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DESIGN OF A WASTEWATER PURIFICATION SYSTEM BASED ON FREEZING

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D. Sc. (Tech.) Emil Kurvinen

ABSTRACT

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Freeze crystallization is a natural and environmental friendly alternative to other conventional wastewater purification processes. In this study, the main objective is to determine the critical issues with direct and indirect form of freeze crystallization and to develop a pilot plant model for a freezing based wastewater purification plant. For this purpose, experimental studies were conducted on crystallization and separation of wastewater by direct contact freezing (DCF). Cold air from a vortex tube was used as the refrigerant for convenience. The main issues identified were formation of ice lumps at the point of dispersion and insufficient heat transfer at four bar pressure. The issue was mitigated by using Teflon as base material due to its ice-phobic properties. To further resolve the issue, polyurethane coating was used and as per calculation, air pressure of 20 bar is required through multiple inlet points in order maintain continuous ice production. Furthermore, experiments suggested that the usage of a universal stirrer with dynamic axial and radial flow also improves the ice formation rate.

The second phase of the research comprised of designing a pilot plant model for the wastewater purification plant for a production rate of 10 kg ice per hour. Based on the experimental learnings, an energy efficient process flow for the plant was created by utilizing the cold energy from brine concentrate and pure water for precooling purpose and the total power consumption of the plant was estimated. Lastly, the crystallizer and separator for the DCF based plant were modeled and assemble into the pilot plant layout including secondary mechanical components such as pumps, compressor, heat exchangers and piping.

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LIST OF SYMBOLS AND ABBREVIATIONS

LIST OF SYMBOLS

A	Heat transfer area
b	Width
C_p	Specific heat
D	Diameter
$E_{Precooling}$	Estimated power required for precooling
E_{REFRI}	Estimated power for required for refrigeration
H	Height
h	Height
ID	Inner diameter
m	Mass
N	Number of plates
P	Power
Q	Heat transfer rate
ΔT	Change in temperature
$\Delta T1$	Change in temperature in first liquid in heat exchanger
$\Delta T2$	Change in temperature in second liquid in heat exchanger
T_{in_cold}	Inlet temperature for cold liquid in heat exchanger
T_{in_hot}	Inlet temperature for hot liquid in heat exchanger
ΔT_{LMTD}	Log-mean temperature difference
T_{out_cold}	Outlet temperature for cold liquid in heat exchanger
T_{out_hot}	Outlet temperature for hot liquid in heat exchanger
U	Overall heat transfer coefficient
ww	Wastewater

LIST OF ABBREVIATIONS

3D	Three dimensional
AISI	American Iron and Steel Institute
CDCC	Cooled Disc Column Crystallizer
CFC	Chlorofluorocarbon
CFD	Computational fluid dynamics
CH_3CF_3	1,1,1-trifluoroethane
CH_3CH_3	Ethane
$CH_3CH_2CH_3$	Propane
$CH(CH_3)_2CH_3$	Isobutane
CH_3CHF_2	1,1-difluoroethane
CH_2F_2	Difluoromethane
CHF_2CF_3	Pentafluoroethane
CH_2FCF_3	1,1,1,2-tetrafluoroethane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
Conc.	Concentrate
DCF	Direct Contact Freezing
DFMA	Design for manufacturing and assembly
ECF	Eutectic Freeze Crystallization
FC	Freeze Crystallization
FEA	Finite element analysis
HCFC	Hydro Chlorofluorocarbon
HE1	Heat exchanger 1
HE1	Heat exchanger 2
HMPE	High Modulus Poly Ethylene
H_2O	Water
IEEE	Institute of Electrical and Electronics Engineers

ISO	International Organization for Standardization
NaCl	Common salt/seawater
Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium Sulphate
NH_3	Ammonia
PE	Polyethylene
PMMA	Poly (methyl methacrylate)
POD	Point of dispersion
PVC	Polyvinylchloride
R	Residence time
SCWC	Scrapped Cooled Wall Crystallizer
WWTP	Wastewater Treatment Plant

1 INTRODUCTION

Wastewater (ww) processing and purification has been an integral part of human civilization since the Industrial revolution. Over the years, the most perceptible development in this field occurred in the 20th century (Henze, Ekama and Brdjanovic, 2008). Some of the major sources of treatable water are sewage, Industrial wastewater (from chemical, mining and pharmaceutical industries), and seawater. Based on the type of contaminant (solid, liquid or microbial), different technologies are used for the purification which can be broadly classified as filtration, membrane technology, ultraviolet disinfection, precipitation and evaporation by heating. Although each method have their respective advantages and disadvantages, the energy consumption and capacity of the Wastewater Treatment Plant (WWTP) play a key role in the selection of a particular process.

Apart from the above mentioned processes, a naturally occurring phenomenon of wastewater purification is freezing (Rane and Padiya, 2011). For countries in proximity to polar region similar to Finland, freezing of water bodies occurs naturally due to the cold environment during the winters (Finnish Meteorological Institute, 2017). Although the purity level largely depends on the rate of freezing, various level of purification is expected from the natural freezing itself (Hasan et al., 2017). In recent times, this has given rise to exciting ideas about how to harvest and collect the naturally formed ice for further processing and purification. On the other hand, there is a possibility of simply adapting and recreating the same process in an artificially controlled environment. In a general way, this research aims at applying the concept of natural freezing in an artificial setup to perform industrial wastewater purification.

In the years 1960, the concept of using freezing for wastewater purification was introduced in the industrial scale (Steinhoff et al, 1960). However, the developments were restricted to initial phase and could not attain proper commercialization. In the recent years, there has been a newfound interest in the application of artificial freezing or crystallization for purification of wastewater or desalinization. (Gao et al., 2004.)

1.1. Freezing process

In general terms, the process of transferring cold energy into water results into formation of either a complete solid block of ice, or a semi solid solution called ice slurry with millions of ice crystals in it as shown in Figure 1. Although the latter might require a controlled rate of cooling, it is arguably much easier to transfer the slurry for further processing than a block of ice.

(a) (b)

Figure 1. Different form of ice as obtained in the laboratory (a) Block of ice (b) Ice slurry

The freezing technique works on the principle of isolation of the ions of impurities present in the solution by crystallization (McCloskey et. al , 2012). As the solution approaches its freezing point, the pure water separates itself from the inclusions and start forming ice crystals until the freezing point is achieved and additional heat energy is extracted in the form of latent heat. The impure solution, also known as brine, is mostly trapped in inter-crystalline space or pores resulting in the formation of a semi liquid solution of ice slurry (Erlbeck et al., 2017). The ice slurry is collected from this section and could be further processed in a separator from where it is dried and melted in the final stage to obtain water of required purity level. The concentrated brine solution is collected from both the primary crystallizer and the separator for utilization of its cold temperature. It should be noted that in this study, the 'pure water' refers to water that has less contaminants than the initial solution (ww).

1.2. Objective of the research

This objective of this study is correlated with the initial stages of product development of a wastewater purification system based on freezing. In order to construct any industrial scale unit, a systematic design approach is followed based on the product life cycle shown in Figure 2. (Pahl and Beitz, 2007.)

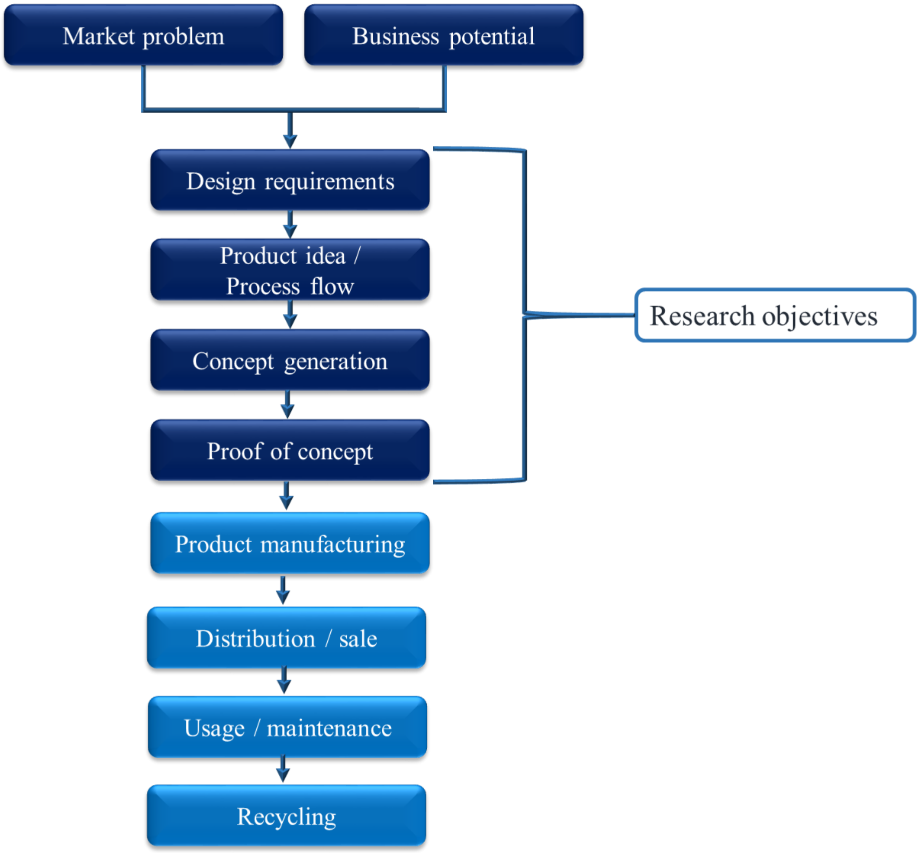


Figure 2. Product life cycle (Pahl and Beitz mod., 2007)

This study aims to identify the design requirements and challenges involved in the process, develop a product concept and carry out the design for a proof of concept for a freezing based wastewater purification system. Typically, a freeze crystallization plant includes the following equipment:

In Figure 3 the wastewater stream is the input and the pure water is the main output with concentrated brine as the secondary output. The rest of the blocks signify the primary equipment utilized in freeze crystallization plant. The wastewater is stored in the storage tanks before being precooled via the heat exchangers. The precooled wastewater is further cooled in the crystallizer to form ice slurry which is pumped into the separator. The ice is separated from the concentrated brine in the separator and passed through the melter to be extracted as pure water. This research consists of the equipment design and process flow development of the plant by understanding the design requirements and developing concept as per systematic product development process (Figure 2).

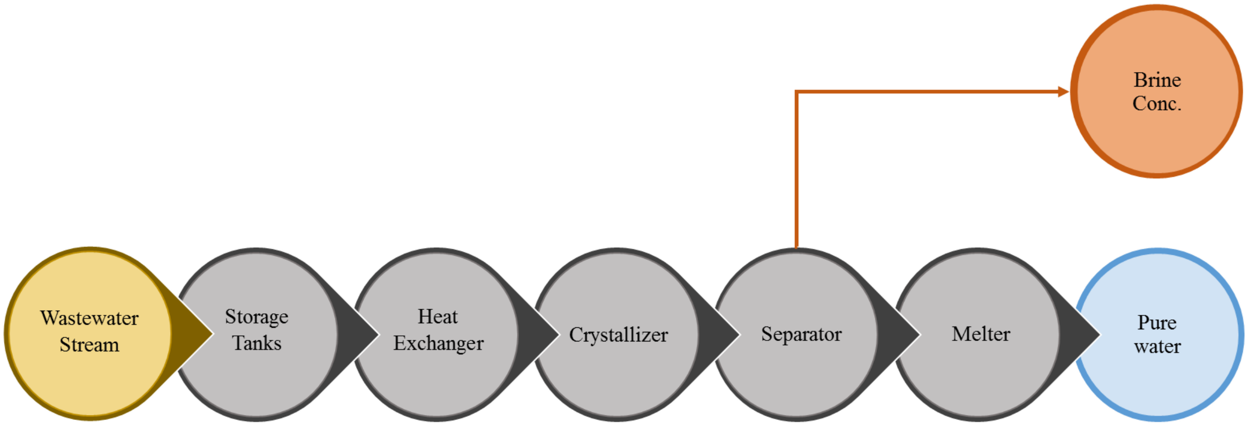


Figure 3. Overview of freezing based wastewater purification system (FC technology process mod., 2017)

Furthermore, the objective is to design the process of freezing and purification as a continuous cycle in order to use the set up as a mobile device. This way, the wastewater stream from any predetermined plant is connected to the inlet of the purification system and purified water is obtained at the outlet of the system (Figure 3). (FC technology process, 2017.)

1.3. Motivation

This project mainly offers motivation from two different perspectives. Firstly, from the technical point of view, the project offers challenges in terms of its diversity. Understanding the process of purification by crystallization requires a great deal of interdisciplinary knowledge, combining the mechanical aspects with the corresponding feasibility analysis in terms of chemical engineering. Figure 4(a) shows a simple experiment performed in the winter simulation laboratory of Lappeenranta University of Technology. It shows how the ice formation purified the colored solution of nickel sulphate. From the chemical perspective, similar to color, other factors such as COD (Chemical oxygen demand), turbidity and conductivity can be neutralized through freeze crystallization and considering the fact that the process is similar to natural freezing, there is no additional usage of chemicals which makes the process environmental friendly. Figure 4(b) shows the industrial application of freeze crystallization by applying the principle of indirect cooling.

Secondly, this research work includes indirect cooling in the precooling of wastewater after which the actual freezing is performed in the crystallizer. To systematically derive the design parameters for the crystallizer, calculations in terms of heat and energy exchange is required. In addition to that, such a system comprises of quite a few auxiliary components like a compressor, a heat exchanger unit, a melter and one or more pumps for precooling and post treatment. Selecting each of these individual component to build the entire mobile system seems like a challenging task. (Erlbeck et al., 2017.)

(a) (b)

Figure 4. (a) Ice formation from nickel sulphate (NiSO4) solution in laboratory (b) Industrial output via freeze crystalization (FC technology process, 2017).

In the current market where some of the technologies used for purification of wastewater are evaporation, membrane filtration, precipitation and ion exchange, introducing an alternative approach in terms of purification by crystallization seems promising from the business perspective. Since only heat transfer is taking place in the process and there is no involvement of chemical reactions, it is environmentally safe and friendly. All these keys features of this process in terms of its environmental advantages and technical challenges make it a very unique project, hence providing the motivation for the research.

1.4. Research problem and research questions

The two basic factors determining the efficiency of a water purification device are its productivity and the purity level of the output water. In terms of productivity, the primary concern here is to establish continuity in the process of freezing and purification as shown in Figure 5.

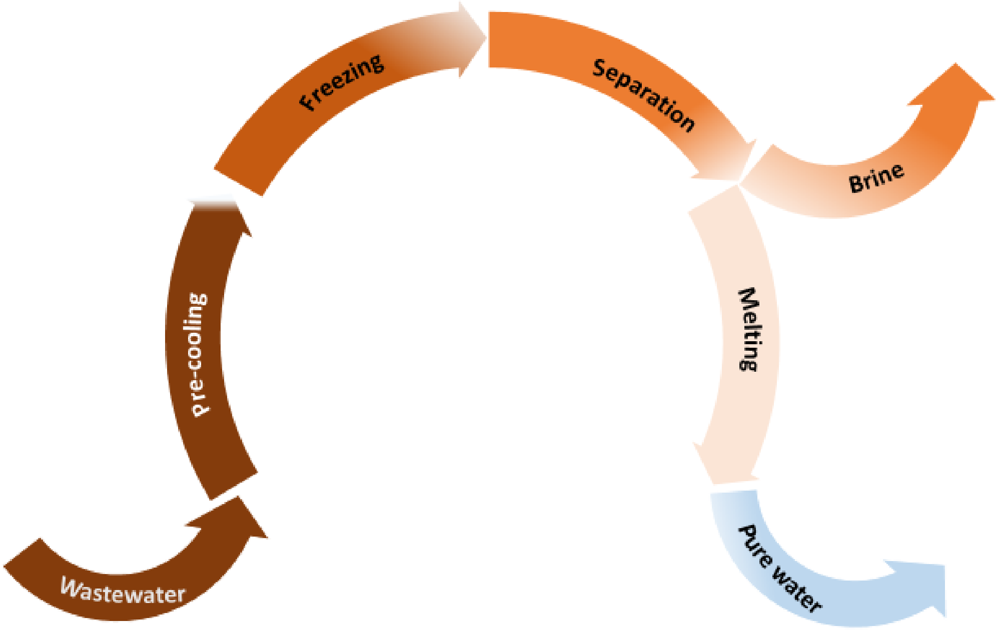
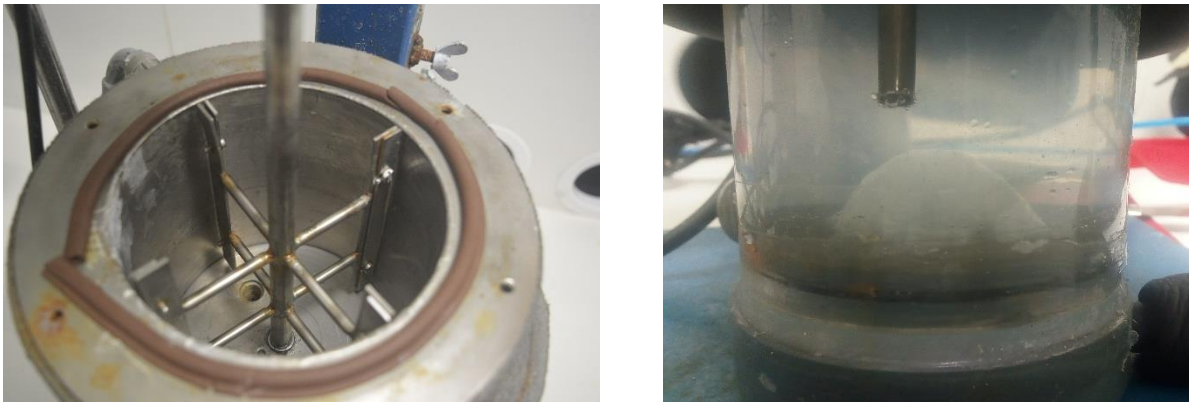


Figure 5. Continuous Process flow diagram

Here the process starts with the wastewater being precooled at the inlet to near freezing temperature followed by freezing and separation of the ice from the brine. The continuity of the process is important because the purpose of this device is to serve as a mobile unit which limits the capacity for the tanks and chamber used. Therefore, the productivity of the system depends directly on how much volume of water can be purified for a given time which in turn depends on how much ice can be formed and successfully separated from the solution.

For ice formation, both direct and indirect cooling processes are considered. However, both the processes have their respective constraints and limitation. In indirect cooling, ice formation occurs at the inner surface of the container and acts as an insulator itself. Hence, it requires a scrapping system to continuously remove the ice formed on the surface of the crystallizer as shown in Figure 6 (a). Although systems using indirect cooling can be better controlled in terms of range of temperature, the scrapping mechanism is an additional complicacy which also increases the power consumption. The alternate approach is to conduct the ice formation using direct cooling. There are a couple of research problems associated with direct cooling as well. Firstly, the surface close to the point of dispersion supplies cold energy to the solution via conduction. This is typically the method of heat transfer used in indirect freezing system. Although through super cooling the solution, ice formation can be obtained in the solution itself, eventually ice will certainly form in the cold plate. The time required to form ice scale on the cold surface is referred as induction time. The longer the induction time is, the longer ice-scale free operation is obtained. Once the ice layer is formed at the point of dispersion, it prevents further cooling of the liquid by acting as an insulator. This problem has to be mitigated in order to establish the process of continuous freezing and purification. From design perspective, the problem can be associated with quite a few factors, namely, type of coolant used, pressure at the point of dispersion and method of dispersion, design and position of the point of dispersion.



(a) (b)

Figure 6. (a) Scrapping unit attached to crystallizer (b) ice scaling at inlet leading to blockade in direct cooling unit

Secondly, the material selection for the crystallizer is also significant challenge in preventing scaling. The idea is to select a material with low thermal conductivity to prevent loss of the cold energy, along with a coating of ice-phobic material to minimize this effect. Furthermore, the wastewater purification system need to be designed to deal with, for example industrial wastewater, wastewater from mining industry, bio-waste and seawater. Along with the crystallizer and the separator, the heat exchanging unit, the pumps, pipes and other auxiliary units have to be designed in such a way that the material could resist failure due to contact with the versatile ingredients of the wastewater. (Rane and Padiya, 2011.)

Based on the above queries, the main research questions are:

I. What are the obstacles in attaining continuous ice formation and separation? What are the ways to resolve those issues?
II. What can be an energy conservative way of process flow for a pilot plant designed for freeze crystallization based wastewater purification?

III. What are the primary and secondary components required from the functional aspect of the pilot plant?
IV. How is it possible to estimate the energy requirements for the entire process?
V. What are the driving parameters in the process which needs to be controlled?
VI. How could be the overall sizing and dimensioning of the primary components established for the proof of concept?

1.5. Scope

The idea of this research is to design a plant which can be transported easily to different locations. This limits the scope of the project to mobile units only eliminating factory based units. The study is limited to the designing of a proof of concept of a water purification system based on continuous process of freezing and separation. Along with the units used for freezing of wastewater and separation of ice, the scope also includes the sizing and estimation of required auxiliary units for the basic set up of the pilot plant.

2 GENERAL METHODOLOGIES

This chapter includes a detail study of the different methods that can be utilized in this research or correlated research studies. The main objective here is to devise a step by step approach to design a proof of concept for a pilot plant to be used for wastewater purification by freezing. The chapter takes a general approach in establishing the different options and criteria that can be studied and in order to come up with a proof of concept for a similar plant based on freeze crystallization.

2.1 Literature review

In literature review, the objective is to go through the previous research data available in the specific area of interest and understand the versatile concepts and methodology employed by the researchers. In this section, the overview and development of application of freeze crystallization has been discussed and the relevant research related to indirect and direct cooling has been reviewed. Similarly, this section also covers both mobile and well as large scale industries which have used freeze crystallization as a method of purification. A systematic literature review procedure is used to study and condensate the previous and prevailing research. In the following sub-sections, the methodology for performing a systematic literature review and the findings by applying this methodology will be discussed.

2.1.1. Systematic literature review methodology

In this section, the method to perform a systematic literature review is presented so that a relevant set of documents with the prime objective of finding the working principle of the freeze crystallization. Majority of the search for relevant research work was conducted using Wilma Finna search portal, a national electronic library services used in most of the universities in Finland (Wilma finna, 2017). Through this portal, various databases, books, journals et cetera are accessible. The systematic search is executed on the following scientific databases:

- Directory of Open Access Journal
- IEEE
- Science direct (Elsevier)
- SCOPUS
- Free Patents Online

- Doria (LUT's publication)

Apart from the above mentioned databases, Google scholar was also used to obtain additional information from books, manuals and general articles related to this topic. The entire search was conducted based on the following criteria:

- The keywords used for the search are "freeze" and "crystallization" "purification" and "freezing", "desalinization" and "freezing", "freezing technique" and "natural freezing".
- Scientific articles, journals, conference papers, patents, books and other relevant documents have been considered for the study.
- Documents only in English language are considered for this study. Furthermore, for any of the search operations coming up with more than five hundred search results for a given keyword, only the first five hundred items are considered for review.
- For the review purpose, publications from as old as 1960 are also considered. This was done simply to analyze the huge scientific contribution and advancement that occurred in the field of in the latter half of the 20th century.

Combining the systematic approach and the above mentioned criteria, the initial results are obtained. These results are screened based on the title of the article, the language, the abstract and finally the actual content of the publication. The articles retrieved from this screening process (Figure 7) were thoroughly studied and the inputs are summarized in section 2.1.2.

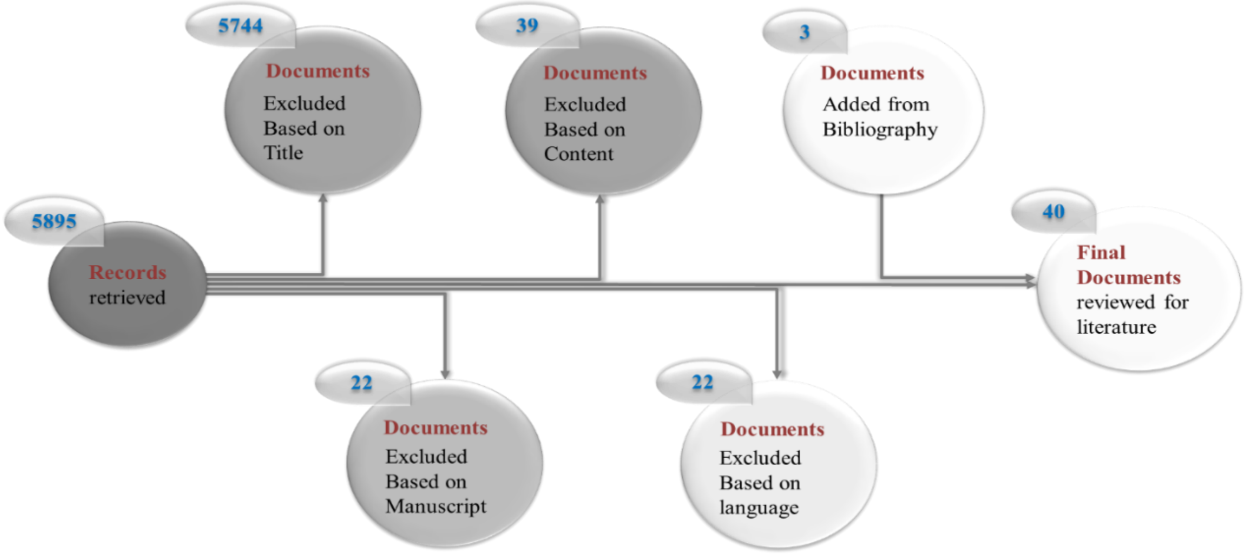
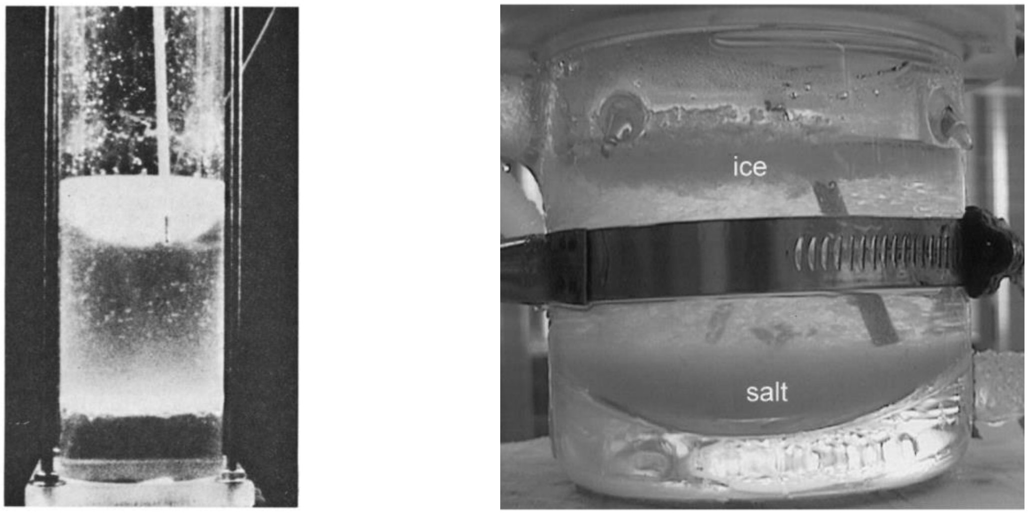


Figure 7. Flow chart for screening performed in literature review

2.1.2. Findings from systematic literature review

In the field of continuous artificial freezing, most of the research are based on the concept of direct or indirect cooling. The chronological development in the field of freeze crystallization has been adequately studied in a recent article by Szpaczyński, White and Côté (Szpaczyński et al., 2017). The authors described the extensive research conducted in 1960's about the two stage purification process used for freezing – crystallization and separation. The basic principle was that the ice crystals grew by gathering water molecules, adding them to the already formed ice structure and rejecting impurities. The researches in the 1960's were mostly based on the principle of freeze crystallization by direct contact freezing (DCF). One of the first reports related to an industrial application of this method of purification was published by Karnofsky and Steinhoff (Karnofsky and Steinhoff, 1960). Based on their laboratory work, they came up with a plant design capable of producing 37854.11m^3 of fresh water per day from seawater. Later in the 60s, Baker also identified freeze concentration as a valuable approach by demonstrating purification procedures for mineralized industrial wastewater (Baker, 1967). However, in the 1970's, direct cooling based project were further enhanced to execute eutectic freeze crystallization (EFC) in certain cases involving desalination (Stepakoff and Siegelman, 1973; Stepakoff et al., 1974). In this process, brine solution is further cooled, concentrated and dried later on to recover salt crystals as an additional output as shown in Figure 8 (a).



(a) (b)

Figure 8. (a) Eutectic separation of sodium chloride dihydrate and ice (Stepakoff et al., 1974). (b) EFC system showing ice float to the top and salt to the bottom (van der Ham et.al, 1997).

In the past thirty years, the research work shifted more towards indirect cooling based eutectic systems. Furthermore, the studies conducted by Dickey et al. suggested that the salt exclusion rate depends on the concentration of the solution which in turn can be improvised by proper mixing (Dickey et al., 1995). Therefore, a mixing phenomenon was also incorporated along with the indirect cooling system. In early 21st century, Wakisaka, Shirai and Sakashita designed an indirect cooling system for creating solid layers/blocks of ice with a number of square shaped freezing columns for utilizing the maximum area in the ice making device and for ease of extraction (Wakisaka et al., 2001). Van der Ham, Seckler and Witkamp continued the trend and came up with a cooled disc column crystallizer (CDCC) and later on, Rodriguez Pascual et al., invented a novel design based on EFC and indirect cooling and named it scrapped cooled wall crystallizer (SCWC) (van der Ham et al., 2004; Rodriguez Pascual et al., 2010). A revised model, one each for CDCC and SCWC have been already designed and published.

From the design point of view, the journals from 1960 to 1980 have been very informative for direct cooling based systems. For example, Karnofsky and Steinhoff have mentioned extensive details about the ice crystallizer, melter and compressor which has been beneficial in the current research as references. For coolant dispersion a glass filter pump is used as nozzle. The crystallizer used was 18 inches long and had an inner diameter of 3.5 inches. This provided an estimation for the height to diameter ratio for the crystallizer design. The melter was also designed to be four feet long having an inner diameter of six inches. Both the crystallizer and the melter were made of a transparent polymer known as Lucite or polymethyl methacrylate. The coolant used in this case was Butane which was compressed using a rotary single stage sliding vane compressor. (Steinhoff et al, 1960.)

In another report, Stepakoff and Siegelman listed down the benefits of a eutectic system based on direct contact cooling. According to the report, such a system has low specific energy requirement and is virtually resistant to corrosion due to its low operating temperature (Stepakoff et al., 1973). In a follow up study, Stepakoff et al. performed experiments to establish desalination in a continuous eutectic freezing process based on direct contact freezing. The salt solution used was sodium sulphate decahydrate (Na_2SO_4. 10 H_2O) and Freon R-114 was used as the coolant. All these systems were based on direct cooling for the initial freeze crystallization part (Stepakoff et al., 1974). In another journal, Williams et al. described the different types of freeze crystallization processes i.e. direct contact freezing (DCF) and indirect contact freezing and vacuum freezing.

Figure 9 depicts a schematic diagram showing the process flow of a direct contact cooling based desalination system:

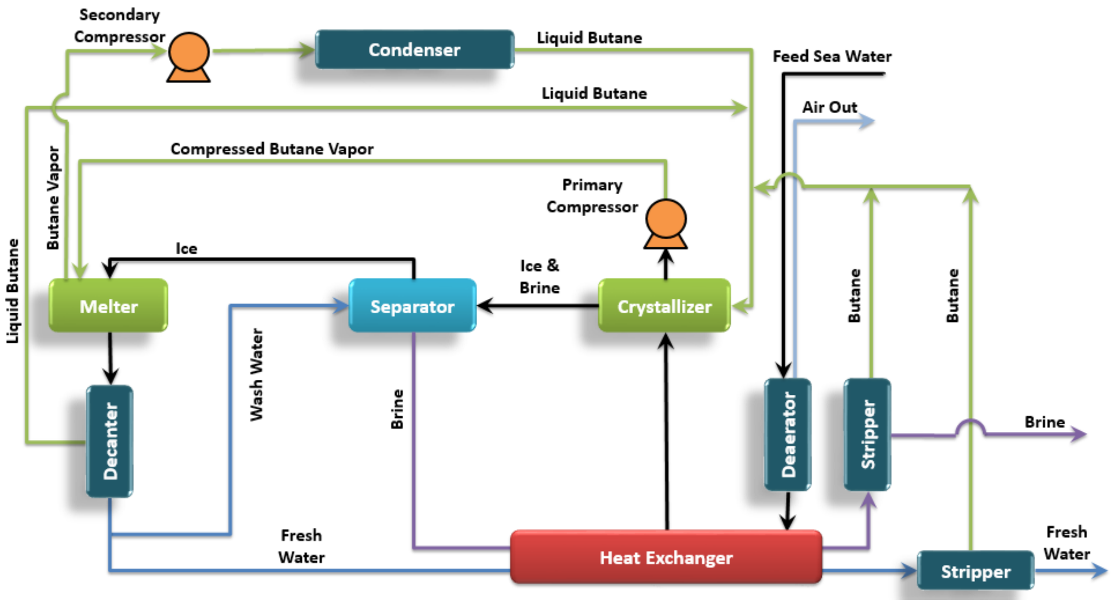


Figure 9. Schematic diagram of a direct contact freezing process (Mod. Williams et al. 2015)

In this system, liquid butane was used as a refrigerant for direct cooling due to its immiscibility with water. The liquid butane is then dispersed into the crystallizer via a nozzle and due to the temperature difference, the liquid refrigerant evaporates once it comes in contact with the seawater. This leads to transfer of cold energy from the refrigerant to the seawater, hence cooling it below the freezing point and leading to the formation of ice crystals. The ice and brine solution is then pumped into the separator where the ice is separated from the brine by natural gravity and a wash down with some amount of fresh water (5% of the total fresh water output). Meanwhile the vapor butane is compressed and hence heated in the process. This heat is utilized in the melter to melt the ice from the separator. The butane from there in its mixed liquid and vapor form is passed through a secondary compressor and condensed to be reused in the cycle. In order to conserve energy, the system utilizes the cold from the brine as well as pure water to heat the feed water through a heat exchanger in the beginning of the cycle. Therefore, as per this research, the system has a high production rate at low power consumption. However, even though the system employs a couple of strippers to remove possible amount of butane retained in the outlet water, the output is still classified as non-potable. The majority of energy consumption occurs in compressing the refrigerant. (Williams et al. 2015.)

In a similar setup described in a patent, the butane is converted into its liquid form by using cold energy from an aqueous solution which in turn gets cooled via heat exchange with methane or liquid natural gas (Pat. US 3835658 A, 1974).

Williams et al. also describes the working of an indirect cooling based desalination process as shown in Figure 10:

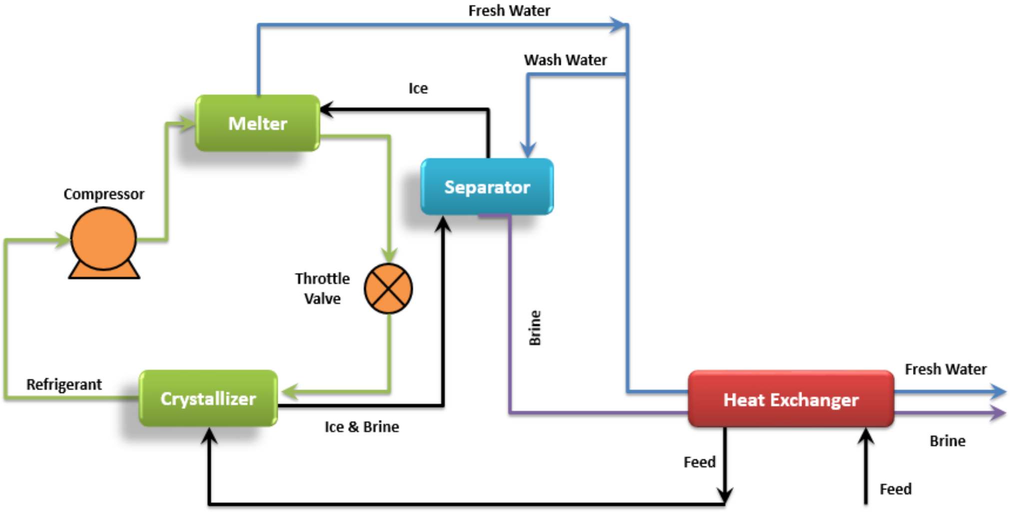


Figure 10. Schematic diagram of an indirect contact freezing process (Mod. Williams et al. 2015)

Over all, the process flow appears to be quite similar to direct cooling. However, since there is no direct contact of the coolant with the wastewater, refrigerants other than hydrocarbons can be used. Furthermore, for experimental studies, artificially created solutions can be used instead of actual wastewater. For example, Wakisaka et al. performed an experiment based on indirect cooling and used a 2600-5800 ppm solution of commercial glucose as the treatable water for experimental purpose for the very first time in this field of research. The coolant used in this case was Flon C318 and the system yielded 135 kg on average from one batch operation of 70 min (Wakisaka et al., 2001).

From the operational point of view, the refrigerant cycle simply captures the heat from the wastewater in the crystallizer and utilizes the same heat to perform the melting of the ice crystals in the melter. Therefore the crystallizer acts as an evaporator whereas the melter acts as a condenser. The compressor capacity ensures that the refrigerant is at the desired temperature, both at the freezing and melting stages. According to Williams et al., the energy consumption is comparatively higher due to resistance offered by the medium between the coolant and the wastewater (Williams et al, 2010).

The third method described in the research work was vacuum freezing process. Figure 11 shows that the feed water passes through a deaerator (to ensure removal of any dissolved air) and a heat exchanger before entering the crystallizer. A vacuum is created in the crystallizer which vaporizes a part of the water, hence creating a refrigerating effect by drawing the heat from the remaining solution and initiating ice formation.

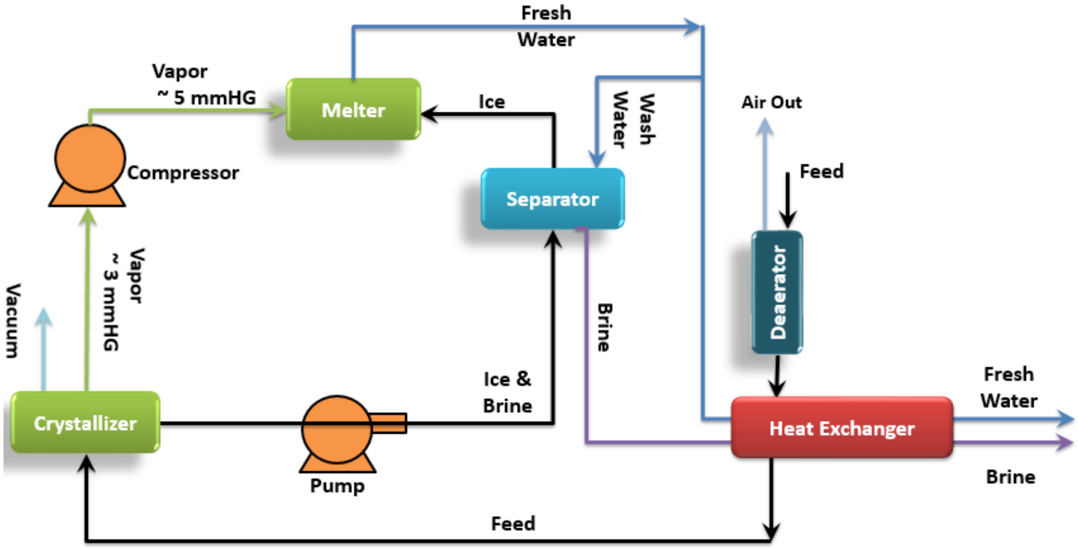


Figure 11. Schematic of a vacuum freezing process (Mod. Williams et al. 2015)

According to Rane and Padiya, by maintaining the pressure and temperature at triple point for the feed water (considering a 3.5% by weight salt solution, the values would be approximately 0.51 millibar and -2.1°C respectively), continuous ice formation is achieved. The total pure water recovered from the system is a combination of the ice melted in the melter and the water resulting from the compressed vapor. Therefore, theoretically, the production rate is quite high and associated costs are quite low due to usage of water itself as coolant. However, designing the compressor is the most complicated part of such a system as majority of the power consumption occurred in the compression stage. (Rane and Padiya, 2011.)

Each of the processes are discussed in details and compared to one another by Rane and Padiya, and as per the comparison, direct freezing process using a hydrocarbon refrigerant like n-butane has the lowest energy consumption amongst the existing processes (Rane and Padiya, 2011).

After crystallizer, the next major operation in freeze crystallization (FC) is separation. Here the ice is separated from the brine for further processing. In some of the modern indirect contact freezing processes, for example, the cooled disk column crystallizer, gravity based separation occurs in the crystallizer itself and the ice crystals are washed down to obtain higher purity level (van der Ham, et al., 2004). Even in direct contact freezing, some of the fresh water (approximately 5 %) from the outlet of the melter is circulated back to the separator to rinse down the ice crystal before it is passed onto the melter as shown in Figure 9, Figure 10 and Figure 11. Another interesting technique for separation has been mentioned by Adeniyil et al. in the design for HybridICE® HIF filter. Figure 12 explains the working principle of the filter and gravity based separation system. Ice and brine solution from the crystallizer is pumped into the separator from the bottom. Due to the continuous inflow in the column, the level of the slurry mixture rises with time. The inner column is provided with a filter wall at a particular zone such that the ice crystals are retained and the brine solution can pass through. Therefore, as the slurry rise to that height, the brine flows through the filter and is pumped out whereas the suspended ice crystals are piled up at the top. With more and more ice piling up, the brine get further drained off simply due to gravitation. Finally, the ice is collected from the top with the help of a rotating scrapper driven by a motor. Therefore, the process attains purification by utilizing filtration and gravitation and eliminates the requirement of a washing procedure which means all the fresh water can be recruited as outlet. The mass flow rate and the concentration of the solution are the primary factors that drive this system. Higher mass flow input facilitates higher output in terms of volume of ice. However, with higher output, the residence time of the solution in column is reduced. In this case, the purity of solution is adversely affected. On an average, for a 2% sodium chloride solution, a flow rate of 30 l/min yields 2.25 kg/min of ice with 83% of sodium chloride removal. The speed of the scrapper rotor also determines the amount of ice outlet. If the scrapper is too slow, it generates a reverse force on the solution causing it to move downwards. This compressive force has an adverse effect on the quality of the recovered water (Adeniyil et al., 2013).

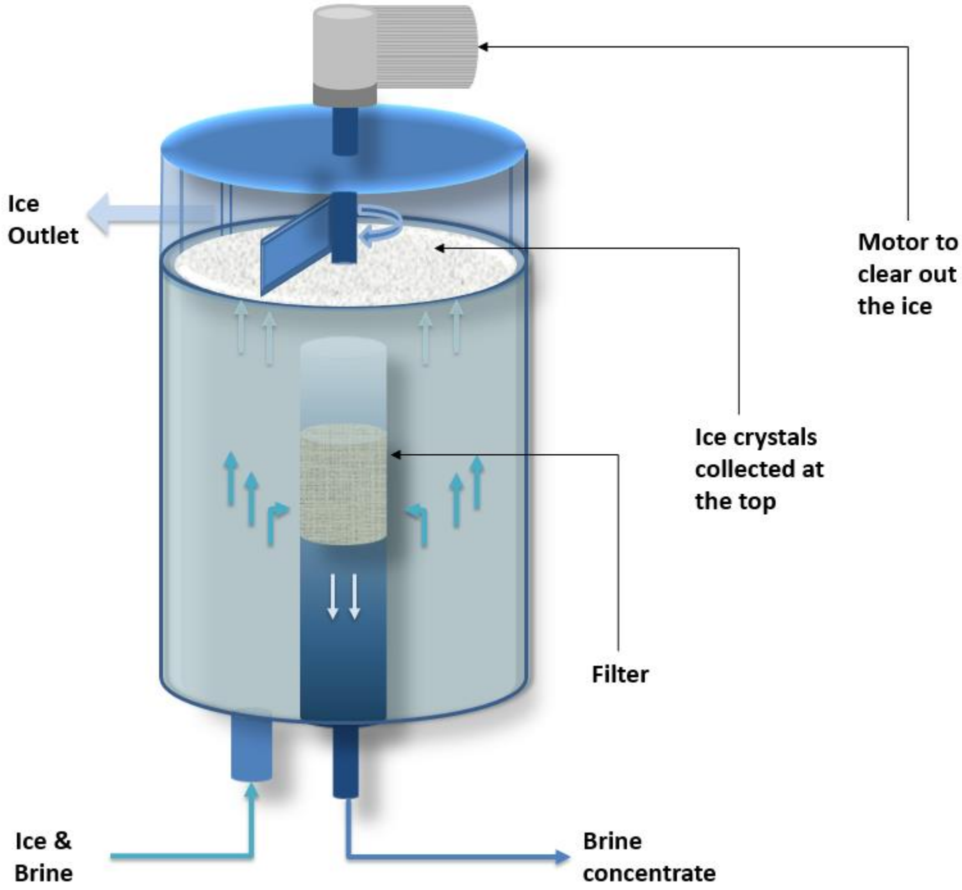


Figure 12. Schematic diagram of the HybridICE HIF filter (Mod. Adeniyil et al., 2013)

Overall, the literature review was very informative regarding the different methods of freeze crystallization. Some of the previous research work provided insight related to design, working phenomena and material selection for the crystallizer and the separator as well. These information have been taken into account and are incorporated in different steps of the current research.

2.2. Ice nucleation

The process of freeze crystallization is initiated by ice nucleation. Similar to any other crystalline material, ice crystals are formed only in the presence of critical numbers of nuclei in the solution. Once the nucleation is triggered, the ice crystals adds water molecules to its structure and grows accordingly. Any form of impurity collected in the crystal structure will lead to internal stresses and therefore the ice keeps on adhering the water molecules whereas the rejected dissolved impurities get concentrated into unfrozen liquid. This eventually leading to a larger crystal of pure water as shown in Figure 13. (McCloskey, John P and Karlsson, Jens OM, 2012.)

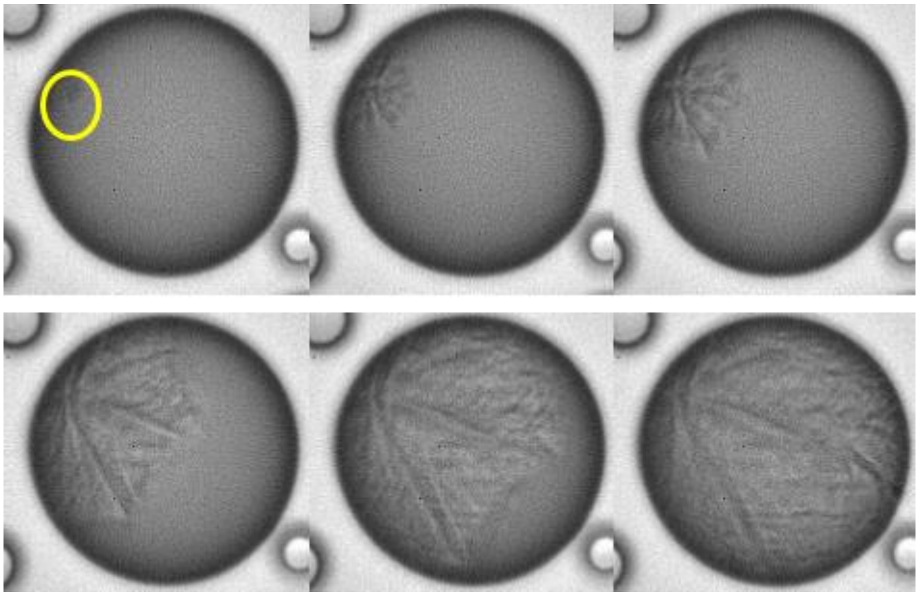


Figure 13. Ice crystal formation via nucleation (initiating at yellow circle) in a water droplet at a temperature -37.5°C, recorded at 53,333 frames/s. (Mod. McCloskey et. al , 2012)

From literature review, it can be established that the ice crystal formation and rejection of contaminants is promoted by slowing down the rate of freezing (Szpaczyński et. al, 2017). Another key factor is type of nucleation and how it is initiated. The process of nucleation can be subdivided into three parts:

- Primary homogenous nucleation, where the process is initiated spontaneously in a system without the presence of any crystalline material.
- Primary heterogeneous nucleation, where nucleation is triggered by the presence of a solid interface of a foreign material (seed).
- Secondary nucleation, where small ice seeds are introduced to initiate nucleation.

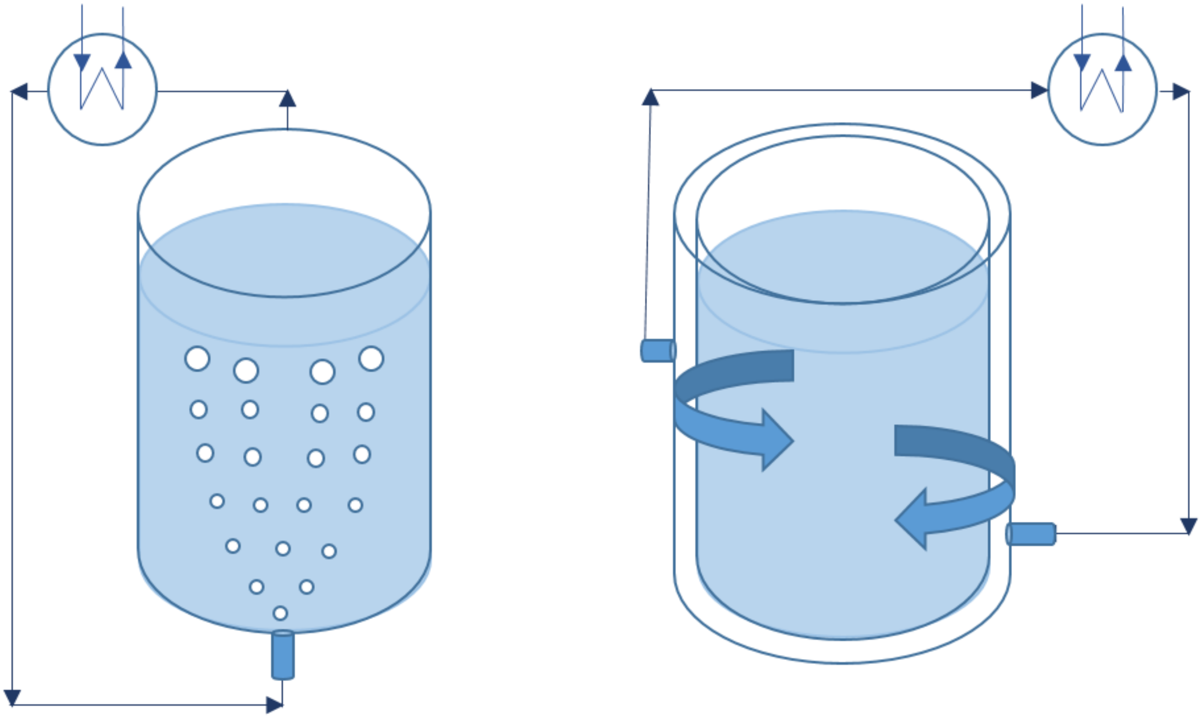
In case of primary homogeneous nucleation, ice crystals tend to adhere to the cold surface of the container instead of forming a slurry in the solution. Furthermore, the number of nuclei formed is higher resulting in small crystal size which negatively impacts the purity level. On the other hand, secondary nucleation operates at low supersaturation and the saturation level can be controlled by the time of insertion of ice seed. This makes it possible to obtain larger crystals which makes separation from the brine concentrate much easier. Hence both the rate of freezing and the method of nucleation can be considered as important criteria for the design of the pilot plant. (Randall and Nathoo, 2015.)

2.3. Freeze crystallization processes

The process of purifying water by freezing can be categorized as follows:

- Direct contact freezing (DCF), where the coolant (liquid or gaseous) comes in direct contact with the wastewater for heat transfer.
- Indirect contact freezing, where the coolant comes in contact with the container holding the wastewater and heat transfer takes place through the container via conduction.

Figure 14 shows a simple schematic diagram each for a direct contact cooling and an indirect cooling system.



(a) (b)

Figure 14. Schematic diagram of (a) Direct contact cooling (b) Indirect cooling

Based on the type of freezing process, the next step is to compare the different refrigerants suitable for this process.

2.4. Refrigerants/ Coolants

In case of direct contact freezing, refrigerants can be used both in the liquid as well as in gaseous form. Based on the literature review, general criteria for selecting a liquid refrigerant are:

- Heat transfer coefficient (U)

  The heat transfer coefficient defines the cooling capacity of the refrigerant and directly effects the crystallization rate which in turn effects the production rate of the unit
- Miscibility

  In case of direct freezing based wastewater purification, it is important that the refrigerant used leaves no traces in the main water stream once it is extracted from the crystallizer (Randall and Nathoo, 2015). Furthermore, based on the origin, wastewater contains complex organic and inorganic compounds at varied concentration such as phenolic compounds, polycyclic aromatic hydrocarbons, salts, metallic residuals, ammonia, cyanide and thiocyanate (Wang et al., 2011). Therefore, refrigerants having inert behavior to these probable chemicals present in the wastewater stream are more suitable.
- Safety factor

  Based on their affinity to combustion at 21°C and 101kPA, refrigerants are classified into class 1, 2 and 3 respectively, class 3 being the highest flammable refrigerant. Similarly, the refrigerants which show toxic results at a concentration of 400 ppm are considered as class B whereas the ones with no toxic effects at that concentration are considered as class 'A' refrigerants. The combination of these factors account for the safety of usage and need to be considered while choosing any refrigerant. (Domanski, 1998.)

Most of the refrigerants used are based on chlorofluorocarbon (CFC) or hydro chlorofluorocarbon (HCFC). However, due to their ozone layer depletion effects, the CFCs and HCFCs, along with other refrigerants based on halons, methyl bromide, carbon tetrachloride and methyl chloroform are being phased out of industrial and commercial usage by 2020 as per the Montreal Protocol. Some of the environment friendly alternatives are listed in (Domanski, 1998.)

Table 1 below. The hydrocarbons are particularly adept for this application because of their immiscibility and inert behavior towards contaminants generally found in wastewater. Hence they are a viable option for a liquid refrigerant based direct or indirect cooling system. (Domanski, 1998.)

Table 1. Classification of natural compound based refrigerants (Classification of Refrigerants mod., 2017).

Classification	Base compound	Composition or chemical formula	Safety class
Inorganic compound			
R717	ammonia	NH_3	B2
R718	water	H_2O	A1
R744	carbon dioxide	CO_2	A1
Organic compound			
Hydrocarbons			
R170	ethane	CH_3CH_3	A3
R290	propane	$CH_3CH_2CH_3$	A3
R600a	isobutane	$CH(CH_3)_2CH_3$	A3
Hydrofluorocarbons (HFCs)			
R32	difluoromethane	CH_2F_2	A2
R125	pentafluoroethane	CHF_2CF_3	A1
R134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3	A1
R143a	1,1,1-trifluoroethane	CH_3CF_3	A2
R152a	1,1-difluoroethane	CH_3CHF_2	A2

However, it must be noted that using a liquid refrigerant demands proper safety precautions which might require expensive equipment and laboratory infrastructure. In case of indirect cooling, liquid refrigerants are the only option although since the coolant cycle can be maintained independent from the flow of the wastewater, the maintenance is simpler. In case of direct cooling, the crystallizer design is more complex as it has to facilitate the mixing of the liquid refrigerant with the wastewater and then proper channeling of the vapor coolant back to its refrigeration cycle. Here, it should be noted that such a process can be complex and expensive. Therefore, in order to conduct preliminary tests on functionality and performance of direct contact freezing, using cold air as a coolant is a low maintenance and safer alternative. (Domanski, 1998.)

Once the type of cooling, nucleation technique and the type of refrigerant to be used are finalized, the next step is to identify the functional requirements of the pilot plant.

2.5. Pilot plant: Design requirements and process flow

Once the freezing technique and coolant are finalized, before moving on, it is important to lay down the list of tasks that the design should perform. Based on the design criteria, the variables related to the process flow can be properly defined. Some of the key design requirements to be defined before designing pilot plant are:

- Production rate: The production rate will define the capacity of the plant along with other factors like sizing of individual equipment, overall plant size and costs related to initial set up and logistics. Although, the production rate for a plant might vary largely (largest plant produces up to 1.57 million liters per hour fresh water output), for a pilot plant it is suitable to keep that value to a minimum for convenience (10 to 100 l/hour). Once the parameters and process flow is established, the model can be scaled up to the required capacity. (Steinhoff et al, 1960.)
- Purification level: The purification level of the output liquid needs to be predefined based on the application. For potable water, the purity level required is approximately 99.9% whereas for industrial reuse, the purification level can be anywhere above 95% depending on the type of industry. Based on the purity level, the residence time (R) for the crystallizer and the separator needs to be calculated which would directly affecting the size and dimensioning of those components.
- Type of wastewater: Depending on the type of source, wastewater might contain organic, inorganic or microbial contaminants. Crystallization has been used for constituents like NaCl (Common salt/seawater), Na_2SO_4 (Sodium Sulphate), Na_2CO_3 (Sodium carbonate), ammonium, phosphates, heavy metals (Pb2+, Mn2+, Ni2+,Cu2+, Ag+, etc.) and softening of water by removal of calcium and magnesium ions (Lu et al., 2017) . However, material selection for the components (heat exchangers, pumps, crystallizer, separator, etc) and piping needs to be considered based on the composition of the wastewater.
- Size and Dimensions: The overall size or space for the plant depends on its functionality. In case of large scale discontinuous production, fixed installation factory sized unit are more adept. On the other hand, for a continuous mobile unit with low production rate, the space required for the entire system is comparatively quite small. The objective of making the process of freezing and purification continuous is to ensure that the device can be built as a mobile unit and not a single installation factory sized unit. For ease of transportability

across different modes like ship, railways and roadways, the entire system is desired to be designed to fit an intermodal container which has a ISO standard dimension of 40’ x 8’ x 8’ (12 meters x 2,4 meters x 2,4 meters) for international mobility containers (Pat. US 5816423A 1998, p.2). This can be considered as the maximum size possible to consider the solution as mobile. For a container of these dimensions, the actual foot print or useable volume will have a length of 12.032 m, width of 2.352 m and height of 2.385 m respectively. Figure 15 below shows a typical intermodal container used for international transportation as per ISO standards. Presets

Figure 15. Typical intermodal container

Once the requirements of the pilot plant are clear, the process flow can be devised. Typically a freeze crystallization process incorporates ice nucleation and crystallization, ice crystal separation, ice washing, and melting units as well. The overall process flow does not vary much irrespective or the type of cooling(direct / indirect) Figure 16 presents a schematic process flow for direct contact freezing system.

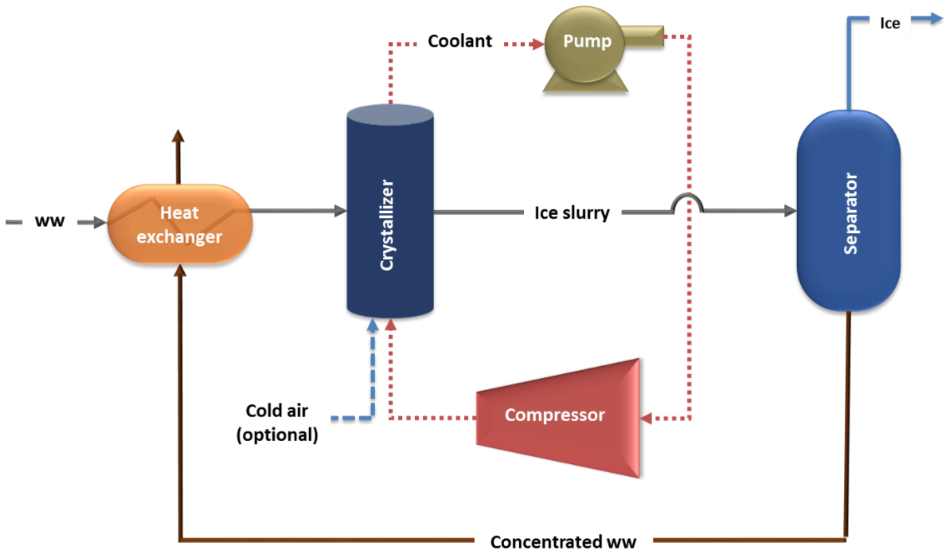


Figure 16. Direct contact freeze crystallization method.

In direct contact freezing, Wastewater is initially precooled by exchanging heat with the formed ice. Pre-cooled ww is then super cooled by direct contact with the coolant/refrigerant, which is then pumped, compressed and recycled. Cold air can be used as an alternative to coolant in which case the refrigerant cycle can be eliminated. Ice nucleation takes place in the crystallizer due to the super cooling of ww. Ice crystals are then retained in the ice crystallizer to achieve the desired crystal size and then separated from the concentrated ww. Ice crystals might be washed to remove the adherent liquid from the crystal surface if the required purification level is not obtained.

The same process flow is applicable for indirect cooling as well only with minor changes. Here no intimate mixing takes place between the refrigerant/coolant and the product to be frozen. Instead, the refrigerant is circulated in a jacketed column crystallizer and it transfers the heat via conduction through the walls of the crystallizer. Ice scale forms on the inner surface and is scrapped with the use of a scrapper and the slurry goes into the separator for the final step.

The process flow needs to be optimized based on the type of freezing, coolant used and the design requirement of the plant. The process flow helps is establish the correlation and arrangement of the different equipment in the plant. Once the process flow is understood the next step is to calculate the energy requirements for each individual part of the process based on which the sizing and structural design parameters could be defined.

2.6. Energy calculation: Heat exchanging and refrigeration cycle

The first part of the process flow cycle can be identified to be the heat exchanging cycle. In most cases, the temperature at the wastewater source can be much higher than its freezing point, hence requiring some form of precooling to speed up the process. This is performed by using heat exchangers. The process also helps in utilizing the cold energy stored in the system (in the form of cold concentrated brine and/or pure water). Figure 17 shows a simple heat exchange where cold energy from concentrated brine is used to precool input wastewater.

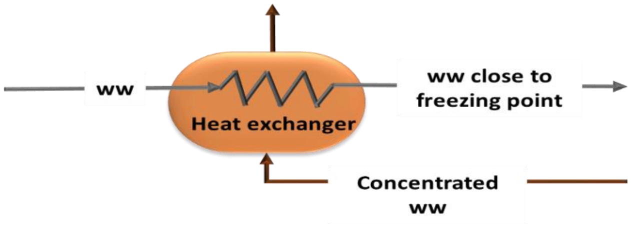


Figure 17. General heat exchanging cycle

In order to completely avoid usage of any external energy, the cold energy required for the precooling will be provided by the output of the system itself which can be calculated as:

$$P = mCp\Delta T \tag{1}$$

Where m is mass, C_p is specific heat in constant pressure and ΔT in the desired change in temperature. Therefore, if power 'P' is equivalent to the required energy, the energy of the system is conserved.

Now, the size and specific type of heat exchanger can be derived from the formula:

$$Q = UA\Delta T_{LMTD} \tag{2}$$

Where Q is the heat transfer rate, U is the overall heat transfer coefficient, A is the heat transfer area and ΔT_{LMTD} is the log-mean temperature difference. The heat transfer Q is equal to the power P derived from equation (1). The log mean temperature difference for counter current flow can be generalized as:

$$\Delta T_{LMTD} = \frac{(\Delta T1 - \Delta T2)}{\ln({}^{\Delta T1}/_{\Delta T2})} \tag{3}$$

Where $\Delta T1$ and $\Delta T2$ are the desired change in temperature for each of the two liquids passing through the heat exchanger respectively. The next unknown factor is the overall heat transfer coefficient U. A wide range of values can be considered for U based on phase of the fluids involved in the heat exchange. Similarly, based on the fluid combination (both gases, gas and liquid or both liquid), the suitable type of heat exchanger can be identified. It should be noted here that for any generalized heat exchanger application in the precooling process which involves heat absorption from concentrated brine and /or purified water will most probably involve 'liquid to liquid' fluid pair. Therefore, in Table 2 the suitable types of heat exchangers, namely plate heat exchangers and spiral heat exchangers are listed with their pre-established range of values for overall heat transfer coefficient respectively.

Table 2. Overall Heat transfer coefficient for liquid to liquid heat exchangers (Overall heat transfer table mod., 2017)

Types	Application	Overall heat transfer coefficient 'U'	
		W/m^{2}K	Btu/ft^2 °Fh
Plate heat exchangers	Liquid to liquid	1000-4000	150-700
Spiral heat exchangers	Liquid to liquid	700-2500	125-500

Now from equation (2) the area required for the heat transfer can be determined which for a plate and shell heat exchanger, is equal to the product of the surface area and number of plates. So if the height and width of the plates are denoted by 'h' and 'b' respectively and 'n' denotes the number of plates, then n, the area of heat transfer coefficient is given by:

$$A = h \cdot b \cdot n \qquad (4)$$

Once these values are determined, manufacturers can be approached for custom built plate heat exchangers as per requirements.

Apart from the heat exchanging cycle, the second part of the freeze crystallization process is the cooling/refrigeration cycle. For simple systems using cold air for freezing purpose, an open loop refrigeration cycle can be used since compressed cold air can be generated independently and fed into the crystallizer and the outlet air can be simply released into the atmosphere without any safety related concern. On the other hand, for a liquid refrigerant, a complete closed loop refrigeration system is a prerequisite. Ideally, a single stage refrigeration cycle consists of four stages: compression, condensation expansion and evaporation as shown in Figure 18.

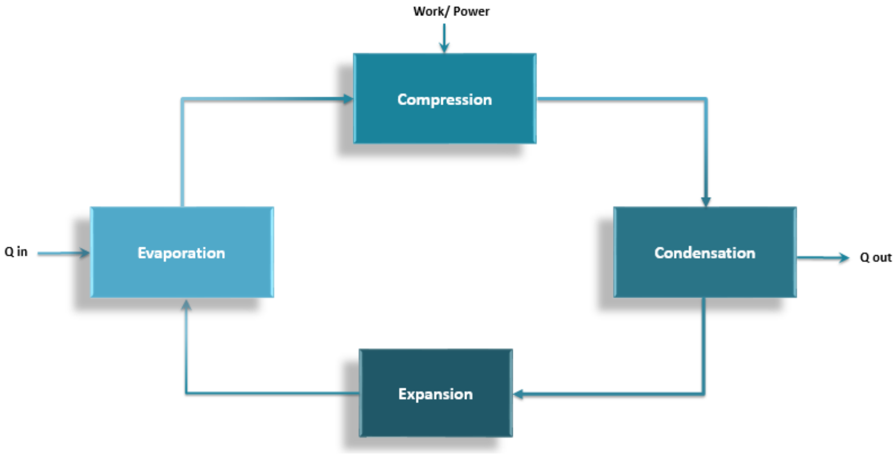


Figure 18. Ideal single stage refrigeration cycle

In case of indirect contact freezing, the refrigeration cycle is quite similar to the ideal one. As shown in Figure 18, the liquid refrigerant is maintained at a fixed temperature in a closed loop and the heat is extracted from the wastewater by passing the coolant through the outer layer of a jacketed column crystallizer. However, in case of direct contact freeze crystallization, the refrigeration cycle is slightly modified. Here, the evaporation step occur in the crystallizer whereas the part of the condensation is also utilized for melting the ice and forming pure water. Therefore, any general refrigeration unit using liquid refrigerant can be probably modified to produce the required amount of refrigeration power to fit in as the refrigeration cycle for such a system. For this, firstly the required power for the refrigeration unit to maintain the pre-established production rate has to be determined. Then the evaporation and expansion step could be replaced by the crystallizer (Figure 19).

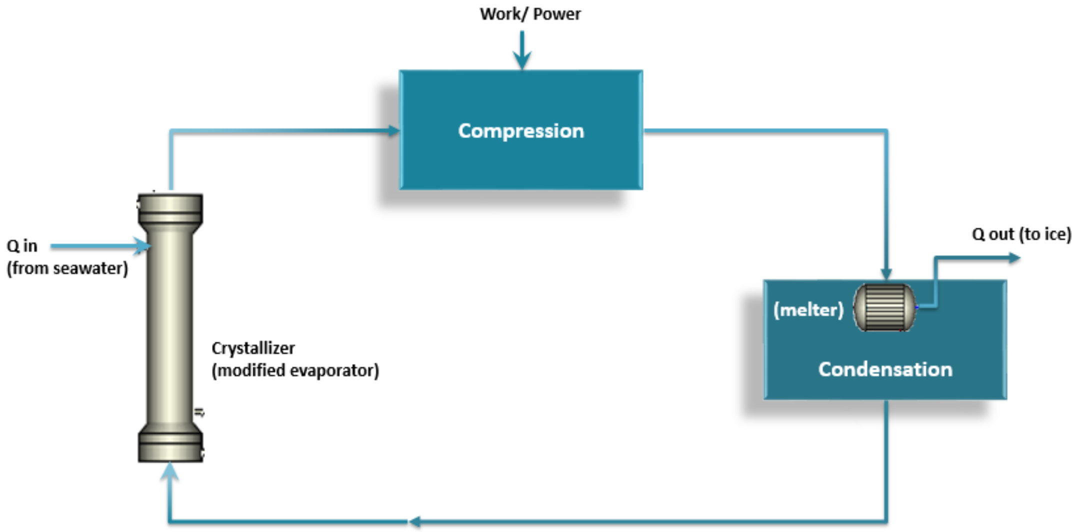


Figure 19. Modified single stage refrigeration cycle

For a cold air based system the refrigeration cycle is open loop as air from the crystallizer can be directly released into the atmosphere. The only energy required is for the compressor to high pressure air which can be cooled by using vortex tube technology. In vortex pipe, compressed air is introduced at around 5-7 bars into a spin chamber where the air revolves toward the hot end. Some of the air escapes through a control valve as hot air while the rest bounce back forming another smaller vortex and coming out of the other end as cold air. These units work without any external energy and commercially optimized units can generate temperature ranging from -50 °C at the cold side to 127 °C at the hot side of the tube. (Behera et al., 2005.)

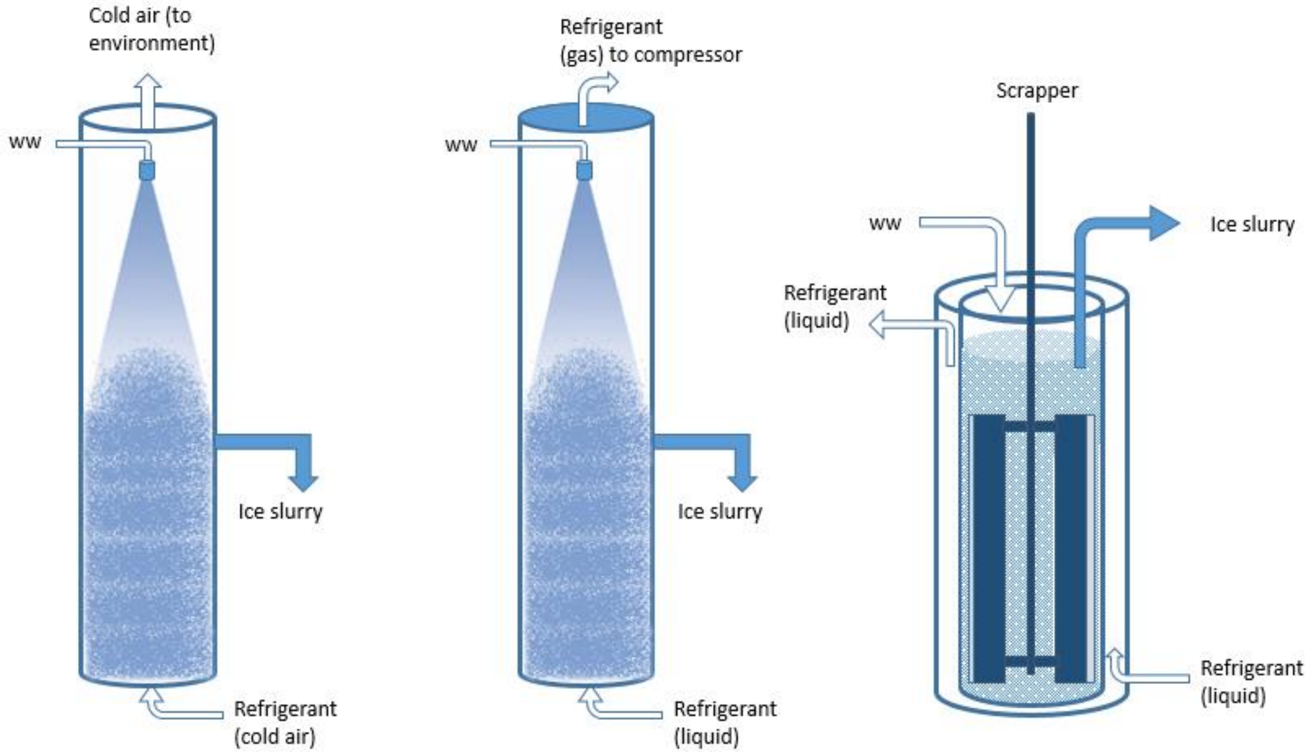
The behavior and power requirement of the refrigeration cycle can be approximated by simulating the conditions in a thermodynamic simulation software named Aspen Tech. The coolant type, pressure of the coolant and the rate of production are primarily required as input determining the power requirement of the refrigeration unit. Once the required power is estimated, manufacturers of refrigeration unit can be approached with the idea of designing a refrigeration cycle as per requirement.

2.7. Design of primary components

The two primary components in the process are the crystallizer and the separator and this topic deals with some generalized guidelines in designing these two components.

2.7.1. Crystallizer

The crystallizer is ideally a column where the ice slurry (mixer of ice and unfrozen concentrated wastewater) is formed. Its design is largely dependent on the freeze crystallization process that is employed. As shown in Figure 14 of section 3.2, direct cooling process requires a single cylindrical column whereas indirect cooling requires a jacketed column and a scrapper arrangement. Figure 20 below shows schematic diagrams for direct cooling using cold air, direct cooling using liquid refrigerants and indirect cooling.



(a) (b) (c)

Figure 20. (a) DCF using cold air (b) DCF using liquid refrigerant (c) Indirect freezing

Typically the air cooled direct contact freezing system are simplest because of minimal safety concern even though there is the innate drawback of low rate of heat transfer when compared to liquid coolants. The cold air can be simply released into the environment whereas in case (b), the vapor refrigerant has to be carefully guided back to the compressor (or a filter in some cases). The column used for direct cooling are usually tall and cylindrical in shape driven by the formula:

$$H/_{ID} = 10 \quad (5)$$

Where *'H'* is the height and *ID* is the inner diameter (Erlbeck et al., 2017). The wastewater can be introduced simply from the top or through a spray nozzle for accelerated cooling while the cold air/ refrigerant is introduced from a single point/ multiple points from the bottom of the chamber. The cylindrical volume from the base to the ice slurry extraction point determines the residence time *(R)* of the solution. Residence time can be simply controlled by controlling the inflow of wastewater depending on the ice formation rate. The higher the heat transfer coefficient *(U)* for the refrigerant, the smaller is the residence time and hence the smaller is the required volume. Furthermore the residence time directly controls the size of the ice crystals which in turn controls the purity level (Söhnel and Mullin, 1988). Once the residence time is determined, the ice slurry exit point can be located. Considering the safety factor and volume required for coolant and ice hold up, the entire volume of the cylinder is simply doubled. The wastewater inlet and ice slurry outlet are of the similar diameter while the refrigerant inlet is considerably smaller for maintaining high pressure. The material for the column is usually some form of transparent plastic material (PMMA, PE, lucite etc) whereas the base can be made of harder plastic like PVC or Teflon. (Steinhoff et al, 1960)

On the other hand, in case of indirect freezing the crystallizer is usually a two layered jacketed column where the coolant is passed through the outer layer and wastewater is poured into the inner chamber. Dimensionally, the crystallizer in this case can be quite shorter than the one used in DCF because firstly, here no spraying is required and secondly the ice is formed at the inner surface of the column which is then scrapped and pumped out constantly. Hence the resident time is controlled by the flow rates of the pumps alone and not by the size of the chamber. In terms of material selection, the cylindrical column is generally made of variables grades of stainless steel for ease of heat exchange. The scrapper blades are designed to exert adequate normal force on the inner surface of the heat exchanger to remove the ice layer. However, for wear prevention on the surface of the container, softer material (high density plastics) like high modulus poly ethylene (HMPE) are considered to be suitable. The refrigerant cycle is controlled externally to maintain the coolant at a fixed low temperature. (Rodriguez Pascual et al., 2010.)

2.7.2. Separator

Next in design is the second stage of freeze crystallization or the separator. The working mechanism for the separator is relatively simple and the design parameters are the same for both direct and indirect freezing. The separation of ice from brine can be achieved either with the help of gravitation or by introducing a wash down mechanism. Figure 19 shows schematic diagrams for both. In both the cases, the ice and brine slurry from the crystallizer can be introduced from the bottom of the separator. In gravitational separation, an outlet for the concentrated brine is located along the wall of the tube or as a filter to an inner tube. Different position of the tube gives different purification levels. Once the brine is filtered out, from that point upwards the ice keeps piling up due to continuous inlet of slurry. The remaining brine from the ice at the top drains down due to gravity leaving purified ice at the top. In some cases, a percentage of pure water (approximately 5%) is used to further wash down the piled up ice, hence increasing its purity level. Once the ice is collected at the top, it is channeled out using a rotating conveyor mechanism and then collected in a melter. (Adeniyil et al., 2013.)

2.8. Auxiliary components

Apart from the primary components, a number of auxiliary parts are required from the basic mechanical aspect of the plant.

- Heat exchanging cycle
  - Reservoir tank(s) for wastewater storage as input to the system and precooled wastewater (capacity dependent on production requirements).
  - Heat exchanger(s) to utilize the cold energy from brine and/or fresh water output to precool the input wastewater. Preferably shell and plate or spiral heat exchanger for better liquid to liquid heat transfer (size and energy calculation dependent on processing capacity or production rate).
  - Minimum 2 - 3 basic centrifugal pumps (one for transferring wastewater from storage tank to precooling units, one from for transferring liquid from precooling units to tank and one more for transferring from tank to crystallizer). The number of pump required will be more depending on the number of heat exchangers used. (Size and energy calculation dependent on processing capacity or production rate).
  - Pipes and fittings
  - A secondary external heat exchanging system (can be an indirect cooling unit) to kick start the process.
- Modified single stage refrigeration cycle

- One Compressor. It can be gas compressor for cooling by cold air. For compressing liquid refrigerants, hydraulic compressor is a viable option.
- One plate and tube heat exchanger integrated in the refrigeration cycle as the melter to use up the heat from compressed refrigerant to melt and mobilize the ice gathered from the separator.
- Vortex tube (only for systems using cold air as refrigerant).
- One ice slurry pump (from crystallizer to separator), three centrifugal pump (Brine from separator to heat exchanger/ outlet, pure water from melter to heat exchanger/ outlet) and one low temperature operational pump (to transfer liquid refrigerant back to crystallizer).
- Pipes and fittings.

3 CASE STUDY FOR DIRECT AIR COOLING SYSTEM

This chapter deals with the development of a freeze crystallization system based on direct cooling by air. The different methodologies listed in the earlier chapter are studied and based on a step by step selection of method for each individual stage of the design, the direct cooling case has been developed. As discussed in the previous chapter, some of the parameters are required to be predefined in order to design and optimize the system accordingly. (Domanski, 1998.)

Table 3 shows the design requirements and predefined parameters set for this specific case study.

Table 3. Design requirements for case study of direct air cooling system

Design Parameters	Presets
Production rate	10 kg Ice per hour
Method of nucleation	Primary homogeneous nucleation
Method of crystallization (FC)	Direct contact freezing (DCF)
Coolant used	Cold air
Purity level	minimum above 95%
Wastewater	NaCl / Na_2SO_4 solution at varied concentration (maximum up to 3.5% w/w representing seawater)
Process flow type and mobility	Continuous process and mobile unit
Maximum dimension for pilot plant	Intermodular container (12 meters x 2,4 meters x 2,4 meters)

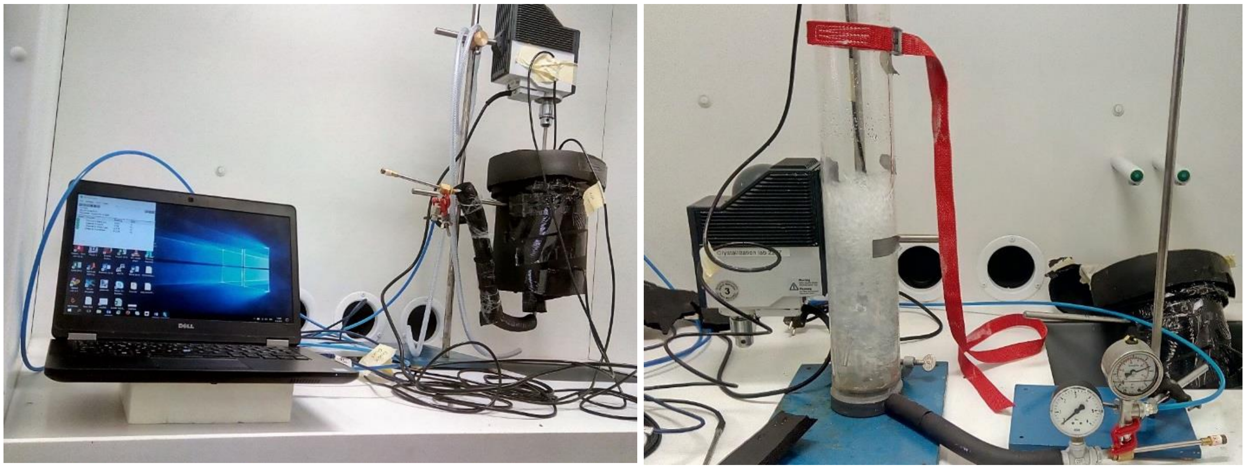
The production rate is chosen to be 10 kg/ hour for ease of experimentation. Once the functionality of the plant is verified and validated, it can be scaled up as per higher production requirements. Similarly, primary homogeneous nucleation is chosen for the pilot plant to avoid the complication of constantly inserting ice seeds in the solution in the crystallizer. For the process of freeze crystallization, direct contact freezing has been chosen for the purpose of experimentation and learning because there are only a few concrete and successful application of this particular type of cooling available in the literature. Considering the practicality of the process, it is a fair assumption that the freeze crystallization unit will find its suitable application as a first level purification system of a multilevel purification unit. Therefore, the output water is required to be least pure enough for industrial reuse or direct feed to a secondary filtration system. The wastewater type was chosen as sodium chloride (NaCl) or sodium sulphate (Na_2SO_4) solution for ease of availability and experimentation. Wastewater from nearby industries could be also used based on availability. Other than that, the mobility aspect of the pilot plant demands that the process flow should be continuous and there is a limitation of size to facilitate ease of transportability.

3.1. Preliminary laboratory experiments

Once the design requirements were finalized, the next step is to understand the primary components and process flow before moving onto pilot plant design. Therefore, preliminary laboratory tests are conducted to understand the working principle of the crystallizer and separator and understand its real time based problems and requirements. For ease of experimentation, simplicity of design and safety concerns, the initial tests are performed using cold air as a coolant in the winter simulation laboratory of the chemical department of Lappeenranta University of Technology. Based on the situation and complexity of experiments, the tests for the crystallizer were divided into three phases whereas the separator was tested in a single phase.

3.2. Conceptual testing for direct cooled crystallizer

DCF based tests have been conducted to understand the working principle of the crystallizer. In order to perform tests, a couple of different crystallizers were used as shown in Figure 21.



(a) (b)

Figure 21. Types of crystallizer (a) 1 l Stainless Steel column (b) 2.5 l PMMA column

During the first phase of the study, most of the experiments are conducted using the stainless steel AISI 316 column as the crystallizer. Apart from that, a vortex pipe is used to generate cold air which is used for the cooling purpose. Four temperature sensors connected to a PT-104 Pico log unit are monitored using a laptop for temperature readings. Cold air at subzero temperature is used as refrigerant for these tests and all the equipment involved are insulated using regular Styrofoam.

3.2.1. Phase 1

The initial experimental runs are conducted in the steel crystallizer. The following parameters are identified to control the setup:

- Pressure – A couple of pressure gauges are installed, one for the air flow into the entire system and one for the cold air flow. The maximum available pressure is 6 bars.
- Flow rate – A flow meter is introduced to gauge the flow for different pressure readings.
- Nozzle design –To determine the optimum way of distributing the cold air into the chamber, different variety of nozzles are used. The outlet diameter of each nozzle is different facilitating individual bubble size for each nozzle. The experiments are going to help in understanding the rate of cooling, ice formation and the maximum cooling achievable for each individual type of nozzle fora given value pressure. For the first phase of experiments on the crystallizer, experiments are conducted using a metallic sintered nozzle and a fritted disc shown in Figure 22.

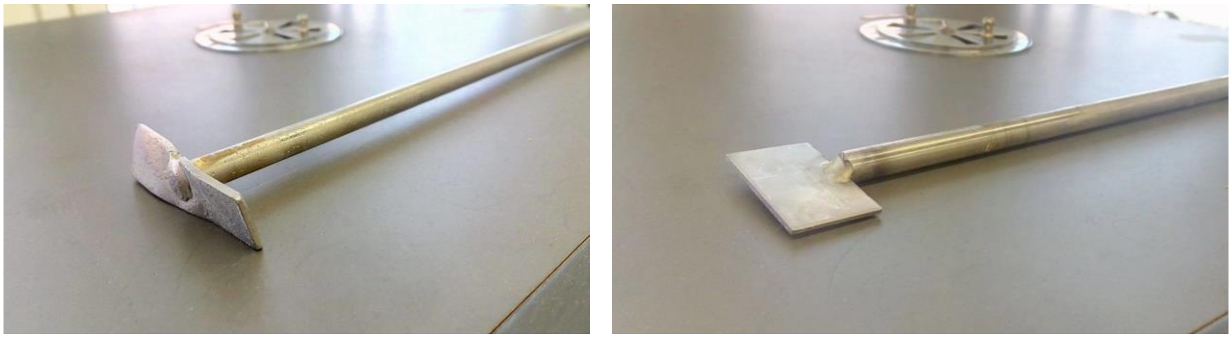
(a) (b) (c)

Figure 22. (a)Sintered metallic nozzle (b) Sintered nozzle extended by 25mm (c) Fritted disc nozzle

While using the sintered metallic nozzle, the exposure of the nozzle to the solution in the chamber is also changed. Initially, the nozzle is located at the base of the chamber as shown in Figure 22(a).

Later on, it was brought higher by 25mm into an extended position where more of the nozzle is exposed to the liquid (Figure 22(b)). The fritted disc nozzle is a part of a chemical gas washing equipment which is inserted from the top of the chamber. As shown in Figure 22(c), the cold air enters through the glass pipe shown by the yellow arrow and then spreads into the solution via the micro holes in the fritted disc present at the bottom.

- Mixing – In case of a single inlet, there were concerns related to the size of the air bubbles and inadequate mixing or distribution of the cold energy. In order to facilitate proper mixing, two different types of stirrer, axial (a) and radial (b) stirrer shown in Figure 23 are tested individually in combination with a single inlet nozzle.



(a) (b)

Figure 23. (a) Axial stirrer (b) Radial stirrer

For experimental purpose, three different types of solution are used: pure water, dilute sodium sulphate solution (1.5 % v/v Na_2SO_4) and actual wastewater procured from a Finnish company named J. M. Huber. The first runs were performed with the fritted disc arrangement and the results are shown in the results chapter in Table 4.

Table 4. Results from fritted disc nozzle arrangement of crystallizer

Dispersion type	Solution	Air pressure (bars)	precooling time	Pre cooled temperature (°C)	Ice formation	freezing time	Type of ice
Fritted disc	Pure water	3.5 - 4	31 mins	-6.5	Yes	112 mins	Hard ice clustered at POD
	Na_2SO_3 (1.5%v/v)	3.5 - 4	31 mins	-6.5	Yes	85 mins	Soft Ice at POD and in the solution
	Wastewater from J.M. Huber	3.5 - 4	30 mins	-6.5	Yes	60 mins	Soft ice formed at PO in the solution

For each of the different solution sample, almost all of the ice was formed at the dispersion point due to the exposed surface area provided by the glass rod. Although the ice grew softer with higher impurity, the ice was still quite irretrievable as shown in Figure 24.


(a) (b) (c)

Figure 24. Ice formation (a) Hard cluster with pure water (b) Soft cluster with sodium sulphate solution (c) Some ice in the solution with wastewater sample from J.M. Huber.

Next, the steel nozzle is considered for spraying the cold air. First the sintered nozzle is located at the base. After that, it is extended into the solution by 25 mm and then the nozzle is relocated to the base and stirrer is introduced for better mixing. The results are summarized in the results chapter in Table 5.

Table 5. Results from sintered nozzle arrangement of crystallizer

Dispersion type	Solution	Air pressure (bars)	precooling time	Pre-cooled temperature (°C)	Ice formation	freezing time	Type of ice
Steel Nozzle (sintered) located at base	Pure water	3.5-4	25 mins	-11	No	-	No ice
	Na_2SO_4 (1.5%v/v)	3.5-4	45 mins	-7	Yes	65 mins	Soft ice at POD
	J.M. Huber	3.5-4	41 mins	-7	Yes	85 mins	Soft ice at POD
Steel Nozzle (sintered) extended by 25 mm	Na_2SO_4 (1.5%v/v)	3.5-4	52 mins	-6.5	Yes	45mins	Soft ice at POD
Sintered nozzle at base with stirrer	Pure water	3.5-4	20 mins	-3	Yes	115 mins	Hard Ice block
	Na_2So_4 (1.5%v/v)	3.5-4	24 mins	-3.5	Yes	60 mins	Hard ice at POD
	Wastewater from J.M. Huber	3.5-4	21 mins	-3	Yes	30 mins	Ice slurry

As the remarks under ‘type of ice’ suggests, most of the ice formation occurred at the point of dispersion, especially without the stirrer and for the extended nozzle case. However, by using a radial stirrer for the sintered nozzle at the base, a significant amount of ice slurry was created for the wastewater sample. The 300 ml of wastewater solution was converted into ice slurry in an overall time period of approximately one hour (Figure 25).

Figure 25. Ice slurry formation with radial stirrer and sintered nozzle arrangement

The results obtained from the final tests of this phase was positive. However, a couple of problems emerged from the test:

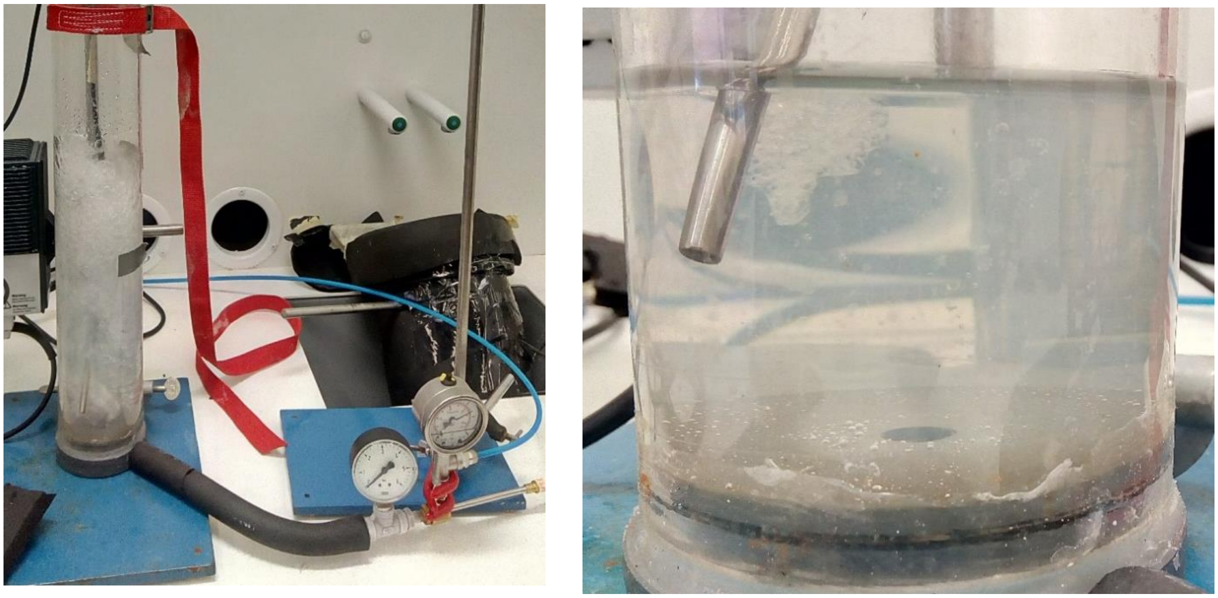
- There was still some amount of ice formation at the point of dispersion which slowed down the entire process by reducing the amount of air flowing into the chamber with time.
- The radial stirrer was also acting a scrapping device to skim off the ice formed at the base and form the slurry. This procedure was undesirable as it caused additional energy loss and instability due to vibration in the system.

3.2.2. Phase 2

For phase two of the experimental study, the following objectives are predefined based on the results from phase 1:

- To achieve faster cooling
- To find out a way to prevent the formation of ice cluster at the point of dispersion.

In the previous setup, a large amount of cold energy was absorbed by the crystallizer as it was made of steel which has a thermal conductivity of 50 W/mK. In order to achieve faster cooling by reducing the heat loss, a tall column made of low density polyethylene (thermal conductivity of 0.33 W/mK) is used as the crystallizer this time. Figure 26 shows the experiment being performed in the plastic crystallizer. For most of the experiments, the cold air is passed into the solution through the single inlet point at the base as shown in Figure 26 (b). Furthermore, in order to achieve more realistic results, sodium sulphate solution of 2 – 2.5 % v/v concentration was used in this case.



(a) (b)

Figure 26. (a) Polyethylene tall column used as crystallizer (b) Polyethylene base part with single inlet point of dispersion

a) Induction time

For the initial runs performed with this setup, the cooling rates obtained were better than the steel chamber. Some of the data related to the tests are:

- Precooling temperature: on an average, it took approximately 15 - 20 minutes to achieve a temperature of -7 °C inside the crystallizer before pouring the solution.
- Ice formation took approximately 30 mins in most cases with pure water or 2 – 2.5 % v/v sodium Sulphate solution.

However, the problem of ice growth at the point of dispersion persisted as shown in Figure 27.


(a) (b)

Figure 27. Ice formation at point of dispersion for (a) Pure water (b) Sodium sulphate solution

The small amount of ice blocked the passage of cold air, hence preventing the cooling of the entire solution and hampering the ice generation process. Based on the experiments, it was learned that the bottom plate was cooling down faster than the solution or the wall of the column and the plate was conducting cold energy to the solution. This is typical in any type of indirect freezing system. Even though super cooling of the solution is achieved at first and ice forms in the solution, eventually ice layer will form in the cold plate after a while. The time required to form ice scale on the cold surface is known as induction time. The longer the induction time is, the longer ice-scale free operation is obtained.

b) Insulation

In order to increase the induction time, the conduction of the cold energy from the bottom plate (indirect cooling) had to be restricted as much as possible such that the only source for cooling the solution is the cold air. To achieve that, a layer of insulation was added on top of the base plate. The insulation layer consisted of a layer of polystyrene (styrofoam with thermal conductivity of 0.003 W/mK) and two layers of paraffin wax sheets (thermal conductivity of 0.25 W/mK) as shown in Figure 28.

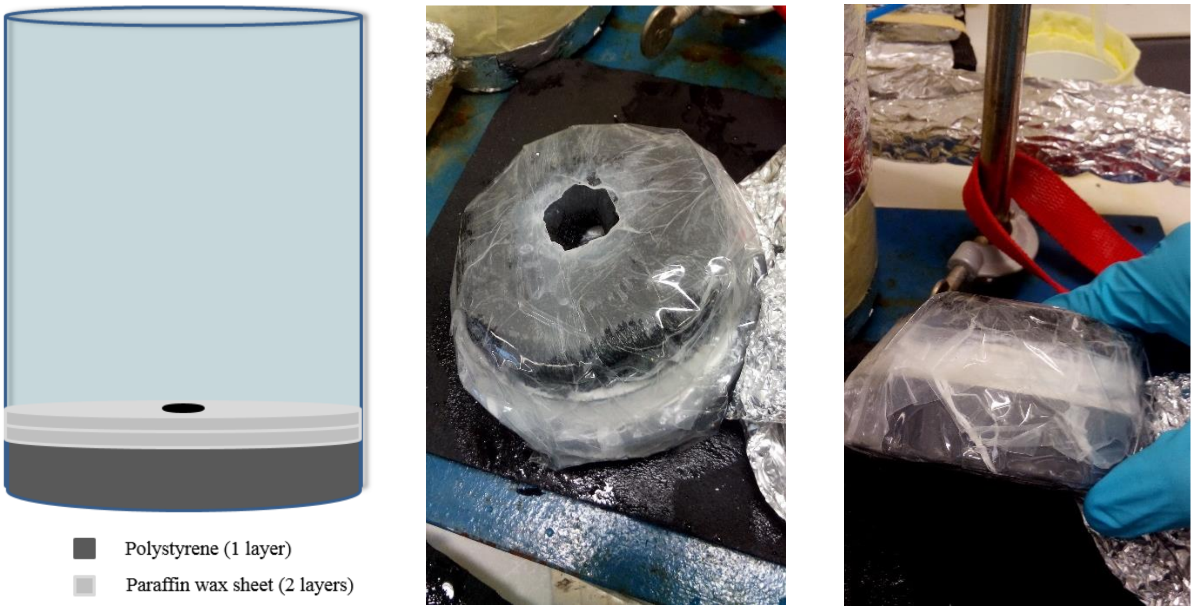
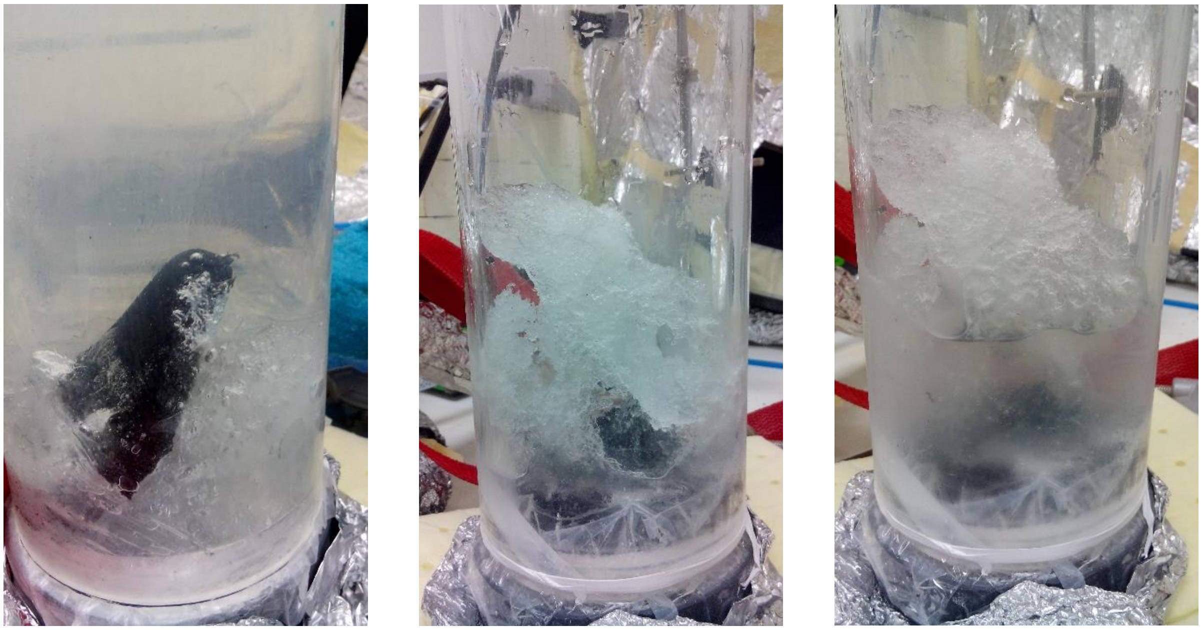


Figure 28. Insulation provided at the base of the crystallizer to increase induction time

With the insulation at the base, further experiments were conducted. The results were not as expected. In most cases, the paraffin layers and the Styrofoam insulation got ruptured as ice formed in and around the layers of insulation (Figure 29(a)). In some cases, structural growth of ice was observed attached to the insulation layer itself as shown in Figure 29(b).



(a) (b) (c)

Figure 29. (a) Ruptured insulation (b) and (c) Ice structures formed above the insulation layer

c) Material Selection and coating

From the above experiments, it was clear that attaching the cut out of insulating substances to the base will not serve the purpose in an actual working plant. However, the study provided some insight for the functional requirements of the crystallizer based on which the material selection can be made. The ice-phobic characteristic of a part depends on the surface roughness and surface energy. The surface energy directly depends upon the stress formed between the layer and the surface of the material and lower the stress, higher is the ice-phobic characteristic. Two of the most prominent commercial products showing high ice-phobic properties are Wearlon and Nussil. The article also mentions viscoelastic rubber and Teflon as suitable material to mitigate stickiness of ice. Any of these materials could be used for the design of the base plate in the crystallizer for the pilot plant. Similarly, higher surface roughness increases the scaling of ice which probably explains the ice formation on top of the Styrofoam layer as the surface was quite rough. The ice-phobic properties can be further improvised by proving some sort of coating on the inner surface of the base plate. Along with a proper surface finish, the usage of oil impregnated polymers and polyurethane (PU) can be considered as a cheaper option for ice phobic coating purposes. (Susoff et al., 2013.)

For experimental purpose, a Teflon base plate was designed in the workshop. An additional layer of Teflon spray was applied before performing experiments for phase 3 as shown in Figure 30.

Figure 30. Teflon base plate with additional teflon spray coating

3.2.3. Phase 3

The main aim of this phase of experimentation is to identify the reason behind low amount of ice formation in the solution. For this purpose, the temperature profile of the liquid is studied along the length of the column based on the hypothesis that the liquid at the top of the column is not getting enough cold energy for the ice to be formed in the solution. Two different probes are used across the length of the column in contact with the solution while another probe is used to record the he temperature of the liquid at input.

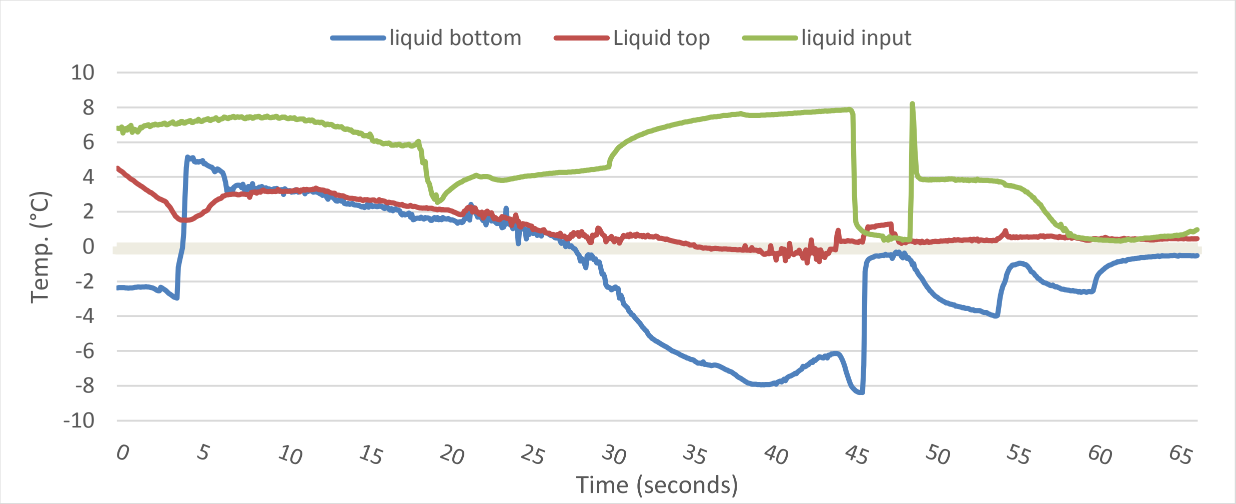


Figure 31. Temperature profile of liquid along the length of the column.

As evident from the graph in Figure 31, the temperatures of the liquid at the bottom and the top vary within a range of 2 to 10 °C. This variation might be the reason behind the fact that no ice is formed in the solution and any ice formed would swiftly melt away because of the high temperature at the top region of the solution.

In order to counter this problem, the solution was circulated from the bottom to the top using a peristaltic pump. The flow rate was depicted by the rpm of the pump. The same experiment was performed for variable speed of pump rotation. Figure 32 and Figure 33 show the temperature profile of the solution at circulation speeds of 20 and 50 rpm respectively.

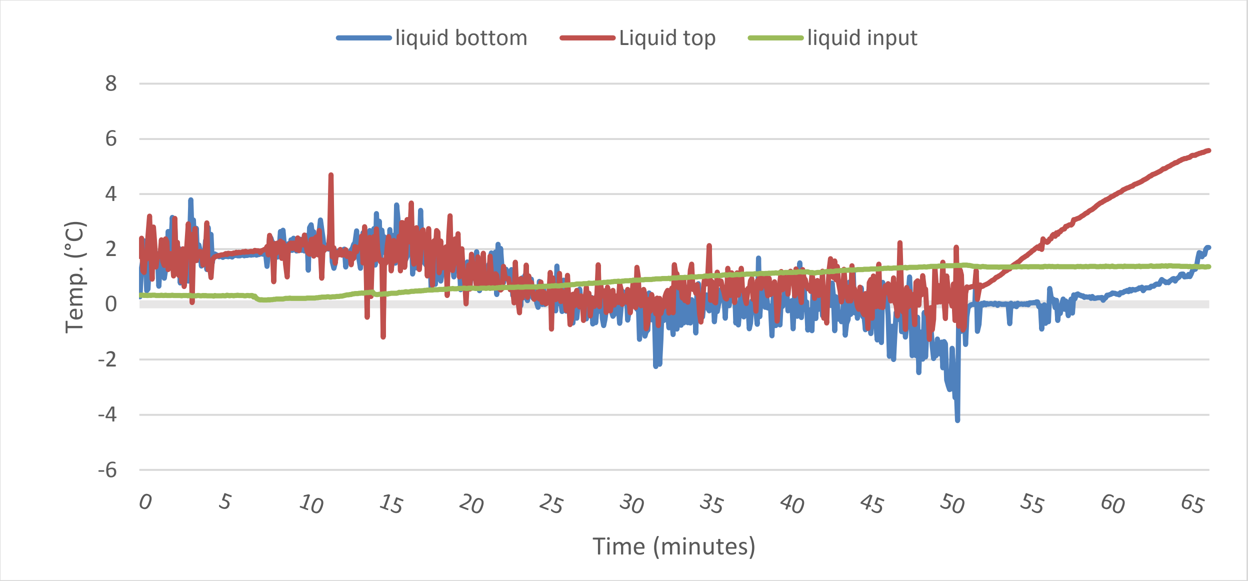


Figure 32. Temperature profile with circulation at 20 rpm

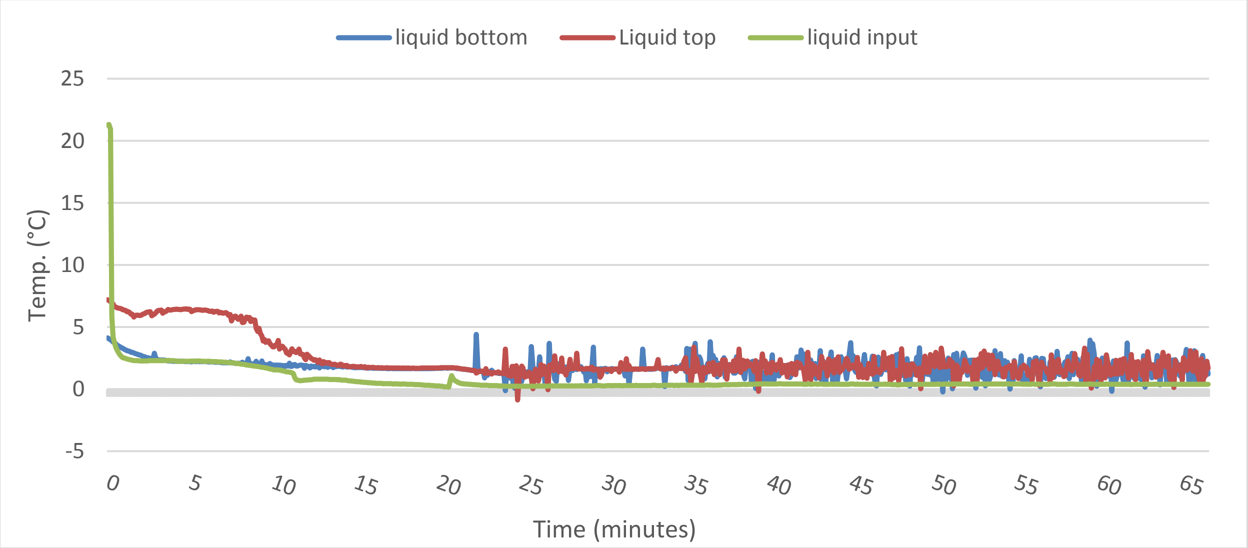


Figure 33. Temperature profile with circulation at 50 rpm

From Figure 32 and Figure 33, it is evident that temperature maintenance throughout the solution can be attained using circulation. The extensive fluctuation in the curves are due to the continuous splashing of liquid inside the crystallizer caused by the high air pressure. However, from Figure 32, at the speed of 50 rpm, the temperature of the solution seemed to remain on the positive (0 to

2 °C). Hence, it might be preferable to keep the circulation speed on the lower side (below 20 rpm).

Another method to speed up the freezing process is by showering technique. Here instead of starting with a stagnant amount of solution, the solution is sprayed from the top of the column through a spraying plate. The small droplets traveling through the length of the tall column exchange energy with the cold air is a much efficient manner. By showering the solution and then following it up with circulation, ice formation has been initiated in as fast as 15 minutes with a precooled chamber at -7.5 °C. However, on continuous cooling for longer period of time, the ice is formed in the shape of a block instead of a slurry. A typical test run combining all these parameters is shown in Table 6 and the results are shown in Figure 34 (b) and (c).

Table 6. Results from a test run including showering followed by circulation for 90 minutes

Solution grade	Precooling		Showering time	Circulation		Ice formation	
	Temperature achieved	Duration		Speed (peristaltic pump)	Duration	Amount	Type
Na_2SO_4 2% v/v	-7.5 °C	10 mins	16 mins	10 rpm	90 mins	28 % of solution	Ice block

However for a limited duration of time, the block formation can be averted and along with an attached layer of ice at the base (mildly attached because of the Teflon base and Styrofoam insulation attached to the base), approximately 10 % of ice can be observed floating in the solution as shown in Figure 34(a). Although it should be noted that some of the ice in that 10% could have actually formed at the point of dispersion and later got released as a small ball of floating ice due to the air pressure at the inlet.

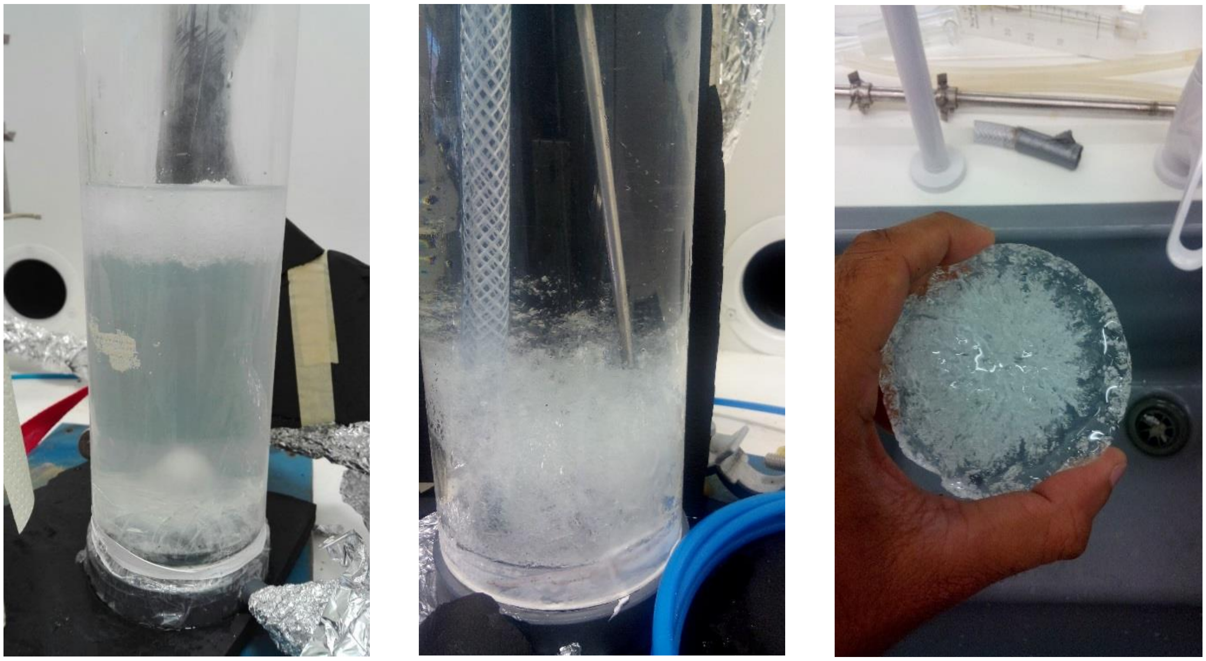

(a) (b) (c)

Figure 34. (a) 10% ice formed in the solution with circulation and showering (b) and (c) Ice block formed in 90 minutes test run

3.3. Conceptual testing for separation

Indirect cooling based tests are performed to study the ice formation through super-cooling and to conduct experimental runs on the separator design. The reasons for using indirectly cooled crystallizer over directly cooled one is simply because operationally it is convenient to pump out the ice slurry from an indirect system. Furthermore, since it is just a preliminary laboratory test (not the actual pilot plant) for the separator, the method used in the crystallizer is not quite relevant here.

An interesting idea for separation has been mentioned in the section 2.2 of the literature review chapter. There, the design and the working principle of the filter and gravity based separation system of HybridICE® HIF filter has been elaborated (Adeniyil et al., 2013). A similar system is built in the laboratory to perform tests related to the separator as shown in Figure 35. In this system, the brine can be filtered and channeled out via one of tubes attached to the side of the column while the ice rises to the top and purification occurs due to gravity.

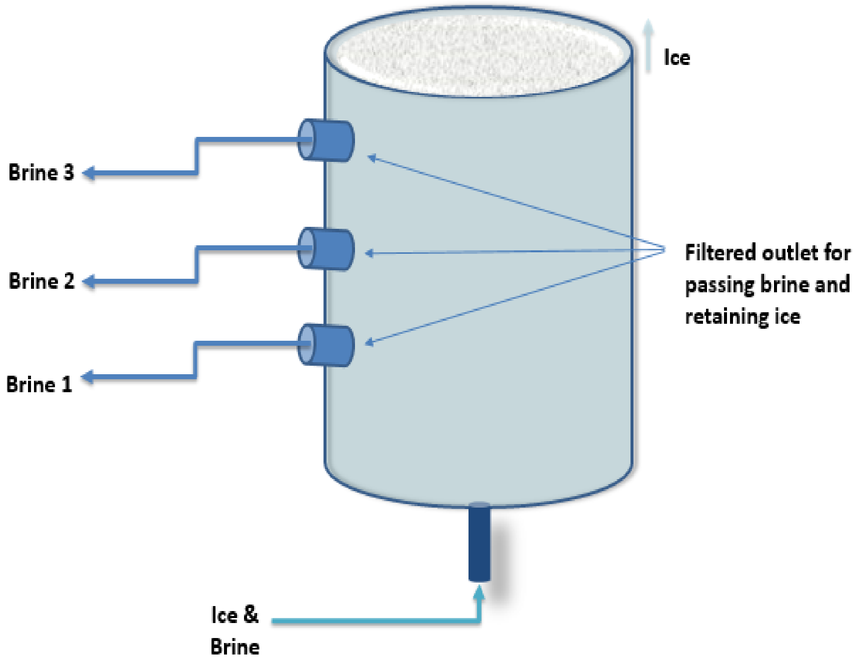
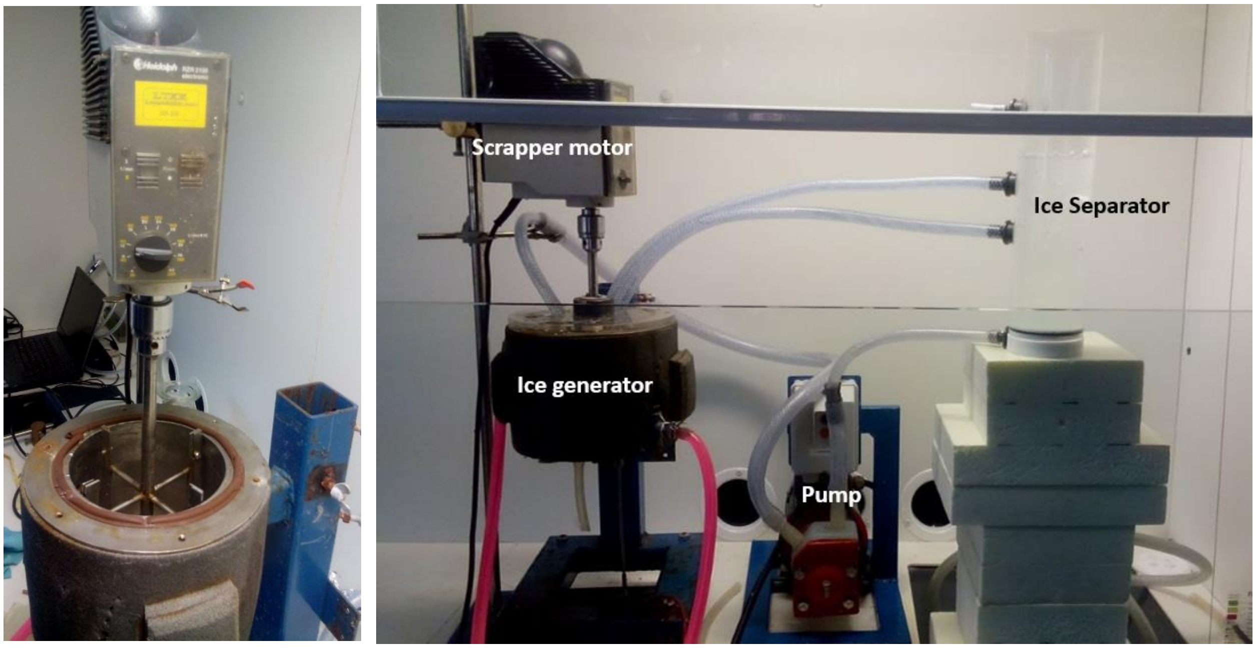


Figure 35. Schematic of ice separator used with indirect cooling system for experimental study.

In a test case, sample sodium sulphate solution of different concentrations (1 % v/v, 2 % v/v and 3% v/v) are used to create super-cooled solution in the indirect cooling system. The system uses ethylene glycol based controlled cooling where the refrigerant was set at a preset temperature of -7 to -5°C. For ease of circulation total 5 liters of solution is prepared and to maintain the continuity during the test, two of the brine outlets are connected back to the ice generator via pipes as shown in Figure 36(b). A centrifugal pump discharging at 7 l/min is used to pump the ice and brine mixture to the separator. The outcome of this experiment are discussed in the result chapter in



(a) (b)

Figure 36. (a) Ice generator for indirect cooling system (b) The separator coupled with ice generator for tests

The test results came positive for sodium solution of 3 % v/v concentration. Ice particles were formed in the solution after super-cooling was achieved at -1.8 °C. The ice slurry created by the scrapper got collected in the separator and brine was recirculated via the outlet tubes. Further testing of the system related to purity level of output ice remains to be conducted. This can be determined by testing the concentration of the brine from each individual outlet as brine at each individual outlet would have different concentration hence establishing different level of purity for the outlet ice.

3.4. Pilot plant specifications

After analyzing the practical aspects of direct contact freezing through simplified air cooled laboratory tests, the process parameters for the crystallizer and the separator are more definable. Next in order to develop the process flow for the pilot plant, the methods mentioned in section 2.5 are utilized which is discussed in the result chapter under section 4.2.

3.4.1. Heat exchanging cycle

Similarly for calculating the energy consumption and modeling the pilot plant, the method inputs from section 2.6 are used. The heat exchanging comprises of the first half of the entire process.

For this process the input water is passed through two individual heat exchangers to absorb the cold energy from the outlet pure water and the brine concentrate as shown. Therefore by precooling the water using the cold energy generated in the system itself, the overall efficiency of the system is improved. Considering seawater as the input with 3.5 % sodium chloride (NaCl) concentration at a temperature of 25 °C, the mass flow and exchange correlated with the change in temperature is shown in Figure 37. It shows how 100 kg/hr of seawater can be cooled from ambient temperature of 25 °C to approximately -2.1 °C (very close/ equal to the freezing temperature).

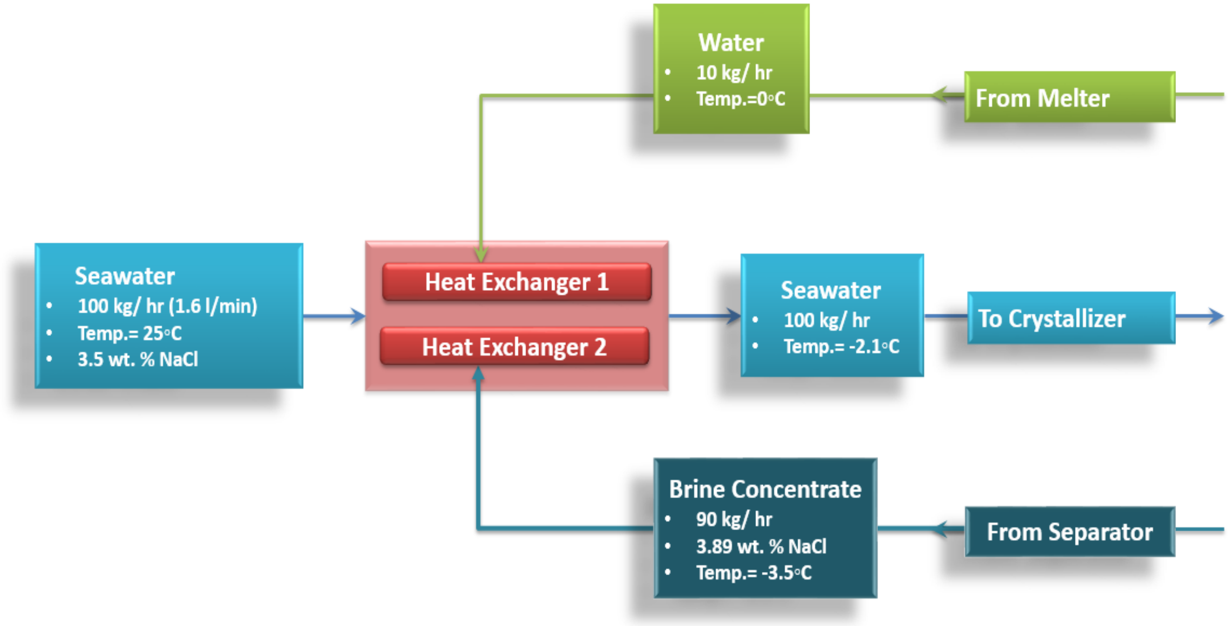


Figure 37. Precooling solution using heat exchanger

The cold energy required for that is provided by exchanging heat with the outputs from the system itself: 10 kg/hr of pure water at 0 °C and 90 kg/hr of brine concentrate at -3.5 °C. The calculations to back up the values are as follows:

From equation (1) in section 2.6, power required to cool 100 kg/hr seawater from 25°C to -2.1°C,

$$P_{req} = mCp\Delta T = (100\ \text{kg/hr})*(4100\ \text{J/kg/K})*\ (27.1\ \text{K}) = 3\ \text{kW} \qquad (6)$$

- Extracted power from temperature change 10 kg/hr water (0°C to 25°C)

$$P_{water} = (10\ \text{kg/hr})\ (4200\ \text{J/kg/K})\ (10\text{K}) = 290\ \text{W} \qquad (7)$$

- Extracted power from temperature change of 90 kg/hr conc. brine (-2.5°C to 20°C)

$P_{conc.\ brine}$ = (90 kg/hr) (4000 J/kg/K) (22.5 K) ≈ 2200 W (8)

Therefore, from equation (6), (7) and (8),

$P_{water} + P_{conc.\ brine}$ = 2200 W + 290 W= 2490 W ≈ P_{req}

So in ideal design, with an additional 500W of energy from one the heat exchangers, the total energy requirement to precool 100 kg/ hr of seawater from 25 °C to -2.1°C can be facilitated.

Now, for the heat exchanger 2, cold energy is extracted from concentrated brine and absorbed by sea water. The temperature variation at both ends are shown in Table 7.

Table 7. Temperature of hot and cold liquids throughout the heat exchanging process

Temperature (°C) for hot liquid(Sea water)	
T_{in_hot}	25
T_{out_hot}	-2.1
Temperature (°C) for cold liquid (conc. brine)	
T_{in_cold}	-2.5
T_{out_cold}	20

For counter current flow

$\Delta T1 = T_{in\_hot} - T_{out\_cold}$ = 25.00-20.00 = 5.00 (9)

$\Delta T2 = T_{out\_hot} - T_{in\_cold}$ = -2.10 - (-2.50) = 0.40 (10)

Therefore,

$\Delta T_{LMTD} = (\Delta T1 - \Delta T2)/\ln(\Delta T1/\Delta T2) = 1.82$ (11)

Now the heat transfer rate for heat exchanger 2 is

$Q = P_{conc.\ brine}$ = 2200W. Assuming the overall heat transfer coefficient, U, to be the same in this case for ease of calculation, from equation (2) from section 2.6,

$Q = UA\Delta T_{LMTD}$

$2200 = 2200 \cdot A \cdot 1.82$

A = 0.49 = 70cm· 70cm (12)

Therefore the area required for the heat exchanger 2 (between sea water and concentrated brine) is 70cm by 70cm. Similarly in case of heat exchanger, as the heat transfer is approximately 1/7th of the current scenario, the required area can be approximated as 0.07 or 27cm by 27cm

3.4.2. Refrigeration cycle

To determine the power requirements for the refrigeration cycle, the method of process simulation is utilized as described in section 2.6. For this purpose, process simulation software Aspen tech is used. Once the software is finalized, a list of required input data is prepared. This list as shown in Table 8, consist of some constant factors related to the production capacity (10 kg/hour) and physiochemical properties of the refrigerant used i.e. cold air. Additionally, there are certain variables which can be varied with respect to each other for optimization. These are the desired temperature difference (can be controlled by varying the vortex tube model and adjusting hot air exhaust valve) and air pressure and volumetric flow rate (adjustable based on the compressor).

Table 8. Data for calculating power requirement of a refrigerant unit to produce 10kg/ hour of ice

Constant factors	
Gas constant, R	8,314
Freezing point of solution (K)	271,15
Total amount of solution (Kg)	100
Mass fraction of ice	0,1
Amount of ice produced (kg)	10
Factor of compensation (heat loss)	1
Heat required for freezing	3,34E+06
Variables	
Temp-air inlet	-8
Temp-air outlet	-1
ΔT air	7
Mole of air of freezing	16453,20
Mass of air (kg)	477,14
Air pressure (Bar)	20
Air pressure (Pa)	2026500
Volumetric air flow rate (L/min)	300
Volumetric air flow rate (m3/min)	0,3
Air flow rate (mol/min)	272,4
Time calculations	
Required time for freezing (min)	60,4
Time for initiation of freezing (hr)	1,0

Based on the simulation for a temperature difference of 7 °C $(\Delta T\ air)$ and air pressure of 30 bar and 300 liters per minute volumetric flow rate, it is feasible to create 10 kg of ice per hour with an initiation time period of one hour.

In terms of energy consumption, the vortex tube provides the cold temperature air without any external energy source. This cold energy is utilized in the crystallizer for phase transfer and ice formation. Hence the only external energy required in this case is for the compressor to generate 20 bar of compressed air from air at room temperature and pressure which is roughly estimated to be 3-4BHP or 2kW.

Therefore, $$P_{compressor} \approx 2\text{kW} \qquad (13)$$

Considering safety factor for instability of performance of vortex tube and 40% pressure loss at the hot air end, energy requirement for refrigeration cycle,

$$P_{refri} = P_{compressor} * 1.6 \approx 4\ \text{kW} \qquad (14)$$

3.4.3. Plant equipment

Due to the continuity of the process of freezing and separation and low production rate, the possibility to reduce the overall sizing of the equipment is higher. Therefore, initially the volume and size of the crystallizer is estimated based on which the sizes for the other components are determined.

For the crystallizer, In order to freeze sea water (pre-cooled at -2.1°C) to ice at almost the same or marginally less temperature, the latent heat of phase transition should be provided by the refrigerant which is cold air in this case. This heat for 10 kg/ hour of ice will approximately amount up to 1 kW.

$$\text{Energy required for 10kg ice/hour} \approx 1\text{kW} \qquad (15)$$

The second key factor is the flow rate of sea water based on which the size of the column can be determined. The prerequisite flow rate for seawater is set at 100kg/hr with an ice generation rate of 10%. By breaking down the flow rates into basic units,

$$\text{Seawater flow rate} = 1.66\ \text{kg/ min} \approx 1.66\text{l/ min} \qquad (16)$$

Ice production rate = 2.77 gm/s (17)

Another key factor for crystallization is the residence time (*R*). It is the time duration taken up by a fluid element to travel from the inlet to the outlet of the column. Inside the crystallizer, the residence time determines the crystal size, the amount of ice formed and its properties. Depending on the heat transfer coefficient of the refrigerant and the droplet size of the seawater, the residence time might be needed to be increased or decreased to control the production rate. The value of residence time also proportionately effects the dimensioning of the crystallizer.

For initial calculation, considering R = 2 min,

Then, liquid volume in the crystallizer = 1.66 * 2 = 3.32 (18)

Adding up the additional volume for coolant, bubbling and ice hold up as 60%,

Total volume of crystallizer = 3.32 * 1.6 ≈ 6 liters (19)

Therefore for the crystallizer column we have,

$$\frac{\pi D^2 * H}{4} = 6\ l$$

Therefore for a meter tall crystallizer the diameter for the column would be *D* = 0.09m =9cm (20)

Based on these calculations, the modeling for the crystallizer is initiated which is further described in the result section under section 4.3 along with the separator and other auxiliary components. The models were created in 2013 and 2017 versions of Solidworks.

4 RESULTS AND DISCUSSION

The chapter includes the results obtained from the three phases of laboratory experiments and a summary of the 3D model of the pilot plant including the primary and auxiliary components. Each section of this chapter is correlated with the research questions introduced in section 1.4 of this study. Firstly, the three phases of laboratory experiments are included to analyze the continuous ice formation and separation.

4.1. Ice formation and separation

The key solutions obtained from the direct contact freezing tests for ice formation in crystallizer are:

- Although circulation might not be feasible in the pilot plant model, showering technique will be used to attain faster cooling. To make sure that the droplets get enough time rapidly acquire cold energy while traveling down the tube, the crystallizer is designed with a height to diameter ratio of 5:1 or more.
- The base of the crystallizer is designed of Teflon and smoothly coated with polyurethane. External insulation for the whole system can be provided by using polystyrene (Styrofoam).
- To counter the effects of induction, the adhesive force between ice and the crystallizer surface needs to be reduced. For this, material having hydrophobic properties (Teflon) can be used with polyurethane coating on the inner surface for prevention of ice scaling.
- Based on the experiments, Temperature gradient between the cold air inlet and the wastewater, ΔT air needs to be low (4 to7 °C) and the pressure needs to high (3-4 bar) for ice formation in the solution. Therefore, by using cold air at -5°C temperature and a pressure of 4-6 bars via multiple inlets points inside a crystallizer (Teflon base coated with polyurethane, PMMA column and outer coating of Styrofoam) with wastewater at approximately -1°C, ice slurry can be obtained. The results from the simulation in aspen tech (*Table 8*) suggest a temperature gradient of 8°C which is quite close to the experimental results. However, for a single inlet the pressure suggested in the simulation is around 20 bars to form a continuous column of air in the solution which can be subdivided into 4 different inlets of 5 bars pressure each. Another way of obtaining ice

slurry is by using a radial stirrer with sintered nozzle (Table 5, Figure 25). However combing a stirrer arrangement along with the showering process might be geometrically complicated and hence, only one of the two options can be integrated in a system.

4.2. Process flow and energy consumption

Figure 38 shows a continuous process flow map for the pilot plant showing a feasible combination of the heat exchanger and the refrigeration cycle in a schematic process flow diagram.

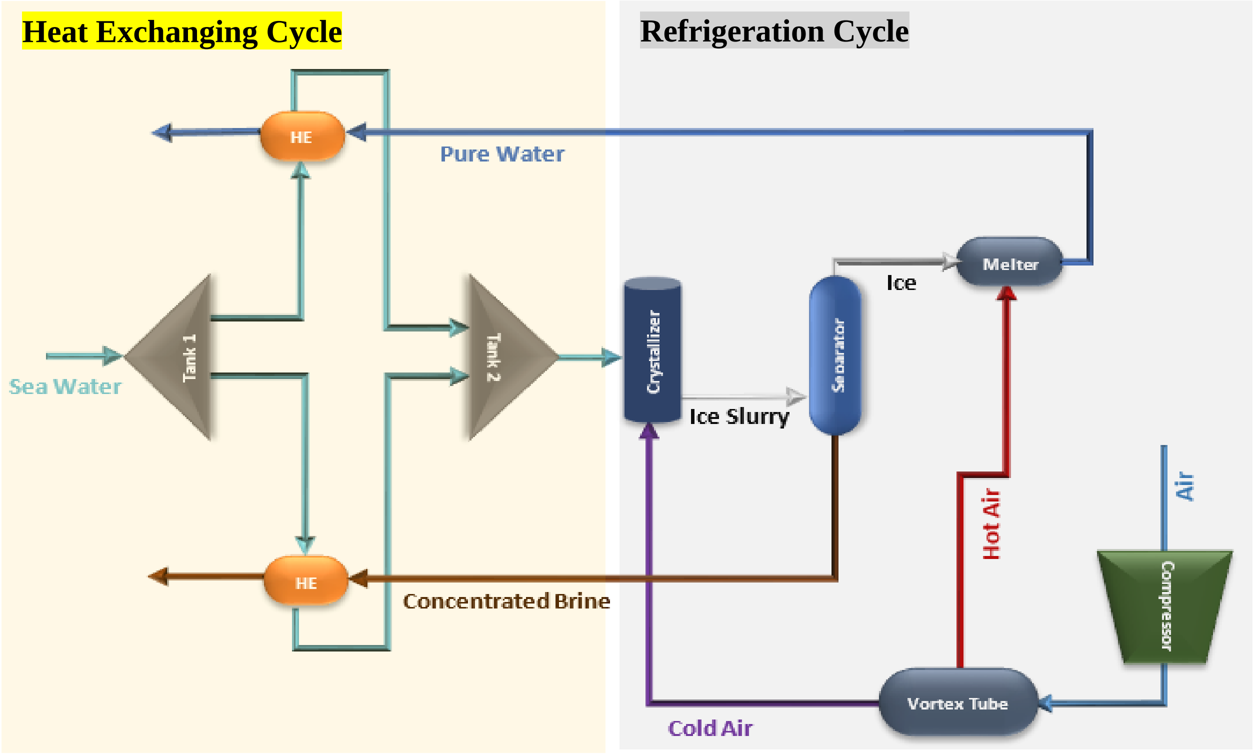


Figure 38. Process flow diagram for the pilot plant

The process flow diagram gives a rough estimate about the different equipment required to support the functional aspects of the plant. All the additional installation are added to the crystallizer and separator in this process map. To optimize the system in terms of its energy consumption, the cold energy generated in the form of ice and concentrated brine is self-utilized to precool the wastewater before it enters the crystallizer. Furthermore, as stated earlier, cold air is used as the refrigerant in the system because of its stability, safety and ease of operation. This means that the refrigerant cycle can be a simplified open loop as there is no phase conversion for the refrigerant.

In this process, the seawater or wastewater is stored in tank 1. From there, it is distributed and passed through two heat exchangers, HE1 and HE2 for precooling purpose. The required cold energy is provided by pure cold water and the concentrated brine coming out of the system for exchangers HE2 and HE1 respectively. Once the wastewater is close to its freezing point, it is again collected from both the heat exchangers in a tank 2 from where it is pumped into the crystallizer. Here, the freeze crystallization (FC) process begins. The precooled wastewater is broken down into small bubbles and showered from the top of the tall column while cold air is pumped from the bottom end into the crystallizer. As soon as the precooled wastewater droplets make contact with cold air (approximately at -5 °C), ice crystals are formed. The result will be a slurry of brine and ice whereas the refrigerant, i.e. cold air, is liberated into the atmosphere. The slurry mix is pumped into the second stage of FC in the separator where the brine is separated from the ice and is sent back to the HE1 for exchanging the cold energy with a part of the inlet water. The ice from the separator is sent off to a melter from where the cold water output is passed through heat exchanger HE2 before it is collected as outlet. In the melter, the heat is supplied from the hot air outlet of the vortex tube. The cycle continues as air is constantly compressed in the compressor and cold air from the vortex tube is fed back to the crystallizer to preserve the continuity of the process.

Next for energy consumption, the heat exchanging cycle is almost completely energy conservative (as per calculations in section 3.4.1.) with a spare energy requirement of 500W. The other half of the process including the refrigeration cycle requires the bulk of the external energy. Now based on the output of section 3.4.2., the estimated power required for the modified refrigeration cycle is

$$E_{REFRI} \approx 4 \text{ KW} \tag{20}$$

In order to provide a rough idea, a normal household refrigeration unit has a power requirement of 1 ton or 3.5kW. Therefore, as the refrigeration requirement for this project is relatively minimal.

In order to determine the overall energy consumption the energy requirements from all the individual components should be combined. From section 3.4.1, external energy required for precooling,

$$E_{Precooling} = 0.5 \text{ kW} \tag{21}$$

For crystallization, no additional external energy is required because theoretically, the entire energy for latent heat of ice formation is provide by the evaporation of propane. Hence,

$$E_{Crystallization} = 0 \tag{22}$$

Also, for the refrigeration cycle, the mechanical efficiency of the compressor needs to be taken into account. Therefore, considering all the above equations and assuming a safety factor of 0.5, the total energy requirement is summarized in Table 9.

Table 9. Pilot plant energy estimation

Energy units	Value in kilowatts(kW)
$E_{\text{Precooling section}}$	0.5
$E_{\text{Crystallization}}$	0
E_{Refri} /Efficiency	8
Other auxiliary equipment	0.5
Total Energy required	9
Safety factor	0.5
Final Energy Requirement	10

Therefore, considering a safety factor of 0.5 and excluding the coefficient of performance (COP), theoretically, the maximum energy required by the pilot plant is 9.5 or 10 kW

4.3. 3D modeling for pilot plant

Based on the design specifications and the process flow discussed in sections 3.4 and 4.2 respectively, a 3D model for the pilot plant is designed. The overall plant from the mechanical point of view occupies a volumetric space of approximately 2 m^3. The 3D model comprises of primary and auxiliary equipment. The primary components i.e. the crystallizer and separator along with the melter, tank 1 and tank 2 have been designed based on the design calculations whereas other auxiliary parts, for example pumps, pipes, compressor, motor assembly and heat exchangers, vortex tube are approximated from drawings, actual parts or models obtained from manufacturer’s catalogs or design library of Solidworks. For modeling purpose, Solidworks version 2013 and 2017 were used.

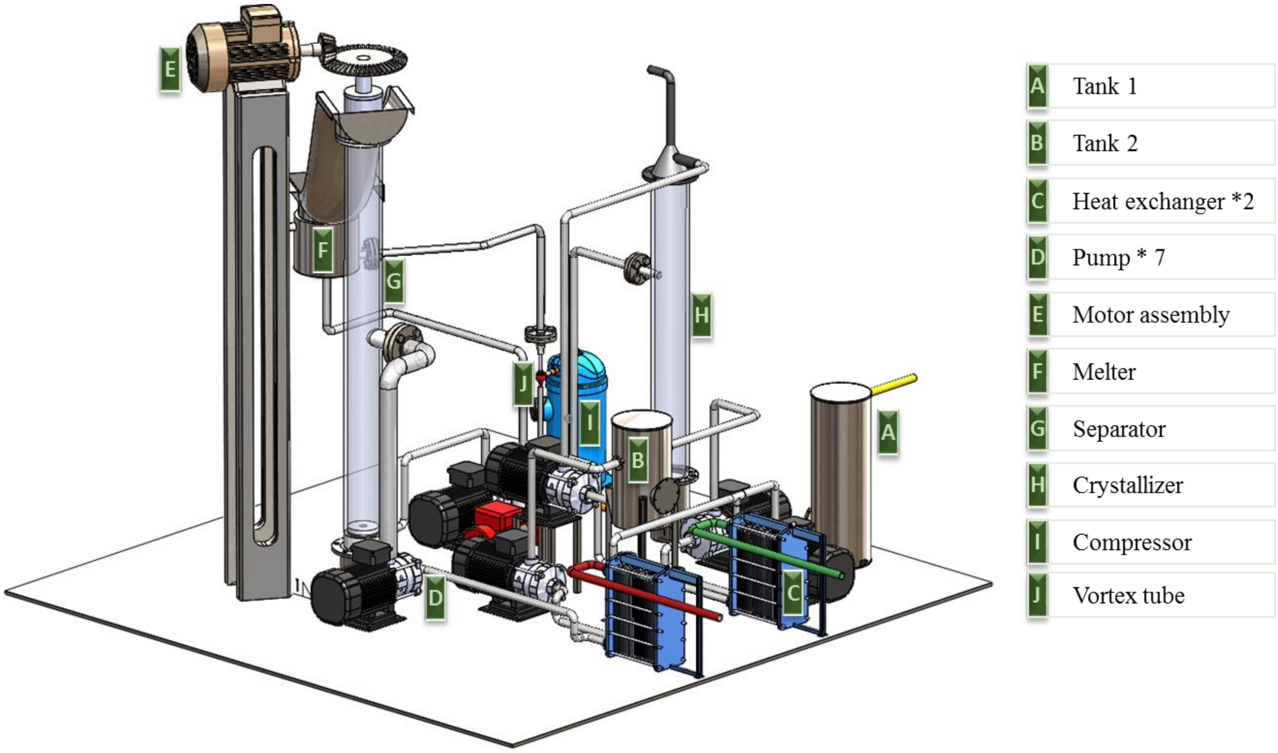


Figure 39. 3D model of pilot plant

Figure 39 shows the 3D model of the pilot plant with listing of the main equipment or subassemblies. The parts are assembled on a base plate of 2 m^2 area with necessary supporting structures welded to the base.

- Tanks

Figure 40. Storage tanks 1 and 2

The tanks are used for storage of inlet wastewater and precooled water respectively. Wastewater is initially stored inside the larger tank at ground level (tank 1 of 10 liter capacity) to provide a continuous supply. From there the wastewater is passed through the two heat exchangers using pumps and then collected in tank 2 (6 liter capacity). The tanks are provided with 20mm inlet and outlet holes with slide on flange connectivity for convenience of assembly and piping. Each tank is provided with side holes for ease of cleaning. The tank 2 is located roughly 50 cm higher than the base for convenience of arrangement and liquid transfer. AISI 316 grade of stainless steel is a suitable choice of material for these parts.

- Heat exchangers

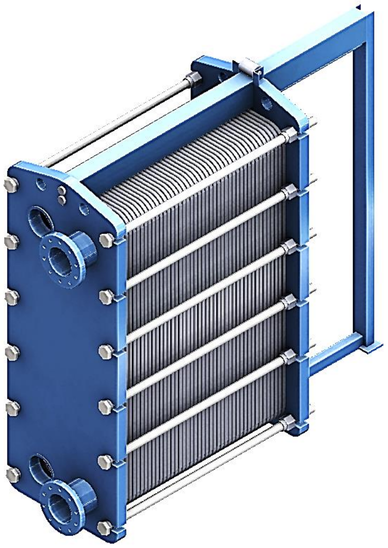
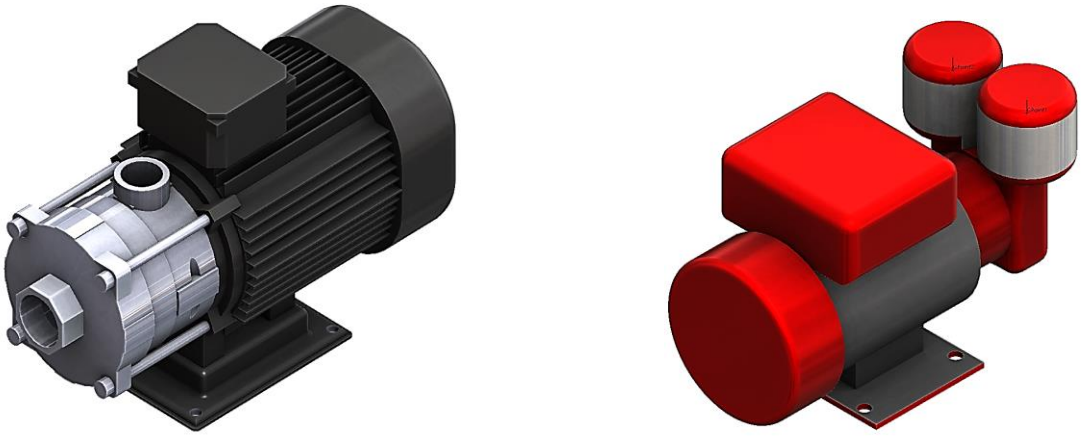


Figure 41. Plate heat exchanger

Two heat exchangers are used for precooling the wastewater by transferring cold energy individually from the brine and the pure water. The heat exchanger modeled in this pilot plant are manufactured by Sondex, a Denmark based heat exchanger designing company. Based on the cross sectional area calculations in section 3.4.1, the model design has been approximated from S4A model of gasketed plate heat exchanger manufactured by the company. However, this model of heat exchanger is for demonstration purpose only and detailed collaboration with the manufacturers is required to identify the exact customized heat exchanger required for this purpose. (Plate heat exchangers, 2017)

- Pumps.



(a) (b)

Figure 42. (a) Centrifugal pump (b) Water booster pump

There are 7 pumps installation required in the pilot plant. These are:

- Tank1 to heat exchangers 1 and 2
- Heat exchanger 1 to tank 2
- Heat exchanger 2 to tank 2
- Tank 2 to crystallizer
- Crystallizer to separator
- Separator to heat exchanger 2
- Melter to heat exchanger 1 (water booster pump)

For the first 6 cases, regular horizontal, hydraulic, end suction centrifugal pumps with low end capacity (10 – 30 L/min) are suitable. The centrifugal pump in Figure 42(a) is based on aproximations from the manufacturing catalog of DHF 4 series models manufactured by Doochpump limited. The energy efficiency of these pumps can be further increased by using additional variable freuency drive in the pumps like the DHFNQ and DHFSQ models. (Dooch pumps, 2017.)

Additionally, in order to propel water from the melter to the heat exchanger, a water booster pump is used to compensate for the pressure drop in the melter . This model (Figure 42.(b)) has been designed form the solidworks 2017 inbuilt library model for demonstration.

- Crystallizer

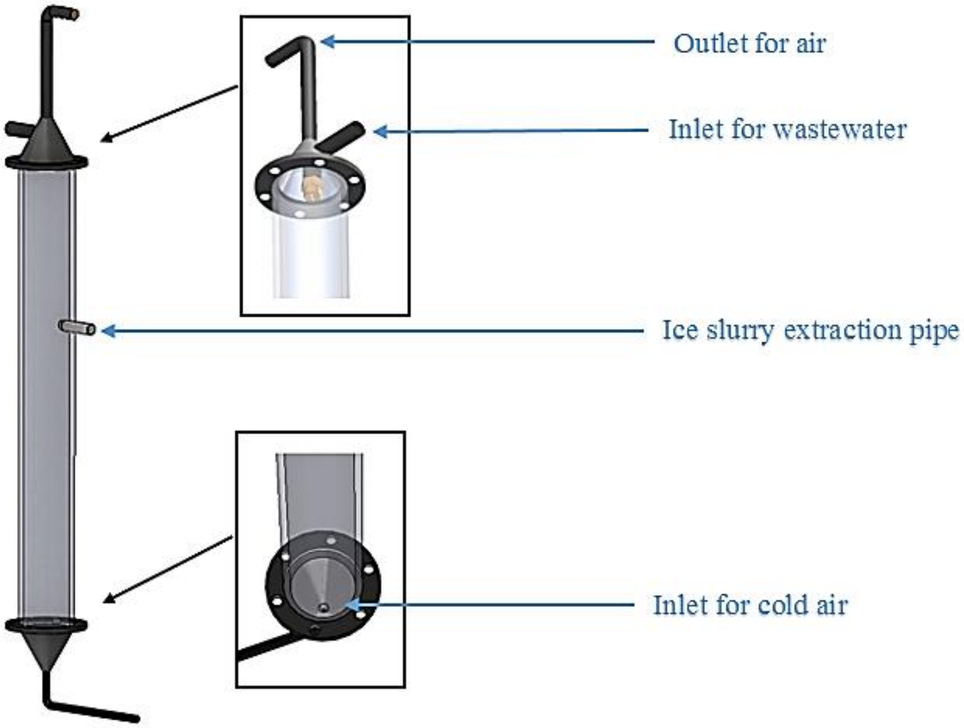


Figure 43. Crystallizer

The crystallizer is built with a volumetric capacity of approximately 6 liters based on the calculations in section 3.4.3 with a diameter of 90 mm and a height of 1000 mm (approx.). The conical ends facilitates proper channeling of the cold air as it enters and leaves the chamber. There is a single inlet at the bottom of the crystallizer for the cold air from the vortex tube. For efficient mixing and cooling (as stated in section 5.1), the wastewater is introduced from the top end in the form of shower by using a standard spray nozzle. This maximizes the heat transfer between the two medium because of the additional exposed surface area. The cylindrical part of the tube is designed to be made of transparent polyethylene for visual convenience and good insulation properties. On the other hand, Teflon is more suitable for the end cones as these parts have higher susceptibility to ice layer formation. An additional 2 mm spray coating of polyurethane can be considered for the inner surface of the lower cone to further reduce the chances of ice clustering at the bottom of the channel, which was a major issue in the experimental systems. The cold air is dispersed into the atmosphere from the top vent after passing through the wastewater. The ice slurry extraction point is located at about 2/3rd of the length of the column giving the solution a residence time of approximately two minutes. The additional volume at the top is provided to accommodate for the foam and bubble built up due to the pressurized air being released in the column. To minimize the amount of external heat loss, it is advisable to wrap the crystallizer column with a layer of Styrofoam.

- Separator

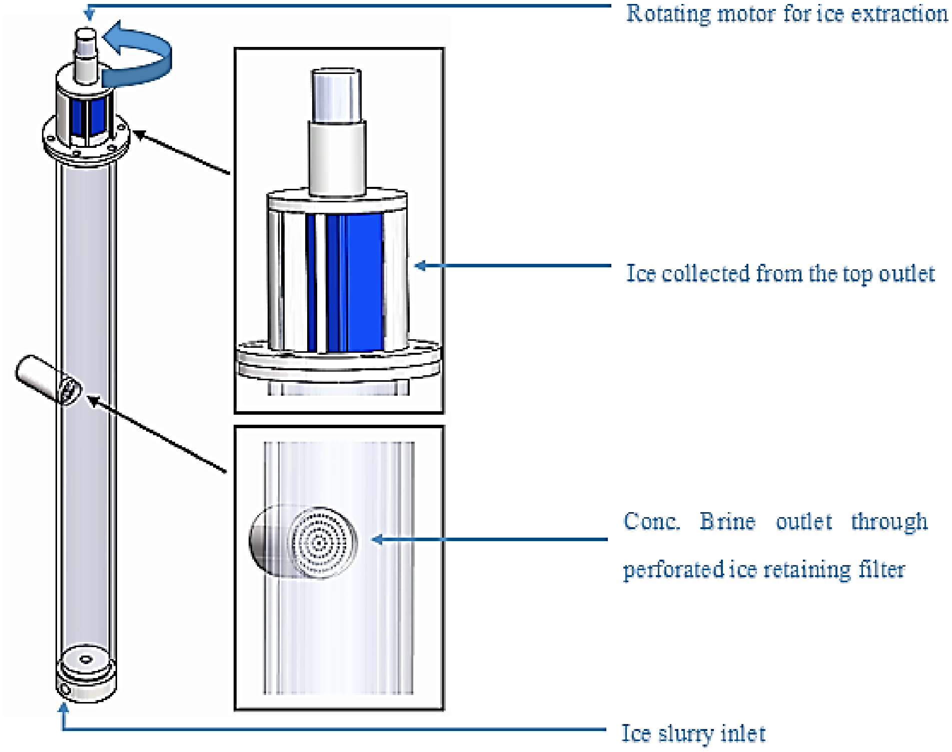


Figure 44. Separator

The separator has roughly the same volumetric capacity as the crystallizer. The only difference is that it is about 200 mm taller. This provides higher residence time (three to five minutes) forming larger crystals, hence allowing the gravitational filtering to take place properly in order to achieve better purity. The base is designed to be made of Teflon with 15 mm channels serving as inlet for ice and brine slurry. In the lab tests, as the brine and ice kept on rising, often there was a clogging problem with the brine outlet due to its small diameter which adversely affected the separation process. Keeping that in mind, the brine outlet has been provided with an outlet diameter of 50 mm for conveniently pumping out the concentrate. The ice rises up to the top of the chamber. Three sets of blades mounted on a vertical rotating shaft drive the crystals out through a cut out in the top lid and moves the ice to the melter.

- Melter

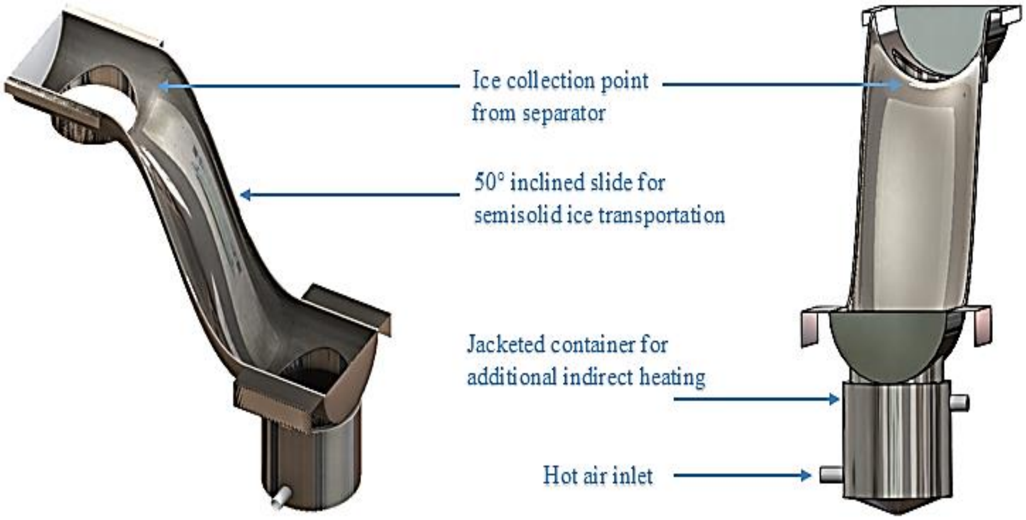


Figure 45. The melter (slide and container arrangement)

The melter is typically a part where the ice is melted back to pure water (close to the freezing point) which is further used in one of the heat exchangers for precooling purpose. In conventional melting process, ideally the ice is melted through direct contact condensation using the heat from refrigerant vapor used as coolant in the main crystallization process (Brian, Smith and Petri, 1968). However, in this current setup, the possibility of heat extraction is quite limited for hot air from the vortex tube with an overall heat transfer coefficient of 2.183 W/m^{2}°K. The stainless steel sliding arrangement of ice in this case has a surface area exposure of $0.25m^2$ to speed up the heating process along with the hot air of the vortex tube. The 50° incline ensures that the ice built up from the separator is transported is semi solid stage into the 160 mm x160 mm jacketed container at the bottom where it is further melted into pure water. The pure water is extracted from the bottom of the container via a water booster pump and delivered to the plant outlet after passing through the precooling stage.

- Compressor

The majority of energy requirement in the refrigeration process is consumed by the compressor for producing a minimum of 30 bar pressure range at a minimum flow rate of 420 liters/min (considering 40% lose as hot air in vortex tube). Based on these requirements, two different compressor manufacturers, “RIX industries” of the United States and “Danfoss Group” from Denmark were consulted.

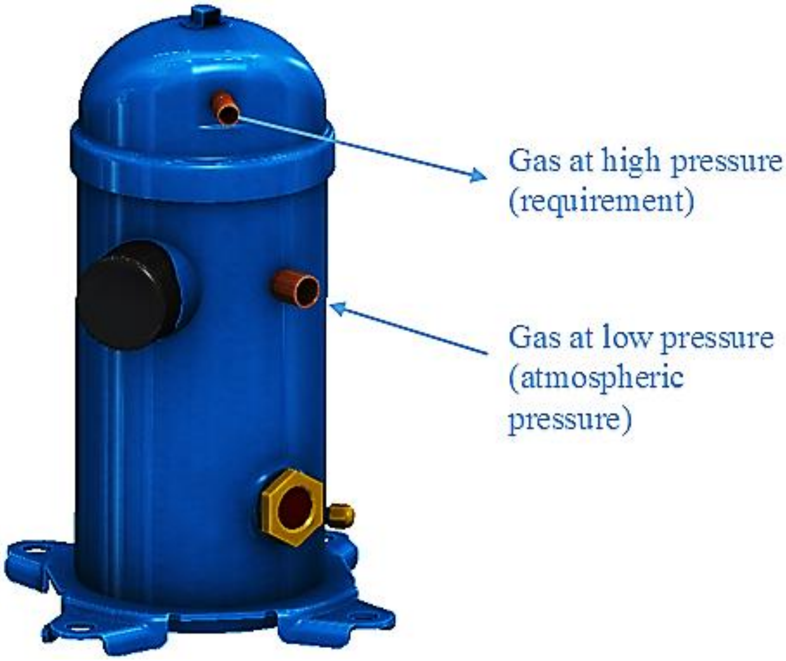


Figure 46. VSZH044CJ (approximated model) air compressor by Danfoss.

By these calculations, the power required by the compressor is approximately 4-5 BHP (4kW) with a two stage compression process (High pressure compressor, 2017). Two standard compressor suitable for this range are the 2V3B-4.1V-HP-P1 and VZH044CJ.

Table 10. Specifications of 2V3B-4.1V-HP-P1 and VZH044CJ compressors

Name	Manufacturer	Power (kW)	Lubricant	Pressure max. (bar)	Flow (L/m)	Stages	Dimension (mm)
2V3B-4.1V-HP-P1	RIX Industries	7.5	Oil Free (Air cooling)	172	283	3	1143 x 59 x 1219
VZH044 CJ	Danfoss	6	R410A refrigerant	90	266	1	359 x 135 x 241

For ease of demonstration and due to its smaller dimensions, an approximated model (based on manufacturer’s catalog) of the VZH044CJ compressor designed by Danfoss has been included in the pilot plant for demonstration. The dimensions of the model are roughly assumed based on the data provided in the company’s sales catalog (Danfoss, 2017).

- Vortex tube

Vortex tubes are used because of there maitenance free, low cost and simple functionality. A stream of pressurized air is used directly as the inlet and normally, two individual streams, one hot and one cold, are released at each end of the vortex tube.

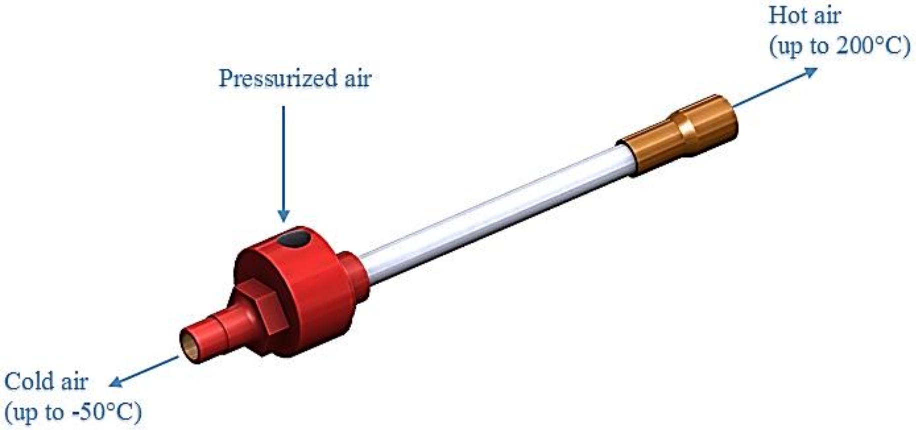


Figure 47. Typical vortex tube

Vortex tubes can be both manufactured independently as well as procured from manufacturing companies like ex-air. Empirical studies have shown that for a 12mm diameter vortex tube, the minimum amount of cold temperature can be attained by keeping a cold end diameter of 6mm and an overall L/D ratio in the range of 25-35 (Behera et al., 2005).

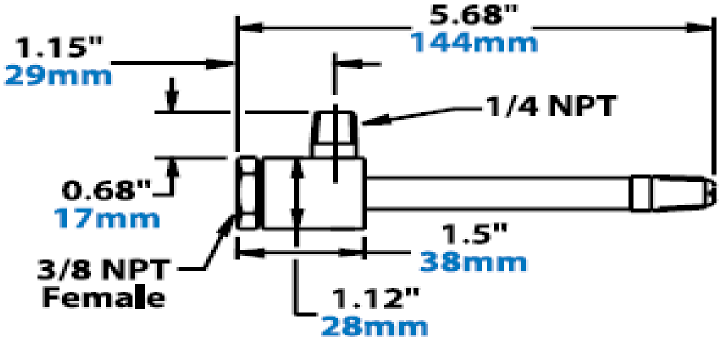


Figure 48. M3200 series of vortex tube without muffler (Exair vortex tubes, 2017).

The commercial products have high efficiency and models can be easily upgraded due to interchangeability of parts. For this particular scenario, model M3240 of the 3200 series of vortex tube designed by ex-air is quite suitable. An approximated model from Figure 48 has been used in the pilot plant model. (Exair vortex tubes, 2017.)

- Pipes, joints and connections

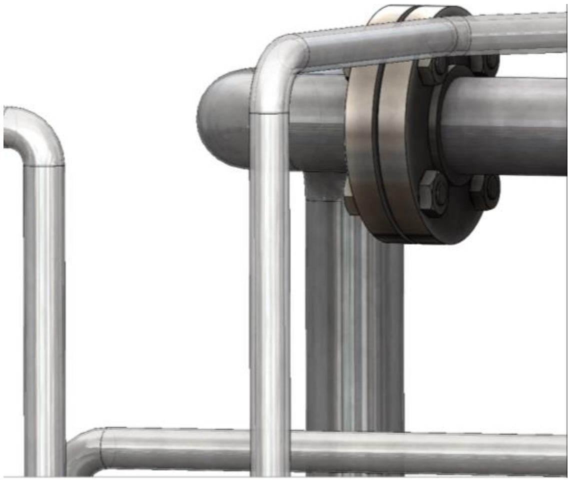


Figure 49. Piping and flange

The piping is designed of clear polyvinyl chloride (PVC) for convenience of visibility and better insulation. The specific properties are:

Table 11. Suitable characteristics of Polyvinyl chloride piping (Parker.com, 2017).

Parameters	Values
Pressure Range	19 to 55psi
Maximum Operating Temperature	79°C
Brittle Point	-40°C
Color	Clear
Hardness	Durometer 83+/-3 Shore A
Toxicity	Non-toxic FDA Listed

Most of the pipes used in the pilot plant have a uniform diameter of 20mm, the only variations being the one taking out the brine from separator (50mm) and the inlet for compressed air to the crystallizer (12mm). Other than that standards bents, T-joints, reducers and slip in flange couplings are used as per requirement.

5 CONCLUSION

The basic foundation of this research was to establish a wastewater purification system based on freeze crystallization and at the same time estimate the requirements, identify the shortcomings and propose feasible solutions to those problems. In the introduction chapter, a few research questions were established based on which the study was conducted. Those questions were:

I. What are the obstacles in attaining continuous ice formation and separation? What are the ways to resolve those issues?
II. What can be an energy conservative way of process flow for a pilot plant designed for freeze crystallization based wastewater purification?
III. What are the primary and secondary components required from the functional aspect of the pilot plant?
IV. How is it possible to estimate the energy requirements for the entire process?
V. What are the driving parameters in the process which needs to be controlled?
VI. How could be the overall sizing and dimensioning of the primary components established for the proof of concept?

Therefore in retrospective observation, it can be concluded that the study summarized the possible answers to the above mentioned research questions. To identify the obstacles in the freeze crystallization process, the laboratory tests were conducted which clearly indicated that ice scaling at point of dispersion and slow rate of cooling were the primary concern in the ice formation part. These issues of ice scaling is addressed by introducing Teflon (ice-phobic in nature) with 1mm polyurethane coating as the base cone material for the crystallizer and combining it with highly pressurized inlet air (approximately 20 bars). The rate of cooling is also improved with the increase in pressure of the inlet air. As per the aspen tech simulations, the 20 bar pressure is sufficient to produce 10 kg of ice in an hour with the temperature difference of 7 degrees (sections 3.4.2 and 4.1). In the separation process, the only issue faced was the blockade of the filter used for separation of concentrated brine. This is eliminated by using a 50mm diameter pipe and a pump for continuous brine extraction.

Once the crystallizer and the separator were established as the primary components, the study was focused on the secondary equipment and establishing an energy efficient process flow and estimate the total energy requirement. Most standard secondary equipment (pump, piping, welding flanges, storage tanks, vortex tube, compressor and heat exchangers) have been incorporated into the process flow with the help from knowledge based on literature and experimental runs (sections 5.2 and 5.3). The only exception is the custom built melter which is specifically designed to utilize the heat energy generated from the vortex tube. This along with the utilization of cold energy from the extraction liquid in the precooling section ensures that approximately 1/3rd of the systems energy is conserved. A majority of the energy consumption occurs in compression the cold air and the total amount of required energy is estimated at 9.5 to 10 kW (section 5.2).

In terms of driving parameters, the entire process is driven by the formation of ice which in turn is dependent on the pressure and temperature of the input air. Hence it is imperative to control the temperature of the input air so that the mean temperature difference between the cold air and the ww solution is below 5°C. This can be controlled by tuning (opening or closing) the hot air exit valve in the vortex tube as required. Simultaneously the pressure is required to be adequate (approximately 20 bars) to avoid ice scaling at point of dispersion. While the compressor output can be regulated to control the pressure, some the pressure head loss can be controlled using the hot air exit valve of the vortex tube as well. Another important driving factor is the residence time in the separation column. As stated in section 2.5, higher residence time yields larger crystals which results in higher level of purification. The current residence time is set at approximately three to five minutes but this can be further varied by altering the flow rate into the separation column.

Finally, the 3D modeling of the equipment is carried out to establish a conceptual layout of the power plant. The primary and customized equipment (crystallizer, separator and melter) have been designed based on the design calculation carried out in the research whereas the rest of the standard parts are designed based on dimensions and drawings provided in information brochures available at websites of independent part manufacturers (sections 3.4.3 and 4.3).

5.1. Future scope of research

This study was aimed at designing the initial proof of concept and there are few areas where further studies can be conducted for improvisation:

- Carrying out design for manufacturing and assembly (DFMA):

In this research, the idea of process flow, estimation of energy consumed and design of proof of concept have been carried out in the virtual aspect based on knowledge from experiments and literature. The next step could be performing design review, design validation and finally moving onto the manufacturing and assembly of the actual parts. This stages could be further utilized to predict some of the upcoming challenges for the pilot plant (for example, life time expectancy, maintenance, backup process flow etc.).

- Process optimization: alternative options for refrigerants

In this research, cold air is used as refrigerant due to its ease of maintenance, stability and simplified process flow. However, compressing and using cold air leads to a high amount of energy consumption which is not uncompetitive in terms of current market scenario. As a viable alternative, using hydrocarbon based liquid refrigerant (for example propane based R290 or n-butane based R600a) considerable amount of energy saving can be achieved (Rane and Padiya, 2011). There could be a few interesting challenges in terms of integrating the liquid refrigerant cycle with the direct cooling system of the pilot plant which can be studied in the future. One more variation can be added to the crystallizer itself by introducing a stirrer and learn its effect on the rate of crystallization.

- Design optimization: Incorporating finite element analysis (FEA) and computation fluid dynamics (CFD)

The current design is a conceptual pilot plant which can definitely use further optimization. In terms of design, FE analysis can be carried out to identify the various loads on each individual parts and eliminate some the risks associated with functionality of the plant reconfirm the suitable materials and dimensions. On the other hand the dynamics of the fluid flow (both refrigerant and wastewater) can be studied as a final step to optimize the design. Considering the fact that the fluids would go through multiple phase changes throughout the continuous process, it is quite an interesting as well as challenging scope for study in the future.

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APPENDICES

APPENDIX I

The different databases used for literature review along with the keywords and number of articles retrieved are listed below:

Database	**Keywords**	**Number of documents found**	**Number of documents excluded**				**Number of documents included**
			By Title	**By Abstract**	**By Content**	**By Language**	
Directory of Open Access Journal	"freeze" AND "crystallization"; "purification" AND "freezing" ; "desalinization" AND "freezing"; "Freezing technique"; "natural freezing".	255	226	4	2	21	2
IEEE		1177	1171	1		1	2
Science direct (Elsevier)		231	219		3		9
Free patent online		389	351		34		4
SCOPUS		1094	1077	3			11
Doria		249	241	6			2
Google scholar		2500	2459	8			7
Summation		5895	5744	22	39	22	37
Documents added from bibliography							**3**
Total documents retrieved for literature							**40**

APPENDIX II

Pilot plant layout in perspective to a 6 foot tall operator