θ = angle of inclination of column plate from the vertical
θ^* = angle of inclination for best performance
ρ = mass density
σ = $(\sigma_e + \sigma_s)/2$
σ_e, σ_s = mass flow rate from the enriching, stripping section
Δ' = $\Delta\sigma/H_0$, reduced separation
σ' = $\sigma L/K_0$, reduced flow rate
σ'_c = reduced critical flow rate above which inclination decreases the performance

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Freezing Process Based on the Inversion of Melting Points due to Applied Pressure

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A new freezing process for the desalination of seawater is being developed which utilizes a unique way of upgrading heat energy where there is no gas phase involved. This method takes advantage of the abnormal melting point curve of water. Water melts at a lower temperature under a higher applied pressure (that is, (dP/dT) melting < 0), while an ordinary substance melts at a higher temperature under a higher applied pressure (that is, (dP/dT) melting > 0). Due to this difference a substance which melts at a temperature lower than the freezing point of an aqueous solution may melt at a temperature higher than the melting point of water at a sufficiently high pressure.

Thus, a suitably selected working medium can be used to form a cyclic auxiliary system which can be incorporated with the main system to: remove the heat of crystallization of water in the partial freezing of an aqueous solution by melting the working medium at a low pressure, and to supply the heat for melting the ice by solidifying the working medium at a sufficiently high pressure.

The essential requirements of any successful freezing process to produce fresh water at a low cost are: removal of the heat of crystallization in the partial freezing operation, upgrading of the heat thus removed so it can be reused to melt ice, and control of the ice crystal size and shape, and separating and washing the ice so formed. All conventional freezing processes have two features in common (*1* to *7*). First, the heat of crystallization of water in the partial freezing operation is removed by vaporizing a liquid, either by vaporizing water under a vacuum or by vaporizing a refrigerant. Second, the removed heat is upgraded by compressing the formed vapor to raise its condensation temperature. Thus, the heat of condensation can be used to supply the heat required in the melting of ice.

A new, distinctive freezing process which also achieves these effects has been originated by Cheng and Cheng (*8*). Due to the difference in the effect of applied pressure on the melting point, a substance which melts at a temperature lower than the freezing point of an aqueous solution may melt at a temperature higher than melting point of water at a sufficiently high pressure. Therefore a working medium can be selected to form a cyclic auxiliary system to remove the heat of crystallization in the partial freezing operation and to supply the heat required to melt the ice.

The process is distinct from the conventional freezing process in that it deals only with condensed (liquid and solid) phases. This has a considerable effect on the energy requirements of the process and favors the control of ice crystallization.

A flow work exchanger has recently been introduced to improve energy efficiency in the pressurization of a feed fluid and the depressurization of a product fluid in a high-pressure processing system composed only of condensed phases (*9*). This exchanger draws flow work (PV) from a volume of discharging fluid and, after the necessary upgrading, transfers it to an equivalent volume of a feed fluid. Such a flow work exchanger can be adopted within the process to improve its energy efficiency.

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The Struther-Umano direct contact controlled crystal process produces large granular ice crystals and is based on the principle of crystallization in the bulk of a well-fluidized slurry at low supersaturation (*10, 11*). In their process, subcooling is kept low by agitating mechanically the ice slurry with cold liquid butane. Major subcooling due to rapid vaporization is avoided and the heat transfer from brine to butane is mainly liquid-liquid. The same principle of crystallization can be readily embodied in a freezer for the present process, since only condensed phases are involved.

The fact that a working medium may be selected from nonvolatile hydrocarbons, which can be supplied from the petroleum industry at a low cost (as low as less than 5¢/lb.) (*12, 13*), is an additional advantage. It is worth noting that the latent heat of fusion of a straight chain hydrocarbon in the range of $C_{12} \sim C_{18}$ is particularly high (40 to 60 cal./g.) (*14*), so the amount of working medium required in the process is reasonably low.

The nonvolatility of the working medium and the atmospheric pressure operation in the partial freezing account for the low cost of the freezer. In addition, the production of large, granular ice crystals makes crystal dewatering and washing easier.

This process should not be rejected because it employs a high-pressure operation, since a reverse osmosis process is also operated in the same pressure range. In fact, the equipment cost for this process will be much lower than the equipment cost for a reverse osmosis process.

THEORY

The shape and direction of a univariant P vs. T curve for the melting point of a pure substance and the eutectic temperature of a binary mixture are given by the Clausius-Clapeyron equation (*15*).

The melting point is seen to be raised (positive slope) by P if the solid is denser than the liquid; a negative slope is found in a few cases, such as water, bismuth, and gallium, where the liquid is denser than the solid. According to Bridgman (*16*), the melting point of water drops by 1°C. with an increase of about 100 atm. in the applied pressure, and the general tendency of all systems is to have a positive slope of the fusion curve, the average value being 50 to 60 atm./°C.

The present process employs a substance or mixture of substances as a working medium. It is so selected that its melting point is lower than the freezing point of the aqueous solution from which fresh water is to be separated under applied low pressure. However, when the applied pressure exceeds a certain value, the melting point is raised to exceed the melting point of water under the same applied pressure.

If the melting point of substance A is lower than the melting point of substance B and if solid A is contacted with liquid B, directly or indirectly, solid A will melt and liquid B will be solidified by the heat exchange between them. Therefore a substance or mixture of substances which may be used as a working medium to absorb heat of crystallization at a low pressure by melting itself can be used to supply the heat of fusion of ice at a sufficiently high pressure by solidifying itself.

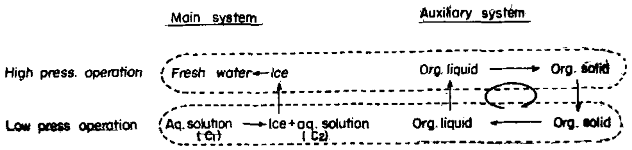

Fig. 1. Coupling between a main system (aqueous solution system) and an auxilliary system (working medium system).

TABLE 1. PRESSURE TO BE APPLIED TO OBTAIN THE RELATIVE SHIFT IN THE MELTING POINTS REQUIRED FOR HEAT REUSE

Concentration of the aq. solution, %	Freezing point at 1 atm., °C. (*17*)	Relative shift in the melting points required for heat reuse	Pressure to be applied, atm. Case A	Case B
1.0	−0.58	0.98	31.4	26.9
1.5	−0.85	1.25	41.6	35.7
2.0	−1.13	1.53	50.8	43.6
3.0	−1.72	2.12	69.5	60.1
3.5	−2.05	2.45	81.4	69.6
4.0	−2.35	2.75	91.6	78.7
5.0	−2.97	3.37	109.5	94.0
5.5	−3.3	3.7	123.6	105.7

Figure 1 illustrates the general process and shows that partial freezing of an aqueous solution can be coupled with the melting of the working medium by the following procedure:

At low pressure: Aq.Sol. + Org.Solid → Ice + Conc. Aq.Sol. + Org. Liq.

The melting of ice is coupled with the solidification of the working medium through the following procedure:

At high pressure: Ice + Org.Liq. → Fresh Water + Org.Solid.

By considering the overall effect, the working medium operates in cycles to reuse heat by drawing the heat of crystallization and transferring it to the melting of ice. Some work has to be supplied to the system in order to conform to thermodynamic requirements.

The pressure required to make heat reuse possible is related to the concentration of the aqueous solution and the temperature differences allowed in the low- and high-pressure transformations; Table 1 illustrates such relations. Temperature differences for the heat exchanges have been assumed to be 0.2°C. Case A is applicable where a common substance whose melting point is raised by 2°C./100 atm. is used as the working medium. Case B is applicable where a rather unusual substance, such as a mixture of benzene and naphthalene, whose melting point is raised by 2.5°C./100 atm., is used as the working medium.

SELECTION OF A WORKING MEDIUM

The working medium to be employed can be either a pure substance or a mixture of substances. It may have a sharp melting point, such as a eutectic point, or it may have a melting point range. It will be desirable to select a mixture whose melting point range approximates closely the range of the freezing point of the aqueous solution during the freezing operation. It is then possible to use a multistage direct contact between the systems and to maintain a small temperature difference between the two systems in each stage. The energy consumption for the process will thus be reduced.

An ideal working medium should have the following qualities: a proper melting range, a very low solubility in water, a large value for the latent heat of fusion, a low $\left(\frac{dP}{dT}\right)_{\text{melting}}$ value, nontoxicity, cheapness and ready availability. Theoretically, any substance which has a proper melting point (or melting range) and has low solubility in water can be used to form a cyclic auxiliary system to render heat reuse possible. But the problem of economy will probably limit the practical working medium to a hydrocarbon or mixture of hydrocarbons.

Phase diagrams (solid-liquid equilibrium) for binary systems of saturated hydrocarbons have been reported by

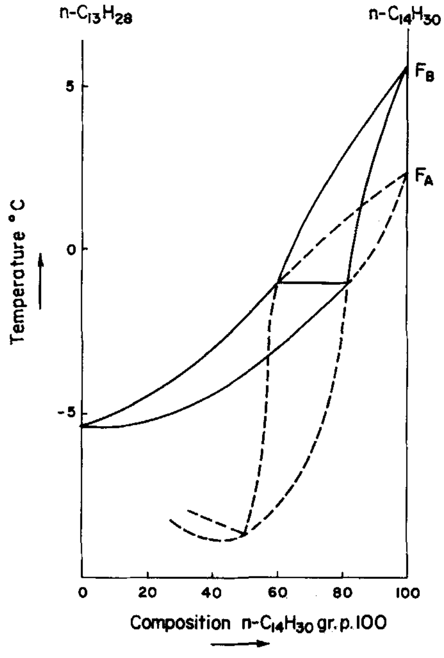

Fig. 2. Phase diagram for tridecane-tetradecane system (*18*).

Salzberger (*18*). It is reported that alkanes of C_{12}-C_{13}, C_{13}-C_{14}, and C_{14}-C_{15} form continuous solid solutions, complicated with transformations at even C ends. Figure 2 shows the phase diagram of the *n*-tridecane–*n*-tetradecane system. It can be seen that a mixture of tridecane and tetradecane of proper composition (say 40 to 60% tetradecane) meets the required melting range. One can obtain the linear paraffins readily by urea extraction or molecular sieves from many petroleum stocks. The latent heat of fusion of higher *n*-paraffin hydrocarbons is particularly high, around 50 to 60 cal./g. for even C-number hydrocarbons and around 40 cal./g. for odd C-number hydrocarbons (*14*). The weight of hydrocarbon required to absorb the heat of crystallizing 1 lb. of water is thus 1.3 to 2 lb. The manufacturers have estimated the long range price of *n*-paraffin hydrocarbons for quantities of several million pounds per year to be within 4.5 to 5¢/lb. (*12*, *13*). Manufacturers should be able to formulate still lower cost mixtures out of hydrocarbons of less commercial value in the future.

Naphthalene forms eutectic mixtures with many substances (*19*, *20*), and the eutectic temperatures are in the range suitable for the desalination of seawater. A mixture of benzene and naphthalene is a nice system because it has a low $\left(\frac{dp}{dT}\right)_{\text{melting}}$ value and is readily available. There are objections to its use as a working medium, however, because it has a slight but significant solubility in water, is toxic, and has rather high volatility. Use of this mixture as a working medium will require aftertreatments to remove it from both the product fresh water and from the reject salt solution. The eutectic mixture of cyclohexane and naphthalene is a workable medium since its eutectic temperature is −3.6°C. (*20*). The main disadvantage of this system is its low latent heat of fusion, which is 7.466 cal./g. (*21*).

Working media may be made from alkylnaphthalenes. A partial list of promising alkylnaphthalenes is given in Table 2 with the pertinent physical properties (*22*). Since the density of an alkylnaphthalene is so close to that of an aqueous solution, elaborate equipment may be required for its separation.

Table 2. Promising Alkylnaphthalenes for Working Media

Name	Melting point, °C.	Density	Solubility
1,2-Dimethylnaphthalene	−1	1.013	Very slight
1-*n*-Octylnaphthalene	−2	0.9427	Very slight
2-*n*-Propylnaphthalene	−3	0.9770	Very slight
2-*n*-Hexylnaphthalene	−3	0.9479	Very slight
1,3-Dimethylnaphthalene	−4	1.0063	Very slight
2-*n*-Pentylnaphthalene	−4	0.9561	Very slight
2-*n*-Butylnaphthalene	−5	0.9659	Very slight

PROCESS DESCRIPTION

The block diagram of Figure 3 shows the process divided into a low- and a high-pressure operation. An outline of the operation of the process is as follows:

The aqueous solution feed is heat exchanged with the outgoing streams, namely, product water and reject concentrated brine. The feed and the recycle working medium (in either a solid state or a slurry form) are then sent into a low-pressure converter (ice maker).

In order to balance all of the inefficiencies of the process plus the reversible work for separation, a refrigeration step would, by necessity, have to remove a certain amount of heat from the process. Some of the heat should be removed from the lowest temperature level in the whole process.

In the converter, the working medium melts and ice forms from the aqueous solution. This ice is separated from the mother liquor and is washed in a vertical wash column, as in the conventional freezing processes. The concentrated saline solution undergoes heat exchange with a feed solution before it is discharged. Ice so formed is again contacted with the working medium (in the liquid state) and the mixture is pressurized sufficiently to invert their melting points. Ice melts to form fresh water and the working medium solidifies and floats on the surface of the fresh water. The fresh water is separated from the working medium and they are depressurized separately.

The size of the equipment for this process is very small compared to the conventional freezing processes, because only condensed phases are involved in the process. The volume of the working medium to be transferred in the process is 0.05 to 0.1 cu. ft./lb. of water produced compared to the 4 cu. ft./lb. of product in the isobutane process and to the 5.6 cu. ft./lb. of product in the *n*-butane process (*3*).

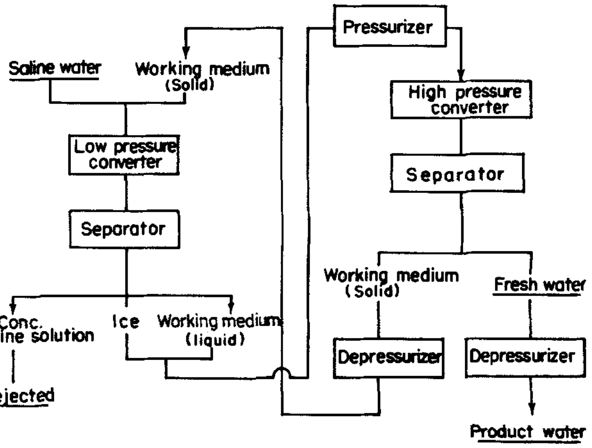

Fig. 3. Flow diagram for desalination of saline water by high-pressure inversion of melting point.

Low-Pressure Phase Transformation

The low-pressure phase transformation takes place according to the following equation:

$$\text{Aq.Sol.}(C_1) + \text{Org.Solid} \rightarrow \text{Ice} + \text{Aq.Sol.}(C_2) + \text{Org.Liq.}$$

Four condensed phases are involved in the transformation: an aqueous solution, ice, an organic liquid, and an organic solid. The organic solid is supplied from the high-pressure operation to be described. An excess of organic working medium may be used and the organic solid can be transferred in the processing in a slurry form. Ice formed in the phase transformation is suspended in the mother liquor.

As has been described previously, the Struther-Umano direct contact controlled crystal process attempts to control ice crystallization so as to encourage a favorable crystal habit by holding subcooling to a small amount. The same principles can be readily incorporated in the present process. When a mixture is used as a working medium, both the freezing point of the aqueous solution and the melting point of the working medium vary during the low-pressure operation due to the changes in the concentrations of the two solutions. It is, then, thermodynamically better to use a countercurrent operation in contacting the two systems.

It might be pointed out that this low-pressure operation has much in common with the liquid-liquid extraction operation, since both deal with condensed phases. The experiences gained in the extraction field may be incorporated into the present process. An efficient freezer may result by combining the Struther mechanical agitation with some multistage extraction set up: A continuous contact extractor with or without mechanical agitation, such as a spray tower, a baffle tower, a perforated plate tower, a rotating disk contactor, the Oldshue-Rushton extractor, the Scheibel extractor, or a pulse extractor, may be modified and used in this process (23).

High-Pressure Phase Transformation

The high-pressure phase transformation takes place according to the following equation:

$$\text{Ice} + \text{Org.Liq.} \rightarrow \text{Fresh Water} + \text{Org.Solid.}$$

Again, four condensed phases are involved in the transformation: water, ice, an organic liquid and an organic solid. The organic liquid is contacted with ice and the mixture is pressurized sufficiently so that the required transformation takes place. Excess organic liquid is used so that the organic solid produced is suspended in it to form a slurry. Fresh water and the organic slurry are depressurized separately.

Less control of crystal formation is required in the high-pressure transformation as contrasted to the partial freezing of an aqueous solution in the low-pressure operation. In the high-pressure transformation, excess organic liquid is used. The organic solid formed is preferentially wetted by the organic liquid and is suspended in it. The suspension is separated from the fresh water and can be directly transferred to the low pressure operation. The fresh water formed does not wet the organic solid surface and is rejected from it. Fresh water produced can be easily separated from the organic suspension due to its nonwetting characteristic and to the difference in densities.

SUMMARY

In addition to those common to all freezing processes, the present process has the following advantages:

1. An efficient low-cost crystallizer can be constructed due to the condensed phase operation.
2. The cost for washing ice crystals can be reduced since large granular ice crystals can be produced in the crystallizer.
3. Energy requirements can be reduced because of the condensed phase operation and the adoption of flow work exchangers.
4. No gas stripping, such as deaeration, propane stripping, butane stripping, is required.
5. No explosion-proof plant set-up is required because the working medium is nonvolatile.
6. A large capacity plant can be constructed.

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NOTATION

H = molar or specific enthalpy change for fusion
P = pressure
PV = flow work
T = temperature

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