is because as the solution is supercooled; by decreasing the solution temperature, the solution becomes less stable and more supersaturated (increased driving force) thus increasing the probability that nucleation will occur spontaneously. The stochastic nature of nucleation has been noted by Jiang and co-workers (2008), Chen and co-workers (1999) as well as by Nyvlt and co-workers (1970). Beyond this region is a region where only primary nucleation will occur (3).

Seeding

There are two seeding approaches that can be used to promote crystallization. The first involves the addition of seed material at a temperature just below the solubility line (Mullin, 2001). Subsequent cooling will result in crystallization occurring at some temperature below the solubility line.

The second approach involves cooling the solution until a temperature within the primary and secondary nucleation region (region 2 in Figure 3) is reached and at which stage the seed material is added. This approach usually always leads to crystallization occurring at the moment the seed material is added. However, because operation is occurring in the stochastic region of the phase diagram, there is a possibility that spontaneous nucleation will occur before the desired seeding temperature is reached. In this case, small irregular crystals would form and a rapid consumption of the supersaturation would occur. This obviously also depends on the degree of supercooling.

The advantage of operating within this region (2) is that as a solution is cooled further from the solubility line, the theoretical yield increases. Thus operating at a low temperature, and hence in the primary and secondary nucleation region (2), increases the probability that spontaneous nucleation will occur but it dramatically increases the potential yield of solid material.

Ice can be formed without any salt formation by manipulating the system with the addition of ice seed crystals. Ice seeding promotes the formation of ice. Similarly, salt is formed by seeding with salt crystals. Seeding with both salt and ice crystals results in two distinct solid phases (van der Ham et al., 1999).

3. EXPERIMENTAL PROCEDURE

A series of experiments were carried out to investigate the following:

- The stochastic nature of nucleation,
- The potential for selective crystallization in a binary $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system,
- The potential for selective crystallization in a ternary $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ system.

Nucleation Experiments to Investigate Stochastic Nature of the Process

A 3.5wt% sodium sulphate solution was prepared from 99wt% Na_2SO_4 (Merck) and de-ionized water of 18.2m Ω . Ten repeat experiments were carried out using the same solution, reactor configuration and cooling and heating profiles. A Testo 175-177 temperature logging device was used to measure the solution temperature of the reactor. These experiments were performed in a 250ml jacketed glass reactor. The reactor had a four blade baffle installed and used an IKA digital stirrer to provide adequate mixing. The stirrer was a 6 blade Rushton turbine rotating at 300rpm. Cooling was achieved by circulating Kryo40 through the jacket with a Lauda RE207 thermostatic unit.

Figure 4 shows the cooling and heating profile for each experiment. The solution was cooled by adjusting the set-point of the thermostatic unit. The initial set-point was at 0°C and the solution at room temperature was allowed to reach equilibrium at this set point. A cooling rate of 4°C/hours was then applied until the first sudden solution temperature increase occurred. The temperature increased because of the heat given off when the crystals formed (heat of crystallization). The set-point of the thermostatic unit was then increased to 25°C to ensure that all the ice would melt. The duration of the cooling rate profile and heating section was 4 hours. The set-point was then changed back to 0°C and was left at this temperature for 19 hours to ensure equilibrium was once again reached and that the memory effects of the solution were eliminated.

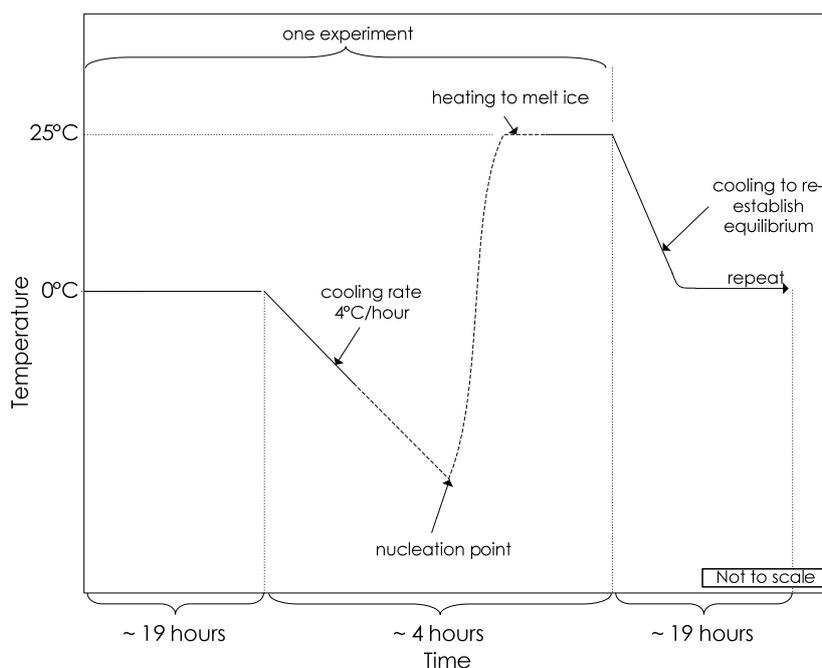


Figure 4. The cooling and heating profiles of the thermostatic unit during the nucleation experiments to investigate the stochastic nature of the system.

Selective Crystallization in a Binary $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ System

A similar experimental setup used during the investigation of the stochastic nature of nucleation was used for these experiments.

Ice seeds were added to a 3.5wt% Na_2SO_4 solution while $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ seeds were added to a 4.5wt% Na_2SO_4 solution. The solutions were prepared from 99wt% Na_2SO_4 (Merck) and de-ionized water of 18.2m Ω . The mass of seeds added was approximately 1g each time. The seed crystals were added at a temperature of -1.8°C which was below the solubility temperatures of both the 3.5wt% and 4.5wt% solutions. This ensured that nucleation would occur.

Selective Crystallization in a Ternary Na₂SO₄-MgSO₄-H₂O System

A 7.8wt% Na₂SO₄ and 45wt% MgSO₄·7H₂O solution was prepared from 99wt% Na₂SO₄ (Merck), 99wt% MgSO₄·7H₂O (Merck) and de-ionized water of 18.2mΩ. This particular solution concentration resulted in a solubility temperature of 14°C for both salts. Seeds were added once the solution temperature was below 14°C to ensure the solution was supersaturated. This concentration was also chosen to ensure that only salt would crystallize with no possibility of ice crystallization. The details of these experiments are illustrated in Table 1.

Table 1. Seed masses (SM) for the ternary Na₂SO₄-MgSO₄-H₂O system.

| Exp # | Na ₂ SO ₄ ·10H ₂ O | Seed Mass(g) | Exp # | MgSO ₄ ·7H ₂ O | Seed Mass(g) |
|-------|---|--------------|-------|--------------------------------------|--------------|
| 1N | No wash | 4.42 | 1M | No wash | 4.42 |
| 2N | One wash | 4.42 | 2M | One wash | 4.42 |
| 3N | Two washes | 4.42 | 3M | Two washes | 4.42 |
| 4N | No wash | 17.66 | 4M | No wash | 17.66 |
| 5N | One wash | 17.66 | 5M | One wash | 17.66 |
| 6N | Two washes | 17.66 | 6M | Two washes | 17.66 |
| 7N | No wash | 35.39 | 7M | No wash | 35.39 |
| 8N | One wash | 35.39 | 8M | One wash | 35.39 |
| 9N | Two washes | 35.39 | 9M | Two washes | 35.39 |

A Testo 175-177 temperature logging device was used to measure the temperature of the solution in the reactor. These ternary seeding experiments were performed in a 1.5L jacketed glass reactor. The reactor had a four blade baffle installed and used an IKA digital stirrer to provide adequate mixing. The stirrer was a 6 blade Rushton turbine rotating at 300rpm. Cooling was achieved by circulating Kryof40 through the jacket with a Lauda RE207 thermostatic unit.

The set-point of the thermostatic unit was set to 12°C and Na₂SO₄·10H₂O seed crystals or MgSO₄·7H₂O seed crystals were added once the solution temperature was lower than 14°C. The set-point was then adjusted to 8°C and crystallization occurred at some temperature during this cooling period. The system was left for 30 minutes once crystallization had occurred, after which the contents of the reactor were removed and vacuum filtered using a Buchner Funnel. The product was washed with 25ml of a saturated solution prepared at the laboratory room temperature (~22°C). The saturated solution was the same as the seed material. Samples of the product were removed after each wash and were analyzed using AAS for both the Na⁺ ion as well as the Mg²⁺ ion.

4. RESULTS AND DISCUSSION

The Stochastic Nature of Nucleation

Figure 5 shows the nucleation temperature for the 10 unseeded nucleation experiments using a 3.5 wt% Na₂SO₄ solution.

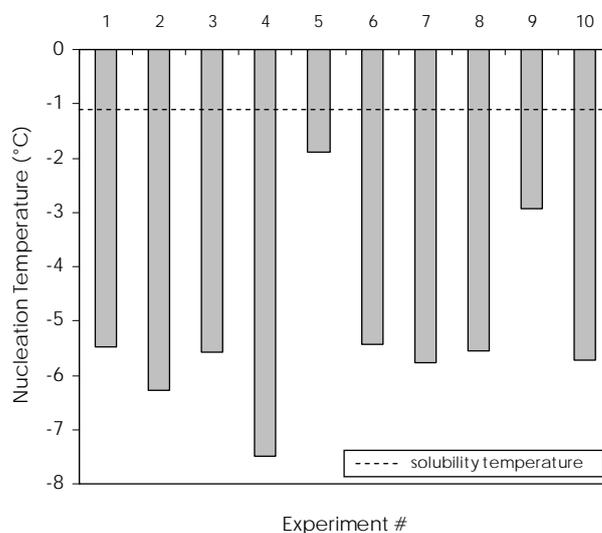


Figure 5. Nucleation temperatures for a 3.5wt% Na₂SO₄ solution.

The ten experiments, with the same solution and reactor configuration, resulted in very different nucleation temperatures. The dotted line represents the thermodynamic solubility temperature (-1.12°C) for a 3.5wt% Na_2SO_4 solution, which is very different to the ten experimentally measured values. This is because the nucleation process is a stochastic event. The crystal nuclei are continuously dissolving and recombining, and only when a critically sized nucleus is achieved does spontaneous nucleation occur (Nyvlt, 1971). This unpredictability in unseeded crystallization does not allow the process to be controlled easily.

Seeding with Ice and Salt

Figure 6 shows the nucleation temperatures during ice and salt seeding in a binary $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system.

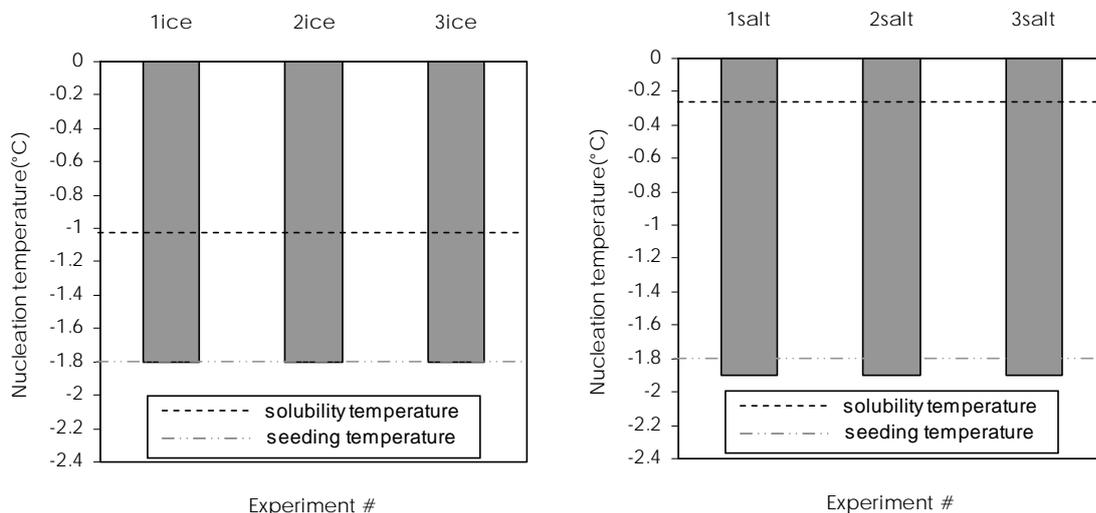


Figure 6. The effect of ice and salt seeding on nucleation temperatures near the eutectic point in a binary Na_2SO_4 system.

Ice seeding resulted in ice crystallization occurring at the exact moment that the ice seeds were added while there was a slight delay in the crystallization process (approximately 2 minutes) during salt seeding thus the actual nucleation temperature was -1.9°C . The possible reason for this is that the time needed to form one molecule of ice is far less than the time needed to form a more complicated molecule of salt along with its waters of hydration. There is thus a slight delay in the release of energy which results in the observed temperature increase. Regardless, ice and salt seeding resulted in reproducible results.

Seeding with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in a Ternary $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ System

Figure 8 and Figure 7 show the salt purity and yield as a function of the number of washes with a saturated sodium sulphate solution while seeding with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

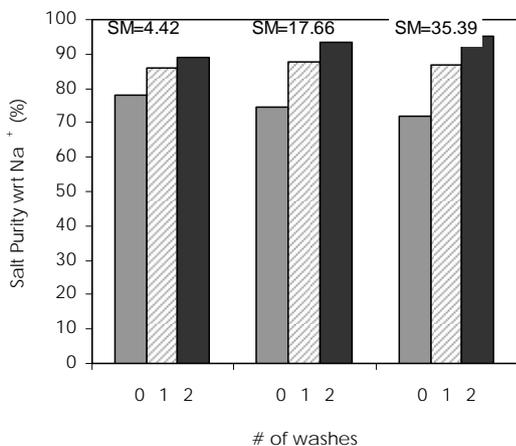


Figure 8. Salt purity with respect to Na^+ as a function of the number of washes.

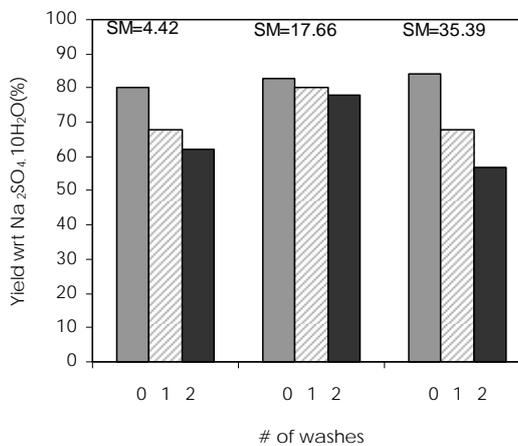


Figure 7. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ yield as a function of the number of washes

The purity of the salt increases with each wash from about 75% to 92% (on average) after two washes with a saturated sodium sulphate solution. The mass of seeds added (SM) does not have a significant effect on the purity. The yield decreases significantly for a SM of 4.42g and 35.39g with each wash from a maximum of around 80% to about 60% after two washes. However, for a SM of 17.66g the decrease in yield was insignificant (83% to 78%) compared to the other amounts of seeds. Thus it would seem that selective crystallization using sodium sulphate seeding is possible in this system with a relatively high purity of 95% after two washes.

The low yield can be attributed to the fact that the saturated solution was prepared at room temperature and not at the temperature of the process (<14°C) thus the salt crystals dissolved. The drop in yield could be prevented by washing the solution with a saturated solution prepared at the same temperature of the process (<14°C).

In this particular system the concentration of Na₂SO₄ (7.8wt%) is significantly lower than that of MgSO₄·7H₂O (45wt%) thus the liquid entrainment and contamination by the magnesium ion would be significant and could explain the low initial purities for these experiments.

Seeding with Mgso₄.7h₂o in a Ternary Na₂so₄-Mgso₄-H₂o System

Figure 10 and Figure 9 show the salt purity and yield as a function of the number of washes with saturated magnesium sulphate solution while seeding with MgSO₄·7H₂O.

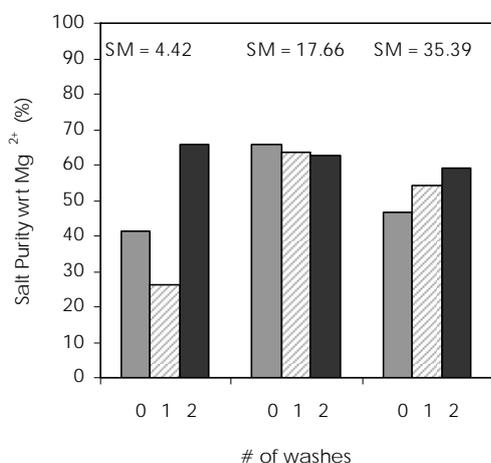


Figure 10. Salt purity with respect to Mg²⁺ as a function of the number of washes.

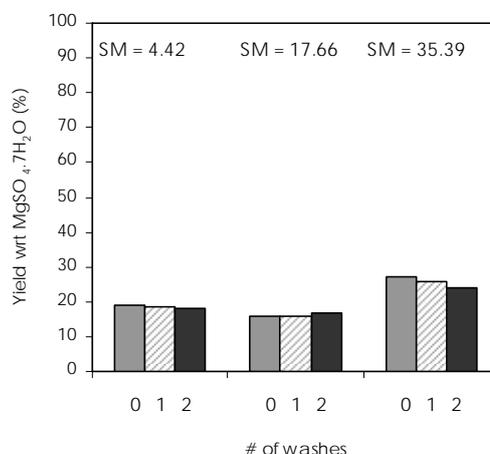


Figure 9. MgSO₄·7H₂O yield as a function of the number of washes.

The highest salt purity (66% and a yield of 16%) was obtained with a SM of 17.66g while the highest yield (27%) was obtained with a SM of 35.39g but the purity was 47%. Only with a SM of 17.66g did the salt purity increase significantly (from 44 to 66% after two washes). The yield was constantly low and never exceeded 30%.

Figure 11 shows a thermodynamic prediction of the yield of magnesium and sodium ions as they crystallize in the form of salts during a cooling process from 25°C to -25°C. The figure also shows the yield of ice. OLI Stream Analyser (OLI Systems Inc, 2009) was used as the simulating tool to predict these thermodynamic results.

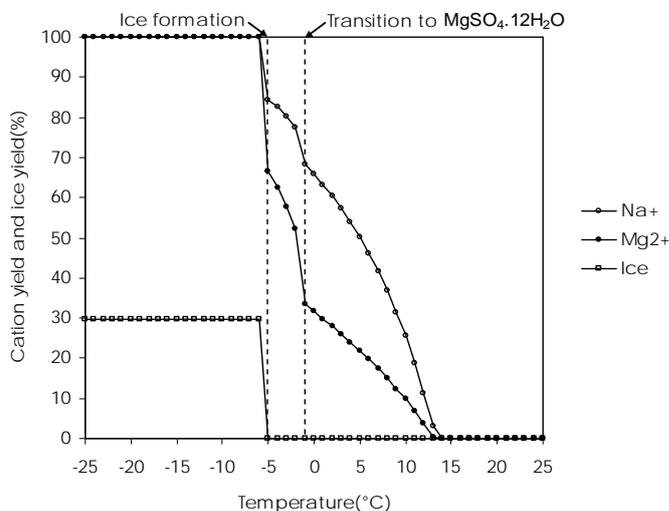


Figure 11. Cation and ice yield for the ternary Na₂SO₄-MgSO₄-H₂O system

The reason for the low yield during the magnesium sulphate seeding experiments could be attributed to the nature of the system as shown by the thermodynamic modelling in Figure 11. The yield of magnesium sulphate will always be low up until the point where the crystals start to transform to $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$. This is the hydrate form of crystal that forms at the ternary eutectic point (the point where $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ and ice will form). Thus, an increase in salt yield will only occur when the crystals are cooled further and allowed to transform to this hydrate. The yield of ice is low (30%) because the majority of the water is used to form the water molecules for the hydrate salts.

The low purity of magnesium sulphate during the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ seeding experiments probably indicates that magnesium sulphate seeding promoted the crystallization of sodium sulphate rather than magnesium sulphate. Thus, it seems that magnesium sulphate seeding does not promote the crystallization of magnesium sulphate in this system. Another possible explanation for the low purity could be attributed to the size and number of seeds added to the system. However, this was not investigated in this study but it is well known that the size and number of seeds does influence the nucleation and crystallization process (Mullin, 2001).

The fact that sodium sulphate seeding did promote the crystallization of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ while magnesium sulphate seeding did not promote the crystallization of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ simply implies that selective crystallization is possible but it depends or restricts which salt must crystallize first. For example, if the majority of sodium sulphate is removed from the process by seeding with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, then the system would become richer in magnesium sulphate. The crystallization of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ would then occur at a lower temperature with little or no sodium sulphate contamination because the system would then essentially be a binary magnesium sulphate system.

5. CONCLUSIONS

Theoretical concepts of Eutectic Freeze Crystallization relating to the yield and thermodynamics were investigated. Salt and ice seeding in a binary Na_2SO_4 system as well as selective crystallization in a ternary Na_2SO_4 - MgSO_4 - H_2O system was also investigated. The following conclusions were drawn:

- Theoretically, the maximum salt yield can only be achieved if a system is allowed to reach eutectic conditions,
- The yield of a component increases as the system is cooled further from the solubility line although the probability that spontaneous nucleation will occur also increases,
- Unseeded experiments are irreproducible and will result in different nucleation temperatures because of the stochastic nature of nucleation,
- Salt and ice seeding in a binary sodium sulphate system results in both salt and ice crystallization,
- Seeded experiments result in reproducible results and therefore allow for better control of a system,
- Selective sodium sulphate crystallization is possible in a ternary Na_2SO_4 - MgSO_4 - H_2O system with a relatively high salt purity of 95% after two washes and with a SM of 35.39g,
- Selective magnesium sulphate crystallization resulted in a low purity (66%) and a low yield (16%) with a SM of 17.66g in the ternary Na_2SO_4 - MgSO_4 - H_2O system,
- Sodium sulphate seeding promoted the crystallization of the desired product while magnesium sulphate seeding did not.

6. REFERENCES

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