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Freeze Decontamination Process: Modeling in a Simplified Case of Completely Mixed Aqueous Phase and Observations with Ultrasonic Agitation in the Liquid during Freezing

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ABSTRACT

Correlations among variables of the freeze decontamination process have not been developed to precisely predict experimental observations of purified solid ice out of a given aqueous solution on a macroscale. A lack of such information has been one of the main reasons for the very small practical application of the process so far. A simplified model has been presented in an effort to take into account the inhomogeneity of the solid phase. Pure ice spikes scattered on a cold surface have been supposed to grow opposite to the direction of heat dissipation, leaving unfrozen liquid channels among them along their length. The ice phase has thus been supposed to consist of pure ice spikes and a quantity of liquid entrapped among them. The liquid at the freezing front and in bulk is supposed to be completely mixed. Volume changes on freezing have also been taken into account. The model has been compared with experimental observations on a specially fabricated apparatus. Temperatures of a cold freezing surface have been continuously lowered while following a -0.0017 K/s gradient during experiments. An ultrasonic mixing technique has been applied to the liquid during freezing to eliminate impurity (cesium nitrate) concentration gradients in the liquid. A comparison of the model with experimental observations has been made with the help of a decontamination factor (DF) [concentration of impurity in the initial liquid/concentration of impurity in the frozen mass (after it has been melted)] versus V/V_0 (volume of unfrozen liquid left at any point during freezing/volume of initial liquid taken) plots. Although a scatter in the experimental results has been observed, there was broad agreement with the model trend. The average value of DF has been as high as 46. The investigation has highlighted the importance of the factors that determine the fraction of pure ice spikes in the growing solid at any point during freezing.

INTRODUCTION

Liquid water is a very good solvent for a wide variety of substances. But its solid form, ice, which has a close-packed hydrogen-bonded lattice, excludes all solutes. The rejection of soluble impurities from a growing ice front and their eventual concentration in the remaining liquid is a problem of theoretical and practical interest (1). Figure 1 illustrates the microstructure of an advancing ice front.

A decontamination process based on freezing pure ice in aqueous solutions is a very promising alternative to conventional evaporation and membrane separation processes. Decontamination of aqueous streams containing volatile, corrosive, toxic, radioactive, and temperature-sensitive substances by this technique at freezing temperatures would eliminate the problems of corrosion, scaling, vapor, and gas handling.

The technique of decontaminating aqueous solutions by freezing has been known for centuries. The inhabitants of Western Siberia and Central Asia freeze saline water in ditches, collect the ice formed, and allow it to

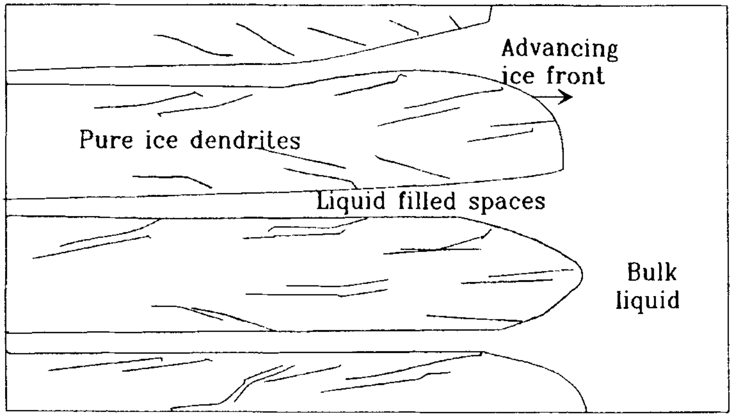


FIG. 1 Microstructure of an advancing pure ice front in an aqueous solution.

melt in the sun. The product is used for watering cattle. Hendrickson and Moulton (2) extensively studied macroscale desalination of seawater by the technique utilized in commercial ice-making machines, and substantially pure ice and a correspondingly higher concentration of salt in the unfrozen part was obtained after simple freezing of seawater. However, the purity of a freeze-decontaminated product was less than what can be obtained by utilizing the alternate evaporation method. Since it is known that ice cannot hold foreign solutes and that complete separation of solutes from ice takes place on a microscale, work to improve the purity of frozen ice on a macroscale has continued to attract attention.

Freezing an aqueous solution is a very complex system. Here, two phases with entirely different characteristics interact. A solid–liquid interface represents a moving heat source with time-varying velocity and structural properties. Very minute quantity of solid impurities sticking on a cold surface, a growing ice–liquid interface, or suspensions in the liquid can have a considerable effect. All of these parameters have not been drawn together so far into a unified model for predicting the eventual decontamination outcome of a given freezing operation.

Mathematical treatments of the phenomena with several restrictive assumptions abound. Almost all of them assume that the ice phase is a homogeneous solid with a certain amount of dissolved impurity. Microscale pure ice structures that do exist are ignored (3–5). On the contrary, microscopic investigations about the mechanism of pure ice growth in solutions have highlighted the existence of these structures (6). It has generally been agreed that a frozen solid with a proper microstructure must be grown if the purity of the ice phase is to be increased. An increase in the dimensions of pure ice spikes or draining the concentrated liquid found among them has been suggested by many workers for that purpose (7). A mathematical model that can take into account the morphology and structure of the ice phase would be helpful in devising an efficient freeze concentration process.

It has been known that agitation in the liquid close to the growing ice front improves its purity. This is attributed to enhanced dissipation of impurities, which are rejected during ice formation, into the unfrozen liquid. A lack of efficient agitation gives rise to a build up of impurities in the liquid at the growing ice front. Continuing ice growth in such a situation results in entrapment of that liquid, which is highly concentrated in impurities, in the solid, and thus impairs process efficiency. A variety of mechanical agitation techniques investigated by a number of workers have not been found effective in avoiding impurity build up close to growing ice fronts.

THE MODEL

This model considers the existence of regions of pure ice and of concentrated solute filling the space in a frozen solid phase. The rest of the unfrozen liquid ahead of such a growing solid phase has been assumed to remain completely homogeneous although solute rejection continuously increases its solute concentration. The fraction of the surface area of growing solid in contact with liquid is assumed constant. i.e., ice is assumed to grow only on the already present pure ice spikes; any new nucleation during ice growth is neglected. That assumption is consistent with the knowledge that ice is the best nucleation agent for itself. No flow of liquid from the bulk ice phase into the bulk liquid phase has been considered. Thus the solute once trapped in ice is assumed to remain there.

In this model (Fig. 2), ice grows on a cylindrical surface of radius r_0. The surface is placed in a volume of solution, and at any time the radius of the ice cylinder formed on the surface is r. The structure of the growing ice front is modeled by a series of holes in pure solid ice that traps liquid. The fraction of the ice front consisting of unfrozen liquid is assumed to be constant. The bulk of the ice phase consists of a number of pure ice spikes holding a quantity of liquid in spaces among them. At any time during freezing the volume of the liquid is equal to V_0 less the volume of liquid used up in freezing pure ice and less the volume of liquid trapped

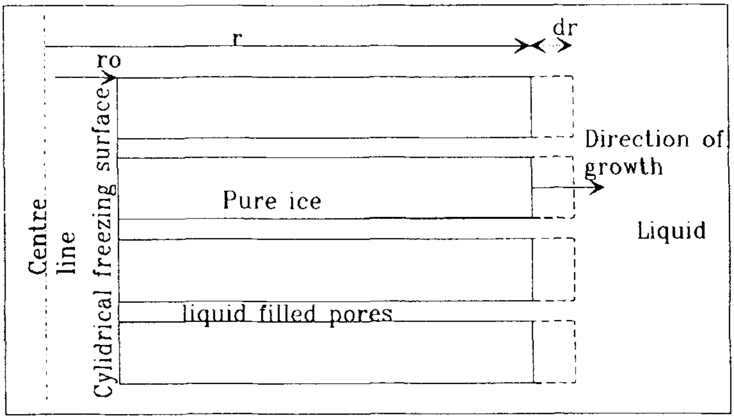


FIG. 2 Description of the proposed model.

in holes in the solid phase. If volume effects of solute mixing (i.e., concentration changes) are neglected, then the volume of liquid ahead of the ice front is

$$V = V_0 - (1 - E)S_i\pi(r^2 - r_0^2) - E\pi(r^2 - r_0^2) \tag{1}$$

Differentiation of V yields

$$dV/dr = -2\pi[(1 - E)S_i + E]r \tag{2}$$

or

$$2\pi r dr = \frac{-dV}{[(1 - E)S_i + E]} \tag{3}$$

As the ice front grows from r to $r + dr$, the volume of pure ice spikes formed is $2\pi(1 - E)rdr$, involving the freezing of a volume of $2\pi S_i(1 - E)rdr$ of liquid water (pure). The growth pushes a mass of solute amounting to $2\pi C_L S_i(1 - E)rdr$ into the rest of the liquid (ahead of the ice front). The addition of that amount of solute in the liquid raises its solute concentration from C_L to $(C_L + dC_L)$ and results in an increase in the solute content of the unfrozen liquid by

$$VdC_L = 2\pi C_L S_i(1 - E)rdr \tag{4}$$

Substituting the value of $2\pi rdr$ from Eq. (3) gives

$$VdC_L = \left(\frac{S_i(E - 1)}{(1 - E)S_i + E}\right)C_L dV \tag{5}$$

or

$$VdC_L = LC_L dV \tag{6}$$

where

$$L = \left(\frac{S_i(E - 1)}{(1 - E)S_i + E}\right)$$

Integrating Eq. (6) with conditions of $C_L = C_0$ at $V = V_0$ gives

$$C_L = C_0\left(\frac{V}{V_0}\right)^L \tag{7}$$

Separation of the solid phase (which will have some liquid entrapped in it, of course) from the remaining unfrozen liquid and thawing gives a purified liquid product of volume $(V_0 - V)$. The solute concentration C_i

of the purified product is

$$C_i = \frac{V_0C_0 - VC_L}{V_0 - V} = C_0 \frac{1 - \left(\frac{V}{V_0}\right)^{L+1}}{1 - \left(\frac{V}{V_0}\right)} \tag{8}$$

At the beginning of freezing, V tends to V_0, making Eq. (8) indeterminate, i.e., zero divided by zero. However, separate differentiation of the top and bottom expressions with respect to V/V_0 gives

$$C_i = C_0(L + 1) \tag{9}$$

Equations (8) and (9) and the definition of the decontamination factor results in

$$\mathrm{DF} = \frac{1 - \left(\frac{V}{V_0}\right)}{1 - \left(\frac{V}{V_0}\right)^{L+1}}, \quad \text{for } V \neq V_0$$

$$= \frac{1}{L + 1}, \quad \text{for } V = V_0$$

DF versus V/V_0 plots for different given values of E are shown in Fig. 3.

EXPERIMENTAL

A specially built microcomputer-controlled cooling apparatus (8) (schematically illustrated in Fig. 4) was utilized for freezing outside a cold cylindrical surface at a constant negative temperature gradient. A 0.087-meter long stainless steel hollow cylinder of 0.04 meter outer diameter was immersed in 0.6 dm^3 of an impure solution contained in a cylindrical container. A solution of cesium nitrate containing 5 kg/m^3 of cesium spiked with radioactive cesium-134 was partially frozen. The temperature at the outer surface of the cylinder was lowered at a constant rate of -0.0017 K/s with the help of a coolant flowing inside it and a 500-W electrical heater also contained inside. The heater power was controlled with the

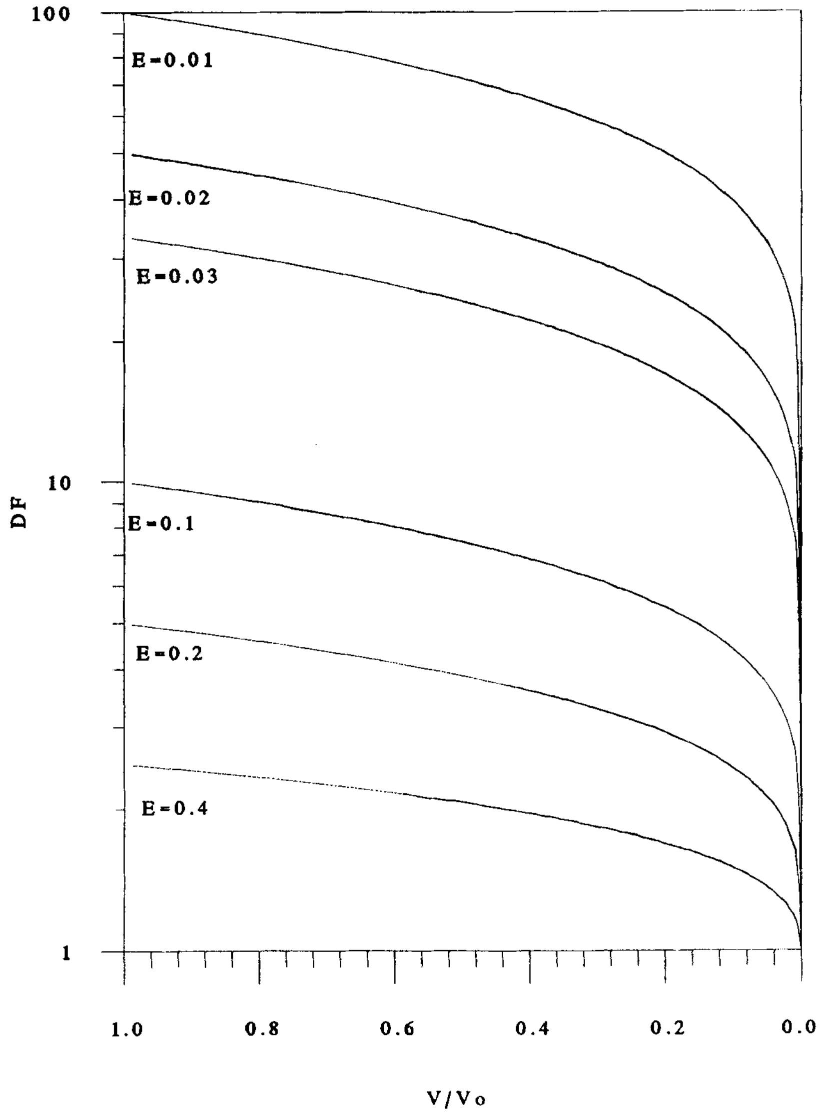
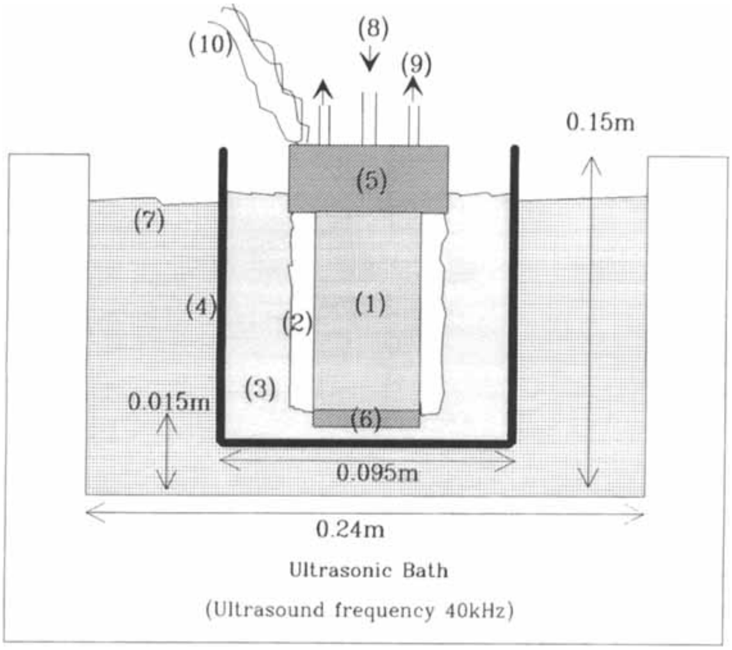


FIG. 3 A few profiles of impurity concentration in the frozen solid for given values of *E*.



(1) Stainless steel freezing cylinder

(2) Ice frozen on the surface of the freezing cylinder

(3) Impure aqueous solution

(4) Glass container holding the impure solution

(5),(6) Thermal insulation

(7) Water as medium for ultrasound

(8),(9) Coolant in and out respectively

(10) Temperature sensor and heater power cables

FIG. 4 Schematic illustration of experimental setup.

computer to produce the required temperature at the cylinder surface during freezing. The cylindrical container holding the impure cesium nitrate solution was partially immersed in water in an ultrasonic bath.

The impure solution was first allowed to cool down to 273.15 K by decreasing the temperature of the stainless steel cylinder. Further cooling and ultrasonic agitation were started the moment the slightest signs of the beginning of freezing at the surface of the stainless steel cylinder were observed. After 45 minutes of freezing, the stainless steel cylinder, with ice sticking on it, was taken out of the remaining impure solution. The stainless steel cylinder with the frozen ice was then immersed in some warm kerosene contained in a separating funnel. The funnel was rotated at about two revolutions per minute so the ice would melt uniformly. The melted ice steadily dropped down to the bottom of the separating funnel. When a quantity of melt, approximately one-third of the amount of ice, had been collected, it was withdrawn and kept in a container. At the same time a new container was used to collect the next sample of melt. The volume and order of each sample were noted. The concentrations of the impurity in the samples were determined with a radioanalytical method. The radioactivity of 0.005 dm^3 portions of those samples due to cesium-134 (counts at 0.0604 MeV gamma energy peak) was measured for 4000 seconds. Values of V/V_0 and DF were then determined for each sample.

RESULTS AND DISCUSSION

The observed impurity concentration profiles (Fig. 5) in the solid phase indicate a large degree of scatter. A precise comparison of experimental observations with the model was not possible; nevertheless, there was some broad agreement in general trend. At a constant negative temperature gradient, the fraction of pure ice in the solid phase $(1 - E)$ does not vary greatly.

The observations of the present study (Fig. 5) also indicate that successive layers of ice had DF values as high as 100. For all runs the overall average DF was 46, while around 35% of the initial impure solution taken (containing 7.3 kg/m^3 of $CsNO_3$) was separated as a purified ice product. This much efficiency for a freezing process can, for instance, purify seawater with total dissolved solids as high as 46 kg/m^3 to a level of 1 kg/m^3 fresh water, which is permissible for public use by WHO standards.

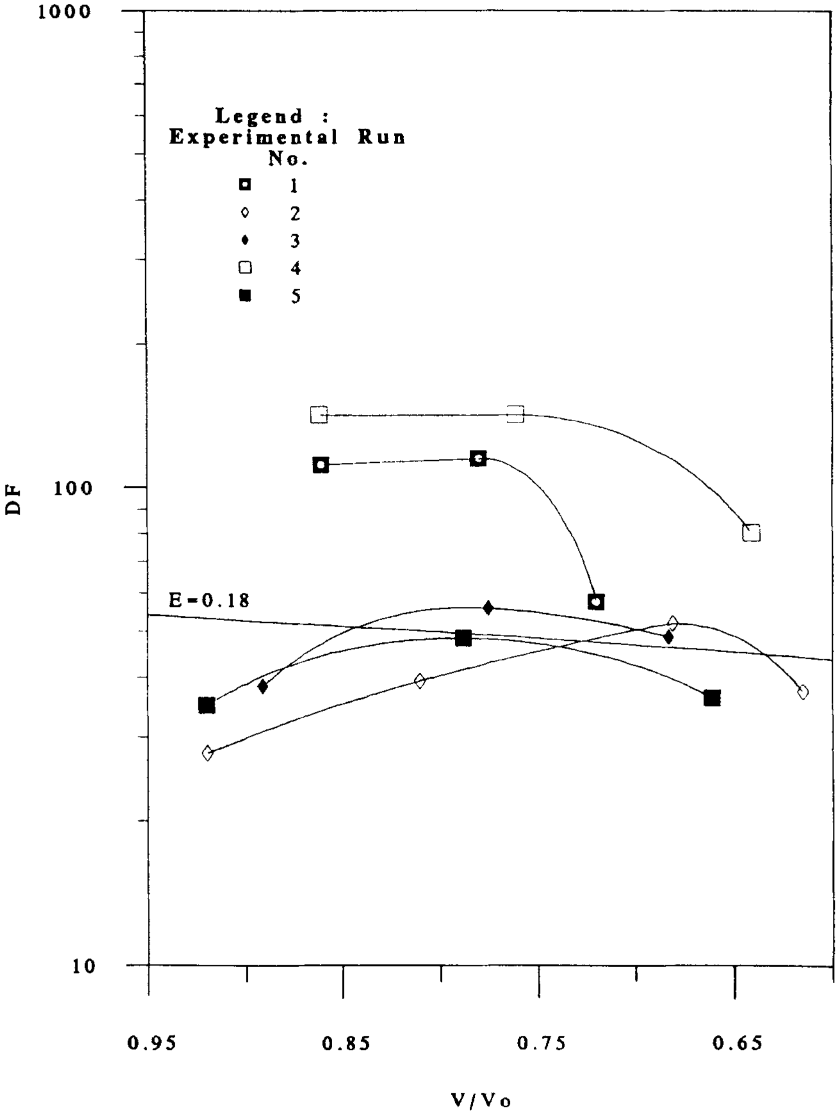


FIG. 5 Comparison of experimental results with the model for a selected value of $E = 0.18$.

CONCLUSIONS

The model is more realistic as far as inhomogeneity of the solid phase is concerned, but total mixing in the liquid ahead of the ice front and no mixing in the liquid entrapped in the solid phase are simplifications that take it far from reality. Properties of the freezing solution, mass and heat transfer characteristics, and supercooling during a freezing operation need to be incorporated to provide values of E in order to predict the observations more precisely. Experimental observation of a high decontamination factor at a macroscale indicates that ultrasound had been effective in dissipating impurity build up at the ice front. The utilization of ultrasound for industrial application needs further investigation, especially to explore the best possible arrangement of ultrasonic source and ice growth direction.

NOTATION

C_i	impurity concentration in melted ice (kg/m^3)
C_L	impurity concentration in unfrozen bulk liquid ahead of the ice front (kg/m^3)
C_0	impurity concentration in the liquid before the beginning of freezing (kg/m^3)
E	porosity of solid phase, i.e., the fraction of the ice front consisting on unfrozen liquid or fraction of the volume of solid phase consisting on liquid-filled pores
DF	C_0/C_i
S_i	specific gravity of pure solid ice, 0.917
V_0	volume of liquid taken before freezing (m^3)

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