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Freezing-Melting Process and Desalination: I. Review of the State-of-the-Art

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Abstract: A thorough literature survey was conducted on the freezing-melting (FM) process for desalination. Collected literatures were studied and analyzed to identify the current state-of-the-art of the FM process, and its practical limitations. The main advantages of the FM process are the requirement of low energy and low temperature operation compared to thermal desalination. Other advantages are less scaling or fouling and fewer corrosion problems, ability to use inexpensive plastics or low-cost material, and absence of pretreatment. The three broad classes of FM process are: direct contact freezing, indirect contact freezing, and vacuum freezing. Different types of processing options in each class are discussed with their operating principles and merits and downsides of each process.

Keywords: Desalination, freezing-melting, FM, direct contact freezing, indirect contact freezing, vacuum freezing, eutectic freezing

INTRODUCTION

Desalination for water supply has grown steadily since the 1960s. In fact, seawater desalination is currently meeting most if not all of the requirements

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of domestic freshwater supply for some countries (especially in the Gulf of Mexico as well as in the Persian Gulf) and is a supplemental source of water for others. Desalination refers to a sea water treatment process that separates water from dissolved salts. Based on the process, desalination plants can be categorized into two types. The first type involves plants that employ a phase-change process. In such plants, desalination takes place while there is a change of phase (i.e., liquid to vapor with boiling or evaporation or liquid to solid with freezing). Plants that follow such a process include the following: (i) Multi-Stage Flash (MSF), (ii) Multi-Effect Distillation (MED), (iii) Vapor Compression Distillation (VC), (iv) Solar Humidification/Dehumidification Desalination (SHD), and (v) Freezing-Melting (FM). The second type desalination plants are those that involve no phase change. In such plants, the extraction of water or salt takes place while the salts or pure water remain in the solution phase. These processes include: (i) Reverse Osmosis (RO) and (ii) Electrodialysis (ED). Buros (1) has categorized the desalting processes into major and minor processes based on their use. Further details of the desalination processes are given by Ettouney et al. (2), Fernandez et al. (3), Hassan et al. (4), UNEP (5), Shwartz and Probstein (6), Singh and Tembrock (7), Thampy et al. (8), and Wangnick (9).

Although the freezing-melting (FM) process is not widely used commercially, the process has some advantages. Perhaps the greatest potential advantage of desalination by freezing is the very low energy requirement compared to that of the distillation processes (10, 11). The reduction in energy costs results because the latent heat of fusion of ice is only one-seventh the latent heat of vaporization of water. FM separation could save 75 to 90% of the energy required by the conventional thermal process (12). The costs of concentration by evaporation and FM are listed in Table 1. The FM processes have the advantage of a low operating temperature, which minimizes scaling and corrosion problems (10, 13, 14). Inexpensive plastics or low cost materials can be used at low temperature (11, 13, 15, 16).

Table 1. Comparing operating costs of various concentration processes

Application	Cost per 1000 kg (1 m ³) water removed	
	Evaporation	Freezing-melting
Fruit juice concentration	\$5.40	\$2.00
Sugar production	\$8.47	\$1.32
Desalting seawater	\$1.85 ^a	\$0.93
Caustic soda concentration	\$2.23	\$1.06
Black liquor concentration (for paper-pulp processing)	\$3.15	\$1.52

^aNow it is \$0.84 in modern plants in UAE.

Source: Chen (121).

A very high surface area and high heat transfer coefficient can be achieved with a direct contact between the brine and refrigerant. It has general absence of pre-treatment, low chemicals requirement and is insensitive to fouling and nature of solution (15, 17), and low ecological impact (16).

Traditionally, the disadvantages of freeze concentration compared to evaporation and reverse osmosis have included higher initial investment and capital costs and higher operating costs during the ice separation (18). The exhaustive list of all other disadvantages is (19): (i) Retention of undesirable flavors and aromas (initially present in the feed saline water) that may come into the produced fresh water (20); (ii) Freezing process needs to include the growing, handling, and washing of ice crystals and the need for mechanical vapor compressors; (iii) Compressors represent an expensive method of furnishing the energy requirements of the system (10); (iv) Probably the greatest deterrent to general acceptance of the freezing process is the fact that large plants cannot be designed and optimized with confidence, due to the complexity of the unit operations in the freezing unit, melting unit, and wash-separation column; (v) Trapping of salt solution in the ice during crystallization needs crushing and re-crystallization of ice; (vi) A progressive increase in the concentrations of the dissolved substance, and non-condensable gases; (vii) High-quality energy is required for crystallization compared to low quality energy used in many evaporation processes; (viii) Certain amount of fresh water is required to wash ice for reducing salt content in the produced water; and, (ix) a minimum knowledge is needed on ice crystallization and growth in a slurry system, on practicalities of handling ice slurries, on good methods for complete separation of ice from brine, and on hydration behavior. The objective of this paper is to review the state-of-the-art of the FM process.

STATE-OF-THE-ART OF FREEZING-MELTING PROCESS

General Description

The general claim of the freezing-melting process is essentially that it is capable of removing water by freezing it out from saline solution as ice crystals. Ideally the ice formed should be free of salts. Fresh water can be produced by partially freezing seawater, and then physically separating the ice crystals from the residual concentrated brine, and melting the ice to form the product water. Ice crystals formed under the appropriate conditions can be very pure. A refrigeration system is required to remove from the brine the heat of fusion of the ice. The quantity of heat, which must be removed from the freezing unit, is essentially equal to that which must be added to the melting unit (10, 15). The FM process is accomplished in two major stages: ice crystallization (stage I), and separation and melting (stage II) (Figure 1). In stage I, nucleation occurs at a suitable supercooling temperature.

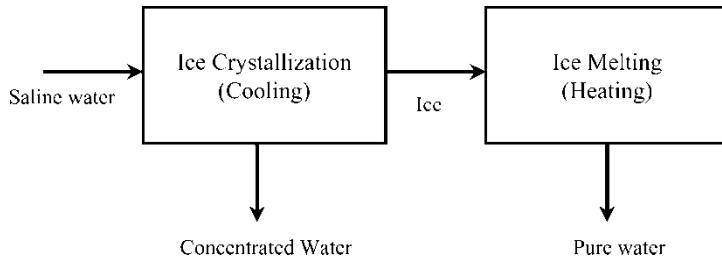


Figure 1. Freezing-melting Process.

The nuclei in solution grow to become large ice crystals in a crystallizing unit. In stage II, the crystals are separated from the concentrate by a separator (mechanical) and then ice melting gives pure water. In general, the components of the FM process are: (i) a pre-cooler to cool the feed water, (ii) a crystallizing unit, where sufficient heat is removed from the process fluid to crystallize up to 15% of the mass, and (iii) a *crystal separator and purifier*, where the crystal is separated from the unfrozen concentrate and washed with a small amount of the melted product to remove any adhering concentrate from the surface of the crystal. The separated concentrate is recycled to the freezer to provide desired recovery. A *heat pump* takes heat out of the freezer and transfers it either to cooling water or to the cold crystal (melting-unit) that is removed from the purification section. A *feed heat exchanger* is usually employed to pre-cool the feed by using the cold product and the concentrate, thus reducing the load on the heat pump.

Historical Development

The Danish physician Thomas Bartholinus (1616–1680) was apparently the first to report that water obtained by melting ice formed in seawater was fresh. Almost at the same time, Robert Boyle (1627–1691) reported the same observation, foreseeing the phenomenon as a source of fresh water and the Jesuit Athanasios Kircher (1602–1680) discussed the reason why ice formed in the sea is fresh (21). The reason of getting fresh water from ice is due to the rejection of salts at the interface. Freezing in large bodies of water occurs in nature on the surface of oceans, lakes, and bays. The combined heat transfer associated with heat removal by the environment, and latent heat release at the water-ice interface results in natural convection flows of water. Freezing seawater releases fluid at the water-ice interface, which is denser than the bulk water. The resulting solute buoyancy force therefore acts downward. This solute buoyancy force is in addition to the thermal buoyancy force. Flow visualization revealed that the flow was downward, below the freezing surface. The convection heat transfer rate is

found to be strongly affected by solute rejection upon freezing (22). At the end of the 18th century, the Italian scientist Anton Maria Lorgna (1735–1796) described a method to purify sea-water and impure water by freezing and then melting of the ice. In 1786 Lorgna published his first paper on water desalination by freezing, wondering why nobody had previously applied it in an artificial process imitating what nature does so well and easily in the cold seas by producing blocks of fresh water ice from sea water. He also identified that only one single freezing of seawater produced an ice block having salinity much less than sea-water salinity but not nil. Thus he pointed out the need for multi-stage freezing-melting processes to obtain salt-free water (21).

The method of water purification by freezing-melting was not of practical interest before the development of refrigerating machines. It was only possible in the coldest regions and seasons. The interest in the process of obtaining fresh water from sea-water by freezing was revived in the late 1930s and an experimental desalting plant has been operated for some years near Rome by the Istituto Superiore di Sanita. The plants operated by the indirect freezing process and later revealed themselves to be of limited practical interest in comparison with the direct freezing desalination procedures. The FM process was first used commercially in the 1950s. Research in the 1960s and 70s in desalination, petroleum, and food processing applications provided many technical innovations (23).

Classification of Freezing-Melting Processes

A wide variety of FM systems are currently on the market (24). Further details of the different types are available in Heist (12), Deshpande et al. (25), Maguire (16) and Chowdhury (24). In general, the FM process occurs in a crystallizer, although control of ice formation and growth has been obtained in numerous ways. A classification of the different FM processes is given in Table 2 based on whether there is direct or indirect contact of refrigerant with the solution.

Direct Contact Freezing

Direct-contact crystallizers provide for intimate mixing between the refrigerant (such as freon and butane) and the product to be frozen. The refrigerant in the liquid form under pressure is expanded through a nozzle into the product liquid, where it vaporizes at lower pressure. This vaporization provides a refrigeration effect and causes formation of ice and/or solute crystals within the product. A typical direct FM system (shown in Figure 2) is composed of ice nucleation, a crystallizer allowing subsequent growth of these nuclei up to a size suitable for separation, an ice crystal separator, a washing unit, and a melting unit (14, 26).

Table 2. A possible classification of freezing-melting processes

A. Direct contact freezing
B. Indirect contact freezing
a. Internally cooled
1. Static layer growth system
2. Layer crystallization unit on rotating drum
3. Progressive crystallization unit
4. Dynamic layer growth system
5. Suspension crystallization
b. Externally cooled
1. Supercooled feed
2. Ripening vessels
C. Vacuum freezing

Conventional Direct Contact Freezing

A direct contact freezer uses a spray of refrigerant by jet impact through a nozzle. The main advantages are a high production rate per unit volume at a low driving force, small power consumption, absence of moving parts and a compact and efficient unit (27). The successful design of a direct contact freeze desalination plant significantly depends upon the availability of a suitable refrigerant (28). There are certain thermodynamic, chemical, physical and economic requirements, which the refrigerant must meet in order to be suitable for use in the process. These are: (i) the refrigerant should have a normal boiling point of -4°C or less and vapor pressure below $2.8 \times 10^5 \text{ Pa}$ (2.8 atm) at room temperature, (ii) the refrigerant should

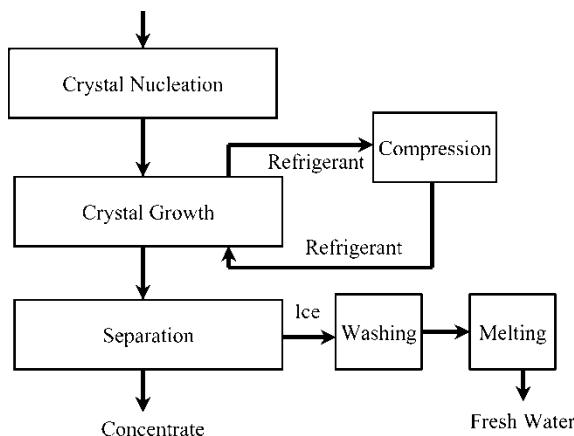


Figure 2. Schematic of basic direct contact FM process (14).

be nontoxic, preferably non-flammable and chemically stable in seawater, (iii) the fluid should be virtually immiscible in water and should possess such molecular size factors so as not to form a hydrate under the freezing conditions employed in the process, and (iv) the refrigerant should be cheap and readily available from commercial suppliers (29). The details of thermodynamic properties of normal butane at refrigeration temperatures have been compiled by Kurnik and Barduhn (30). The refrigerants that could be used are: butane, carbon dioxide, nitrous oxide, Freon-114, and Freon-318. Freon-114 and Freon-318 are a better choice based on the above factors. However these materials are relatively expensive when compared to other refrigerants such as butane. Antonelli (31) developed a process where liquefied natural gas (LNG) evaporates and generates power. Part of the sea-water is frozen and the ice produced is melted at ambient temperature. It is possible to couple a FM process to a LNG vaporizer (32). In many cases, gas companies import huge quantities of LNG, which is vaporized from a low temperature to the ambient temperature at the terminals, and then transported through gas pipe lines. In this case sea water could be used as a source of heat for the vaporization of the LNG. The cost could be substantially reduced if sea water could be cooled from the ambient temperature to near freezing.

The butane evaporation involves at least three phases: liquid butane, butane vapor and liquid brine and its mechanism is correspondingly complex. Simpson et al. (33) studied the evaporation process of refrigerant by describing the dynamics of the bubble motion in a more meaningful way, and recorded this more readily with the visual evidence of the bubble's motion. The rate of evaporation of butane droplets increased rapidly with a diameter ratio compared with the initial one, up to a critical value, and then gradually with the $1/6$ power, implying that evaporation was controlled by the heat transfer through the transient liquid butane film on the inside surface of the bubble (33).

Orcutt and Hale (34) used mathematical models to study the operational-design economics of a freezing process and to predict the best operating conditions. Optimization computations showed that the economics of the process operation depended largely on the temperature maintained in the freezer and the overall difference in refrigerant and equilibrium freezing temperature. An analysis of the linearized freezer dynamic equations showed the freezer to be stable and did not indicate regions of difficult control. The cost of the washer-melter is influenced by the operation of the freezer, which determines the value of crystal size. The freezer operating costs depend on the brine temperature, which influences both the crystal size and the refrigerant vaporization rate.

The choice of a suitable refrigerant for the process is important. From the viewpoint of cost and stability, the hydrocarbons with four carbon atoms have been recommended. When n-butane is used, the operation is to be carried out carefully because it is at a vapor pressure lower than atmospheric pressure,

while i-butane has a considerably higher vapor pressure than atmospheric pressure and can form solid hydrate in contact with a aqueous phase under specific conditions. The formation of hydrates result in the elimination of the ice crystals formed. The mixture with less than 73.8% i-butane cannot form a hydrate at -0.7°C with 1.6% NaCl aqueous solution, and this limiting ratio increases with increasing temperature (35).

Ice Crystallization-Unit

The direct FM process could be continuous or batch. Energy recovery is one of the important aspects of the process. The butane FM process employs butane as the immiscible refrigerant (Figure 3). The refrigerant in liquid form under pressure is expanded through a nozzle into the product liquid, where it boils at lower pressure. The vaporization of butane in the freezer removes heat from the brine, causing a portion of it to freeze as tiny ice crystals (Figure 4). Another option is to use vacuum to vaporize a portion of the water, which then provides the refrigeration effect for lowering the temperature of the product and causing ice crystallization to occur. This process is able to reduce the residence time in crystallization unit to at least half compared to flash freezing (28). These types of processes are mainly utilized for the concentration of chemicals and seawater desalination (10, 36). It is rarely used in the food industry for a number of reasons. The major reason is that a vapor-liquid interface is created, resulting in a subsequent loss of volatile flavors and aromas. The product then has no superior quality advantages over that produced by evaporation (14).

The ice nucleation unit produces small ice crystals, which are transferred into the crystallization unit and grown larger by ripening (i.e., nucleation) at the expense of the smaller ones. In the crystallization unit, the formation

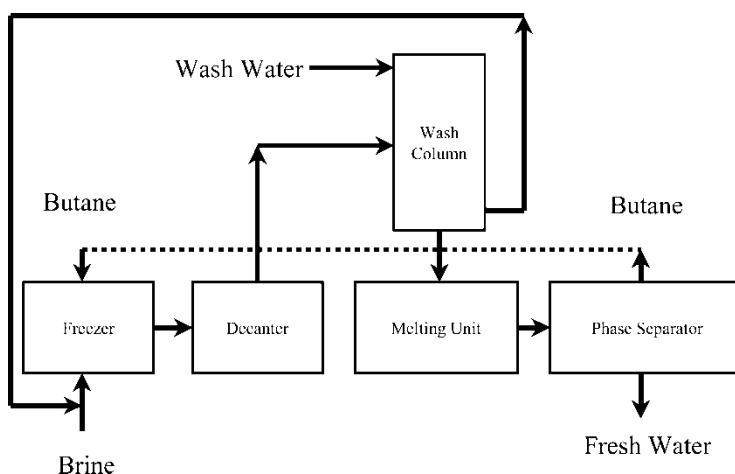


Figure 3. Simplified flow diagram of a butane FM process.

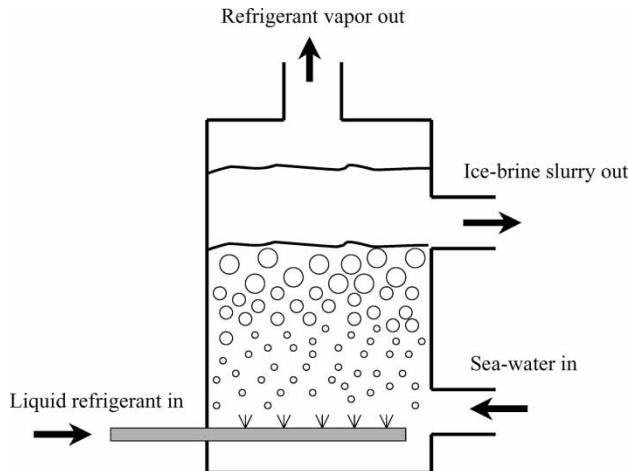


Figure 4. Schematic diagram of a direct freezing-unit (118).

and growth of ice crystals should be controlled in such a way that a uniform distribution of large ice crystals suitable for separation is formed. The optimum size distribution for most separators is a monodisperse distribution (narrow range of sizes) with a large mean size. This facilitates the washing step and reduces the amount of product carryover into the separated ice stream. The more efficient the separation process, the less carryover of salt into the separated ice stream, and the more economical the overall process is. The ice crystals are then collected and transferred to the ice crystal separator and washed with water to remove the brine from the ice crystal surface. The key technology in this system is how to grow ice crystals in the crystallization unit large enough to facilitate the separation between the ice crystals and solutes (37). From a separation point of view, the formation of a few large ice crystals is desirable. Supercooling and secondary nucleation were identified to be major factors preventing ice crystals from growing large (38–40). Very high supercooling can create a large number of smaller new crystals. Lower rates of supercooling are, therefore, desirable to prevent excessive nucleation. Lower nucleation rates are required to produce reasonably large ice crystals at an acceptable residence time (25). Thijssen (41, 42) suggested adjusting the agitation rates, within certain limits, to lower the nucleation rates, since high mixing rates may promote a smaller size due to mechanical damage. Garabedian and Strickland-Constable (43) found that fluid shear does not produce crystal breeding, and collision of a single crystal in pure water produces high rates of nucleation. Polycrystals may well be formed by agglomeration or growing together of fine crystals, but little is understood about agglomeration. The nucleation rate at low stirring rates is determined primarily by the cooling rate, while with intensive stirring it depends primarily on the hydraulic factor (44). Polymers could

suppress the secondary nucleation of ice crystals, thus a larger crystal size could be achieved. The suppression depends on the types of polymer and concentration, and is related to the increase of viscosity (39).

The circulation pattern of the ice slurry in the freezing-unit by direct contact vaporization of an immiscible refrigerant can profoundly affect the quality of the product crystals (45). Stripping of butane from products has been accomplished in a packed tower with liquid effluents containing less than 0.2 ppm butane, which meets some standard (28). Landau and Martindale (36) reported initial bench scale studies of novel butane freezers, the most promising of which used a draft tube. The butane introduced at the bottom gave good vertical movement to the slurry and 25% ice suspensions could be handled. It was found quite unnecessary to use a mechanical agitator and the unit operates satisfactorily without any additional agitation and a comparatively small flow of butane vapor, purged in near the bottom of the crystallizer, greatly improves the mixing and ensures reliable operation under all circumstances. This small flow of vapor (containing a negligible amount of incondensable gas and little super heat) is still effective in causing circulation even when the pressure in the bottom half of the crystallizer is above the vapor pressure of the butane (46).

Barduhn (28) concluded that the following points should be considered in designing secondary refrigerant freezers: (i) adequate dispersion of the liquid refrigerant into the brine is of paramount importance, (ii) normal butane is the cheapest and probably the best refrigerant and does not form any hydrate, (iii) short residence time does not necessarily lead to small crystals and poor wash ability, (iv) the plant should be designed to handle short contact times, and (v) several methods of agitation should be included in the design.

Some of the best possible ways of mixing could be: (i) use of fine spray nozzles to introduce the liquid refrigerant under the brine, (ii) pump vapor from the vapor space through spargers which reintroduce it under the brine, (iii) pump the entire liquid content of the freezer rapidly around a closed path, and (iv) use conventional mechanical agitators. The last method is the most difficult to scale up and furthermore multiple mixers appear to complicate the design and increase costs in large plants. The combination of (i) and (ii) could be a viable option (28).

The ice production rates in a spray freezer can be 10 to 30 times those in stirred tanks. Refrigerants and salt water are sprayed into a low-pressure space and slurry forms virtually instantaneously, but the particle size averages only 40 microns and the ΔT (temperature gradient between the refrigerant and the slurry) is very large at 18°C (47). In the case of RC-318 (C_4F_8) the ice crystal size was a strong function of the salinity and a marked size maximum occurred at about 0.5% NaCl. A similar phenomenon is also noted in single crystal growth rates from many aqueous solutions (48). At least two factors, namely diffusion and a surface adsorption, could be the rate controlling in a continuous crystallizing-unit (49). Depending on the liquid depth and temperature conditions in the freezer, several liquid refrigerant zones may

exist (50). Refrigerants at depths sufficient to suppress vaporization are said to be in the *inactive* zone. Vaporizing refrigerant is in the *active* zone, and if liquid refrigerant accumulates on the surface of the slurry, it is said to form an *excess* zone. Nucleation occurs mainly in the active zone, while crystal growth proceeds throughout the entire brine. The depth of the active zone can be calculated from the relationship between the refrigerant vapor pressure and temperature. It is good to prevent the formation of an excess zone, which generally interferes with good freezer control (34).

The Exchange FM process was developed by Johnson et al. (15). The crystallizing-unit is a horizontal vessel, operating at atmospheric pressure, consisting of three distinct sections: (i) an ice-brine and hydrocarbon disengaging section, (ii) an agitated or contacting section, and (iii) a brine and hydrocarbon disengaging section. The brine entering the agitated section is broken up into small droplets by turbine agitators and counter-currently contacted with a partially solidified stream of normal straight chain hydrocarbons. The melted hydrocarbon, which contains entrained brine, flows into the disengaging section where separation is effected by gravity and electrostatic coalescence. The electrical coalescer is a horizontal unit consisting of three vertically stacked grids. Applying ultrasound to crystallizing systems offers a significant potential for modifying and improving the process. The most important mechanism by which ultrasonic can influence crystallization is ultrasonic cavitation, which is particularly effective for inducing nucleation. Using ultrasound to generate nuclei in a relatively reproducible way offers a well-defined starting point for the crystallization process, and allows the focus to be on controlling the crystal growth for the remainder of the residence time in the crystallizing-unit. This approach can successfully manipulate crystal size-distribution, hence modifying solid/liquid separation behavior, washing, and fresh water purity (51). Adding an ultrasonic system in the crystallizing-unit could be tested although it has not yet been applied in the FM process.

Ice Separation

Separation devices can be classified as: presses, gravity drainage, centrifuges, filter, and wash columns (41, 42, 52–55). Filtration has proven less effective for crystal separation. It also cannot be used for washing the crystals. In many cases, screens or filters showed a history of freezing up (brine freezing in the openings of the lace) (12). Arulampalam et al. (56) investigated the effect of various physical parameters on the efficiency of separation and purification. The important factors controlling the separation efficiency of the columns were the axial diffusion of impurity and the mass transfer between the adhering and free liquids around the crystal phase. Modification of the screw conveyer was necessary to facilitate crystal removal.

Before the ice crystals can be melted they must be separated from the brine. The brine adheres to the ice crystals by means of interfacial tension.

Conventional methods used for the separation of crystals from their mother-liquor prove to be either too slow or too expensive (55).

Wash Columns

After the crystals are formed in the crystallizing-unit, the crystal/liquid slurry is separated into concentrated liquid and other crystalline components and impurities are washed from the crystal surface, producing pure crystals. To perform the separation, a wash column is used. There are two types of wash column: pressurized and gravity. In the pressurized wash column, the crystals raise to the top and hydraulic pressure forces a wash liquid, derived from the melted pure crystals, to flow down. The applied pressure also squeezes the concentrate through a filter at the bottom of the column. As the wash liquid flows down the column it removes impurities from the surface of the crystals. At the interface between washed and unwashed crystals, called the wash front, the wash liquid comes in contact with colder crystals and crystallizes on them. In this way, the wash liquid does not mix with the concentrated liquid. Effective washing of ice is one of most difficult unit operations in the FM process.

The gravity wash column is simpler in design, but larger than the pressurized wash column. Its greater height creates the pressure needed to compact the ice bed. It works in much the same way as the pressurized column but at lower pressures. An ice pack is still formed and moved hydraulically up the column. The performance of wash columns depends on the crystal size and shape and on the id having the wash water seek the path of least resistance and channel through the crystals unevenly.

In order to overcome the difficulties associated with surface tension forces, clean fresh water can serve as a displacing liquid. The displacement process can best be pictured by considering a gravity drainage separation process. The separation by drainage is greatly improved when, in addition to draining the brine from the bottom of a batch of ice crystals, one adds pure water to the top of the batch and lets the water filter through the interstices of the ice bed to displace the remnants of brine. Bosworth et al. (57) suggested a continuously operating separation device based on the displacement principle. In this device the slurry of the brine and ice crystals is introduced into the bottom of a vertical column from which the brine drains through screens at the bottom. The ice crystals move upward by their own buoyancy force forming a porous ice plug at the top of the column where wash water is added from the top. As the ice plug moves upward through the layer of wash water, the brine is displaced from the interstices of the porous ice plug and the salt-free ice crystals are harvested at the top of the column and transferred to the melting-unit. The rise of the ice crystals in the column is, however, rather slow. There is a limiting velocity for a particle moving through a fluid by buoyancy (or gravity) forces alone. This limiting velocity determines an upper limit to the production rate for such a gravity wash column, a value which is much too low for economically

viable desalination water conversion. Hahn et al. (58) modified the wash column separator described above to allow the moving brine to provide the driving force for moving the ice particles upward. The discharge screens are located in the vertical walls of the column, about midway between the top and bottom.

Wash columns have been successfully used for both separating the crystals produced in the crystallization section as well as purifying them. They are classified as the flooded column and the drained column. The ice crystal slurry is fed to one end of the column, and the mother-liquor withdrawn from the same side. The compacted ice bed is forced towards the other end of the column, where it is melted by means of a grid of internally heated pipes. A portion of the melt water is used to wash the crystals moving counter currently in the column (25).

The ice wash column could be drained and flooded types with either rectangular or cylindrical shape. Tall screens are desirable and contouring of the ice surface with the scraper can be very useful. Much higher production rates were possible by cutting out a slot in the center of the column, which fills with wash water or by cutting a deep V-shaped trough in the ice with the scraper (28). In a typical hydraulic piston washer-separator column, the ice-brine slurry is fed to the bottom of the column and moves upward. The ice builds up a porous plug until it fills the entire top of the column; the brine flows out of the column through filter screens situated laterally part way up the column walls. As the slurry is fed to the column, ice is added to the bottom of the porous plug and the brine flows through the plug. The pressure drop of the brine flowing through the plug causes the ice to move upward, and is harvested at the top of the column, usually by scraping. The washed ice is melted and a portion is recycled to the top of the washer separator as wash water. This wash water moves downward by gravity and some of it leaves the column through the filter screens with the brine from the slurry, but the greater part clings to, and is harvested with, the washed ice (6, 34).

The production of fresh water increases with the increase of ice crystal size, the ice plug length above the screens, the concentration of ice crystals in the slurry, and the external mechanical restraining forces on the ice plug. It is also found to increase with a decrease in the ice plug length below the screens, where this length is shown to be an independent parameter for certain slurry feed conditions, such as gravity feed. Shwartz and Probstein (55) provided design criteria for minimizing the capital cost for a given production rate. The theoretical analysis helped to establish the optimal operating conditions for high production rates, sufficiently low salt content in the product, and minimum loss of fresh water. At pressures below about 1.05×10^5 Pa (1 atm), the driving force in the melting-unit becomes so low that the required melting-unit cross-sectional area increases to large values, which are uneconomical (34).

Centrifuges have also been used to separate the ice crystals from the concentrated liquid. Filtering centrifuges utilize the difference in specific gravity

between the ice crystal and the liquid concentrate to separate ice from liquid with the liquid being forced through the filter basket by centrifugal force. Generally, a water rinsing is required to assure that there is no salt carryover. For food liquids, there is some loss of volatile flavors and aromas due to the airspace created during the separation. It is important to have large ice crystals to ease the ice-crystal separation from the concentrated solution phase (58–61).

Ice particles from liquids during the FM process can be separated by a filter. To increase efficiency, vacuum is normally applied to pull liquid across the filter. The vacuum filter has been used for separating the ice slurry made by direct freezing and vacuum FM systems (62–64). Solids carry over is one of the problems for the wash column. However the Grenco system for separation can give up to 100 ppm purity (65). This wash column operates continuously with counter current flow of ice and concentrate. The ice crystals are transported to the upper levels of a vertical column by some natural or applied force, where they are then separated by a scraping device. A small portion of the ice is melted and allowed to pass back down the column, giving the washing effect. The concentrate is removed through a filter at the bottom of the column.

The slurry of the ice crystals in brine is pumped to a wash separation column, where the brine and the ice crystals are separated with the consumption of a small amount of wash water. The washed ice is then sent to the melter-condenser, where it is melted by direct contact condensation of the compressed butane vapor. The primary compressor must compress the butane vapor in order to attain its condensation temperature in between the brine freezing point and the ice melting point. The two liquid phases formed in the melting-condensing unit are separated by a decanter, the liquid butane being returned to the freezer and the liquid water representing the product, except for a small amount that is used as wash water and leaves the wash-separation column with the reject brine stream. The net wash water consumption is about 2% (10).

Melting Unit

The Melting-unit is difficult to characterize although it appears to be a straightforward process. Direct contact melting is easy to achieve. However, the scaling-up is difficult. In the case of dumped bed, the characterization of heat transfer data is difficult due to the drainage of water and refrigerant from the bed. An indirect melting-unit requires a heat transfer surface, which reduces the attainable efficiency when compared with the direct contact melting-unit (15).

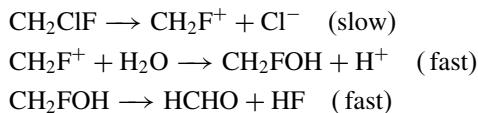
Lloyd applied the concept of integration in order to optimize the space use and to permit adjacent processes to share boundaries. A commercial design using two integral vessels for four main processing steps has been formulated. It showed that capital cost could be reduced by around 20%. Different commercial equipments are available based on this concept.

Refrigerant-Brine Interactions

The refrigerant is contaminated by the brine spray carryover from the crystallizing-unit, which adversely affects compressor performance. Thus it is necessary to develop separating devices between the crystallizing-unit and the compressor. These separators must remove ice containing an evaporating refrigerant, so simple demisters are not permissible because of ice plugging problems attendant to this condition. The dissolved refrigerant is rather easily removed by vacuum stripping of the effluent stream, which can be polished to meet environmental effluent standards by carbon absorption if necessary.

It is important to make certain that during the operation of the process, excessive losses of refrigerant do not occur as a result of entrainment and solubility of Freon in the water, and from irreversible processes such as hydrolysis. In addition if the rate of hydrolysis of the Freon refrigerant is too large, undesirable levels of soluble fluoride could build up in the product water. Stepakoff and Modica (29) developed the solubility data of Freon in order to predict the rate of hydrolysis, which is a function of dissolved Freon in water. They found that the economic loss by hydrolysis is less than 0.26 cents per m³ of water. The solubility of refrigerants decreases with the increase of salinity which is termed as salting out. The hydrolysis rate was decreased to half for a 3% saline solution relative to pure water at the same temperature and pressure. Completely halogenated hydrocarbons are much less soluble than their partially halogenated counterparts. For example, Freon 142b (CH₃CClF₂) is ten times as soluble as Freon 114 at 1 atm, -4°C. The solubility of Freon 14 (CF₄) is about three orders of magnitude less than that of Freon 23 (fluoriform, CHF₃).

The fact that hydrogen-containing Freons are much more soluble than their completely halogenated counterparts can be understood on the basis of hydrogen bonding between the CH group in the halocarbon and the oxygen dipole of the water molecule (66). The simplest mechanism for describing the hydrolysis of Freon is to assume that the rate determining step is a slow ionization to a carbonium ion and a halide ion followed by a faster reaction of the carbonium ion with dipolar water molecules (67). The essential feature of this mechanism is that every carbonium ion, which is formed in the primary step is attacked by water at a much faster rate than by halide ions, i.e., the reverse rate of the primary step is very slow. In the case of Freon 31 the mechanism of hydrolysis can be described by the following equations (68):



The presence of formaldehyde (HCHO) in the hydrolysis of Freon 31 was confirmed by chemical tests, and the rate of formation of chloride and fluoride

were found to be identical (68). Stepakoff and Modica pointed out that a similar effect could occur during hydrolysis of Freon 114. Stepakoff and Modica (69) determined the hydrolysis rate constants for Freon 21 (CHCl_2F), Freon 31 (CH_2ClF) and Freon 114 ($\text{CClF}_2\text{CClF}_2$) based on the three adjustable parameters, the Arrhenius collision frequency, the hydration energy of the carbonium ion and the ionic distance of the closest approach.

Eutectic Freezing

The Eutectic FM process was first proposed at Syracuse University. Barduhn (70) devised the process and Pangborn (71) tested the idea. In a eutectic FM process, salts separate as solids and fresh water from brine as ice. By freezing the water out of these aqueous solutions until they are adequately concentrated to precipitate the salt simultaneously, one ends up with no brine product. The ice and salt crystals nucleate and grow independently and are easily separated since the ice floats and the salt sinks. Using the simple system of sodium chloride and water the essential feature is that at -20°C both ice and $\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystals precipitate from solution as heat is removed.

Laboratory investigation of the eutectic temperatures of various proportions of the ions commonly found in natural waters (Na, K, Ca, Mg, Cl, SO_4 , HCO_3) shows that the process operated well at temperatures not lower than -25°C (71). This approach could avoid the brine disposal problem as well as the production of byproducts such as salts. The main difference between this and the normal freezing process is the presence of the ice-salt separator and the salt filter. Several important variations of this have been proposed (72). Another important difference between normal and eutectic freezing is in the crystallizing-unit. In normal freezing where the product water is the only goal, the freezer operates near -5°C and the temperature lift for the primary compressor is thus about 6°C . A two-stage eutectic FM is more economical (17, 72, 73). The costs are generally much lower than the alternative of reverse osmosis followed by deep well injection of the rejected brine. Moreover, deep well injection could be ecologically unsound. The Eutectic FM process may be one of the meaningful solutions to brine disposal (73). Schroeder et al. (17) pointed that the eutectic FM process is likely to become a very important process in the future when it is better developed. A stirred-tank crystallizing-unit is required, and a hydrocyclone separator and floating wash column are used (73).

The hydro-cyclone separator splits the slurry into a light and heavy cut. The light cut, called the overflow, contains the ice crystals and brine. The heavy cut, called the underflow, contains the salt solids and brine. The salt solids could be separated from the brine, utilizing conventional solid-liquid separators such as filters, and then dried in conventional dryers. The brine filtrate is required for the crystallizer (17). The hydro-cyclone is a compact, simple device working with a low pressure drop. Washing is difficult due to

the small ice crystal size, and low slurry temperature. Schroeder et al. (17) identified the possibility of combination of eutectic freeze and the distillation process and membrane and eutectic freeze processes. The product stream of eutectic freezing would be a brine of low salinity, which would be returned to the distillation plant or membrane process in an actual operation. The cost of the membrane process depends on the brine concentration. The melted ice water from a single freezing step without any washing contains 3 to 6 times less salt than the feed (75).

Indirect Contact Freezers

In the indirect-contact FM process, the energy for refrigeration must be passed through the walls of some form of heat exchanger, and heat transfer occurred through a solid barrier (42, 75). It was found that the growth rate of dendrite type ice in supercooled water cannot completely be understood on the basis of heat-flow controlled-growth mechanisms but has to be explained on the basis of the combined mechanisms of heat dissipation and molecular-growth kinetics (76, 77). The indirect contact system can be classified into those that are internally cooled and those that are externally cooled. Internally cooled crystallizers can be further subdivided into a static layer growth system, a layer crystallization unit on a rotating drum, a progressive crystallization unit, a dynamic layer growth system, and suspension crystallization processes.

Internally Cooled

Static Layer Growth System

In layer growth systems, the liquid from which the crystal mass is grown is stagnant and it is termed as static layer crystallization. The static operation of solution crystallization in this process is very reliable and requires very simple equipment without moving parts and without the need of a solid-liquid separation device. The residence time in this process is large because the mass transfer is only promoted by free convection. Large equipment volumes are required due to the batch-wise operation and the slow crystallization rate (78, 79). The crystal-solution interface per unit equipment volume can be increased by using a plate-type contact surface, but static growth can not be avoided (80). High purification efficiency can only be obtained when relative low rates of growth ($<10^{-7} \text{ m} \cdot \text{s}^{-1}$ or $0.36 \text{ mm} \cdot \text{h}^{-1}$) are established since no stirring is applied. The capital cost of the equipment is high and more economic use can be obtained by carrying out more than one relatively rapid crystallization in series.

Muller and Sekoulove (81) pointed out that the layer freezing process is easier to manage, but the crystal growth upon a cooled surface induces fast crystallization rates and under these conditions rather impure crystal film

may be produced. In spite of this moderate crystal purity, the disadvantages are compensated by the ease of operation, because there are no moving parts and no slurry handling. Two mechanisms of crystal growth were found in a batch crystallizer with an external cooler that contained a large amount of ice crystals. With the first mechanism, the ice crystals grew larger by the usual kind of growth, governed by heat or mass transfer resistance. With the second mechanism, the ice micro-crystals agglomerated and the agglomerates fused into a very large ice crystal (1–3 mm in diameter). The second mechanism occurred not because of the high concentration of ice crystals in the crystallizer but because of long residence times. Large ice crystal agglomerates were not produced when extremely small ice crystals were formed in the crystallizer at the start (59).

Layer Crystallization Unit on Rotating Drum

In layer crystallization with a rotating drum FM process, ice forms in thin layers on the heat exchange surface, and after a suitable period of time for the ice layer to build up, the ice is removed from the surface and is separated by a press from the concentrated liquid remaining. One form of layer crystallizer utilizes a rotating drum immersed in the fluid to be concentrated. Refrigerant is circulated within the drum and causes ice to form on the surface of the drum, which is then scraped free as the drum rotates past a knife (14).

Progressive Crystallization Unit

A progressive crystallization FM process is a method of separating the solvent from a solution based on a concept completely different from the conventional method of layer crystallization described above (82). The progressive FM process utilizes the concentration phenomena of a solute at the ice-solution interface moving from one end of a vessel to the other end (83). It is characterized by having only a single ice crystal in the system so that the separation of the ice crystal from the concentrated solution is very easily done compared with the conventional method of freezing-melting (Figure 5).

The concentration efficiency in the progressive freeze concentration was related to the ice structure of the freezing front. High freeze-concentration efficiency was obtained under the conditions at which a smooth solid-liquid interface is formed. The distribution coefficient depends on the ice structure at the freezing front, and operating conditions represented by the moving speed of the freezing front and the speed of stirring in the solution phase (82, 84). Liu et al. (37) studied the operating conditions of this process on the freeze-concentration ratio and the apparent partition coefficient of a solute between the ice and the solution phases (glucose and/or blue dextran). They found that the efficiency of the process is strongly dependent on the moving speed of the freezing front and the agitation or stirring speed at the ice-solution interface. A lower moving of the freezing front and a higher stirring speed produced a better freeze-concentration ratio. A concentration polarization model was useful to describe the effects of the operating

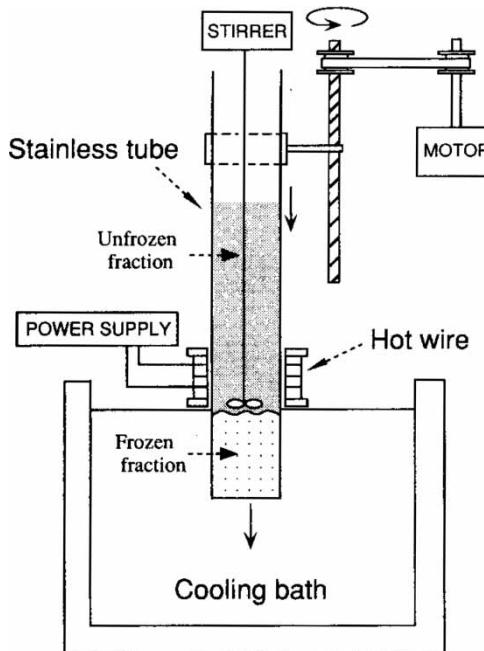


Figure 5. Apparatus for progressive Freezing-Melting Process (37).

conditions on the effective partitioning coefficient (84). Matsuda and Kawasaki (85) investigated the effects of supersonic radiation and the dissolved air concentration in the liquid on the efficiency of separation and concentration of glucose and sodium chloride under various freezing rates. They found that the efficiency was greatly improved by supersonic radiation and increasing dissolved air concentration.

In the progressive freeze-concentration, the major part of the impurity in the ice phase occurs when supercooling occurred before the initial crystallization at the bottom of the sample vessel. Different mechanisms of solute rejection at the interface were observed (86). Ice-nucleating protein (types of anti-freeze proteins) could be used to suppress initial supercooling (37, 87, 88). Curran (75) studied the effects of container geometry on the recovery of product water from indirectly frozen salt water. Salt water was frozen in containers having a circular or rectangular cross-section, then allowed to melt and drain until the residual ice was potable. Thin rectangular cross-sections were found to be more effective than circular cross-sections. The product water recovery was found to increase with increasing ice height up to 60 cm, beyond which the effect of height was negligible.

The growth rates of ice depend on the ionic salts, surfactants, and water-soluble polymers. Michaels et al. (87) identified that both growth-rate enhancements (up to a factor of about five) and retardations (up to a factor

of about three) could be possible in the presence of additives. The type of effect and its magnitude were dependent on the nature of the additive, its concentration, and upon the degree of super-cooling. The effect of solutes may have a consequence of dislocations introduced in the crystal during growth. Recently Miyawaki et al. (89) showed that a tubular ice system with a large cooling surface area was effective as a method for scale-up of progressive freeze-concentration with an increased productivity and high yield. In this method, the slower growth rate of ice and the higher circulation rate gave the lower effective partition constant as was expected theoretically by the concentration polarization model. The effective partitioning constant was also dependent on the initial solute concentration; the higher concentration gave the higher partitioning constant of solute. By the tubular ice system, coffee extract, tomato juice, and sucrose solution were very effectively concentrated to high concentrations with good yields, showing the high potential of progressive freeze-concentration for practical applications.

Dynamic Layer Growth System

In the falling-film type, solution flows down over the wall of the heat exchanger (well-mixed). Crystals are formed on the wall surface under the falling film. Shear caused by solution flow at the crystal-solution interface increases the mass transfer coefficient and promotes the transport of impurities from the interface to the bulk. This process is easy to scale-up because of the modular design. Currently, most of all layer growth processes are used in the chemical industry and seldom in the food industry.

Local equilibrium at the interface exists and solute trapping occurs based on the rate of crystal growth (90). Solutes are distributed between brine and ice crystals. Adsorption on the ice crystal surface and entrapment within the ice may be the major reason for the presence of the solutes in ice. The distribution or coefficient of salt (ratio of salt in brine and ice) is used to determine the solids in the ice and slurry (91).

In the circular tube-type process, ice is formed from a solution flowing through a tube cooled from outside (92–95). Supercooling can be obtained in a liquid before it solidifies when forced to flow inside circular tubes. The maximum supercooling depends on the local tube wall temperature, tube inside diameter, Reynolds number, and a dimensional constant depending on the process (96). The salt entrainment in the ice layer is one of the major problems in the indirect FM process. Janzow et al. (97) studied the salt entrainment in ice crystallized from brine on a flat pellet. First the ice layer thickness increases rapidly, reaches a maximum, then decreases. The phenomenon corresponds to the growth and subsequent melting of dendrites. It was believed that brine adhering to the thin plates of ice and perhaps being retained in the interstices by capillary forces is responsible for the relatively high salt concentration found in the melted ice. A rinsing operation could be applied to the reduced brine content in the ice layer.

Suspension Crystallization Unit

In the suspension crystallization unit, the product to be concentrated is agitated in a vessel cooled by heat transfer through the walls of the jacketed vessel. This vessel may be either a scraped-surface heat exchanger or simply a jacketed kettle vessel. The result of this process is a fluid suspension of ice crystals in the concentrated product, which must then go to a separation device. Independent control of ice nucleation and crystal growth is very difficult in this type of crystallizer (14). Many variations have been investigated to develop a process that allows independent control of ice nucleation and crystal growth (54).

A modification of the process above involves recycling of all or part of the mass in the main vessel. One process recycles the entire crystal slurry through an external heat exchanger, similar to a forced-circulation evaporator, to provide cooling. Nucleation occurs mainly in the heat exchanger, usually a scraped surface, while most of the growth occurs in the main vessel. In a slight variation of this system, only the liquid product from the main vessel is recycled by withdrawing the liquid through a filter. This ice-free liquid is then pumped through a scraped-surface heat exchanger operating at high sub-cooled temperature to promote nucleation of small crystals (50 μm). These fines are then pumped back into the main vessel, where a ripening process occurs. The difference in equilibrium conditions between the fine nuclei and the existing seeds provides the driving force for ripening, which results in the dissolution of the fines and the growth of the seeds as the equilibration process occurs. Large mono-disperse crystals may be formed in this way (14). In the ripening tank, the unstable subcritical ice crystals melt and the latent heat that they absorb in melting causes freezing on the surface of the large ice crystals in the ripening tank (98). As small crystals have a lower melting temperature in solution than larger crystals, the small crystals melt and re-crystallize on the surface of the larger ones.

Externally Cooled

Externally cooled crystallizers employ a heat transfer device external to the main crystallization vessel. One type of externally cooled crystallizing-unit employs a heat exchanger to super-cool the liquid feed so that the cold feed provides the cooling effect in the main vessel. Nucleation and subsequent crystal growth both occur in the main vessel. Conditions in the heat exchanger must be closely controlled to prevent nucleation from occurring where it is not wanted (14).

A modification of the external cooling process involves recycling all or part of the mass in the crystallizer. One process recycles the entire crystal slurry through an external heat exchanger to provide cooling. Nucleation occurs mainly in the heat exchanger, usually a scraped surface heat exchanger, while most of the growth occurs in the crystallizer. Ideally, ice-free liquid is cooled to promote nucleation and generate small crystals by

being pumped through a Scrap Surface Heat Exchanger (SSHE) operating in high supercooling conditions. These fine crystals are then transported with the product into the crystallizer, where a ripening process occurs.

Super-Cooled Feed

A solution is super-cooled in a heat exchanger without ice formation. Ice crystals are formed instantly in a nucleation device before being transported to a separate vessel for growth. The primary aim is to avoid heterogeneous crystallization within the crystallizing-unit. The inside wall of the heat exchanger has to be highly polished or coated with a hydrophobic plastic to minimize changes of minimum nucleation and crystallization within the heat exchanger. The concentrated solution is filtered to effect ice separation. Low energy consumption is claimed (99). Janzow and Chao (100) identified that within a relatively narrow range of super-cooled brine temperatures, large plate-like free ice crystals of up to several inches (~ 10 cm) in length were formed in the bulk of slowly traversing brine simultaneously with the growth of dendrite ice on a cold surface.

Ripening Vessels

It has been reported that ice crystals with 1 mm diameter could be produced by applying the process of ripening (26, 101) with long residence time of ice crystals. Smith and Schwartzberg (102) examined ice crystal size change during ripening. The method of producing large ice crystals, which uses the Ostwald ripening effect, was developed and is now widely used in industry. Shirai et al. (59) and Kobayashi and Shirai (61) proposed another strategy to make large ice crystals by agglomerating the small ice crystals produced. The theoretical analysis of certain FM systems was also carried out by Bayindirli et al. (91) and Ratkje and Flesland (103).

Vacuum Freezing

Vacuum-freezing and vapor-compression systems have been used for sea-water desalination. Water can itself serve as the refrigerant in vacuum freezing (104). In this option a high vacuum is used to vaporize a portion of water, which then provides the refrigeration effect for lowering the temperature of the product and causing ice crystallization to occur. The washed ice is melted by direct contact condensation of the water vapor in the melting-condensing unit. All vacuum freezing processes contain a crystallizing-unit which is a vessel in which ice crystals and vapor are formed simultaneously by maintaining the vessel close to the triple point (when material could not be considered either solid, liquid or gaseous) (0.61 kPa). Based on the method by which the vapors are removed, these may be further classified as: (i) vacuum-freeze and vapor-compression systems, (ii) absorption-freeze and vapor-compression systems, and (iii) vacuum-freeze and ejector-absorption systems.

In the *vacuum-freeze and vapor-compression method*, a mechanical compressor is used to remove the vapor phase. The vapor is compressed so as to permit it to condense either directly as pure crystals or on a heat-transfer surface. In case of *absorption-freeze and vapor-compression*, water vapor is absorbed in a material that has a vapor pressure below the triple point and the absorbent has to be regenerated. A conventional refrigeration cycle can be used to provide the heat necessary to drive off the absorbed vapor. The *vacuum-freeze and ejector-absorption* method uses mechanisms to remove the vapor by an absorption cycle or low-pressure steam ejector. The steam that drives the ejector is also used to regenerate the absorbent. The ejector acts as a thermal compressor to raise the quality of the removed vapor so that the vapor can be condensed (25).

Vapor Compression System

In the vacuum freezing vapor compression process, a large multi-blade compressor is used to compress the vapor from the freezer to the melting-unit. For a plant having a capacity of $227 \text{ m}^3/\text{day}$, the compressor was more than 3 m in diameter and needed a fairly high moment of inertia for starting. For larger desalting plants of perhaps $4000 \text{ m}^3/\text{day}$ and above, it is difficult to find a practical compressor (105). There are two components of a vacuum freezing system: the vapor removal unit to keep the slurry at or below its triple point and a freezing/ evaporation unit to keep ice particles suspended with a fluid slurry/vapor interface. An economical system will have the freezer and vapor removal units of nearly the same capacity, but both are expensive. In principle, a balance between the size of the evaporation and condensation units could be calculated from existing correlations when standard thermodynamics are known, which is difficult. The primary compressor must compress the water vapor from a pressure somewhat below the vapor pressure of water in equilibrium with the brine at its freezing point up to a pressure somewhat above the vapor pressure of pure water at 0°C . An auxiliary refrigeration cycle is needed to remove the excess energy from the system as a standard ammonia cycle removing the heat of condensation of the excess water vapor and rejecting heat to ambient cooling water. Pachter and Barak (106) identified the following module for increasing a compressor's efficiency: multi-compressor modules, direct contact and evaporative feed pre-coolers, and multi-stage heat removal compressors of flexible blade type. Burton and Lloyd (107) examined the design considerations of the primary and secondary compressors. Additionally two other aspects, safety and environment, affecting component specifications were discussed.

Vapor Absorption

In order to maximize the low energy consumption advantage of FM, it is necessary to seek a different solution, for example the vacuum freezing

ejector absorption process (VFEA) can be a solution (57, 108, 109). In an absorptive vacuum freezing process, water evaporates from the freezing solution and condenses on a cold salt solution. Condensing on a flowing cold NaCl solution was found to be an inexpensive water vapor removal method. In this process, water vapor is compressed by a combination of steam ejector and absorber loop with the primary energy source being thermal rather than mechanical. The process incorporates an absorption loop, which raises the pressure and temperature of a portion of the vapor entering the freezer to a level sufficient to drive the steam ejector. The primary and secondary steam discharged from the ejector is at the stoichiometric temperature required to melt the ice. The absorption loop, in raising the freezer vapor pressure from a level slightly more than 400 Pa (0.004 atm) to that of the primary steam, acts as a compressor. The ejector has the advantage of no moving parts and is capable of being designed for larger plants.

The real novelty was in the fact that the water vapor generated in the freezer is recycled through the system to act as the primary steam for the ejector. The addition of heat was completely separated from the process cycle. For a medium to absorb water vapor, a solution of sodium hydroxide is usually chosen as being most appropriate to the pressures and temperatures in the VFEA process. It is also an inexpensive chemical in comparison to alternate choices and is readily available in adequate quantities. The average vapor pressure in the absorber is maintained below the crystallizing-unit pressure to provide the driving force for vapor absorption. The dilute sodium hydroxide solution from the absorber is heated by the concentrated solution in the absorber heat exchanger before it enters the concentrator. The main feature of the VFEA process is that it can use low-grade thermal energy, which may be generated by flat plate solar collectors. This combination would seem to be attractive in remote coastal or inland communities (105).

The low operating pressures, below 600 Pa (0.006 atm), make the effectiveness of this method dependent on keeping the fraction of non-condensable gas in the vapor phase. Air introduced with the feed and from equipment leaks will accumulate near the condensing interface unless removed by a mechanical pump down stream from the condenser. Non-condensable gas entering the vapor space between the freezing slurry and absorbent will be pushed to the absorbent surface by the water vapor flow impeding water vapor condensation (12, 104). In many cases, feed saline water intake is first pumped to a vacuum de-aerator in order to remove dissolved air and other gases before being pumped into the crystallizing-unit (105). The advantage, which offsets the cost of the low pressure compared to the more usual indirect FM is that the freezing slurry is chilled uniformly, without a stationary interface between the coolant and the freezing slurry. Stationary interfaces require constant, costly removal of ice or special interface treatment to keep the ice from reducing heat transfer to the coolant. A cost-effective absorber design often is sufficiently

complicated so that published models and theories are of limited use in predicting performance (110).

High Pressure Melting

Vacuum-Freezing with high-pressure ice-melting process was introduced by Cheng and Cheng (111), and improvements were proposed by Cheng et al. (112). In this process high pressure ice-melting (washed ice) and de-sublimation of the low pressure water vapor are conducted simultaneously and respectively inside and outside a heat conductive conduit. Thus, fresh water is formed inside the conduits and a de-sublimated (ice) deposit is formed on the outside of the conduits, which is then melted. In some cases an in situ desublimate dissolution operation is used. In this case an aqueous solution is brought into contact with the de-sublimated mass and the conduits are depressurized. The de-sublimate dissolves in the aqueous solution and an equivalent amount of ice is formed inside the conduits. It is noted that in the result of the in situ desublimate dissolution operation, the de-sublimate is not recovered as product water. The advantages are: it does not require a compressor or absorption solution for the low pressure vapor, it does not require a regeneration loop or a heat pump (a refrigeration loop) to reuse the heat released in the condensation or de-sublimation of low pressure water vapor in supplying the latent heat of melting ice, the process uses commercially available components and can be operated reliably (11). An extended surface freezer, such as rotating tray freezer used in this process is found to have several advantages over the conventional spray freezer or agitated jet evaporator. These advantages are: (i) there is less losses of driving force due to back-mixing of brine, (ii) the need of a demister is eliminated, (iii) the power input in the refrigeration is saved although a portion of the power is used by stirrer, and (iv) larger crystals can be made so that the crystal washing operation is facilitated (113).

Vacuum Freezing Multiple Phase Transformation FM Process

In case of low pressure below the triple point of water (less than 610 Pa) sublimation occurs and it is called sub-triple point vapor. When a sub-triple point vapor is cooled at constant pressure, it condenses the solid solvent as ice and this operation is called de-sublimation. When a super-triple point vapor is cooled at constant pressure, it condenses as liquid. Cheng et al. (114) proposed a vacuum freezing multiple phase transformation (VFMPT) consisting of vacuum evaporation freezing, sub-triple point vapor desublimation, de-sublimate melting, super-triple point vapor generation, crystal-washing, and crystal melting. A preliminary economic analysis shows that VFMPT process can be more competitive than reverse osmosis and distillation/evaporation in the range of solute concentrations represented by sea water desalination both in terms of equipment and operating cost, and in many applications when concentration is higher VFMPT can be more suitable for

the reverse osmosis process, which requires very high pressure. Advantages identified for the VFMPT process are: high heat transfer rates, low energy input, insensitivity to fouling and corrosion and the ability to handle highly concentrated as well as acidic and alkaline solutions.

MERITS AND DRAWBACKS OF EACH PROCESS

Comparison Between Direct and Vacuum FM Processes

In vacuum freezing the compressor must handle a very large volume of low-density water vapor due to the very low vapor pressure of water, whereas when relatively volatile refrigerant, such as butane is used, the freezer pressure is raised to approximately atmospheric pressure, and the volume of vapor to be compressed is greatly reduced. Furthermore, compressor technology for butane from 0.85×10^5 to 1.05×10^5 Pa (0.85–1 atm) is much better developed than that for water vapor compression from around 400 Pa (0.004 atm). On the other hand, in vacuum freezing, no butane is added to the system, and therefore the complexity and expense of butane recovery, butane make-up, and fire and explosion protection measures are avoided. Hence the relative simplicity of vacuum flash freezing recommends its use, especially for desalination plants of small size (10).

In the case of vacuum freezing, the residence time is not an important variable and the process is more heat transfer controlled requiring agitation. Moreover the melting unit needs a more efficient design for removal of non-condensable gas in the system (28).

The cost of flash freezing for water was reported as \$1.35/1000 U.S. gallons (0.31 €/m³) using 45 kWh/1000 U.S. gallons, (12.5 kWh/m³), 18°C (75°F) sea-water, 1 cent per kWh power and labor at 1/2 man per day (28). The two big advantages expected of all crystallization processes are their indifference to scaling or corrosive feeds and the substantially decreased water cost with decreasing feed salinity.

Comparison Between Direct and Indirect FM Process

Water from a direct refrigerant FM process would contain excessive amounts of volatile refrigerant, which is undesirable in most cases. This process could keep 80 to 140 ppm of butane, up to 3% CH₂ClF, CF₂Cl₂ or other halogenated hydrocarbons (115). These gases must be recovered and recycled down to about 1 to 10 ppm to recover their economic value and/or to prevent explosion hazards, and probably to the 0.1 ppm range to meet public health standards for drinking water (10, 116). When the dissolved gas is to be recovered after removal, it is important that the process be uncomplicated in order to keep the cost low. Simple flashing of the product streams at

reduced pressures is useful, and probably necessary, but not sufficient since the approach to equilibrium in a single stage flash is not very close because of the very short residence times in spray chambers. In this case, lowering the flashing pressure is the key to maintaining the low ppm of the refrigerants. Bajolle et al. (116) designed stripping butane from water in a packed column down to concentrations as low as 0.6 ppm. The mass transfer of butane from the melted water was experimentally shown to be liquid-diffusion controlled. The results obtained are expected to be valid as long as the thermal effects are not significant, that is, as long as the column is operated at a total pressure not below the vapor pressure of water.

The formation of hydrates consisted of two phenomena, which were almost always observed when the freezer was being tested at low driving forces. First, the ice becomes oily, somewhat impalpable, and washing become poor. Operators called this rotten ice. Second, the inventory of butane in the storage tanks dropped steadily. This accumulation of butane in the freezer, washer, or melter could be due to hydrate formation. Insufficient agitation at low temperature gradient can lead to accumulation of the liquid butane in the freezer and it will then carry over into the washer reducing the porosity of the ice bed, thus resulting in poor washing. In some cases, when the refrigerant is well dispersed, it shows no hydrate formation even with 80–20 mixtures of iso- and n-butane. Mixed refrigerants, for which the vapor-liquid equilibrium is normal (i.e., the temperature-composition diagram is lens-shaped), have a disadvantage, since the bubble and dew points differ. In the case of iso- and n-butane this difference at the compositions used is about 1°C. Thus 1°C is added to the total temperature lift of the heat pumping cycle, which adds about 10% to the energy requirement for the primary compression beyond what is needed for a pure or an azeotropic refrigerant. Hydrates may also cause channeling in the wash column.

Hydrate formation is one of the main problems of the direct FM process. The rate of heat transfer among the four phases present in a butane freezer controls the rate of ice production and this in turn is determined mainly by the liquid-liquid interfacial area and the intensity of turbulence in the freezer. The lack of proper liquid dispersion and adequate agitation in the freezer has led to production at low rates per unit volume and has probably caused all the trouble with butane hydrates.

Formation of hydrates is one of the problems that occur in the direct freezing process. Iso- and n-butane may form hydrates. Having two crystal species present (ice and hydrate) is uneconomical for the process since heat must be removed at the lower of the two formation temperatures and rejected at the higher of the two. In the case of ice and iso-butane hydrate, this increases the total temperature lift for the primary compressor by about 2°C, which may increase the energy requirement by as much as 30%. Even more serious than this is the fact that the hydrate reduces substantially the permeability of the crystal bed in the wash column. Butane-1 usually shows less hydration compared to normal butane. Operation on butane-1 was similar to

that with the butane mixture, and hydrates and rotten ice still appeared under certain conditions. In addition, the smell of the commercial hydrocarbon bothers many people, and it costs about 31c per gallon (7 euro cent per liter) as compared to 11c (2.5 €c/L) for normal and 14c (3.2 €c/L) for iso-butane (117). Fernandez et al. (3) found similar rates of formation in hydrates in the case of propane, F-12 (CCl_2F_2) and methyl bromide (CH_3Br). Roux found that F-31 (CH_2ClF) formed hydrate 6 to 10 times as fast as the above refrigerants. The F-31 hydrate crystals were compact rough spheres with average diameters of 150 to 190 microns. Both propane and methyl bromide hydrates are smaller and much more dendrite-type and probably more compressible in beds than other hydrates. Hydrate properties depends on the type of refrigerants.

Homogeneous nucleation of ice crystals requires a subcooling of several degrees and does not occur in the direct-contact freezing process for which brine temperatures are much closer to the freezing point. All new crystals are formed from existing crystals by secondary nucleation processes such as breaking of crystals by collisions or removal of fragile dendrites by fluid shear (45).

The refrigerant compressor limitations and problems are important limitations for the direct FM process. However, they can be eliminated by the use of a new type of compressor known as the hydraulic refrigerant compressor (118). The hydraulic refrigerant compressor does not use lubrication (i.e., it avoids lubricant contamination), and water and water vapor carried into the compressor inlet have no detrimental effect on the compressor. This compressor is highly efficient, and so it avoids the problem of freeze desalination caused by conventional compressors. At the freezer and melting unit temperatures, the pressure of the two-phase n-butane refrigerants is very near atmospheric pressure, which is a large advantage in the freeze desalination system since the pressure vessels need only to withstand very small pressure differences and can be of minimal strength and cost. The advanced technical skills associated with the design, installation, and maintenance of conventional refrigerant compressors are not needed, nor are expensive spare parts storage required. The hydraulic refrigerant compressor is simple, of low cost and low maintenance. It is compatible with the other components of a freezing-melting process.

Comparison of Different Types of Direct FM Processes

Usually a conventional direct contact FM process operates around -5°C , whereas an eutectic FM process operates at -25°C , thus needing more energy for cooling. The main advantage of the eutectic FM process is that it can separate both ice and salts at the same time and avoids the brine disposal problems. With the precipitated salts different by-products could also be produced by the eutectic FM process.

Comparison Between Different Types Of Indirect FM Processes

The performance of suspension growth systems can be improved by adopting a multistage design (119). The main advantages of the multistage plants include lower energy consumption and approximately 50 to 70% lower operating costs than the single-stage process. The loss of soluble solids usually is less than 100 ppm after the washing step in the Genco systems.

The drawbacks of a dynamic growth system are numerous. It includes (i) the need for a large solution circulation rate, (ii) the need for a large crystallizer volume, (iii) multistage operation is required to attain high purity (sometimes 8–9 stages may be needed), (iv) some variables such as the number of stages, the reflux ratio and the maximum thickness of crystal layer need to be optimized and (v) the cost and energy efficiency are adversely affected by the need for repeated operation of a batch procedure. A continuous commercial dynamic layer growth process using a counter-current layer crystallization technique is called the Bremband belt crystallizer (120). The main problem of this process is that it is uneconomical.

A comparison of layer and suspension crystallization growth is given in Table 3 and Table 4. Both layer and suspension processes are governed by the same crystallization laws. This means that the results obtained with both process types will, in principle, be the same when the operating conditions are identical.

In practice, the main advantages of layer growth in comparison with suspension growth come from simple technology with simple design and scale-up. High growth rate can be achieved in layer growth processes because heat is transferred through the solid layer. However, large growth rate usually results in a limited effective distribution coefficient in a single stage. By adding a sweating step and by repeating the operation, high purity can be attained but at higher costs.

The main features of suspension growth option combined with wash column technology are large single-stage efficiency and large net production per volume of equipment and time period. The suspension option also offers a continuous operation, which may result in lower energy consumption.

The progressive FM process can be easily run at atmospheric pressure and is less complex. It gives only one block of ice. Thus separation and the melting process are easy. However, the main disadvantage is that it requires greater processing times and large temperature differentials (75).

CONCLUSIONS

A thorough literature survey was done on the different desalination methods in order to evaluate the Freezing-Melting (FM) process. Desalination refers to a water treatment process that separates water from salt solutions and its use has grown steadily since the 1960s. Based on this process, desalination plants can

Table 3. Comparison between layer and suspension growth (121)

Feature	Layer growth	Suspension growth
Purity attainable	Limited per stage (repetition needed)	High in one single stage
Crystal-solution interface	Small ($10-100 \text{ m}^2/\text{m}^3$)	Large ($10,000 \text{ m}^2/\text{m}^3$)
Growth rate	Large ($10^{-5}-10^{-7} \text{ m/s}$)	Small ($10^{-7}-10^{-8} \text{ m/s}$)
Purification	Solid-liquid separation, sweating and reprocessing in same unit	Solid-liquid separation, sweating and reprocessing in separate devices
Production rate/volume of equipment	Small	Large
Way of operation	Batch, possible continuous	Usually continuous
Technical feasibility	Proven technology	Force transport columns: demonstration phase
Heat transfer coefficient	Small ($50-400 \text{ W/m}^2\text{K}$)	Large ($1,000-4,000 \text{ W/m}^2\text{K}$)
Design	Simple	More complicated
Scaling up	Simple	More complicated
Crystal size (distribution)	Not important	Important
Solid-liquid separation	Simple by draining followed by melting	Extra device needed
Pieces of equipment	One single	Several
Moving parts	Only pumps	More moving parts needed
Transport problems	No suspension handling	Pumping of suspension
Incrustation	No, layer is product	Yes, may be hampering
Flexibility	Multipurpose	More tailor made
Reliability	Restart without loss of product	Loss of product in case of interruption which has to be recycled

be categorized into two types: phase change processes (i.e., evaporation or freezing), and absence of phase change process (i.e., reverse osmosis and electrodialysis). The FM process is essentially capable of removing water by freezing it out from saline solution as ice crystals. In general, the components of FM processes are: (i) a pre-cooler to cool the feed water, (ii) a crystallizing unit, where sufficient heat is removed from the process fluid to form ice crystals, and (iii) a crystal separator and purifier, where the crystals are separated from the unfrozen concentrate, washed, and then melted.

A wide variety of FM systems are currently on the market. These are: (i) direct contact freezing, (ii) indirect contact freezing, and (iii) vacuum freezing. In the case of direct freezing, the refrigerant in the liquid form under pressure is expanded through a nozzle into the product liquid, where

Table 4. Applications of the commercial FM systems for food liquids

Food liquid	Product concentration	System ^a	References
Fruit juice	40–55 wt%	Grenco in USA, Japan, Italy	Grenco (122); Muller (18); Deshpande et al. (25)
Vinegar	12.8–40 wt% acid content	Girder in USA	Staff (123)
	Up to 400-g	Votator	Votator (124, 125)
	48 wt%	Grenco in USA	Wagner (126)
Beer & wine	12.5 wt %	Phillips	Deshpande et al. (25)
	32% by volume	Grenco	Wagner (126)
	4-fold	Grenco in UK	Grenco (122)
Coffee extract	35–48 wt%	Grenco in Brazil, Japan, UK, Switzerland,	Grenco (122); Wagner (126)
Sugar solution	Up to 50 wt %	Grenco	Wagner (126)
Whey	Up to 40 wt %	CSI	Davis (127); Saal (128)
Skim milk	Up to 36 wt %	Grenco	Deshpande et al. (25); Wagner (126); Basta and Fouhy (129)
Whole milk	Up to 38 wt%	Grenco	van Mil and Bouman (130); Basta and Fouhy (129)
Tea extract	Up to 35 wt%	Grenco	Wagner (126)

^asuspension crystallizer i.e., stirred tank with wash column technology.

it vaporizes at lower pressure. This vaporization provides a refrigeration effect and causes the formation of ice and/or solute crystals within the product. The successful design of a direct contact freeze desalination plant significantly depends on its thermodynamic, chemical and physical properties, and its cost. In indirect-contact FM processes, the heat energy for refrigeration passes through the walls of some form of heat exchanger. It is available as two types: internally cooled and externally cooled. In vacuum freezing FM processes, water can itself serve as the refrigerant. Each system has its advantages and disadvantages. In the vacuum freezing FM process, the compressor must handle a very large volume of low-density water vapor due to the very low vapor pressure of water. When relatively volatile refrigerant is used in case of the direct FM process, the freezer pressure is raised to approximately atmospheric pressure, and the volume of vapor to be compressed is greatly reduced. However, in vacuum freezing, direct contact with the refrigerant can be completely avoided. The main disadvantage of direct FM is that water could contain excessive amounts of volatile refrigerant, which is undesirable in most cases. It is also not easy to separate the refrigerant due to the formation of hydrates. In the case of indirect FM, these hydrates could be

avoided but the process is more complex. The choice of a technology is usually based on product quality, operating economy, energy cost, initial investment, and the complexity of the process. The main factors affecting the use of FM process are the capital cost and complexity of the process. This is clearly evident from the wide varieties of alternatives available in the state-of-the art.

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