

A MATHEMATICAL MODEL FOR PURIFICATION OF A CRYSTAL LAYER BY THE TEMPERATURE GRADIENT METHOD

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The purification of crystalline solids by the temperature gradient method was studied by a novel experimental method, and a mathematical model was developed to simulate the process. The experimental method was based on measurement of the impurity concentration profile in the whole crystal layer. Our results show that the amount of impurities in a crystal layer maintained under a temperature gradient decreased with time. This can be explained by a mechanism in which liquid inclusions move under the influence of a temperature gradient. The validity of the mathematical model for the concentration profile was shown through reference to experimental results.

Introduction

Crystallization from a melt onto a cooled surface is increasingly being used for the purification of organic chemicals. A strong disadvantage of the method, in eutectic as well as in solid-solution systems, is that impurities become trapped in the crystal layer as liquid inclusions. The amount of impurities can be reduced to some extent by controlling the growth conditions, but those inclusions remaining at the end of crystallization are wholly inside the crystal layer and cannot be removed by conventional post-purification methods. In recent years the use of a temperature gradient for purification of a crystal layer has been studied.

Whitman⁸⁾ long ago observed that the amount of brine trapped in an ice sample was reduced toward the cold end when the sample was maintained under a temperature gradient. The dominant mechanism for the decrease of impurities, he suggested, was the migration of the inclusions. This was verified experimentally by Harrison¹⁾ and Hoekstra *et al.*²⁾ In these experiments the migration of inclusions was studied by observing the movement of single inclusions in an ice sample under a microscope. Inclusions in the ice sample were incorporated by causing the growing ice to entrap the desired solutions. The thermal gradient was measured by the use of thermocouples frozen in the ice. The velocities observed by Hoekstra *et al.*²⁾ were always less than

the velocities calculated by the diffusion theory.

Yamazaki *et al.*¹⁰⁾ proposed the same mechanism as an explanation of the observation of Toyokura *et al.*^{6,7)} that the amount of benzoic acid included in naphthalene crystals grown from a benzoic acid-naphthalene mixture decreased even while the crystal mass increased. Yamazaki *et al.* proposed that the impurities were diffused into the bulk melt because of the temperature gradient. Because the concentration of impurities was decreased, the contents of the pores were solidified.

The method of analyzing the distribution of impurities in the crystal layer, introduced by Silventoinen *et al.*,⁴⁾ was also used by Yamazaki *et al.*¹¹⁾ Experimental results reported by Yamazaki *et al.*¹¹⁾ are consistent with the results reported in the present work. However, no attempts were made earlier to calculate the distribution of impurities as a function of time in the crystal layer.

1. Experimental Section

The experimental apparatus was a cylindrical crystallizer consisting of a constant-temperature bath with a fines dissolver for feed liquid and of a crystallizer section with a cooled surface on which the crystal layer grew. The apparatus is similar to that used by Yamazaki *et al.*⁹⁾ except that the flow conditions of the cooling medium and feed solution were modified to ensure equal growth on all parts of the crystallizer surface. A schematic diagram appears in **Fig. 1**. A water solution of NaCl was chosen for the feed solution since the liquidus curve and diffusion coefficient are known with considerable accuracy for

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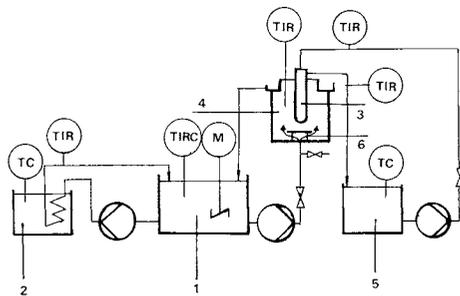


Fig. 1. Experimental apparatus

1) feed tank; 2) fines dissolver; 3) cylindrical crystallizer; 4) overflow tank; 5) coolant tank; 6) plate for modification of flow conditions.

NaCl solution.

The crystal layer was grown to a thickness of about 2 cm. The temperatures of the feed solution and the cooling liquid were 4°C and -7°C, respectively. The mathematical analysis is derived for the case where the crystal layer did not grow further. The final thickness of the crystal layer could therefore be used for calculation of the temperature gradient. The gradient was approximately 350°C/m.

The initial value of NaCl in the liquid phase was 0.5–5 g/dm³ and the volume of the feed tank was large enough to keep the concentration in the liquid phase constant in spite of the impurity rejection by the solid phase. The crystal grown was removed from the crystallizer surface by melting, and impurities were analyzed with an ion chromatograph. In some of the experiments, only the total mass and the average impurity concentration of the crystal layer were measured. In others, designed to give information about the movement of inclusions, the crystal grown was removed by melting it a few millimeters at a time.

Melting was accelerated with warm air to prevent the parts of the crystal layer with higher impurity concentration from melting before the rest of the layer. Each sample was weighed and analyzed separately and the diameter of the crystal layer was measured. From the diameter of the crystal layer, which was used for calculation of the thickness of the sample, the concentration profile was obtained.

2. Mathematical Formulation

2.1 Migration of a single inclusion

The difference in composition between the warm and cold sides of the inclusion can be considered the driving force for the movement of liquid inclusions through a crystalline solid under the influence of a temperature gradient. The concentration gradient of the impurity in the inclusion is determined by the temperature gradient across the inclusion, dT/dx , and the slope of the liquidus curve, dc_i/dT , as specified by the phase diagram. The steady-state movement of the inclusion can be described by a simple diffusion

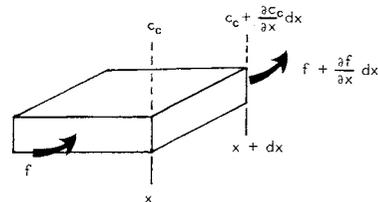


Fig. 2. Mass balance over an element in a crystal layer

equation^{2,3)} if it is assumed that the shape and size of the inclusion remain unchanged. The migration velocity, v , of the inclusion can be calculated from the following equation:

$$c_i(T)v(T) = -D(T) \frac{dc_i}{dx} = -D(T) \left(\frac{dc_i}{dT} \right)_T \left(\frac{dT}{dx} \right) \quad (1)$$

where D and c_i are the diffusion coefficient and the concentration of impurity in the inclusion, respectively. T is the temperature and x is the coordinate in the direction of migration.

The value of the derivative dc_i/dT in Eq. (1) is obtained from the liquidus curve as a function of temperature. The concentration of the impurity in the inclusion can also be obtained from the liquidus curve if it is assumed that there is equilibrium between solid and liquid phases.²⁾ This is not the case because of the temperature gradient, but the error is assumed to be negligible. Tiller⁵⁾ made a more exact solution to the problem, taking into account the lack of equilibrium at the solid-liquid interface. Finite interfacial kinetics lowers the rate of migration below that predicted by Eq. (1).

2.2 Concentration profile of the crystal layer

To evaluate the usefulness of the temperature gradient method in purification we need to be able to calculate the mass of the impurities in the crystal layer as a function of time. We do this by first calculating an impurity concentration profile with time as the variable. With this we can then analyze the experimentally determined concentration profiles, which provide indirect information about the movement of inclusions.

The model described is based on the assumption that growth of the crystal layers has stopped; i.e. time $t=0$ refers to the instant when growth has stopped.

If we assume that the inclusions migrate only in the x -direction (Fig. 2), the mass balance over an element of the crystal layer is defined by

$$\left[\left(f + \frac{\partial f}{\partial x} dx \right) - f \right] dt = \frac{\partial}{\partial t} (-c_c dx) dt \quad (2)$$

where f is the mass flux of impurity and c_c is the concentration of impurity in the crystal layer.

Equation (2) simplifies to the form

$$\frac{\partial f}{\partial x} = - \frac{\partial c_c}{\partial t} \quad (3)$$

The mass flux of impurities is a function of the migration velocity and concentration of inclusion, i.e.

$$f = c_c v \quad (4)$$

Substituting Eq. (4) into Eq. (3) yields

$$\frac{\partial c_c}{\partial t} = -v \frac{\partial c_c}{\partial x} - c_c \frac{\partial v}{\partial x} \quad (5)$$

which, since $v = v(x)$, becomes

$$-v(x) \frac{\partial c_c}{\partial x} - c_c(x, t) g(x) = \frac{\partial c_c}{\partial t} \quad (6)$$

where

$$g(x) = \frac{\partial v(x)}{\partial x} \quad (6a)$$

Equation (6) can be solved numerically by the finite difference method, applying the equation

$$c_{ck}^{t+1} = c_{ck}^t + \Delta t \left\{ v_{k+1/2} \left[\frac{c_{c(k-1)}^t - c_{ck}^t}{\Delta x} \right] + c_{ck}^t \left[\frac{v_{k+1/2} - v_{k-1/2}}{\Delta x} \right] \right\} \quad (7)$$

Here Δx and Δt are coordinate and time steps, and t and k refer to time and position, respectively. This is a simple first-order method but was found to converge into a consistent solution by varying the step lengths. The step lengths necessary were below 20 s and 0.4 mm for Δx and Δt , respectively. The system proved to be unstable with longer step lengths. The value of v_k at each point of the crystal layer is calculated by Eq. (1).

The advantage of a numerical solution is that, at the beginning of aging, any initial concentration profile that is an important parameter for purification can easily be used.

3. Results

3.1 Amount of impurities in the crystal layer

The removal of impurities from the crystal layer is seen in Fig. 3, where the total mass of the crystals and the mass of the impurities are plotted as a function of crystallization time. Experiments show that, after the initial increase, the total amount of impurities in the crystal layer decreases with time; i.e. the amount of impurities in the crystal layer goes through a maximum. In Fig. 3 the mass of crystals is essentially the same for crystallization times greater than 300 min but the amount of impurities starts to decrease after a crystallization time of 100 min.

Figure 4 shows the experimental and calculated masses of impurities in the crystal layer as a function of time for the crystal growth. The experimentally determined mass is seen to remain constant after 14 h, whereas the calculated mass continues to decrease.

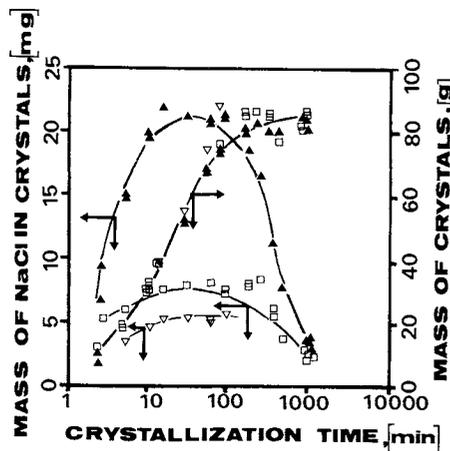


Fig. 3. Total amount of impurities in a crystal layer as a function of time, at various liquid-phase concentrations

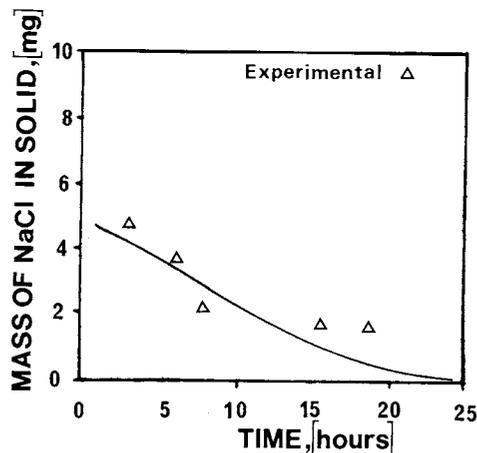


Fig. 4. Experimentally determined and calculated mass of impurities in a crystal layer as a function of time for crystal growth. The starting point of the calculation was two hours after the start of crystal growth, which is indicated by zero. Experimental conditions: Temperature of cooling liquid -7°C , concentration of feed liquid 0.9 g NaCl/dm^3 , thickness of crystal layer 23 mm

The deviation may be due to those impurities which do not migrate with the inclusions and hence represent the minimum concentration of impurities that can be achieved.

The cumulative mass of impurities in the crystal layer is calculated from the concentration profile, which is obtained numerically.

3.2 Concentration profile

Figure 5 shows the impurity concentration in the crystal layer as a function of distance from the cooled surface when time for the growth of the layer is a parameter. It is generally accepted that the crystal layer is purer when the growth rate is lower. This has been assumed to mean that the crystal layer will be purer near the growing surface. Our results show, however, that this is not the case. As seen in Fig. 5, with short crystallization times the NaCl concentration in the ice crystals is lowest near the cooled

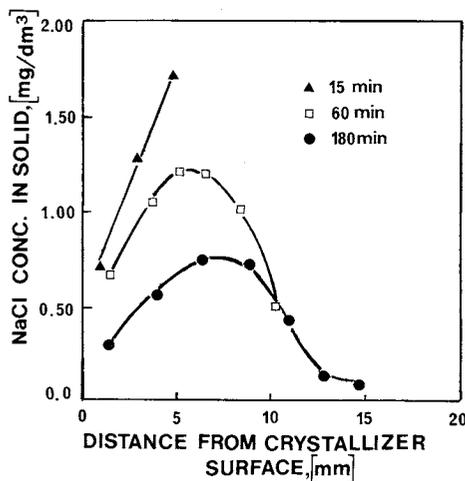


Fig. 5. Concentration of NaCl in ice crystals as a function of the distance from the cooled surface. The layer was grown from 1.6 g/dm³ aqueous solution with different crystallization times.

surface of the crystallizer. With longer crystallization times the maximum is in the middle part of the layer. Similar results are reported by Yamazaki *et al.*¹¹⁾

Two different mechanisms explain these results. First, in the early stages of growth of the crystal layer, the temperature gradient over the crystal layer is high, and there is a strong driving force for the movement of inclusions away from the crystallizer surface. At this stage the part of the crystal layer near the cooled surface is purified effectively. Secondly, in the course of growth, the growth rate and therefore the impurity concentration as well decrease toward the warm surface. When these two effects are added together, a concentration profile with a maximum is formed.

Figure 6 shows the measured concentration profile and Fig. 7 that calculated by Eq. (6). The concentration profile at the beginning of aging shown in Fig. 7 is the experimentally determined one from Fig. 6.

Conclusions

Our experiments show the total amount of impurities in a crystal layer to decrease with time when the layer is grown on a cooled surface and maintained under a temperature gradient. This can be explained by a mechanism in which liquid inclusions move under the influence of a temperature gradient. The experimentally determined concentration of impurities reached a maximum in the middle part of the crystal layer, indicating that the movement of inclusions has a significant effect on the distribution of impurities in the crystal layer and also allows a high level of purity to be achieved in the crystal layer nearest the cooled surface where the temperature gradient in the first part of the growth was greatest.

The migration of a single inclusion can be expressed by a simple diffusion equation. The concentration

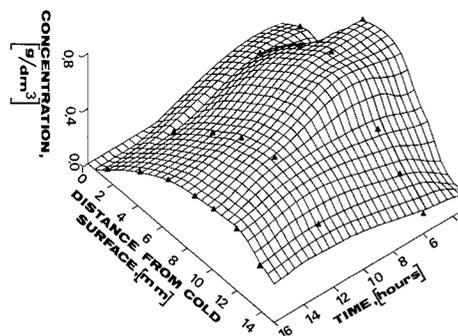


Fig. 6. Experimentally determined concentration profile of NaCl in a crystal layer grown from 1.6 g/dm³ aqueous solution. Some of the experimentally determined values (\blacktriangle) are folded behind the curved surface obtained by cubic spline interpolation

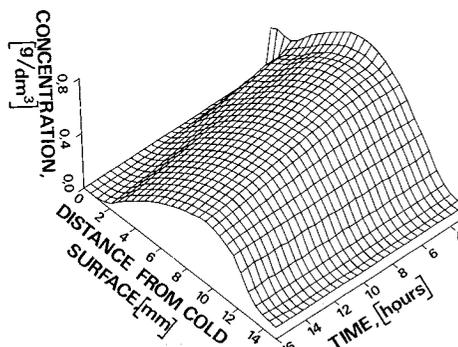


Fig. 7. Calculated concentration profile of NaCl in a crystal layer. The initial concentration profile used in the calculations is the same as in Fig. 6. The difference in initial concentrations shown in Figs. 6 and 7 is due to the data treatment techniques.

profile over the crystal layer can then be calculated with the model we have proposed, based on the mass balance over the layer. Since no parameters for different crystallization configurations are needed the calculation of the purification process is easy.

Nomenclature

c	= concentration of impurity	[kg/m ³]
D	= diffusion coefficient	[m ² /s]
f	= mass flux of impurity	[kg/(m ² s)]
T	= temperature	[K]
t	= time	[s]
Δt	= time step	
v	= velocity of migration of single inclusion	[m/s]
x	= coordinate in direction of migration	[m]
Δx	= coordinate step	

<Subscripts>

c	= crystal
i	= inclusion
k	= position, nodal point

<Superscripts>

t	= time
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ADSORPTION ISOTHERMS OF ETHANE, ETHYLENE, AND CARBON DIOXIDE ON ACTIVATED CARBON FIBER AT ELEVATED PRESSURES

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There is a need for adsorption isotherms at elevated pressures in connection with pressure swing adsorption processes or gas purification processes at high pressures. Equations for adsorption isotherms are required to predict multi-component adsorptions as well as to correlate single-component adsorption data.

The present work describes an experimental apparatus suitable for precise measurement of gas-phase adsorption equilibria at elevated pressures up to 1100 kPa. Ethane, ethylene and carbon dioxide, which are impurities in natural gas, were chosen as adsorbate gases. Single-component adsorption isotherms on a commercial activated carbon fiber, KF-1500, were obtained at 273.15, 298.15 and 323.15 K, respectively, and they are correlated by the multi-site occupancy model.⁸⁾

1. Experimental

1.1 Apparatus

The experimental apparatus used in the present work utilizes a volumetric method. The amount of adsorption (q) is determined from the mass balance calculation by measuring the amount of gaseous substance charged into the system first and that remaining in the gas phase at equilibrium. Since the

gas-phase volume in an adsorption cell was determined by means of helium gas, the adsorption q obtained in the present work is regarded as the Gibbs surface excess whose dividing interface is chosen as the solid surface of the adsorbent.

A schematic diagram of the apparatus is shown in Fig. 1. A gas piston (a) has a total volume of 100 cm³ with 25 turns, which was calibrated by using de-gassed water within ± 0.01 cm³. A Digiquartz pressure transducer (b), model 2000AS of Paroscientific Co. Ltd., has a full range of 1400 kPa and a sensitivity of 0.04 kPa with a reproducibility of ± 0.14 kPa. A gas sampler attachment (c) is connected to a gas chromatograph for analysis of gas-phase composition in the case of multi-component adsorption.

A water bath in which the gas piston (a) and the circulation pump (d) are immersed is regulated to 298.15 ± 0.01 K. The adsorption cell (f), with a 1.073 g activated carbon fiber, is also placed in a water bath, controlled within ± 0.01 K at each adsorption temperature.

Helium gas was used to determine the volume of gas phase including the circulation pump, the pressure transducer, tubing and the void space in the adsorbent. The precise measurement of pressure and use of the calibrated gas piston allowed accurate determination of the volumes.

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