$$S \equiv (h+R)/R$$

$$M = M(G,S) \equiv \frac{2.4\ G^{0.85}\ S^{0.85}}{1+2.4\ G^{0.85}\ S^{0.85}} + \frac{0.5}{GS}$$

$$Z = Z(S) \equiv \ln S - \frac{1}{2}\left(\frac{S^2-1}{S^2}\right)$$

Equation (8) has been evaluated for certain specified values of C_o and G by solving an iteration method but special precautions were necessary. Following the earlier procedure, Equation (8) can be written in D notation and rearranged to be explicit in C_o

$$D\ M = 0.944\ (C_o - 2\ S^2G^2Z)^{2/3}$$

$$C_o = 1.09\ (D\ M)^{3/2} + 2\ S^2G^2Z \tag{9}$$

The speed explicit form is

$$u = 1.09\left(\frac{\sigma}{\rho g}\right)^{1/4}\frac{\rho g(hM)^{3/2}}{\mu} + \frac{\rho g\ Z\ (h+R)^2}{\mu} \tag{10}$$

Given radius, fluid properties, and film thickness, one can calculate the speed by Equation (10) without iteration.

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Crystallization on a Constant Temperature Surface

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In a recent article (*1*) Harriott has investigated the effect of heat and mass transfer on ice crystal growth rates for crystallization in the bulk liquid of a subcooled water and salt solution. He concluded from experiment and theory that heat and mass transfer do affect the crystal growth rates, but that there could be an appreciable crystallization resistance especially at low subcooling (0.01 to 0.02°C.).

This paper presents a similar theoretical analysis (for a two component solution) of the heat and mass transfer effect on the rate of crystallization on a constant temperature surface. This case is of considerable practical importance. It is especially applicable to scraped pipe crystallizers (2) which are used extensively in the chemical process industries.

Crystallization on a cold surface involves conducting the latent and sensible heat through the solid phase to the cold surface.

The following important assumptions will be made:

1. The thermal capacity of the solid phase is negligible, that is, the temperature in the solid phase is linear.
2. There is no driving force required for crystallization, as the interfacial temperature is the true freezing point of the solution.
3. The interfacial heat and mass transfer coefficients are constant.
4. The freezing point relationship can be expressed as the following linear relationship:

$$c = A - B(T) \tag{1}$$

5. The bulk of the liquid is at saturation temperature (realistic for continuous flow devices).
6. The bulk flow contribution to heat and mass transfer is negligible.

The growth rate of the solid phase from a heat balance is

$$k_s\frac{(T_i - T_w)}{x} = \lambda\rho_s\frac{dx}{dt} + h(T_b - T_i) \tag{2}$$

A mass balance on the component diffusing away from the interface is given by Harriott (*1*):

$$K(c_i - c_b) = \frac{c_b}{\rho_b - c_b}\rho_s\frac{dx}{dt} \tag{3}$$

Substituting for $(c_i - c_b)$ in Equation (3) we obtain from Equation (1):

$$T_b - T_i = \frac{c_b}{\rho_b - c_b}\frac{\rho_s}{KB}\frac{dx}{dt} \tag{4}$$

Equation (2) can be rearranged as follows:

$$\frac{k_s}{x}[(T_b - T_w) - (T_b - T_i)] = \lambda\rho_s\frac{dx}{dt} - h(T_b - T_i) \tag{5}$$

Substituting $(T_b - T_i)$ from Equation (4) into Equation (5), simplifying and integrating with the initial condition $x = 0$ at $t = 0$ we obtain

$$x = \sqrt{\alpha^2 + 2\beta t} - \alpha \tag{6}$$

where α, β and ϕ (same as Harriott's ϕ) are as follows:

$$\alpha = \frac{k_s\phi}{h(1+\phi)} \tag{7}$$

$$\beta = \frac{k_s(T_b - T_w)}{\lambda\rho_s(1+\phi)} \tag{8}$$

$$\phi = \frac{hc_b}{\lambda K(\rho_b - c_b)B} = \frac{k_bN_{Nu}c_b}{\lambda DN_{Sh}(\rho_b - c_b)B} \tag{9}$$

Various analogies between heat and mass transfer (3) predict that

$$\frac{N_{Nu}}{N_{Sh}} = \left(\frac{N_{Pr}}{N_{Sc}}\right)^a \tag{10}$$

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Thus ϕ is only a function of fluid physical properties.

Equation (4) is the relationship between x and t; however, it does not indicate immediately what effect agitation (that is, an increase in h and K) has on the crystallization rate. The effect of agitation can be clearly seen by comparing the solid phase thickness with finite agitation (h and K finite) to its thickness with infinite agitation. The thickness-time relationship for the solid phase with infinite heat and mass transfer coefficients is

$$x^* = \sqrt{2\beta t} \tag{11}$$

For a pure component Equation (11) becomes

$$x = \sqrt{\frac{2k_s(T_b - T_w)t}{\lambda\rho_s}} \tag{12}$$

This is the relationship which Heertjes and Gie (4) obtained from a simplified theoretical solution that can be obtained by assuming a linear temperature variation in the solid phase. They also conducted freezing experiments with water and benzene. The experimental data agreed very well with Equation (12).

By substituting x^* from Equation (11) into Equation (6) we obtain

$$\frac{x}{x^*} = \sqrt{\left(\frac{\alpha}{x^*}\right)^2 + 1} - \frac{\alpha}{x^*} \tag{13}$$

For constant α (a particular level of agitation) x/x^* is zero when $x^* = 0$ and approaches unity as $x^* \to \infty$. Thus Equation (13) expresses quantitatively what one would intuitively expect, that mass transfer affects the crystallization rates much more when x is small than when x is large. This suggests that it might be economically attractive in some cases to provide more agitation at the start of freezing than at the end of freezing.

Let us now consider a specific example. Consider a 6% sodium chloride-water solution with $(T_b - T_w) = 10°\text{F}$. With $a = 1/3$ in Equation (10) Harriott (5) has computed $\phi = 1.65$. With moderate agitation a heat transfer coefficient of 200 B.t.u./(hr. sq. ft. °F.) could be obtained; thus $\alpha = 0.048$ in. For a freezing time of one minute $x^* = 0.053$ in. and $x = 0.024$ in. For a freezing time of 1/10 min. $x^* = 0.017$ in. and $x = 0.0034$ in. With sufficient agitation to produce a heat transfer coefficient of 1,000 B.t.u./(hr. sq. ft. °F.), $x = 0.043$ in. for a freezing time of one minute. This example certainly illustrates that the level of agitation can significantly affect the solid phase thickness.

For the above example the solid phase thickness is only 61% of the ice thickness which could have been obtained with the same $(T_b - T_w)$ in pure water.

Heat is transferred from the liquid solution to the interface due to the temperature difference between the bulk solution and the interface. Thus, in many practical cases, crystallization occurs in the bulk solution. It is very important to know how much crystallization occurs in the bulk solution because the properties of crystals grown in the bulk solution are vastly different from crystals grown on and removed from a constant temperature surface.

Gilliland (5) states without proof that for crystallization of sea water (a 6% sodium chloride-water solution would approximate concentrated sea water) on a constant temperature surface more than 99% of the refrigeration would go to form crystals in the bulk solution. The present theory predicts that the ratio of heat transferred from the bulk solution to the total heat transferred is $\phi/(1 + \phi)$. Thus, for the 6% sodium chloride-water solution, the ratio of heat transferred from the bulk solution to the total heat transferred is 0.62. Then only 62% of the total refrigeration would go to form crystals in the bulk solution. To compare the present solution and Sherwood's observation with experimental data would be desirable; however, I cannot find experimental data on crystallization from a multicomponent solution onto a constant temperature surface.

In order to determine if there might be an appreciable crystallization resistance the present theory can be compared with data for growth rates where heat and mass transfer have little effect. Lindenmeyer, et al. (6) have taken growth rate data for pure water on a brass surface. At a bulk to wall temperature difference of 1°C. they obtained growth rates of 0.1 cm./sec. Let us see how the present solution compares with this data.

Differentiating Equation (6) the growth rate is obtained

$$\frac{dx}{dt} = \frac{\beta}{\sqrt{\alpha^2 + 2\beta t}} \tag{14}$$

The maximum rate occurs at $t = 0$. For a 6% salt solution with $h = 200$ B.t.u./(hr. sq. ft. °F.) and $(T_b - T_w) = 1°\text{C}$. the maximum rate is 0.0002 cm./sec. This rate is almost three orders of magnitude lower than the rate measured by Lindenmeyer (6). For this case the crystallization resistance would almost certainly be negligible and it probably would be negligible for crystallization on a cold surface except upon start of crystallization in pure substances and eutectic solutions, where there is no diffusional resistance and where the present theory predicts an infinite growth rate at $t = 0$.

NOTATION

a = exponent in Equation (10)
B = slope of freezing point curve, Equation (1)
c = mass concentration of nonfreezing component
D = diffusivity of mass
h = heat transfer coefficient
k = thermal conductivity
K = mass transfer coefficient
N_{Nu} = Nusselt number
N_{Pr} = Prandtl number
N_{Sc} = Schmidt number
N_{Sh} = Sherwood number
T = temperature
t = time
x = thickness of the solid phase
x^* = thickness of solid phase with infinite h and K
α = parameter defined by Equation (7)
β = parameter defined by Equation (8)
ρ = mass concentration of the solid phase and the bulk solution
ϕ = parameter defined by Equation (9)

Subscripts

i = interface
b = bulk solution
s = solid phase
w = constant temperature wall

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