Eutectic Freeze Crystallization:

Separation of Salt and Ice

Master Thesis

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‘Remember, nothing that's good works by itself, just to please you. You have to make the damn thing work.’

Thomas A. Edison, (1847 - 1931)

Summary

Eutectic Freeze Crystallization (EFC) is a new technology to separate salt and water from a process stream. EFC is in the final development stage and has the potential to be more energy efficient than current separation methods, like evaporative crystallization, used by the industry. Salt and ice are separated in a solid form by their density difference, which allows ice to rise to the surface and salt to sink to the bottom. Currently no knowledge is available on bidisperse settling behavior of salt and ice. The separation of the salt and ice solids in the solution is observed using a HD camera and a 10L transparent test setup filled with a potassium chloride solution.

The separation is a settling process that uses the density difference between salt and ice. Although pure salt and ice crystals are formed, they tend to get entangled. This causes all the visible ice to sink to the bottom together with the salt. This phenomenon was also observed in other setups of 1L and 200L and with a different salt. When the salt-ice slurry is settled on the bottom, the salt and ice can be separated by agitating the slurry with some sort of impulse, created by for instance air. The solids then separate by their density difference.

The salt-ice slurry was examined under the microscope to find a cause for the entanglement of the solids. Irregular shaped extremities, which were observed on the ice crystals, seem to be the reason for the bad initial separation. These irregular extremities are probably caused by kinetic roughening induced by foreign particles, but no definite proof was found for this.

Based on the performed research, a change in the EFC process is suggested. Rather than separating the salt and ice in the crystallizer, it is better to remove both the salt and ice as a slurry through the bottom. The slurry can then be separated in a subsequent vessel, which has less turbulence and gives a place to agitate the slurry, allowing for a more effective separation. This change in the design of the process also provides answers to other design issues like feed entrance location, which should be placed at the top, and heat exchanger configuration, which can now be placed in series.

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Chapter 1 – Introduction

The Netherlands is an agricultural country with a very large amount of life stock. This life stock consists of cows, goats, chickens, pigs and much more. And that creates a problem, all these animals produce more manure than we can cope with. In 2011 the total amount of liquid manure produced in the Netherlands was close to 68 billion [CBS, 2012], most of it was due to cows and pigs.

In the past the animal manure was never a big issue, because the manure was used to fertilize the crops. With the introduction of artificial fertilizers and the increase of the amount of animals for the production of meat and dairy, a surplus of manure was created. Part of the manure is still used to fertilize the fields, but this is only allowed in a small period of the year and there is not enough agricultural land in the Netherlands to use all the manure. The remainder of the manure therefore has to be exported to other countries or disposed of in some other way.

In Delft a new technology is currently being developed for the disposal of pig manure with zero waste remaining. The process consists of a centrifuge step to remove all the organic material and Eutectic Freeze Crystallization (EFC) to further treat the remaining liquid. The remaining liquid contains a lot of salts, like for instance potassium chloride, which should not be discarded in the environment for two reasons. First of all, when too many salts are discarded to the environment in large quantities, this is harmful for the local flora and fauna. Secondly, a lot of the salts that can be separated from this waste stream have an economical value and can thus be sold, turning waste into profit.

Eutectic Freeze Crystallization is a more recently developed technology, where water and salts are separated by reducing the temperature to the eutectic temperature. The big advantage of EFC compared with other separation processes between water and salt is that EFC is more energy efficient, even up to 90% [Van der Ham, 1999]. This technology is currently in the final stage of development, a skid mounted pilot plant is present at the Process & Energy department of the TU Delft.

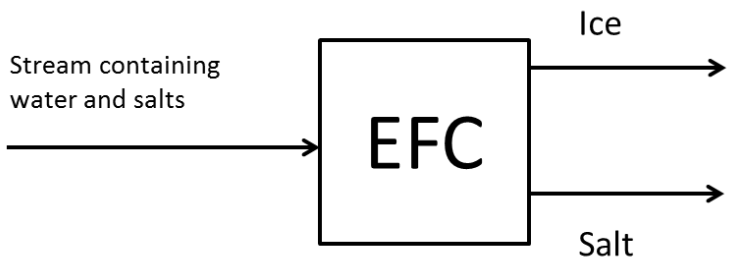

Figure 1.1 – Eutectic Freeze Crystallization

Eutectic Freeze Crystallization

Eutectic freeze crystallization is a separation process based on crystallization at the eutectic point. This can be explained using figure 1.2, which is a typical phase diagram of a salt-water mixture.

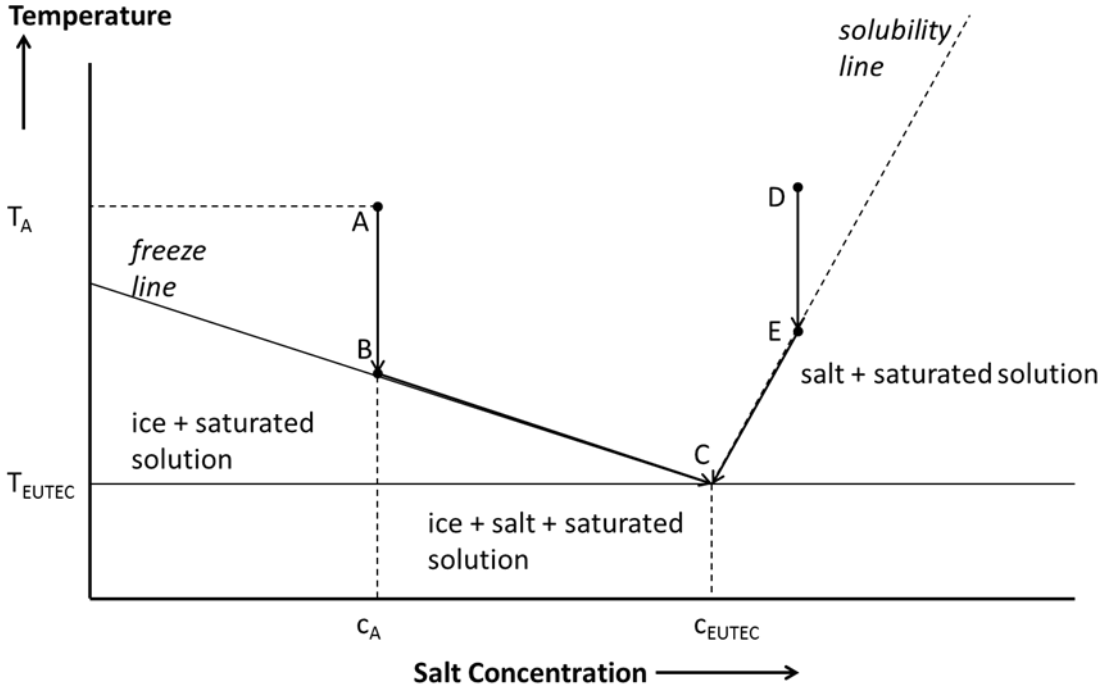

Figure 1.2 – Phase diagram of a binary salt-water mixture

Take a salt water mixture at point A, with temperature T_A and concentration c_A. By decreasing the temperature of this mixture, eventually point B will be reached. At this point ice crystals will start to form. Point B is a point on the freeze line. This line indicates the concentrations with corresponding temperature at which ice is formed in the mixture.

By creating ice crystals, water is removed from the mixture. This means that the concentration increases and the temperature can be decreased again. This is continued along the freeze line until point C is reached. At point C the freeze line intersects with the solubility line. The solubility line indicates the concentration of salt that is soluble in water at a certain temperature. At point C the concentration cannot become any higher without increasing the temperature. When more ice is formed the amount of dissolved salt is too high and salt crystals start to form, the salt is no longer soluble in the water. Point C is also known as the eutectic point.

Of course, the same principle is also possible with a solution where the concentration is higher than the eutectic concentration. This can be seen in point D, the temperature is decreased again, until the solubility line is reached at point E. At point E, salt crystals are formed and the concentration of the solution is lowered. The temperature can now decrease again, this is repeated until the eutectic point is reached again and ice crystals start to form.

Development of Eutectic Freeze Crystallization

The first research on eutectic freeze crystallization was published in the 1970's by Stepakoff [Stepakoff, 1974]. He used direct cooling, where a refrigerant is directly added to the brine to achieve this. This poses some disadvantages, because there is another chemical introduced to the system. Van der Ham [Van der Ham, 1999] was the first to use indirect cooling, and make a working crystallizer called the Cooled Disk Column Crystallizer. He proved that the separation of the ice and salt crystals using EFC is possible. The research was continued by Vaesen [Vaesen, 2003] among others who scaled up the process to 100L in the Scraped Cooled Wall Crystalizer. The most recent development is that of Genceli [Genceli, 2008], who scaled up the process to 220L in the skid mounted third generation Cooled Disk Column Crystallizer and Rodriquez Pascual [Pascual, 2009], who looked at some of the physical aspects of the heat transfer.

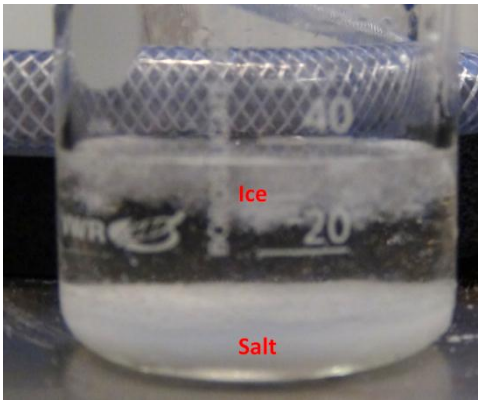

Figure 1.3 – Separation of ice and salt crystals

Recent research is focused on designing the next generation of eutectic freeze crystallizers. This next generation is a crystallizer that can handle process streams on an industrial scale. This requires optimizing the current equipment on the pilot plant scale and identifying possible problems. An example of this is the research of De Graaff [De Graaff, 2012], who did some research to the cause of scale formation on the heat exchangers. The scaling causes the heat exchangers to become less efficient, therefore there is some profit to be made in finding the cause of this scaling and possible ways of preventing this.

Current challenge

The development of an industrial EFC process is nearing and only a few last challenges need to be faced. One of these challenges is the actual separation of the ice and salt crystals. In the 200L pilot plant this is done in a separate vessel, but ideally this should be done in a sort of hybrid crystallization and separation vessel.

In this thesis the separation behavior of salt and ice during an eutectic freeze crystallization process is studied with the goal to get a better understanding of the separation during EFC and get a better understanding of the possibilities for the separation of salt and ice.

To start this research first the known theory was studied, this consist mainly of the settling theory of a single type and multiple types of solids in suspension. This is presented in **chapter 2** in combination with possible influences of crystallization phenomena.

During this research potassium chloride was used as a salt, therefore the crystallization behavior of this salt was briefly studied en described in **chapter 3**. The separation behavior

of salt and ice was observed in a 10 L setup and documented using a HD camera. The results and findings are presented in **chapter 4**.

The observations were used to make some recommendations for an industrial EFC process in **chapter 5** and in **chapter 6** the conclusions and recommendations of this thesis are presented.

Chapter 2 – Gravitational solid liquid separation

Gravity separation processes

Gravity separation is any method of separating two or more compounds from each other using a technique where gravity is the dominant force. Gravity separation is used in a large variety of industries and is usually employed for streams that have formed some kind of suspension. The falling of suspended particles through a liquid is called settling, the termination of this process is called sedimentation.

In general gravity separators are divided in two categories: clarifiers and thickeners. Thickening is used to increase the concentration of solids in a process stream. Clarification is used to remove solids from a process stream [Perry, 2008]. For a stream where the density of the solids is larger than the liquid ($\rho_{solid}>\rho_{liquid}$), this means that in a clarifier the top stream is the product and the bottom stream is the waste stream. For a thickening process the opposite is true.

It is also possible that both a clarification and a thickening process are used at the same time. This is possible when more than one type of solid is present, e.g. the suspension is polydisperse. In an EFC process, there are two types of solids present, ice and a salt. The suspension in an EFC crystallizer can therefore be specified as a bidisperse suspension. In theory the density difference between the different compounds ensures that ice will float to the top and salt will sink to the bottom, which means it is both a clarifying and a thickening process at the same time.

For instance in an EFC process where the salt must be recovered, the ice is removed at the top, which is a clarifying process. At the same time the salt is concentrated at the bottom, which is the thickening process. When water is the desired product, the opposite is true, when ice and salt are both desired products, both streams are a clarifying and a thickening process. For instance, the ice stream would then be thickened by the separation of the ice and clarified by the removal of the salt, while the same could be said about the salt stream.

Theory

The first person who found a solution for the settling behavior of solids in a fluid was Stokes in 1851. He derived an equation for a sphere in a creeping flow using the Navier-Stokes equations. A particle is in creeping flow when the Reynolds number is smaller than one ($Re<<1$). This resulted in the Stokes' equation (eq.2.1) [Kundu, 2008]:

$$v_s = \frac{g d^2 (\rho_p - \rho_f)}{18\mu} \quad (2.1)$$

Where:
- v_s is the Stokes' settling velocity, which is positive when the particle is moving downward [m/s];
- g is the gravity constant [m/s^2];
- d is the diameter of the particle [m];
- ρ is the density of the fluid (f) and the particle (p) [kg/m^3];
- μ is the viscosity of the fluid [Pas].

This equation is still the basis in the field of sedimentation, but it is not ideal. The Stokes' equation describes the velocity of a single particle and does not incorporate the influence from any surrounding particles. Kinch found a theoretical formula for hindered settling, but it was not as accurate as was desired [Kinch, 1951]. Richardson and Zaki finally find an empirical equation, which is very similar to Kinch, but more accurate [Richardson, 1954]. This equation is still in use today and is only on very exceptional occasions altered a bit to fit in very specific cases.

$$v = v_s(1 - \phi)^n \quad (2.2)$$

Where:
- v is the settling velocity, which is positive when the particle is moving downward [m/s];
- ϕ is the volumetric solids concentration [m^3/m^3];
- n is a constant that depends on the Reynolds number and the ratio between the particle diameter and the diameter of the settler [-].

Settling behavior and crystallization

The formulas above give the factors that influence the settling behavior of the solids. From the Stokes' equation, the only variable that can be changed is the diameter of the particle. The densities and viscosity are constant during EFC. (They are temperature dependent, but EFC takes place at a constant temperature.) The diameter is the only variable that can change, it is dependent on multiple crystallization phenomena like growth, agglomeration and attrition. These crystallization phenomena are visually described in figure 2.1. The crystals grow larger when they get more time to grow, they also become larger when multiple particles stick together and form one larger particle. In the case of attrition, large particles become smaller and form new particles. For the settling velocity of individual particles this means that growth and agglomeration can increase the settling velocity, while attrition decreases the settling velocity.

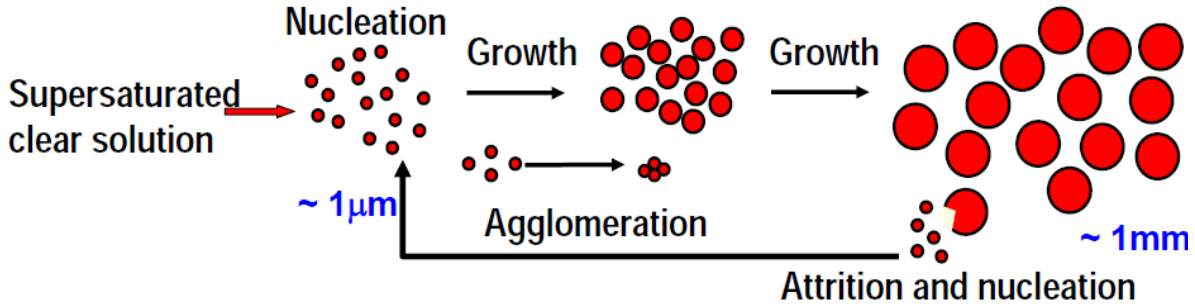

Figure 2.1 – Crystallization phenomena [Kramer, 2010]

From the hindered settling equation (eq. 2.2), it follows that the volumetric amount of solids is also an important factor. The volumetric amount of solids is only affected by the growth and nucleation, because these let the volume of solids increase. Agglomeration and attrition may change the amount of particles, but not the volume.

Another crystallizing phenomenon in EFC that can contribute to the settling behavior is Ostwald ripening. When crystals in a suspension are ripening, it means that the large crystals become larger, at the cost of the smaller crystals. Crystal growth creates heat, so the larger crystals grow and the heat that this produces melts the smaller crystals.

Although all these phenomena have an influence on the settling behavior, one has to keep in mind that not all the crystals will have the same size. In a continuous EFC process the size of both ice and salt crystals will most likely have a normal distribution. For the separation of ice and salt, this means that the effectiveness is limited by the smallest particles.

Settler column

The particle size of the smallest particles is the limiting factor to a good separation. This is because the particle size is largely responsible for the settling velocity and small particles have a tendency to move in the 'wrong' direction when the flow velocity is too high. When ice and salt are separated in a column, the upward flow velocity of liquid should not be faster than the downward settling velocity of the smallest salt particles. In the same way the

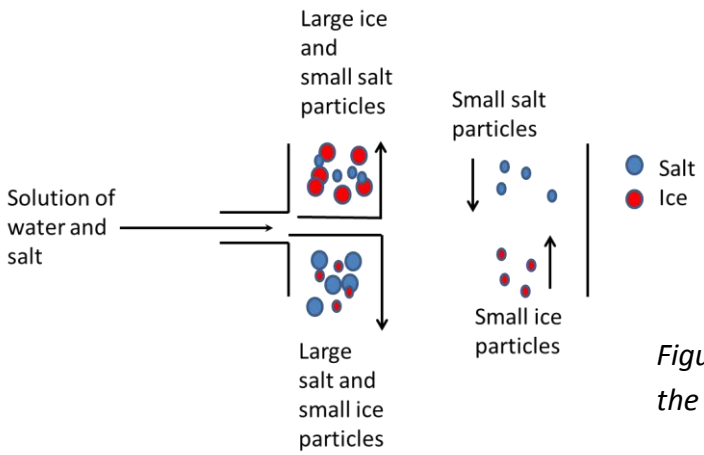

Figure 2.2 – Graphical display of the working of a settler column

downward flow velocity of liquid should not be faster than the upward velocity of the smallest salt particles.

The flow rate of the slurry flow in a settler is usually not controllable, but it does influence the flow velocity in the column. The flow velocity in the column is adapted to the settling velocity during the design phase by choosing a correct diameter for the column. When the diameter of the column increases with a constant flow rate, than the flow velocity will decrease. This is also why in a water purification plant the sedimentation tanks are so wide in diameter.

Most gravity separation equipment deals with only one solid phase and the available literature on polydisperse mixtures is limited to models and small scale experiments like Nasr-El-Din et al.[Nasr-El-Din, 1988 & 1989]. Based on his experiments and model he concluded that for a bidisperse mixture the degree of separation is a function of the feed flow rate, the total amount of solids in the feed and the split ratio. He also found that every feed flow rate has a threshold split ratio, after which the effectiveness of the separation decreases. The split ratio is the ratio between the underflow and the feed flow.

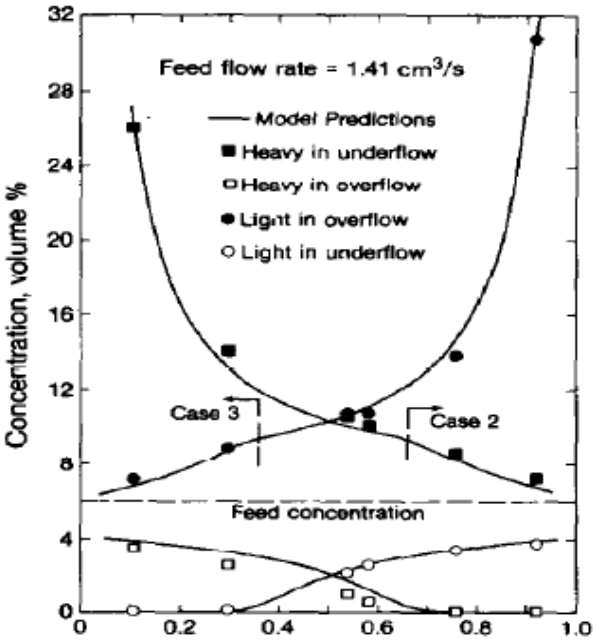

Figure 2.3 – Variation of light and heavy particle concentration in overflow and underflow as a function of the split ratio [Nasr-El-Din, 1988]

The difference between these experiments and the EFC separation is that in the experiments spheres with two distinct densities where used. In the EFC there are no spheres, but irregular forms. Also ice crystals have the tendency to stick together, which could have as a consequence that the ice and salt will disturb the settling behavior of each other.

Washing

A possible solution to the fine particles that are separated in the wrong direction, e.g. fines of salt between the ice particles or vice versa is washing. Washing is one of the simplest cases of a leaching operation and is the most obvious choice for removing fines of salt from an ice slurry. Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, usually permeable, solid phase with which it is associated [Perry, 2008].

The washing of ice slurries is not without difficulties. Problems such as channeling, viscous fingering and ice pack clogging are often seen in practice [Qin, 2008 & 2011].

Channeling occurs when certain areas are less dense packed with ice then others. The washing liquid will then follow the path of least resistance instead of being distributed evenly. This occurs most of the time near the wall and is therefore also known as the wall-effect.

Viscous fingering occurs when the wash front moves unevenly. The interface between the ice and the wash liquid develops into finger-like shapes.

Clogging of the wash column occurs when the ice crystals in the slurry have not ripened enough, they would then tend to stick together. Often two or all three of these problems occur at the same time, for instance when a part of the column is blocked, the wash front is not moving evenly and viscous fingering occurs.

As a washing medium it is not possible to use plain water in an EFC process, because water will freeze at 0°C. Therefore some other fluid should be used, for instance a part of the feed stream that is diluted could be a solution. This could at the same time function as a precooling step for the feed stream.



Figure 1.4 – Viscous fingering [Qin, 2008]

Chapter 3 - Potassium Chloride

KCl – water system

Potassium chloride is a salt that is very common in a lot of waste streams and waste products, such as for instance pig manure. EFC can be used on waste streams to separate the salt from water so that the amount of waste remaining becomes minimal. In this chapter the potassium chloride – water system is investigated in a 1L setup, to get a better understanding of this system.

Potassium chloride is a salt composed of potassium (K) and Chlorine (CL), it is a natural occurring salt that is also known as the mineral Sylvite. Potassium chloride is a harmless salt that is only toxic in excess. It is therefore used as a sodium-free substitute of table salt. On the other hand, intravenous it is very dangerous for the heart muscle and is even used as the third drug in the lethal injection process in the United States [Wikipedia, 2012].

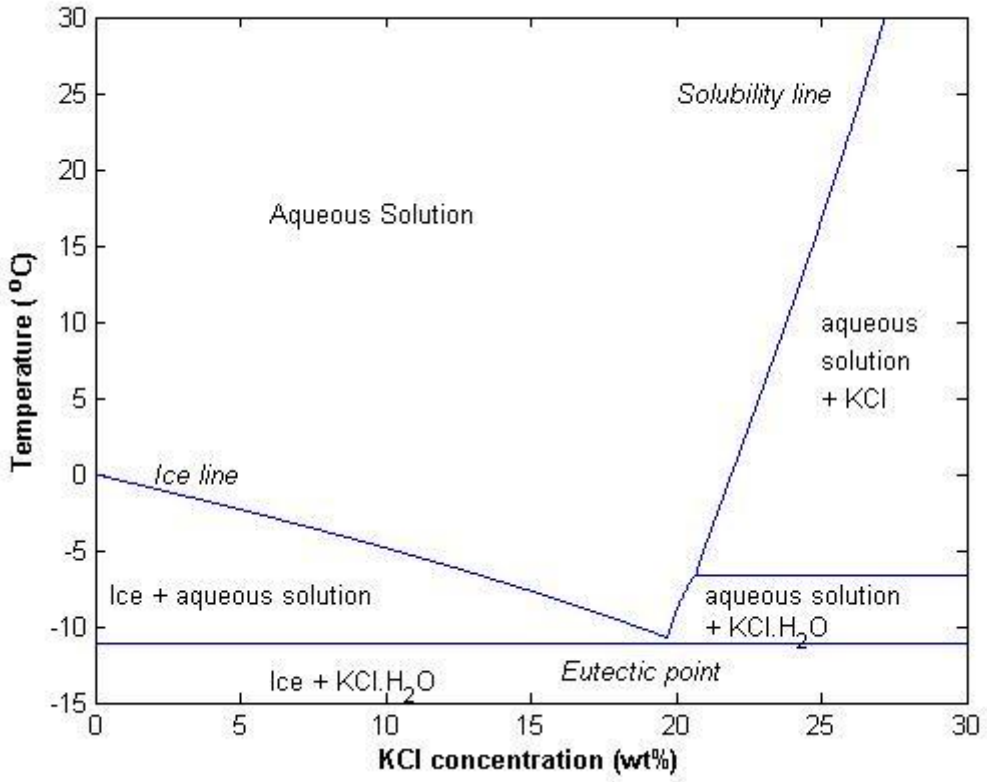

Figure 3.1 – Phase diagram of Potassium chloride and water [Pronk, 2006]

When Potassium chloride is dissolved in water it forms two ions. These ions will bond again when the temperature of the solution drops and form a monohydrate crystal as can be seen in figure 3.1.

$$KCl \leftrightarrows K^+ + Cl^- \leftrightarrows KCl \cdot H_2O \qquad (2.1)$$

Because there is some contradictionary information regarding the eutectic point of potassium chloride an analisys was performed in a 1L setup of the potassium cholide – water system.

Experiment

The analysis of the potassium chloride – water system was done in a setup that contains a beaker of one liter, which is easy accessible for sampling. The solution in the beaker is kept in motion using a stirrer and the beaker is cooled using Kryo 85 refrigerant in a Lauda Proline RP-855 cooling machine. The beaker is insulated with a Teflon coating (figure 3.2). To ensure that the formed crystals do not melt immediately during the analysis, this experiment was performed in a temperature controlled room, where the temperature was set at -5°C. The solution used for the experiment contained 19.1 wt% potassium chloride. The solution was made using demineralized water and the potassium chloride was of industrial technical grade, 99% KCl (KALI).



Figure 3.2 – 1L setup

The solution was cooled to the eutectic temperature and given some time to develop both ice and salt crystals. The salt and ice crystals were observed under a microscope and photographs were taken. Further the ice was washed three times using demineralized water at 0°C. Samples were taken from the ice, wash water and the solution at start and eutectic concentration. These samples were analyzed using an Inductive Coupled Plasma analyzer.

Results

During the 1L experiment the temperature of the refrigerant and the solution was logged every five seconds by Pt 100 temperature sensors on a computer. The result is visible in figure 3.3.

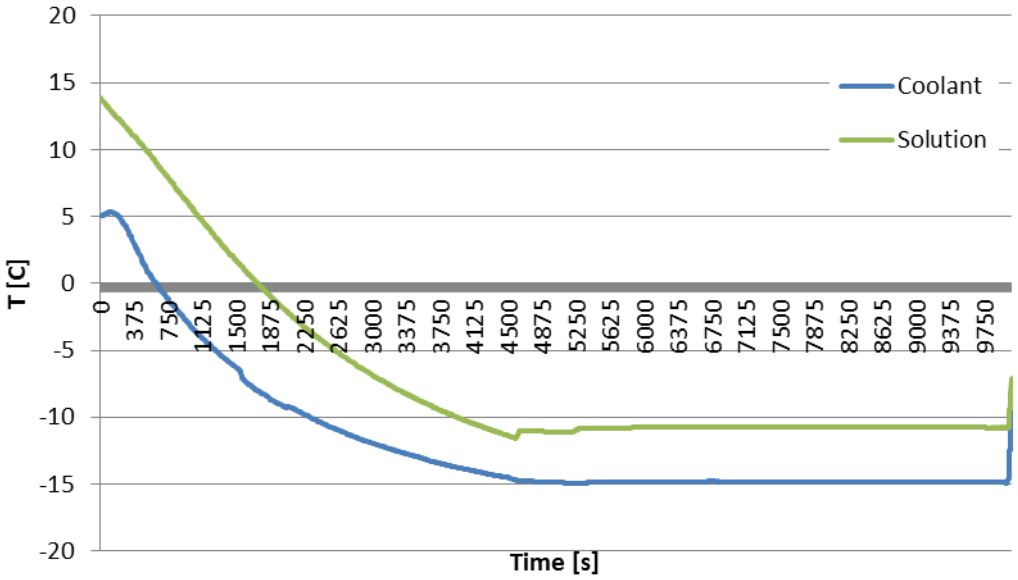

Figure 3.3 – Temperature curve

The temperature of the solution keeps decreasing until after 4500 seconds a small jump is visible and again a small jump at 5250 seconds. These small temperature jumps are caused by the start of the crystallizing of ice and salt. The starting solution has a salt concentration which is lower than the eutectic concentration. Therefore it is safe to say that the first jump indicates the start of ice crystallization, because the ice line is reached first and then followed to the eutectic point. This means the second jump indicates the starting point of the salt crystallization. This is also where the eutectic temperature is reached. According to the temperature graph the eutectic temperature is -10.8^{o}C. This value lies between the values given by Pronk [Pronk, 2006] and Van der Ham [Van der Ham, 1999], which are -10.6^{o}C and -11.1^{o}C respectively.

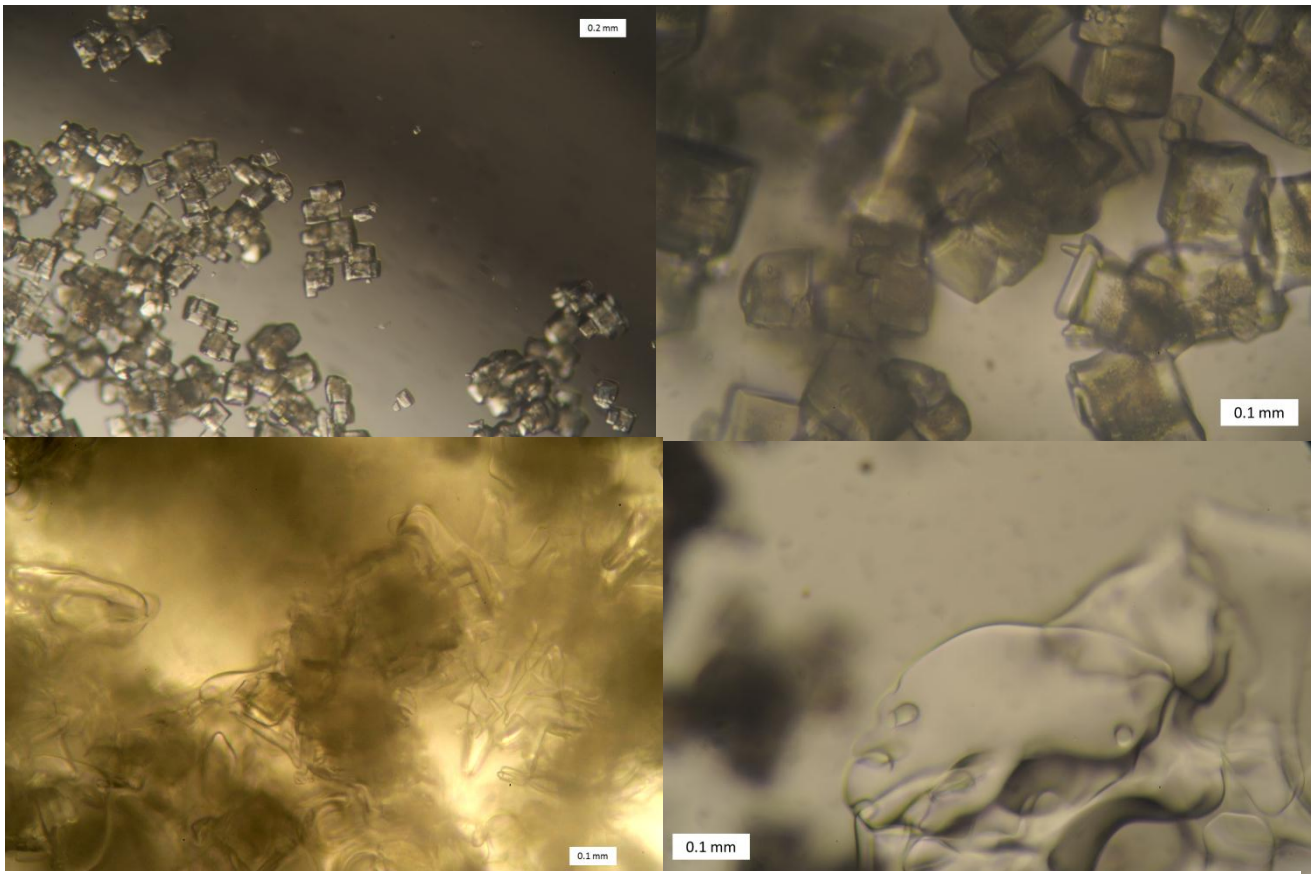

Figure 3.4 – Microscopic photographs of potassium chloride (Top) and Ice (Bottom) crystals

Samples of the crystals were observed under the microscope. In figure 3.4 the results can be seen. In de top potassium chloride crystals with their distinct cubic shape are visible, the bottom crystals are ice, which have a round and more random shape. The color difference in the pictures is caused by modifying contrast and brightness afterwards to enable better visibility of the crystals.

Notice that ice and salt crystals are not present in the same pictures. This is caused by the density difference, which causes ice to float on top of the sample during the observations with the microscope. Pictures with both ice and salt at the same time were made during other 1L experiments. These will be presented in chapter 4.

Samples from the solution at the start and eutectic concentration, as well as ice and wash liquid from all wash steps (indicated as 'ice' and 'liquid', respectively, in the figures below) were analyzed using ICP. These samples were tested for potassium and chloride in a high dilution, where the samples were diluted 10000 times, and for other impurities at a lower dilution, a dilution of 100 times.

Demineralized water at a temperature of 0°C was used as washing liquid. The washing liquid is used to dissolve the salt residues from the ice samples. Samples of the salt were not washed, because no impurities were added initially to the solution.

Figure 3.5 shows the potassium and chloride contents in weight percent of the different samples. When both numbers are combined the total weight percent can be found, this way from the figure it follows that the eutectic concentration found was 19.4 wt%. This is very close to value found in literature, which is 19.8 wt%.

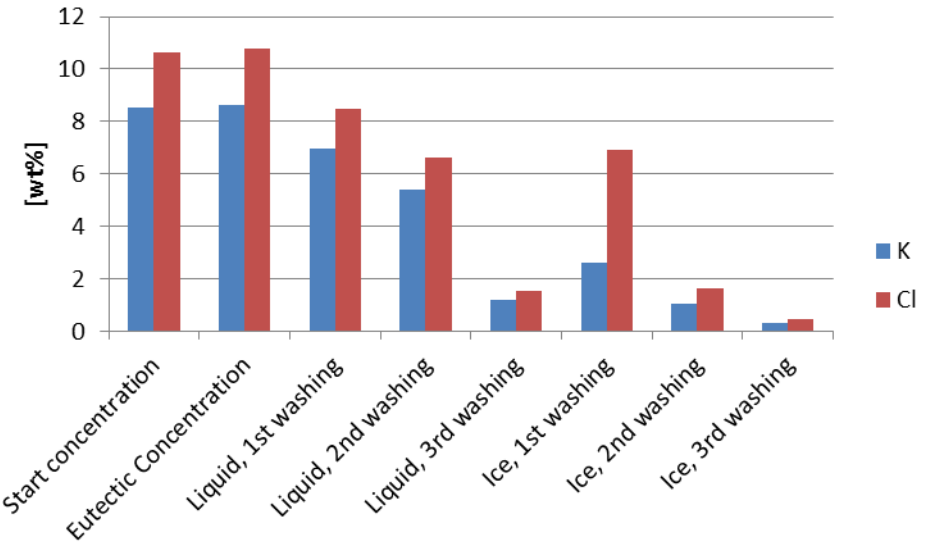

Figure 3.5 – Potassium and chloride content in samples

The amount of chloride in the ice after the first washing is not proportional to to the amount of potassium found, this migth indicate some kind of error and it is therefore better to take the potassium content as a reference here. The salt content decreases drastically over the course of three wash steps. After the third wash step the salt content is decreased to only 0.8 wt%. this means that 96% of the original salt content (19.1 wt%) is removed during the EFC process in combination with the washing.

Figure 3.6 deals with traces of impurities that where found. The impurities displayed in the figure are not the only elements that were found. Aluminium, boron, zinc and calcium, were also present acconrding to the ICP analysis, but these results looked very unreliable and migth be caused by some sort of pollution in the measuring equipement. Therefore they are not displayed in the figure.

The ICP did indicate reliable results for bromine, magnesium, sodium and sulphate. In the figure the peaks of sodium and sulphate clearly stand out above the others. The high presence of these two substances can be explained by the fact that the used solution was used in earlier experiments in another setup. There it is polluted with traces from other experiments. The previous user of this setup did indeed execute some experiments with a sodium sulphate solution [De Graaff, 2012].

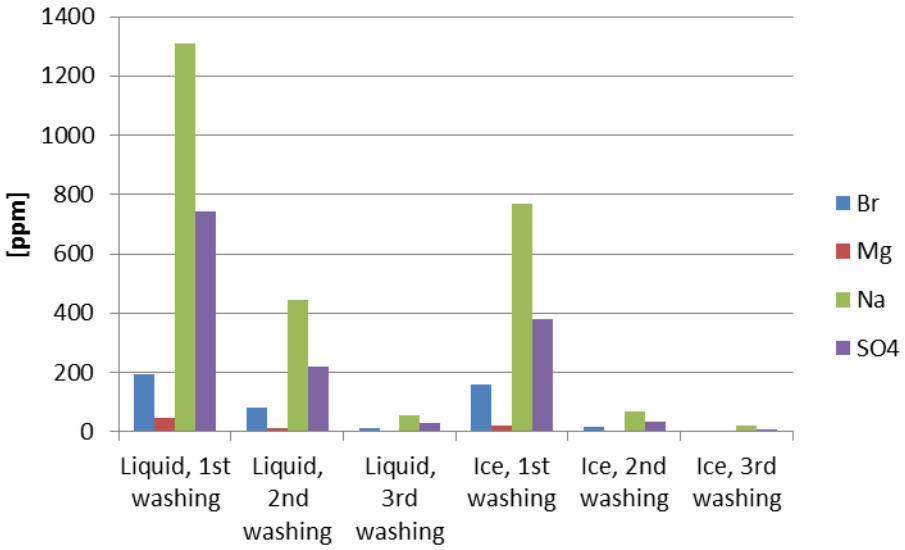

Figure 3.6 – Impurities in the ice and washing liquid

The figure shows the pollutants in ppm (mg/kg). After washing the ice three times almost all the pollutants have disappeared.

Observation

During one of the 1L experiments the solution was cooled to a temperature below -12°C without any sign of crystallization of ice or salt. When the rotational speed of the stirrer was lowered the crystallization started immediately and the solution returned to the eutectic temperature. This might indicate that the rotational speed of the stirrer can influence the temperature at which the crystallization occurs.

Chapter 4 - Settling behavior of ice and salt

Settling behavior

One of the key points of the EFC process is the separation of the ice and salt crystals. In chapter 2 the available knowledge of bidisperse mixtures was presented briefly. The research presented was performed using spherical objects of different densities, this is however an idealization of reality. There are hardly any industrial processes that need the separation of spheres. Therefore observations were performed using a High Definition (HD) camera in a 10L setup to get a better understanding of the behavior of both types of solids and eventually give some suggestions to improve the separation efficiency in an industrial process.

10L Setup

For this experiment the Scraped Cooled Disk Reactor was used. This reactor is a 10 Liter vessel with a heat exchanging plate in the bottom that is scraped with a stirrer. The stirrer is pressed on the plate with an air pressure of 0.2 bar and rotates with a rotational speed of 120 rpm. The heat exchanger disk is cooled with Freezium and a Lauda RK8KP cooling machine to a temperature of -18 ^{o}C. During the experiment the temperature is monitored using Pt 100 temperature sensors, which visualize the temperature via a computer. For the experiment a millimeter scale is applied on the reactor vessel and the settling behavior is recorded using a HD camera (SONY,HDR-130CX, 3.3 megapixels still image recording). The HD film material was analyzed using Splash Pro (Softonic®) and the images were edited with Corel Paint Shop Pro X when necessary.



Figure 4.1 – Crystallization vessel of the 10L setup (Scraped Cooled disk Reactor)

For the experiments a solution of 23 wt% potassium chloride in deminarelized water is used. In order to get enough of both ice and salt crystals a growth time is used to allow the crystals to grow. The growth time is defined as the time from the moment the eutectic point is reached to the moment the cooling machine is turned off. The growth time is visualized in figure 4.2.

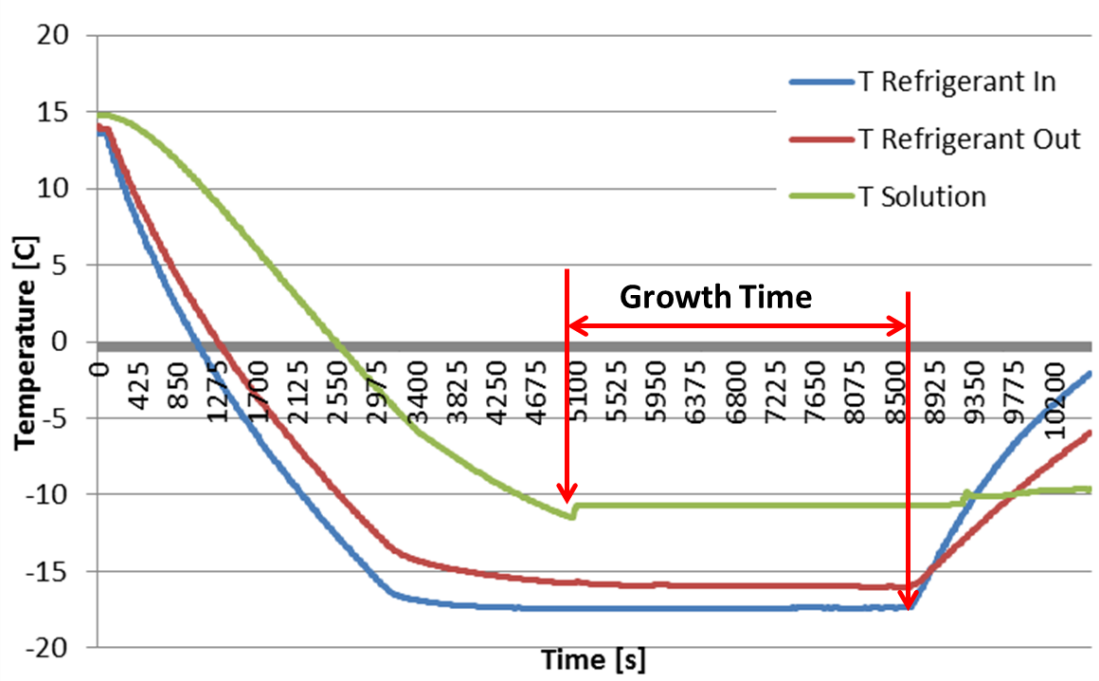

Figure 4.2 – Growth time

In later experiments a solution of up to 19.1 wt% potassium chloride was used to see if there was any difference in separation behavior when the starting concentration is lower than the eutectic concentration. These experiments were unsuccesful, because there was too much ice present before the eutectic point was reached. This filled the entire vessel, which made it impossible to see any vertical movement of salt or ice.

The settling behavior is studied when the scraper is turned off. The created crystals are used for only one experiment and then they are dissolved again. This is done for three reasons. The first reason is that when the scraper is stopped it is immediately frozen to the heat exchanger disk and it takes a long time before one can move it again. Secondly, the ice and salt crystals might bind in some way to each other that would create very large or unusual pieces of crystal, which would not occur in a normal EFC process. Thirdly, when the scraper is finally free to move again, usually the scaling, a layer of ice on the heat exchanger disk becomes detached, this can also influence the settling effect.

Observations of settling behavior

The first instant of the observations not much is visible. The ice-salt suspension is still too turbulent. When the turbulence decreases the first movements can be observed, this is usually the ice, which floats by in cloud-shaped structures. At first sight the ice and salt seem

to separate reasonable well. On the bottom salt is present and in the top ice. But on a closer inspection there are salt crystals falling from the ice. The salt is entangled in between the ice and keeps falling as the ice starts to melt. The ice starts to melt, because the cooling has been shut down.

On closer inspection of the salt particles that fall from the ice, it appears that there is no particular size of the salt crystals that are entangled in the ice. The amount of relative smaller or larger crystals than the average is not very large, but one has to take in to account that crystals in a crystallization process don't all have the same size. They usually follow a normal size distribution.

The images of the salt falling from the ice are presented with the intention to show, that the salt is indeed entangled in the ice. In most of the conducted experiments, there was no ice floating in the top of the crystallizer. The ice was found instead on the bottom of the crystallizer together with the salt. The sinking of ice can be seen in more detail in Appendix A.

The salt can be distinguished from the ice, by a clear difference in shape. The salt particles are shaped liked grains and are very compact, there are no openings of any kind in the salt particles. The ice particles are much larger and look more like snowflakes or clouds, they also have a structure that is open, it is almost possible to look through them (figure 4.9).

In an effort to see if the growth time of an hour could be the cause of the sinking ice, the growth time was reduce to half an hour to see if this has an effect. The thought behind this is that by reducing the grow time of the ice, the ice particles will be less large and thus not be dragged to the bottom by entangled salt particles. The result of the experiment was completely unexpected. Almost the entire crystallizer vessel was filled with ice and it all sank to the bottom (figure 4.11). Only a few pieces of solid ice were visible at the top, but these were most likely part of the scaling that came loose from the bottom.

The fact that all solids are lying on the bottom, however, does not mean that there is no sign of separation visible. On closer inspection there are two layers distinguishable at the bottom. The upper layer is the ice with the salt and the bottom layer is only salt. This means that not all the salt gets entangled in the ice and that the salt which can move freely in the suspension will drop faster than the salt that is attached to ice. This is because the average density of ice entangled with salt is smaller than only salt, therefore the loose salt particles will drop faster.

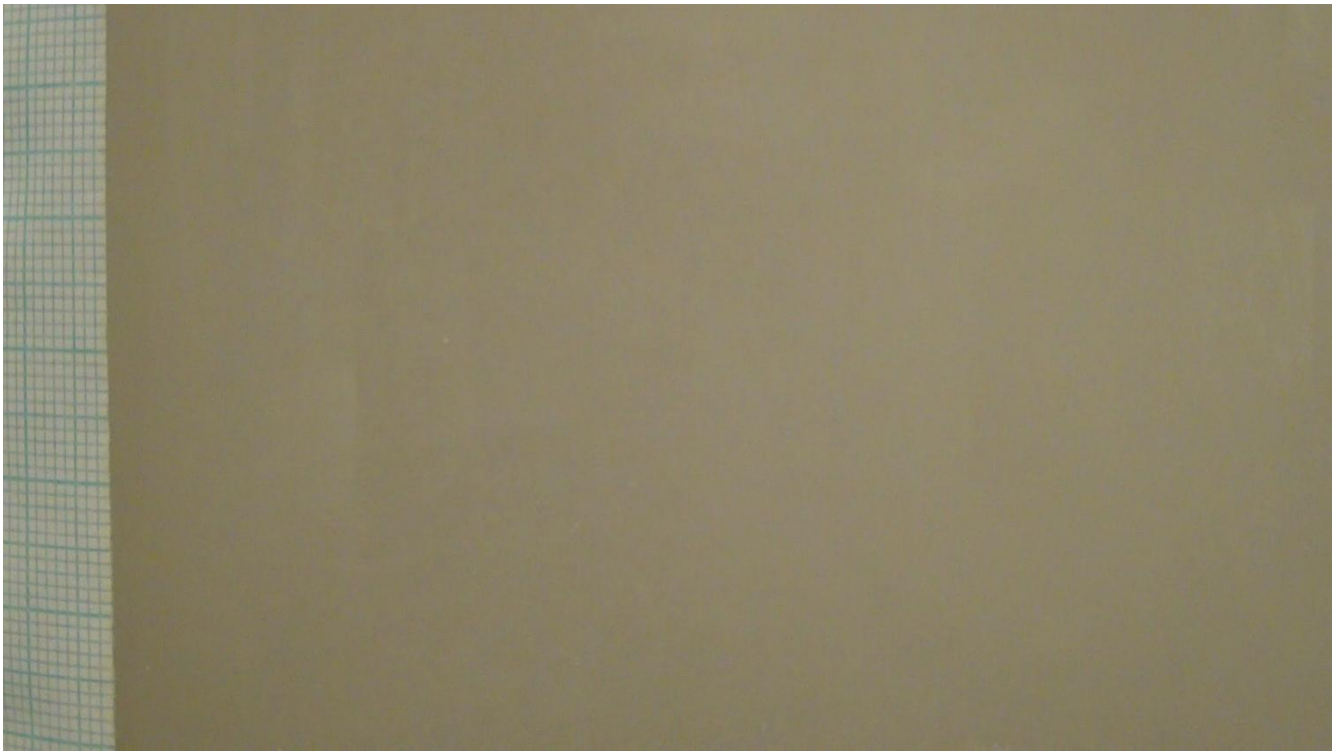

Figure 4.3 – The fog; no form of ice or salt is recognizable



Figure 4.4 – First ice cloud; first clouds of ice are visible, later also salt particles become visible

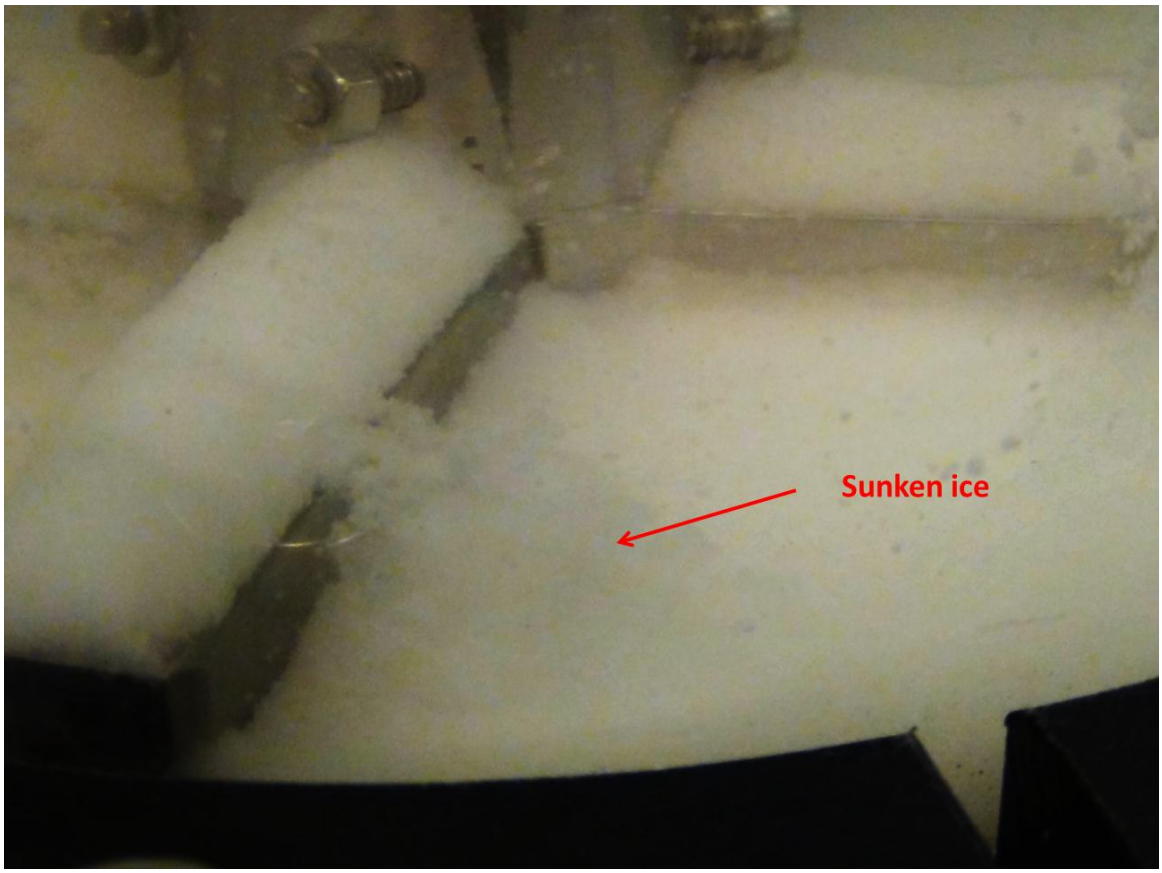

Figure 4.5 – Salt covering the bottom of the crystallizer, also a small amount of ice is visible

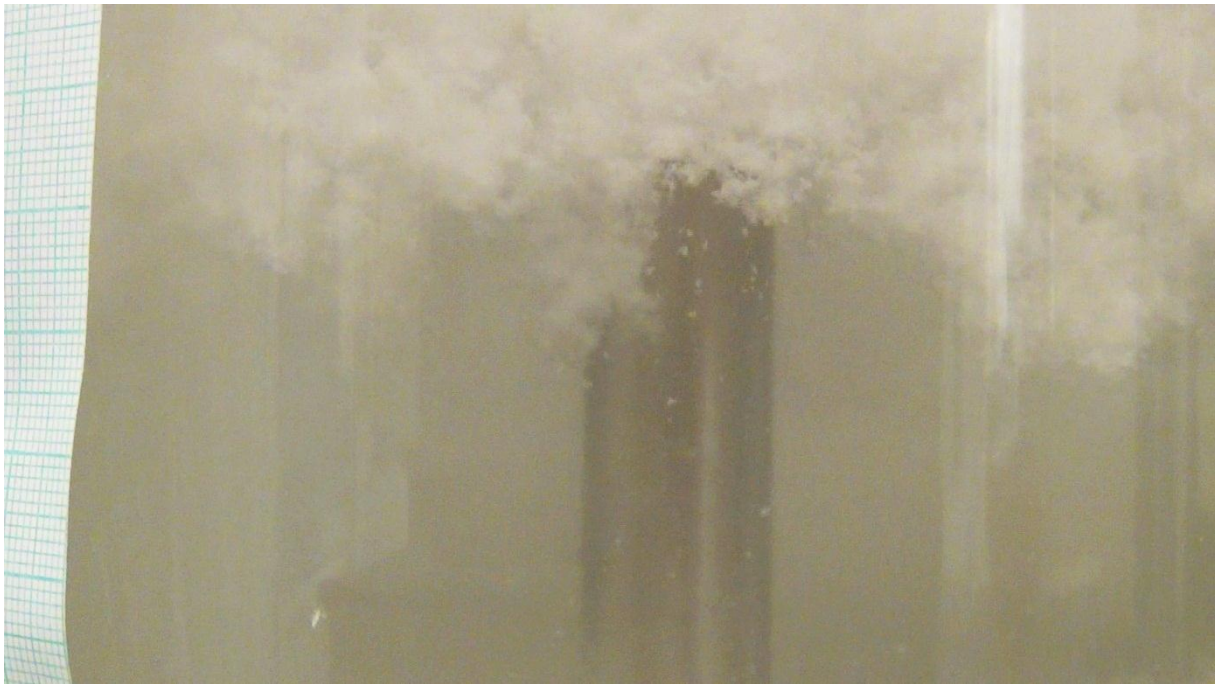

Figure 4.6 – Salt falling from floating ice in the top of the crystallizer

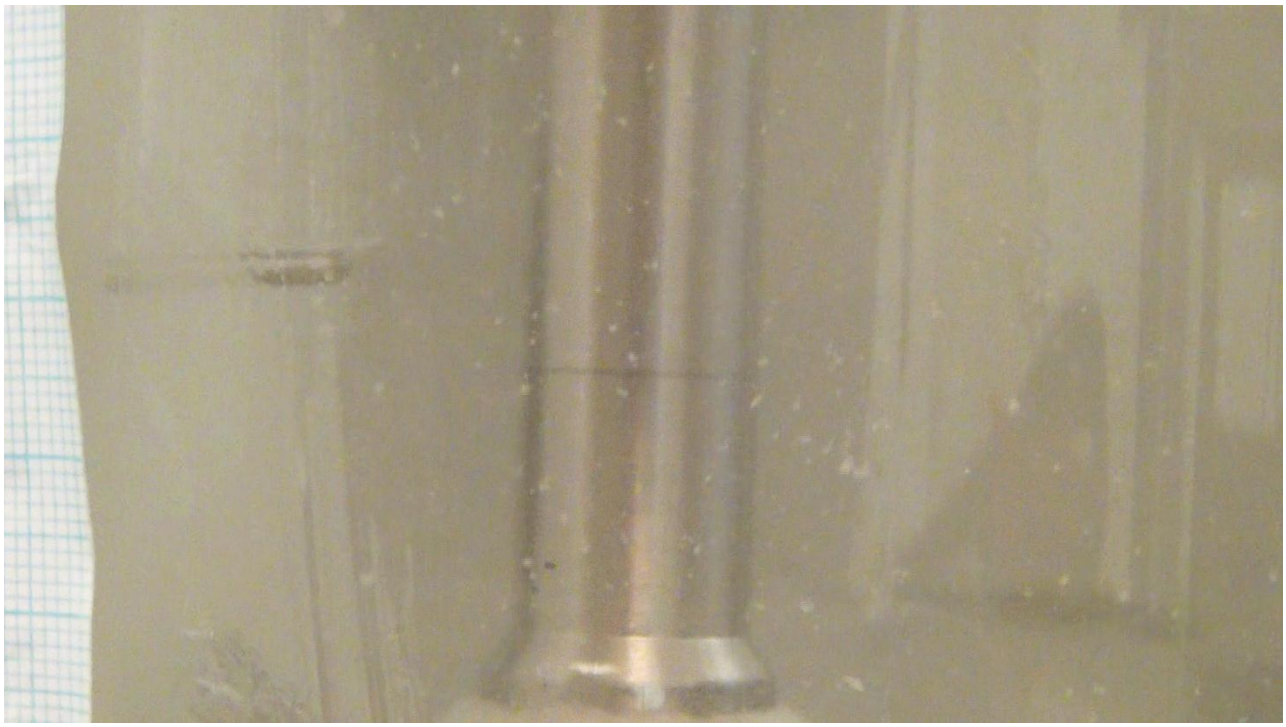

Figure 4.7 – Falling salt of different sizes in the middle of the crystallizer

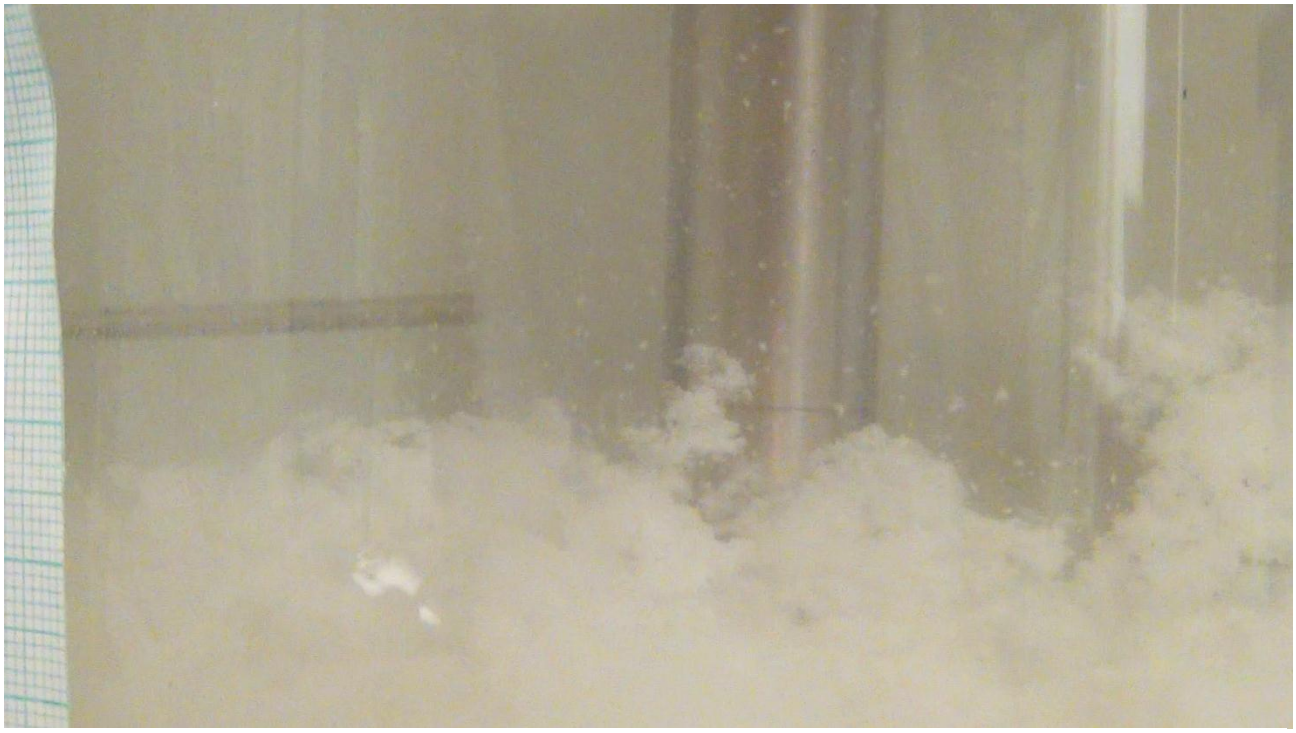

Figure 4.8 – Falling salt at the bottom of the crystallizer

The following photo (figure 4.13) was taken during another experiment [De Graaff, 2012]. It shows the same characteristics as described above. Ice that does not float, in this case the ice is lying on a heat exchanger in the middle. Also the two layers are again clearly visible. The crystallizer in the photo is not the 10L setup, which has been used by the author. It is a 200L pilot plant. The salt used in this experiment is sodium sulphate (Na_2SO_4). From this two things can be concluded, namely that the entangling of salt in the ice is not a phenomenon that only happens in this specific crystallizer, it happens also in other crystallizers and even on a much larger scale. Also it is not just a phenomenon that happens only with potassium chloride, but also with other salts.

Observations of separation

The EFC process is supposed to be used for the separation of salts from water and when both substances lie on the bottom of a vessel, then the separation is not very useful. Therefore different ways of agitating the ice and salt on the bottom of the crystallizer were used for two reasons. First of all, to get a confirmation that the substance on the bottom is indeed ice. Secondly to see if the two could be separated in some way.

The first method to test the ice on the bottom was to use a large syringe and draw a sample from the ice. The sample is deposited in a small beaker. In the beaker a new separation is observed, all ice is floating in the top and only salt is visible in the bottom. Ice is not present on the bottom (figure 4.15).

For the second method the scraper inside the crystallizer setup was used to agitate the ice. Before the scraper could be used, first the heat exchanger was used to melt the scraper loose from the heat exchanger plate. When the scraper could move freely again, it was twisted around manually. The result of this was a clear separation between some of the ice and the salt. Ice flakes floated to the top of the crystallizer, while they lose even more salt on the way up (figure 4.17 and 4.18). The separation by use of the scraper can be seen in more detail in appendix A.

As a third option the ice was separated using an air flow. The scraper in the crystallizer setup is pushed on the heat exchanger plate by air pressure. Due to the wear in the setup, a leak has formed in the lower of the scraper. This leak creates an airflow that was conveniently used, to see what the effect was on the ice in the bottom. The air flow initially stops during some point in the experiment, probably because the leak is covered with salt or ice.

When the ice has settled to the bottom, the pressure in the scraper was increased from 0.2 bar to 0.4 bar. This resulted in an air flow through the ice, which agitated the ice enough to cause a separation (figure 4.20).

The observations above give the impression that although the ice bonds with the salt, it can easily be separated by subjecting the ice to some kind of mechanical pulse. The necessary strength of this pulse is not known and is something that future research should point out.

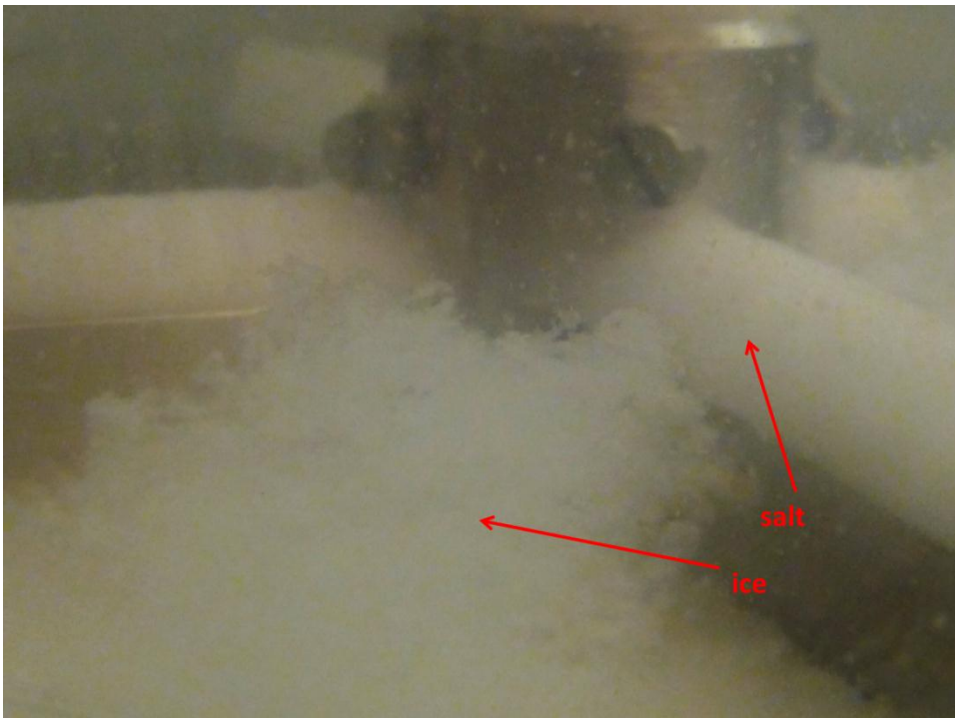

Figure 4.9 – Salt and some ice on the bottom



Figure 4.10 – Ice covering the entire bottom

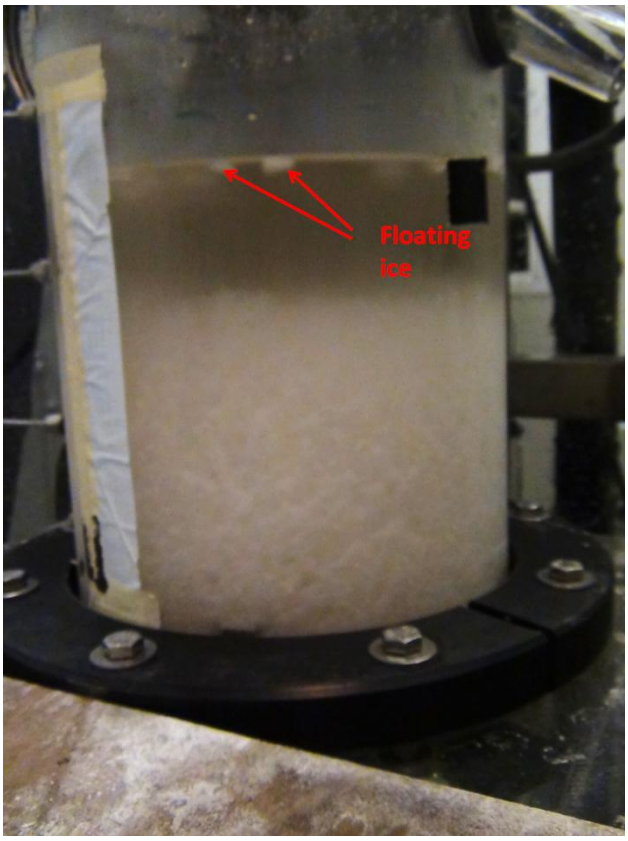

Figure 4.11 – Vessel full with ice after reducing the growth time. Also a few pieces of ice floating at the surface.



Figure 4.12 – two layers are distinguishable at the bottom



Figure 4.13 – Salt and ice resting on the middle heat exchanger in the 200L pilot plant. [De Graaff, 2012]

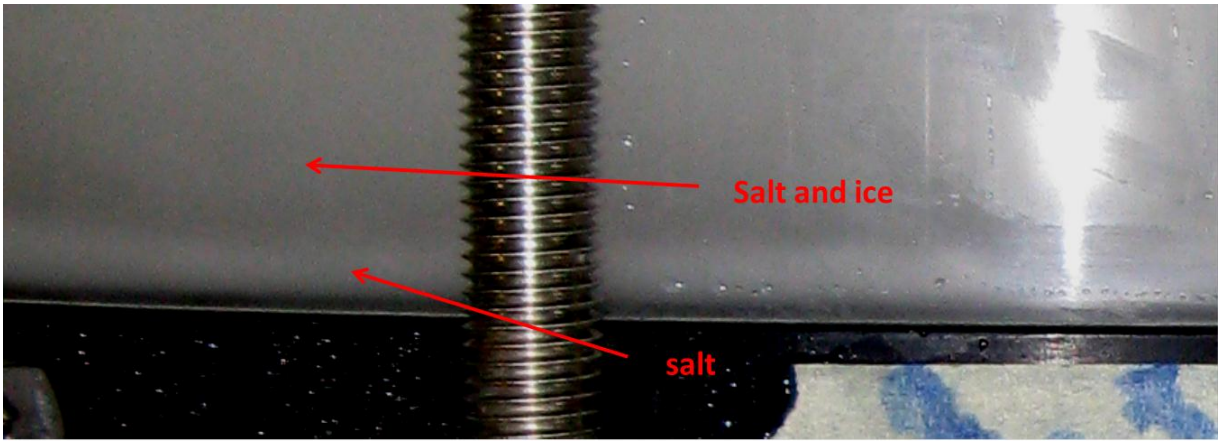

Figure 4.14 – Detail from figure 4.13, two layers are visible again

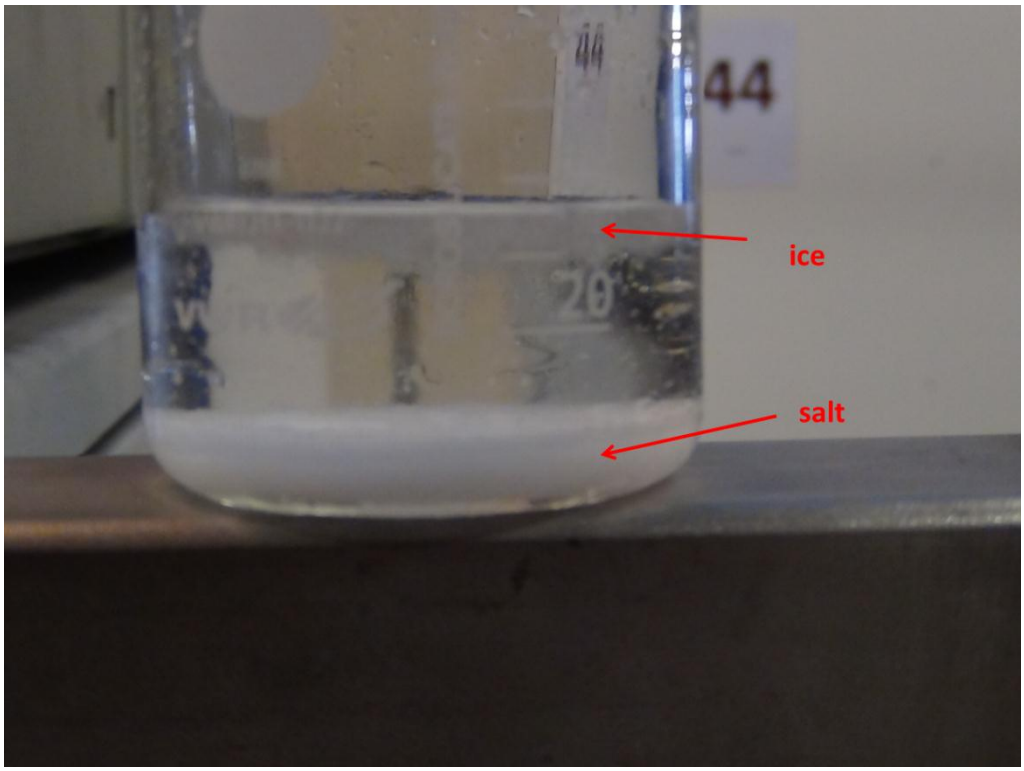

Figure 4.15 – A sample from the bottom of the crystallizer

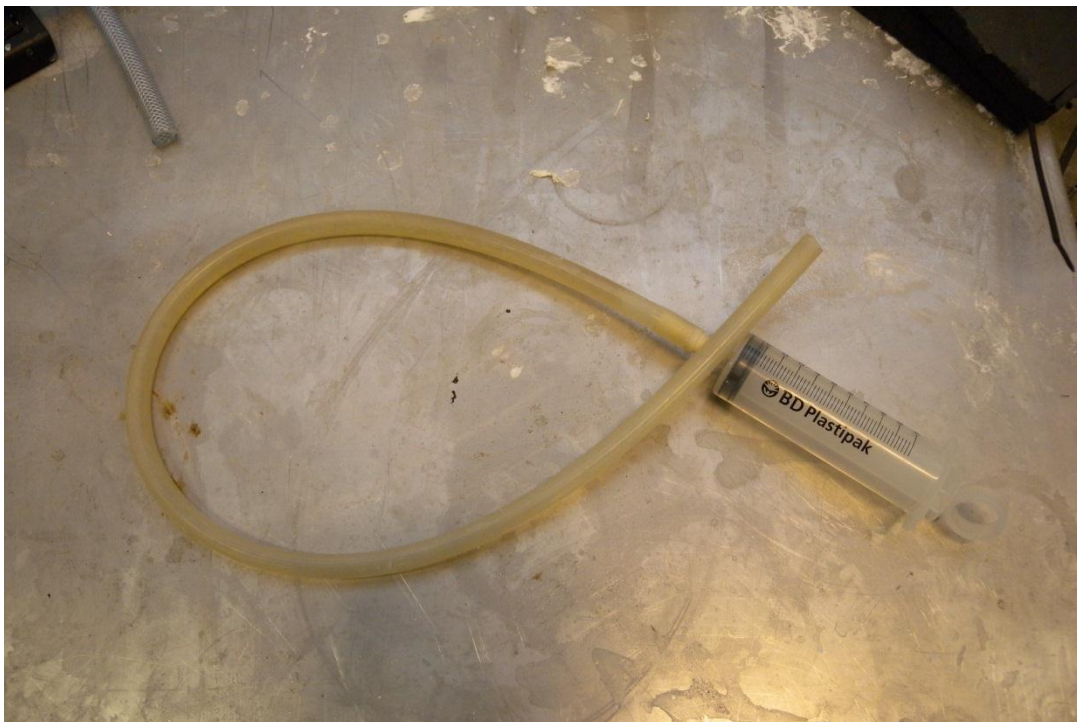

Figure 4.16 – Syringe used for taking samples

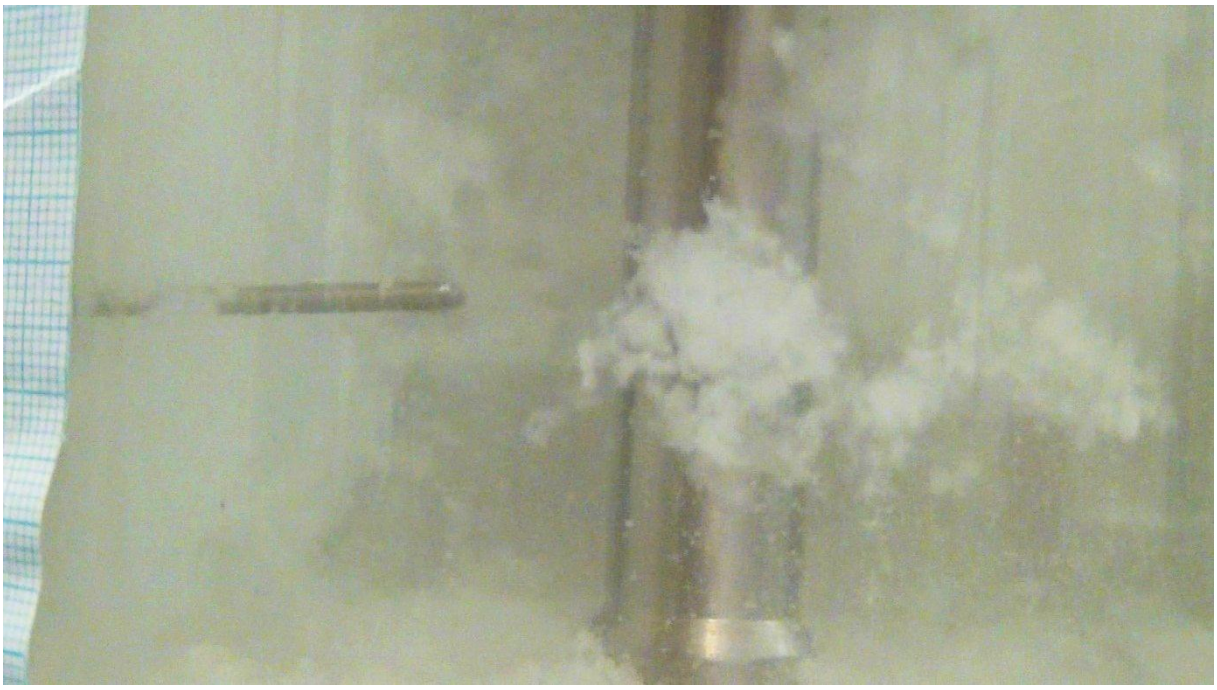

Figure 4.17 – Floating ice after disturbance from scraper

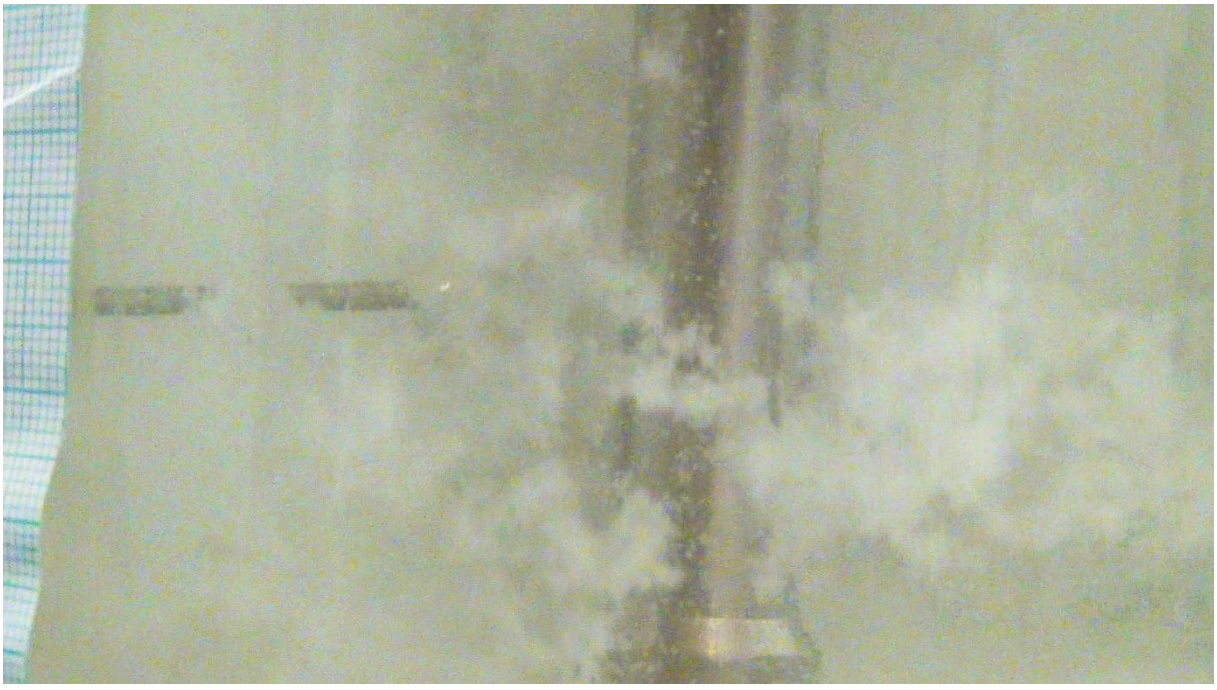

Figure 4.18 – Floating ice after disturbance from scraper, also a lot of salt is falling from the ice clouds

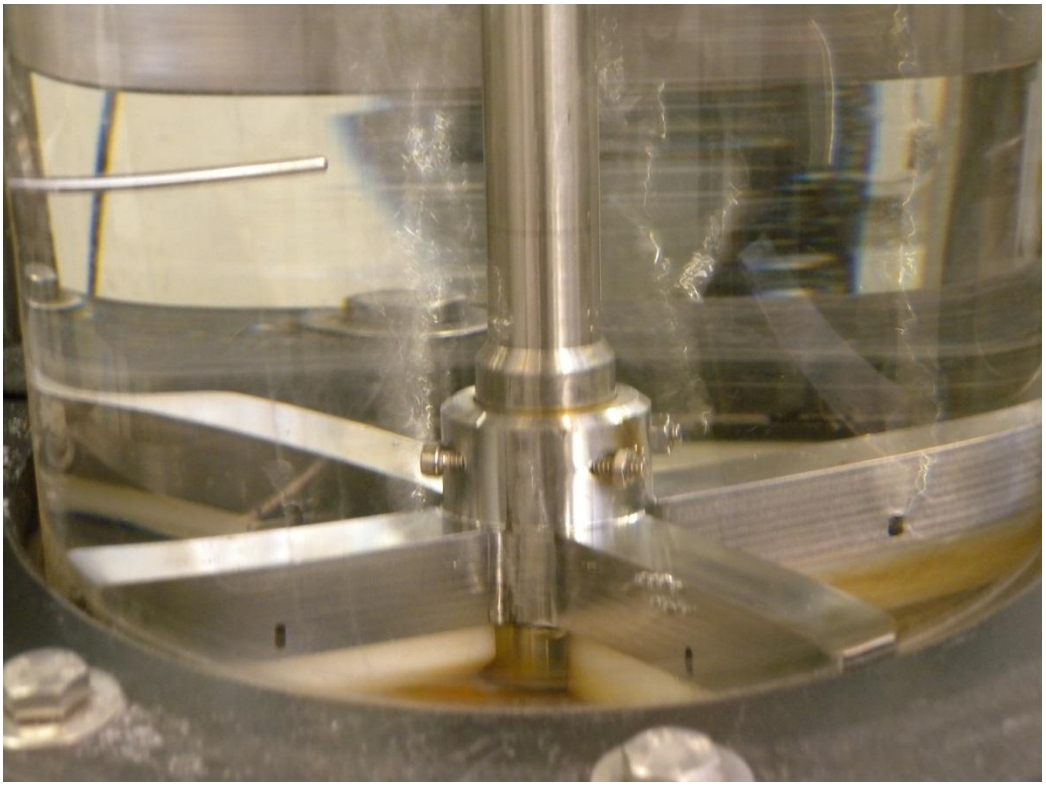

Figure 4.19 – Leaking of air through the scraper



Figure 4.20 – Disturbing the ice-salt slurry using air

Salt ice entanglement

The outcome of the experiments above was quite surprising and no good explanation was available. Therefore some more research was done in the literature to find some sort of explanation for the entanglement of salt and ice. Two possibilities where found, namely the ice that is formed is dendrite ice and kinetic roughening. Both will be explained in more detail below and with the help of some new experiments the possibility of the theory is tested.

First the possibility of dendrite ice formation was looked at. Dendrite ice is ice that looks like snowflakes (figure 4.23). Nagashima and Furukawa [Nagashima, 1997] studied dendrite ice in a potassium chloride – water solution, which indicates that it is possible to have dendrite ice in the previous experiments. Teraoke et al. [Teraoke, 2002] studied the dendrite ice formation in water – ethylene glycol solutions and reports that dendrite ice will form at a supercooling of more than 0.30 K.

During the EFC experiments in the 10L setup the temperature of the solution always drops below the eutectic temperature, before the formation of ice starts. This means that there is supercooling of the solution and therefore dendrite ice is considered a possible cause for the salt entanglement in the ice.

In order to decrease the amount of supercooling seed crystals were used. When seed crystals are used, the energy boundary necessary for nucleation is not present and crystallization starts of ice starts at the eutectic temperature. This is visible in the figure below where temperature profiles of an experiment with and without seeding are visible. The experiment without seeding shows a clear temperature jump, whereas no such jump is present when seeding was applied.

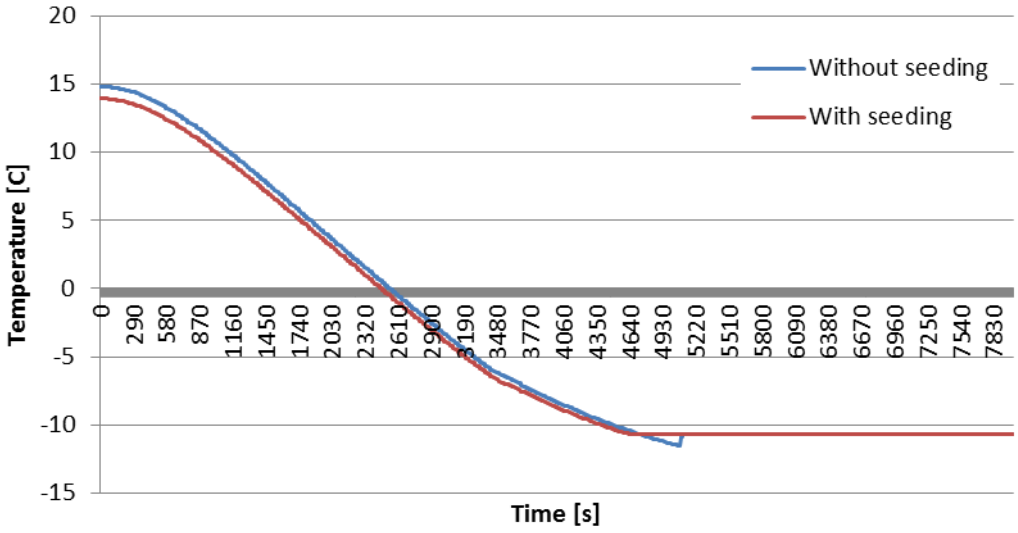

Figure 4.21 – Temperature profile with and without seeding

The result of the seeding experiment is shown in figure 4.22. approximately half of the amount of ice formed displays the normal behavior and sinks to the bottom. The other half of the ice floats to the top. Although the seeding has some effect, there is still ice, which is dragged to the bottom. Since there was no supercooling, but still ice on the bottom, it is unlikely that the formed ice is dendrite ice.

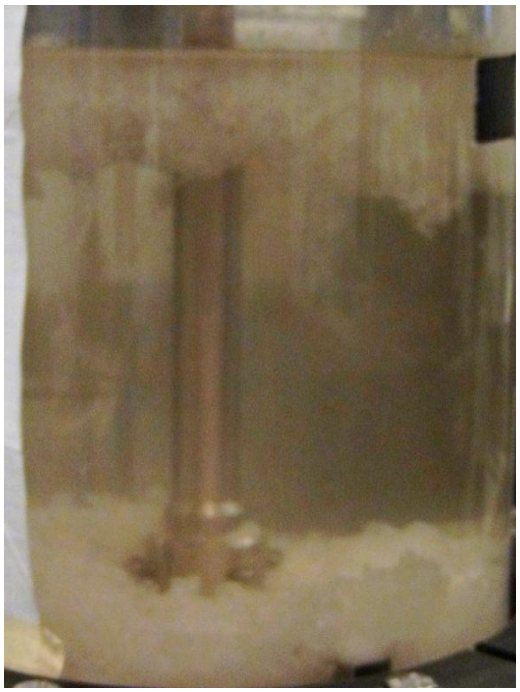

Figure 4.22 – Seeding experiment

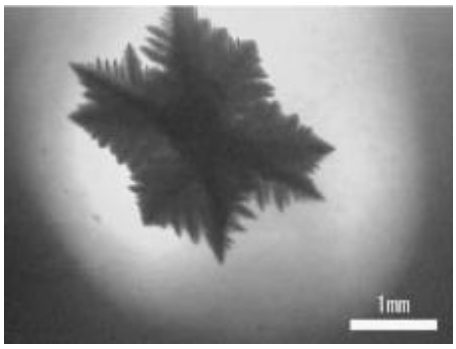

Figure 4.23 – Dendrite ice crystal [Teraoke, 2002]

A second possibility is particle induced kinetic roughening. This phenomenon happens at flat crystals surfaces and a temperature of low subcooling. When a foreign particle, for instance a salt crystals, attached to an ice crystal, it the salt crystal will reduce the amount of energy required for growth very locally (figure 4.24)[Liu,2001]. This results in the growth of spike like elements on the crystals on which salt can easily get entangled.

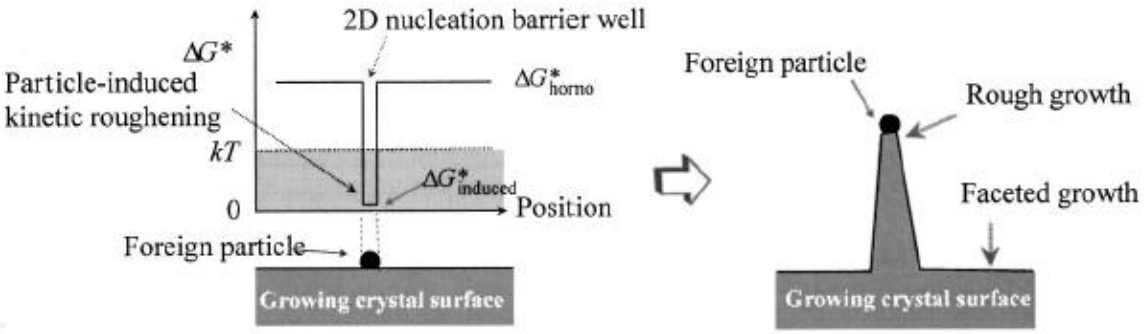

Figure 4.24 – Particle induced kinetic roughening [Liu, 2001]

Because proof of neither dendrite ice nor the kinetic roughening can be seen with the naked eye, some more experiments are necessary in the 1L setup. Here samples can easily be taken and studied under the microscope. The results are discussed in the next section.

A view under the microscope

For this experiment the same solution of 23 wt% potassium chloride was used as in the previous experiment. The 1L setup described in chapter 3 was used again. The refrigerant had a temperature of -15°C and the scraper was spinning with 122 rpm. The solution was cooled to the eutectic temperature. When the eutectic point was reached the cooling of crystals was continued for another 20 minutes. Before the observation through the microscope it was confirmed visually that both the salt and ice had sunk to the bottom.



Figure 4.25 – Visual confirmation of sunken ice in 1L setup

The samples that were used for observation were taken from the top part of the slurry to ensure that both ice and salt were present. First samples were put under the microscope without any treatment. The second sample was washed three times using demineralized water and filtered using a glass filter (por.3). The third sample was washed three times using the original solution and also filtered with the same filter. The washing liquid was cooled to 0 ^{o}C before the washing.

First the photos from the untreated samples were examined (figure 4.26) and there some things that stood out. First, in the top left both ice and salt are visible, which confirms again that it is ice on the bottom. Second, the salt seems to have a layer of ice around it as can be seen in the bottom left by a dark core and a transparent outer layer. Third, the ice in the bottom right has a very spikey and irregular shape, this looks a bit like the expected result of kinetic roughening.

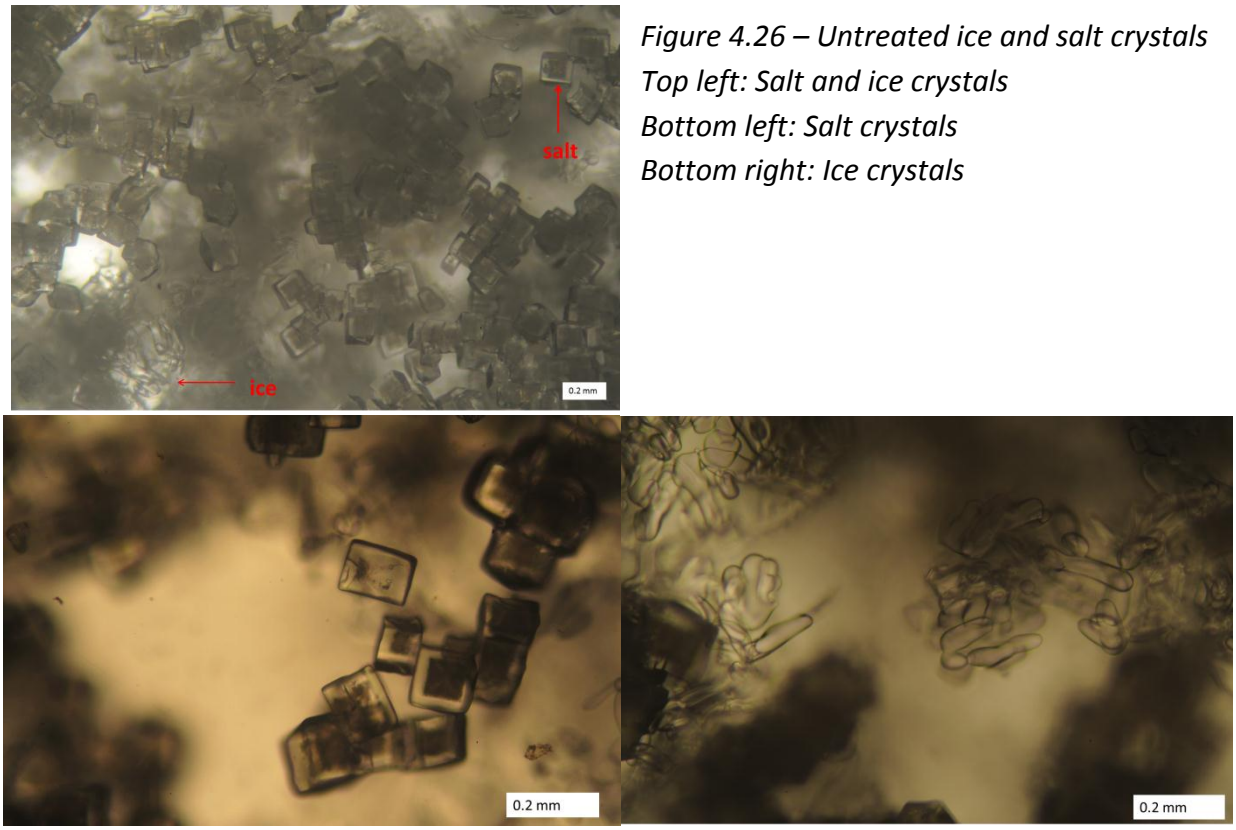

Figure 4.26 – Untreated ice and salt crystals
Top left: Salt and ice crystals
Bottom left: Salt crystals
Bottom right: Ice crystals

After treatment of the sample with demineralized water (figure 4.27) no more salt was found. Also the ice has a very different shape than in the untreated samples. When the sample was treated with salt solution (figure 4.28), there was no more ice present and the salt was still visible.

From these observations it follows that the salt on the photos has no layer of ice around it. If this was the case then there would be salt present after treatment with water and the transparent layer should have disappeared after treatment with solution.

Further the ice looks different from the untreated case, this might be the result of the washing and filtering, where some ripening could have taken place.

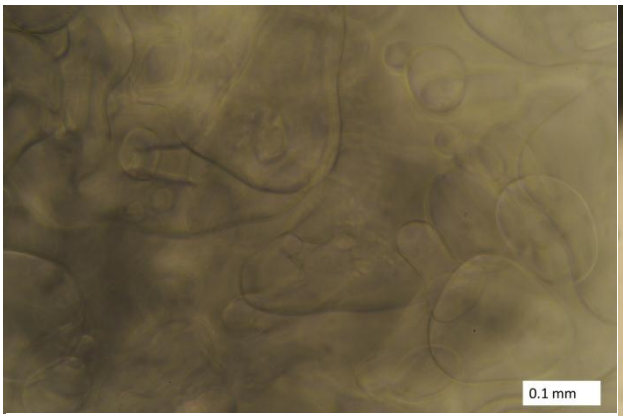

Figure 4.27 – Sample treated with water

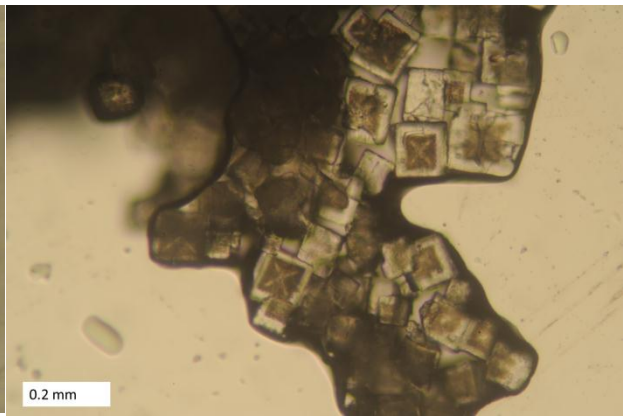

Figure 4.28 – Sample treated with salt solution

Chapter 5 – Industrial scale eutectic freeze crystallization

The findings in the previous chapter shed a whole new light on the EFC process. Therefore some recommendations on the current vision of the EFC process are done in this chapter, based on the knowledge gained during the experiments and the observations made while working on the project. For clarity first a brief description is given of the current EFC process, for this the 200L pilot plant was used as a point of reference.

Current EFC process

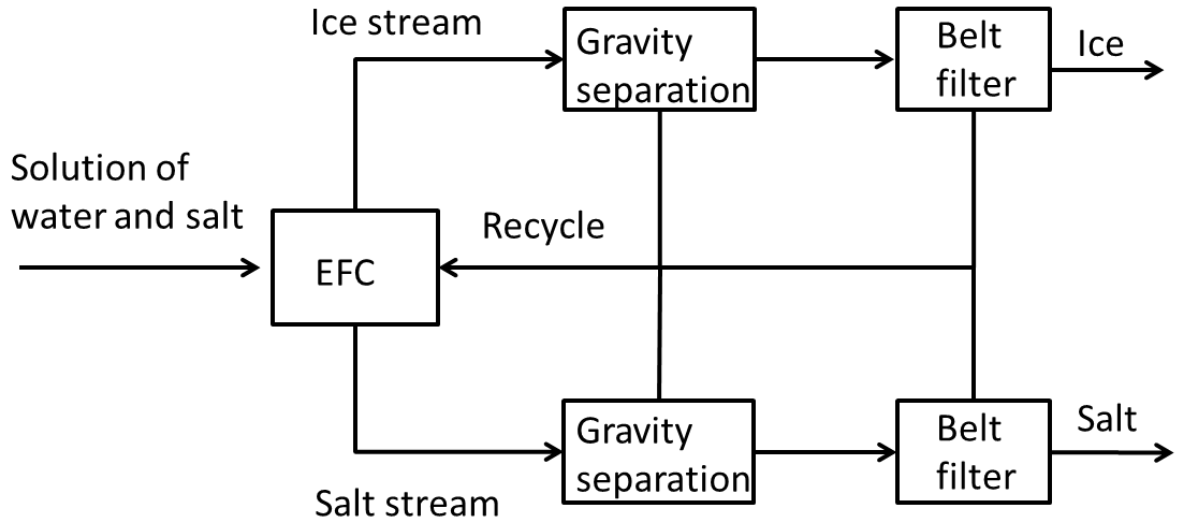

Figure 5.1 – Current EFC process

In the current EFC process the separations of ice and salt is done in the crystallizer by gravity separation. Salt is removed at the bottom and ice is removed at the top. Each stream has to undergo a gravity separation to remove unwanted fines, fines of salt in the ice stream and fines of ice in the salt stream. The salt and ice streams then each go over a belt filter where the mother liquid is removed and the final products of salt and ice remain. The streams with removed fines and mother liquid are recycled back to the crystallizer. The recycle streams are not necessarily combined in one stream as is depicted in figure 5.1, this is done only to keep the figure more readable.

Recommended EFC process

In chapter 4 it was mentioned that there is no real separation between the salt and ice in the crystallizer, therefore both should be removed through the bottom as a salt-ice slurry. The salt and ice can then be separated in a gravity separator, where the slurry is first agitated to speed up the separation. Due to the absence of moving scrapers there is much less turbulence in the separator. Therefore there is less chance that fines are dragged to the wrong stream. This means that one gravity separator will be sufficient. The gravity separator will be discussed in more detail later in this chapter. The ice and salt are separated from

their respective streams by the use of a belt filter and the mother liquid can be recycled to the crystallizer (figure 5.2).

This new configuration has some new advantages, which are not only related to the separation part of EFC. There is only one exit and one entrance in the crystallizer, this means that the heat exchangers can be reconfigured in a counter current setup, which is more efficient. Secondly, only one separator is needed, which will reduce cost and risk of equipment failure.

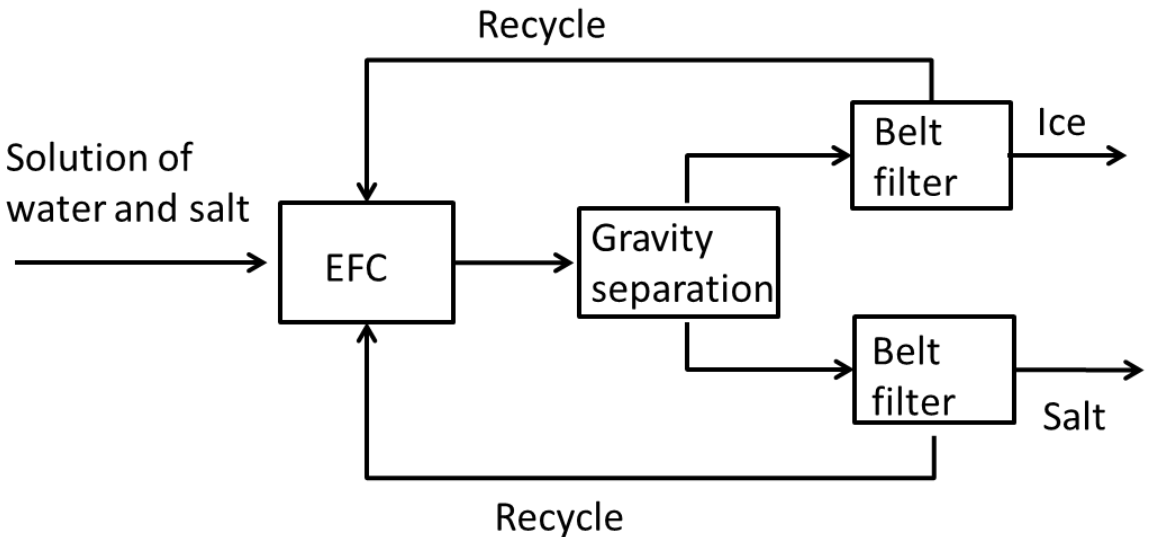

Figure 5.2 – Recommended EFC process

Heat exchangers

Since the salt-ice slurry will be removed from the bottom only, it makes sense to move the entrance of the feed flow to the top of the crystallizer. The two heat exchangers in the old setup are connected parallel, this was done because there was a stream going to the top and a stream going to the bottom and both had to be cooled. In the new setup, there is one stream that has to pass the entire crystallizer. This means that now it makes more sense to use the heat exchangers in series. By doing this the temperature difference between the mother liquid and the heat exchangers will decrease. A lower temperature difference means a better heat transfer coefficient and less torque on the scrapers due to scaling [De Graaff, 2012].

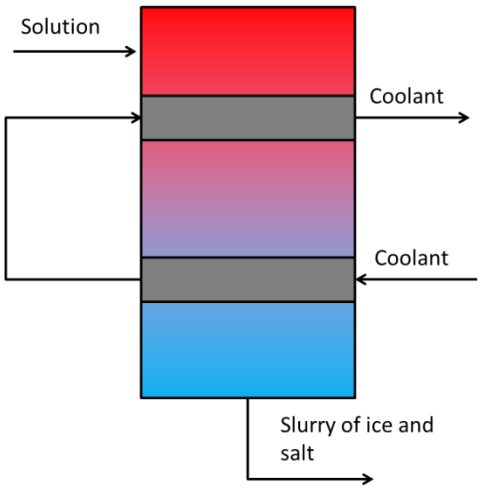

Figure 5.3 – Heat exchanger configuration

Another thing that should be altered in the next heat exchanger design is that it should more open. In Figure 4.13, one can see both ice and salt lying on the top heat exchanger. This

shows the problem that a large quantity of suspended ice gives, if it has a chance to clog something, it will. A more open heat exchanger with less horizontal surface should reduce the risk of clogging. A different thought is that it might be possible to use two different types of heat exchangers. If there is no ice formation in the top section then there is no problem with the current design and only the bottom heat exchangers will need to be redesigned.

Slurry displacement

In the current pilot plant setup there were some problems with the displacement of the ice slurry and the salt slurry. Both were pumped to the belt filters using a peristaltic pump. The problem with these pumps is that the larger pieces of crystal tend to block the flexible tube inside. With the pilot plant setup in mind an Archimedes screw was designed to remove ice from the top. The same type of screw could be used ate the bottom to remove the salt ice slurry. However, it would have to be redesigned, because the screw would have to cope with the pressure created by the weight above it.

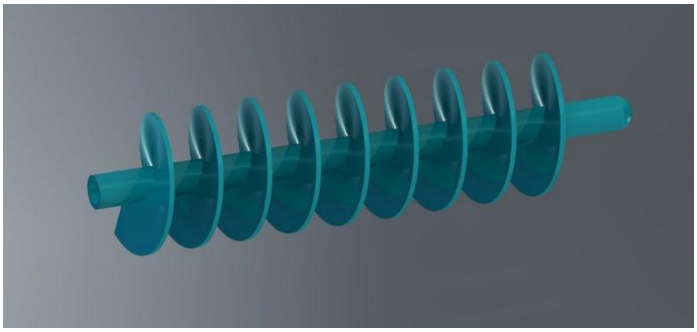

Figure 5.4 – Archimedes' screw

Gravity separation equipment

The design for the separation equipment is based on the observations of the separation behavior of the ice and salt. The salt and ice will enter the separator as a slurry and from the experiments, it is known that this slurry will separate fairly easy when it is agitated. In the experiments the slurry was agitated with the scraper and with air, both techniques were successful. Therefore two options are presented and compared.

The slurry can be agitated with an air curtain, using an air compressor to blow air through the slurry. The advantage of this is that the slurry cannot attach itself to the agitating mechanism, the disadvantage is that an air compressor will always use energy. The slurry can also be agitated, by agitating the slurry in a mechanical manner, for instance using a wire mesh, where the slurry has to flow through. The advantage of this option is that the wire mesh does not use any power, the disadvantage is that especially the ice has a tendency to block the small openings, which would result in a lot of maintenance. This was also observed around the heat exchanger of the 200L setup.

Table 5.1 – Advantages and disadvantages op agitating options

	Air	Mechanical
Advantage	Low maintenance	No energy required
disadvantage	Continuous energy costs	High maintenance

The separator has to work continuous, therefore it is important that it can work almost without stopping. This means that a low maintenance is the most desired and therefore the option of agitating by air is preferred.

For the separation itself, the experiments in chapter 4 have shown, that it takes some time before all the salt has escaped from the ice. To speed this process up, it is necessary that the layer of floating ice is very thin. This can be achieved by creating a large surface, making the separator look more like a trough than a column. This shape also makes sure that all the ice stays approximately the same length of time in the separator. The ice and salt can then both be removed as a slurry, the salt at the bottom and the ice at the top.

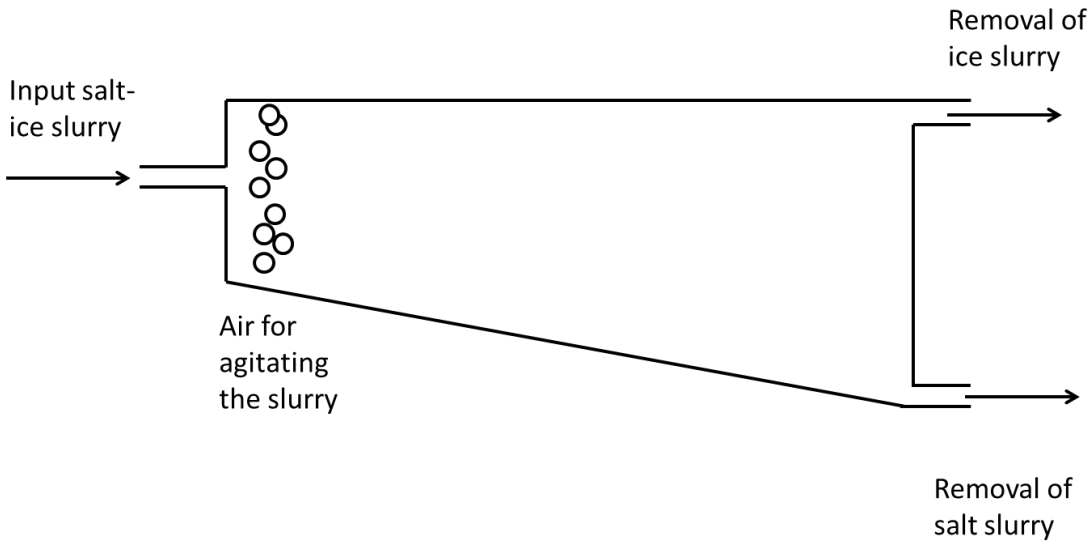

Figure 5.4 – Design of separation trough

The ice crystals will be dragged to their exit with the current created by the removal of liquid at the top. For the salt at the bottom, this is a different story, as it lies on the bottom. To keep the salt moving a descending bottom might work or some sort of conveyer belt. When a belt is used one has to keep in mind that the belt should not create too much turbulence, because this will cause the salt to fly up and make the transport less effective.

It might also be possible to remove the salt using a screw, but this screw will create turbulence. The turbulence could be reduced by covering the screw with a roof-like cover, which would allow the salt to sink to the bottom on the sides of the settler. The cover would then prevent the salt from being dispersed again by the turbulence.

Settler dimensions

The size of the settling equipment is dependent on two dimensions, as was briefly mentioned in chapter 2, namely the diameter of the solids and the amount of solids in the slurry stream. This can be seen in the following figures. Figure 5.5 shows the relation between the diameter of the solids and the velocity and figure 5.6 depicts the relation between the amount of solids and the velocity. The downward velocity is positive in both cases and for the calculations equations 2.1 and 2.2 are used.

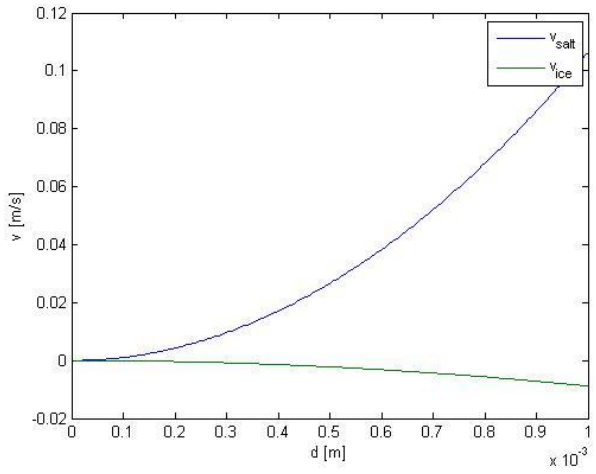

Figure 5.5 – Settling velocity vs. Particle diameter

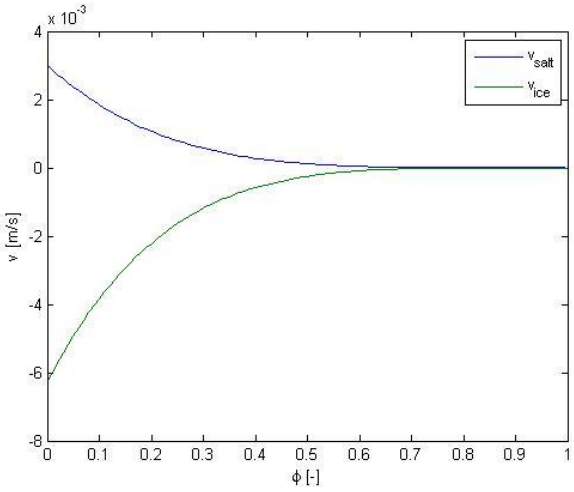

Figure 5.6 – Settling velocity vs. Volumetric solid fraction

The settling velocity of the solid particles determines the difficulty of the separation. When the settling velocity becomes smaller, larger equipment is necessary of smaller flow velocities to enable the separation.

The results of some simple simulations are depicted above to see the influence of the particle size and the solid fraction. In figure 5.5 the diameter of the salt and ice particles is varied with a constant solid fraction (ϕ =0.2). From the figure it can be seen that size has a larger influence on the settling velocity of the salt particles than of the ice particles. This is due to the larger density difference compared to the density of the mother liquid.

In the same manner the influence of the solid fraction on the settling velocity with constant particle sizes (d_{salt} =100 µm, d_{ice} = 500 µm) is visualized in figure 5.6. From this it follows that the solid fraction should be as small as possible to get a good separation.

As an example the required settler diameter was calculated for the separating of potassium chloride and salt. Here it is assumed that the Richardson-Zaki equation (eq. 2.2) is valid for the settling behavior of salt and ice. The properties of the salt ice and liquid can be seen in table 5.2 and the chosen design variables in table 5.3. The sizes of the crystals for the separation where chosen using the work of Himawan [Himawan, 2005] and the density of the ice was found using Melinder [Melinder, 2010].

Table 5.2 - Properties

ρ_{salt}	1984	kg/m^3
ρ_{ice}	918	kg/m^3
ρ_{liquid}	1000	kg/m^3
μ_{liquid}	1.79E-3	Pa s
g	9.81	m/s^2

Table 5.3 – Design parameters

d_{salt}	50	µm
d_{ice}	100	µm
ϕ	0.2	-
Q_f	0.001	m^3/s
Q_u/Q_f	0.15	-

First the Stokes settling velocity can be calculated using equation 2.1 for both the ice and the salt. With this velocity the Reynolds number is determined using equation 5.1

$$Re_i = \frac{\rho_{liquid} v_{s,i} d_i}{\mu_{liquid}} \tag{5.1}$$

Where: i Salt or liquid

The Reynolds number is nessecary to determine the Richardson-Zaki exponent. For Reynolds numbers smaller than 0.2 this is a linear correlation, equation 5.2 (Richardson, 1954).

$$n = 4.65 + 19.5\frac{d}{D} \tag{5.2}$$

Where: d Particle diameter
D Diameter settler

Because the diameter of the settler is of a much larger scale than the diameter of the solid particles (d<<D), this equation can be reduced to a constant of n = 4.65. With this value and a chosen solid content that is not too high to ensure a good separation, the hindered settling velocity can be determined.

The flow split can be estimated, based on the original concentration of the liquid entering the EFC process. For this example the flow split is chosen near the eutectic concentration. When the slurry flow entering the settler is known the minimal required area for separation can be determined for salt using 5.3 and for ice using 5.4.

$$A_{min,salt} = \frac{v_{salt}}{\left(1 - \frac{Q_u}{Q_f}\right) Q_f} \tag{5.3}$$

$$A_{min,ice} = -\frac{v_{ice}}{\left(\frac{Q_u}{Q_f}\right) Q_f} \tag{5.4}$$

The results of these calculations can be seen in table 5.4. There are two minimal required areas, one which allows salt particles of a diameter larger than 50 µm to sink to the bottom and one which allows ice particles larger than 100 µm to rise to the top. In this case the diameter of the salt is the limiting parameter. Therefore the minimal required area for this settler is 3.20 m^2.

Table 5.4 – Results

$v_{s,salt}$	7.50E-04	m/s	$v_{s,ice}$	-2.50E-04	m/s
Re_{salt}	2.10E-02	-	Re_{ice}	1.40E-02	-
v_{salt}	2.66E-04	m/s	v_{ice}	-8.86E-05	m/s
$A_{min,salt}$	3.20	m^2	$A_{min,ice}$	1.69	m^2

Chapter 6 - Conclusions and recommendations

Conclusions

- The eutectic point of potassium chloride is at a temperature of-10.8^{o}C and a salt concentration of 19.4 wt%.(chapter 3)

- The separation in of salt and ice in the crystallization vessel is not feasible, because the salt gets entangled in the ice. This has as a consequence that salt drags the ice to the bottom and prevents a good separation in two separate slurry streams. (chapter 4)

- Salt and ice was observed together on the bottom with different types of crystallizers of different sizes (1L beaker crystallizer with stirrer, 10L bottom scraped crystallizer, 200L cooled disk column crystallizer) and with different salt solutions (potassium chloride, sodium sulphate). This seems to suggest that this phenomenon is not vessel size, crystallizer type or salt dependent. (chapter 4)

- The separation of salt and ice from a settled salt-ice slurry can be achieved by agitating the slurry with some sort of impulse. This can be done by mechanical means, for example twisting a scraper, or by means of a fluid, for instance air. (chapter 4)

- When the ice is separated from the salt at the bottom and floats to the top, it still contains salt which it is disposing as is rises to the top. To ensure an effective separation of the salt and ice, the floating layer of ice should be as thing as possible to allow the salt to fall to the bottom. (chapter 4)

- The salt gets entangled in the ice because the ice forms irregular extremities, probably this is caused by kinetic roughening. (chapter 4)

- When ice crystals, obtained from an EFC process, are washed in a glass filter with demineralized water, their shape changes. The irregular extremities on the crystals that were visible before washing, could no longer be seen and the ice had a more round shape. (chapter 4)

Recommendations

- During an experiment in the 1L setup, the stirrer speed was reduced, immediately after this the crystallization started. Further research should be conducted on this issue, to see if there is a connection between the rate of crystallization and the stirrer frequency.(chapter 3)

- The sinking of both ice and salt was observed in all types of crystallizers (1L, 10L, 200L), but the EFC process had to be stopped to do so. An experiment should be conducted to prove that it is possible to remove ice and salt through the bottom in a continuous process. (Chapter 4)

- Since the ice and salt should be removed from the bottom, logic dictates that the feed should enter the crystallizer at the top.(chapter 5)

- Ice crystals have a strong tendency to conglomerate into large clouds that can clog the flow through the heat exchangers, therefore a more open heat exchanger design, with less horizontal contact surface should be considered. At least for the bottom heat exchanger, since a large quantity of ice crystals is expected here. (chapter 5)

- When the feed flow configuration is changed, it makes sense to change to heat exchanger configuration from parallel to series and to let the refrigerant in the heat exchangers flow counter current with respect to the mother liquid. (chapter 5)

- The peristaltic pumps in the current 200L setup have problems when dealing with large chunks of crystals. This problem can be solved by using a screw pump instead. (chapter 5)

- The salt-ice slurry should be agitated when it enters the separator, to improve the separation. This can be done by creating an air curtain at the entrance of the separator. (chapter 5)

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Appendix A

Sinking ice



Figure A.1 – Sinking ice, t=0 s



Figure A.2 – Sinking ice, t=2 s



Figure A.3 – Sinking ice, t=4 s

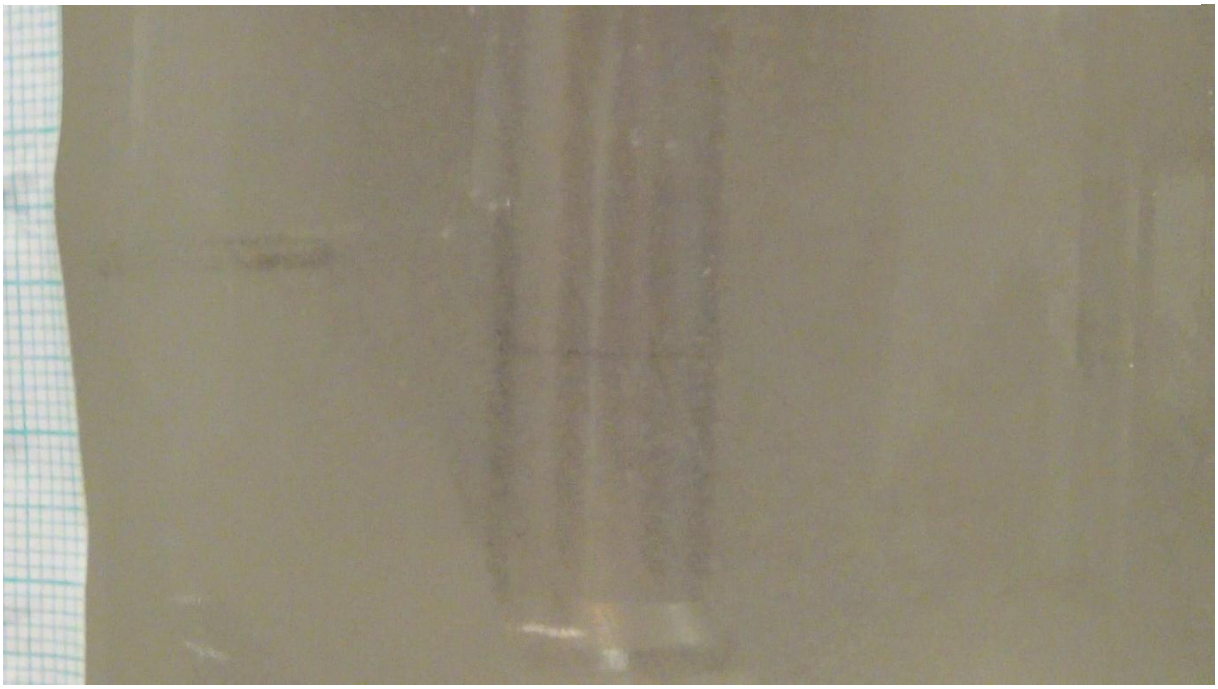

Figure A.4 – Sinking ice, t=9 s

Disturbance by scraper



Figure A.5 – Disturbance by scraper, t=0 s

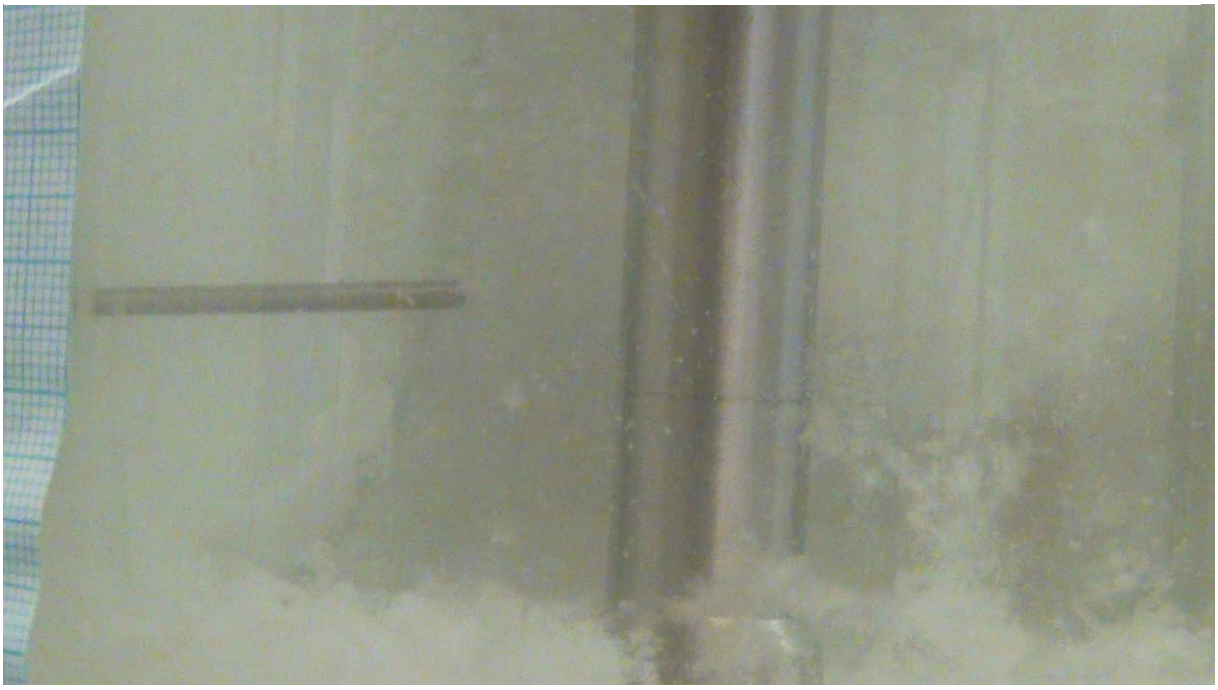

Figure A.6 – Disturbance by scraper, t=2 s



Figure A.7 – Disturbance by scraper, t=5 s

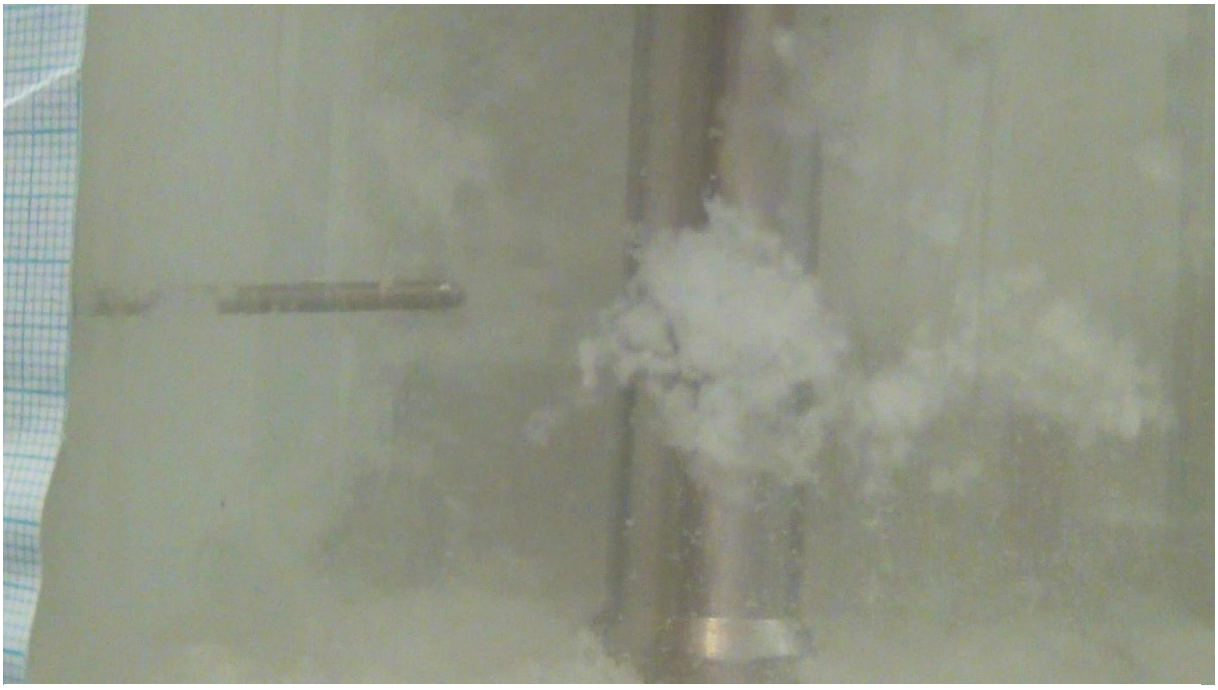

Figure A.8 – Disturbance by scraper, t=7 s

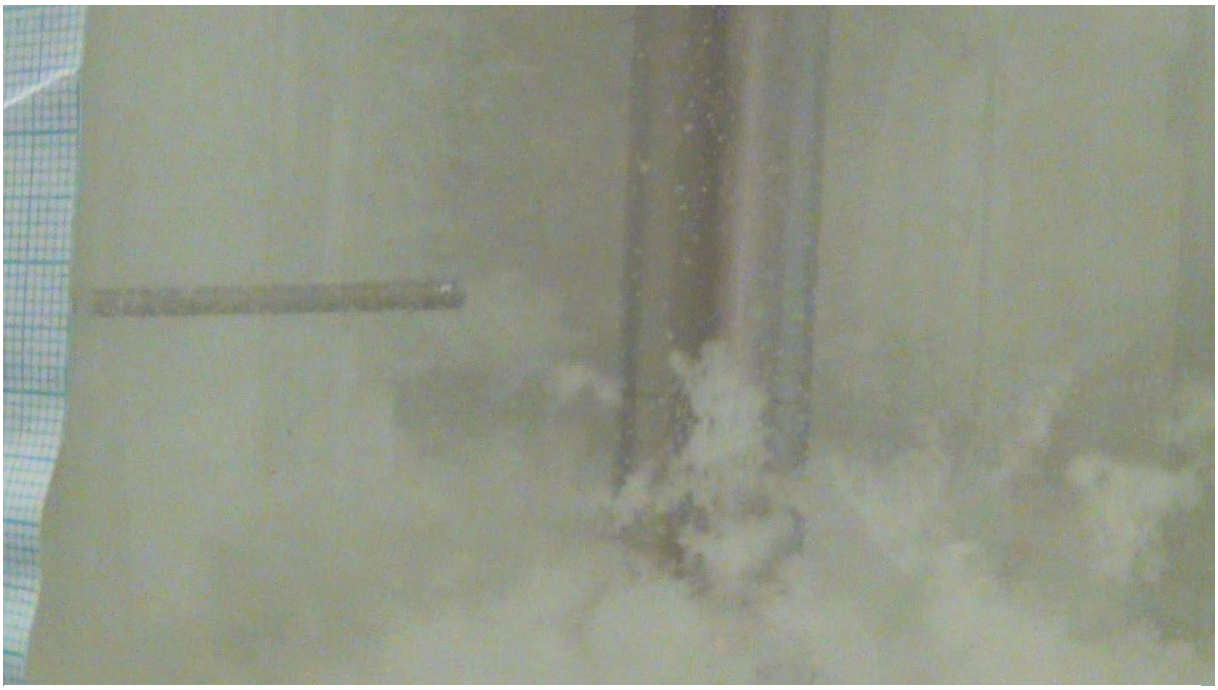

Figure A.9 – Disturbance by scraper, t=9 s

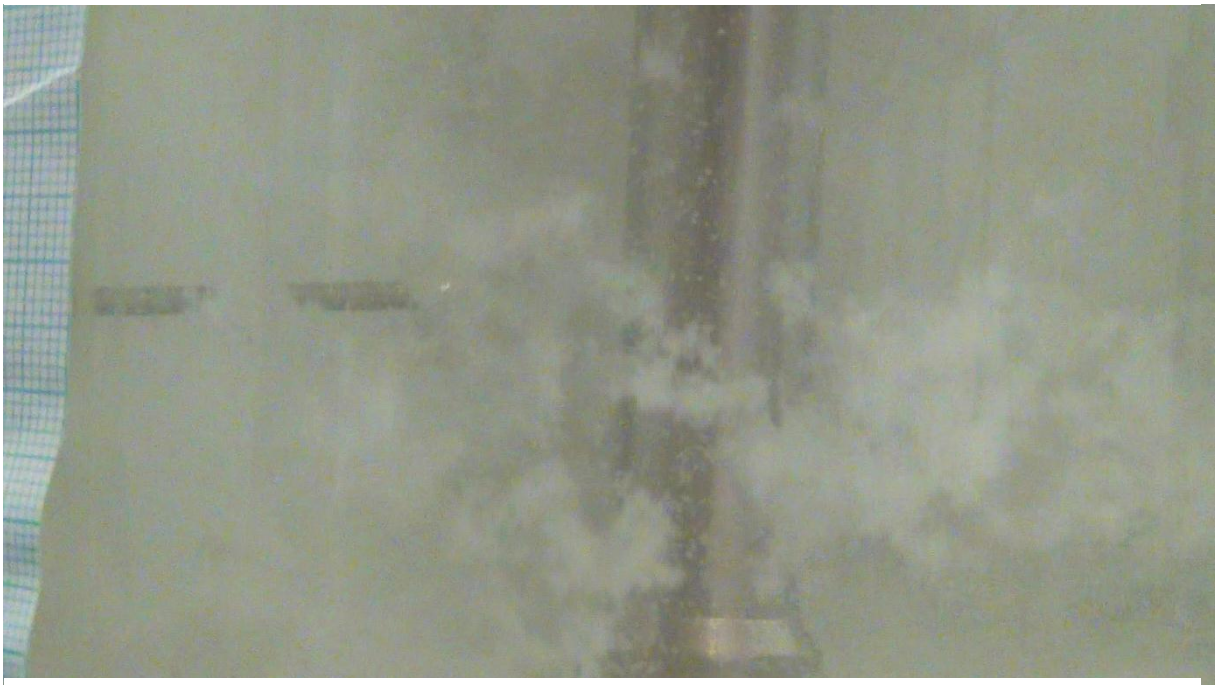

Figure A.10 – Disturbance by scraper, t=11 s



Figure A.11 – Disturbance by scraper, t=14 s

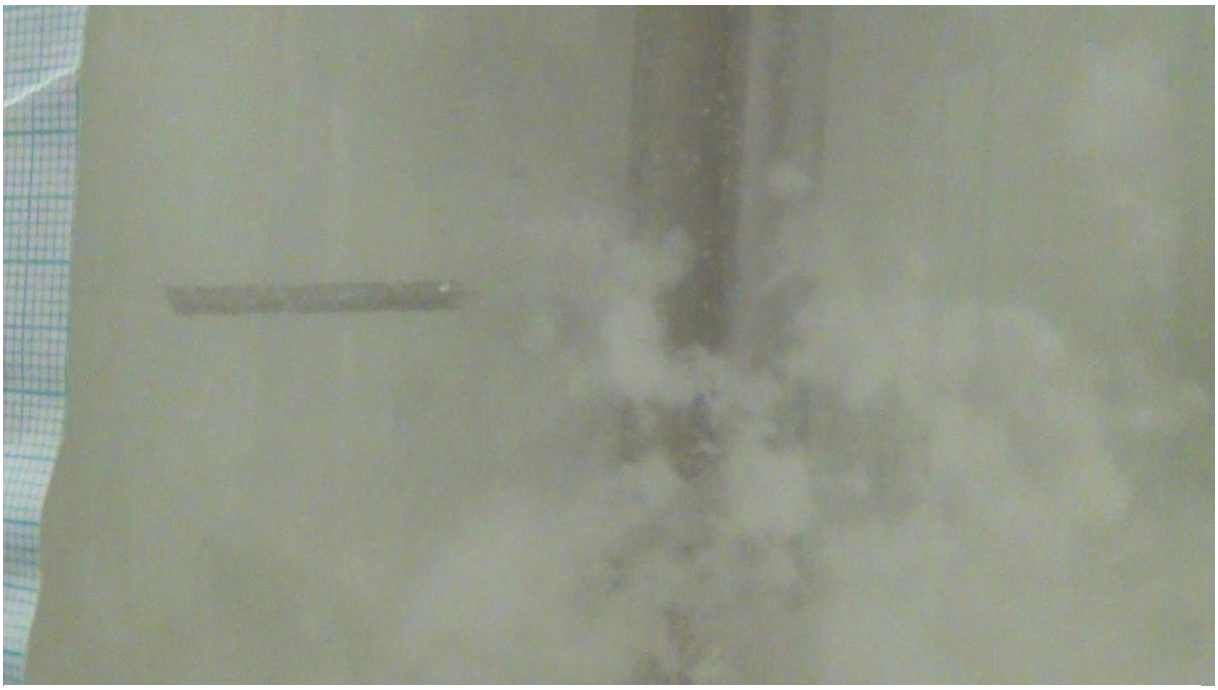

Figure A.12 – Disturbance by scraper, t=16 s



Figure A.13 – Disturbance by scraper, t=18 s

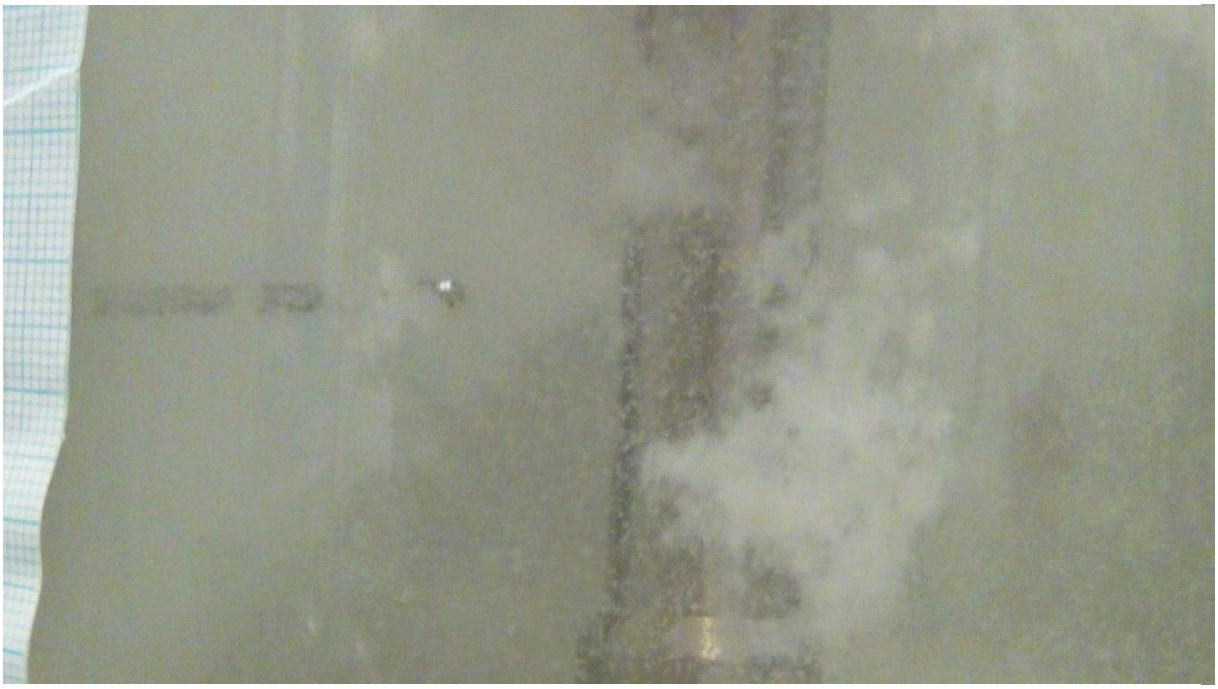

Figure A.14 – Disturbance by scraper, t=22 s