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Ho-Ming Yeh[a]; Wen Hsien Yeh[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, NATIONAL CHENG KUNG UNIVERSITY TAINAN, TAIWAN, REPUBLIC OF CHINA

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The Improvement of Separation in Zone Refining Processes with Zone Length Varied along the Ingot

HO-MING YEH and WEN HSIEN YEH

CHEMICAL ENGINEERING DEPARTMENT
NATIONAL CHENG KUNG UNIVERSITY
TAINAN, TAIWAN, REPUBLIC OF CHINA

Abstract

Adjusting the zone length properly and continuously along the ingot during zone melting substantially increases the separation efficiency by controlling the solute concentration in the liquid zone. Considerable improvement in separation was obtained by employing the process with a partially optimized zone length versus distance.

INTRODUCTION

Zone melting, introduced by Pfann (*4*), is used for the purification of metals, semiconductors, and organic and inorganic chemicals. In this process, separation of impurities is effected by slowly moving a narrow melted zone through an ingot of solid material.

The distribution of impurities along an ingot depends on the value of the distribution coefficient, on the length of the zone, and on the number of zone passes. Davies (*1*) has investigated theoretically the efficiency of the zone refining process in terms of an optimal zone length which is held constant during a given pass. He pointed out that maximum separation with the first zone is achieved when the zone length l_1 is equal to the length of the ingot L, i.e., normal freezing. He then suggested that following a normal freeze, the most effective length for the second zone is $l_2 = 0.3L$.

Zone melting with zone size changing along the ingot has been studied by Jackson and Pfann (*3*) and Wilcox (*7*). In their studies, Wilcox developed a theory for determination of the nonconstant distribution coefficient, while Jackson and Pfann discovered a method for producing a linear gradient of solute concentration by changing the volume of a molten zone.

A more detailed study of the mechanism of separation in zone refining indicates that properly adjusting the zone length as a function of position along the ingot might further improve the separation efficiency. It is the purpose of this work to develop the separation theory and investigate the improvement of separation in a zone refining process with zone length as a function of position along the ingot.

THE BASIC EQUATIONS

The basic differential equation applicable to zone melting processes with constant zone length was derived independently by Lord (*2*) and Reiss (*5*):

$$\frac{l}{k}\, dC_n(x) = [C_{n-1}(x + l) - C_n(x)]\, dx, \qquad 0 \leqslant x \leqslant L - l \qquad (1)$$

This equation is obtained by taking the mass balance within the moving zone ABCD or A'B'C'D' as shown in Fig. 1, and is also based on the following assumptions: (a) constant distribution coefficient, (b) uniform composition in the liquid, (c) negligible diffusion in the solid, (d) solubility of the solute in the melt is not exceeded at any point, (e) the change in density that occurs upon solidification is neglected, and (f) constant length of liquid zone.

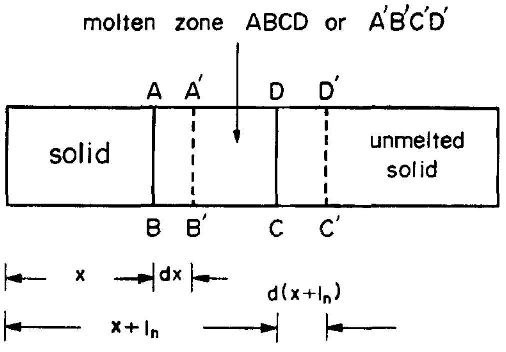

FIG. 1. Schematic diagram of zone melting.

By following the same procedure and under Assumptions (a)–(e), the basic differential equation applicable to processes with adjustable zone length is

$$\frac{dC_n(x)}{dx} + \frac{\left(\frac{dl_n(x)}{dx} + k\right)}{n} C_n(x) = \frac{kC_{n-1}(x + l_n)}{l_n}\left(1 + \frac{dl_n}{dx}\right)$$

$$0 \leqslant x \leqslant L - l_n \qquad (2)$$

and the solute concentration at $x = 0$ is given by

$$C_n(0) = \frac{k}{l_n}\int_0^{l_n(0)} C_{n-1}(x)\, dx \qquad (3)$$

If the following dimensionless variables are introduced:

$$\bar{C}_n(Z) = C_n/C_0, \qquad Y_n(Z) = l_n/L, \qquad Z = x/L \qquad (4)$$

Equations (2) and (3) become

$$\frac{d\bar{C}_n}{dZ} + \frac{\left(\frac{dY_n}{dZ} + k\right)}{Y_n}\bar{C}_n = \frac{k\bar{C}_n(Z + Y_n)}{Y_n}\left(1 + \frac{dY_n}{dZ}\right),$$

$$0 \leqslant Z \leqslant 1 - Y_n \qquad (5)$$

$$\bar{C}_n(0) = \frac{k}{Y_n(0)}\int_0^{Y_n(0)} \bar{C}_{n-1}(Z)\, dZ \qquad (6)$$

For constant zone length, $dY_n/dZ = 0$, and Eq. (5) reduces to Eq. (1).

AN OPTIMAL VARIATION OF ZONE LENGTH

First Pass

Consider an ingot with uniform initial concentration C_0. A molten zone traversing an ingot has two liquid–solid interfaces, a melting interface and a freezing interface. As zone refining progresses, the solute concentration in the molten zone rises for a solute having $k < 1$ and falls for $k > 1$. It would appear, therefore, that to obtain the best separation in the ingot, one must continuously reduce the solute concentration in the molten zone for $k < 1$ and increase it for $k > 1$. In order to meet both situations, the zone length must be as large as possible, i.e., normal freezing for all values of the distribution coefficient. This is the same result as obtained by Davies (*1*).

The concentration distribution resulting from such normal freezing is given by

$$\bar{C}_1^* = k(1 - Z)^{k-1} \tag{7}$$

Second Pass

Following a normal freeze, the mass balance equation and boundary condition for the second pass can be obtained from Eqs. (5) and (6), respectively:

$$\frac{d\bar{C}_2}{dZ} + \frac{\left(\frac{dY_2}{dZ} + k\right)}{Y_2}\bar{C}_2 = \frac{k^2[1 - (Z + Y_2)]^{k-1}}{Y_2}\left(1 + \frac{dY_2}{dZ}\right) \tag{8}$$

$$\bar{C}_2(0) = \frac{k}{Y_2(0)}\int_0^{Y_2(0)} \bar{C}_1^*(Z)\,dZ \tag{9}$$

The concentration distribution $\bar{C}_2$ may be calculated from Eqs. (8) and (9) numerically for any given function of zone length $Y_2(Z)$. An optimal variation of zone length $Y_2(Z)$ will be selected by the following procedures.

(a) First, Eq. (8) is rewritten in the form of a difference equation:

$$\frac{\bar{C}_2(Z + \Delta Z) - C_2(Z)}{\Delta Z} = \frac{k^2[1 - (Z + Y_2(Z)]^{k-1}}{Y_2(Z)}\left(1 + \frac{Y_2(Z + \Delta Z) - Y_2(Z)}{\Delta Z}\right) - \frac{\frac{Y_2(Z + \Delta Z) - Y_2(Z)}{\Delta Z} + k}{Y_2(Z)}\bar{C}_2(Z) \tag{10}$$

(b) Give a value of $Y_2(0)$ and calculate $\bar{C}_2(0)$ from Eq. (9). Then set $\Delta Z = 0.02$ and search for the proper values of $Y_2(0.02)$ by Eq. (10) for minimum $\bar{C}_2(0.02)$ as $k < 1$, or for maximum $\bar{C}_2(0.02)$ as $k > 1$. The proper values of $Y_2(0.04)$, $Y_2(0.06)$, . . . will be calculated by the same procedures.

(c) Similarly, give other values of $Y_2(0)$ and find the corresponding proper functions of $Y_2(Z)$ and $\bar{C}_2(Z)$.

(d) Finally, the best functions of $Y_2(Z)$ will be determined from the proper functions of $Y_2(Z)$ and $\bar{C}_2(Z)$ by the following criteria:

$$\text{Min } I_2 = \int_0^{0.5} \bar{C}_2(Z)\, dZ \quad \text{or} \quad \text{Max } I_2' = \int_{0.5}^{1.0} \bar{C}_2(Z)\, dZ \quad \text{for } k < 1 \tag{11}$$

$$\text{Max } I_2 = \int_0^{0.5} \bar{C}_2(Z)\, dZ \quad \text{or} \quad \text{Min } I_2' = \int_{0.5}^{1.0} \bar{C}_2(Z)\, dZ \quad \text{for } k > 1 \tag{12}$$

The optimal functions of zone length $Y_2(Z)$ and the corresponding values of minimum or maximum I_2 in terms of k have been determimined numerically. The results are presented in Fig. 2 and Table 2, respectively.

Multipass

The optimal functions $Y_n(Z)$ of zone length for the nth pass may be calculated numerically by trial and error from the following equations:

$$\frac{d\bar{C}_n(Z)}{dZ} + \frac{\left(\frac{dY_n}{dZ} + k\right)}{Y_n}\bar{C}_n(Z) = \frac{k\bar{C}^*_{n-1}(Z + Y_n)}{Y_n}\left(1 + \frac{dY_n}{dZ}\right), \quad 0 \leqslant Z \leqslant 1 - Y_n \tag{13}$$

$$\bar{C}_n(0) = \frac{k}{Y_n(0)} \int_0^{Y_n(0)} \bar{C}^*_{n-1}(Z)\, dZ \tag{14}$$

and the following restrictions:

$$\text{Min } I_n = \int_0^{0.5} \bar{C}_n(Z)\, dZ \quad \text{for } k < 1 \tag{15}$$

$$\text{Max } I_n = \int_0^{0.5} \bar{C}_n(Z)\, dZ \quad \text{for } k > 1 \tag{16}$$

CONSTANT ZONE LENGTH

For constant zone length, $dY_n/dZ = 0$, Eqs. (13) and (14) reduce to

$$\frac{d\bar{C}_n(Z)}{dZ} + \frac{k}{Y_n}\bar{C}_n(Z) = \frac{k\bar{C}^*_{n-1}(Z + Y_n)}{Y_n}, \quad 0 \leqslant Z \leqslant 1 - Y_n \tag{17}$$

$$\bar{C}_n(0) = \frac{k}{Y_n} \int_0^{Y_n} \bar{C}^*_{n-1}(Z)\, dZ \tag{18}$$

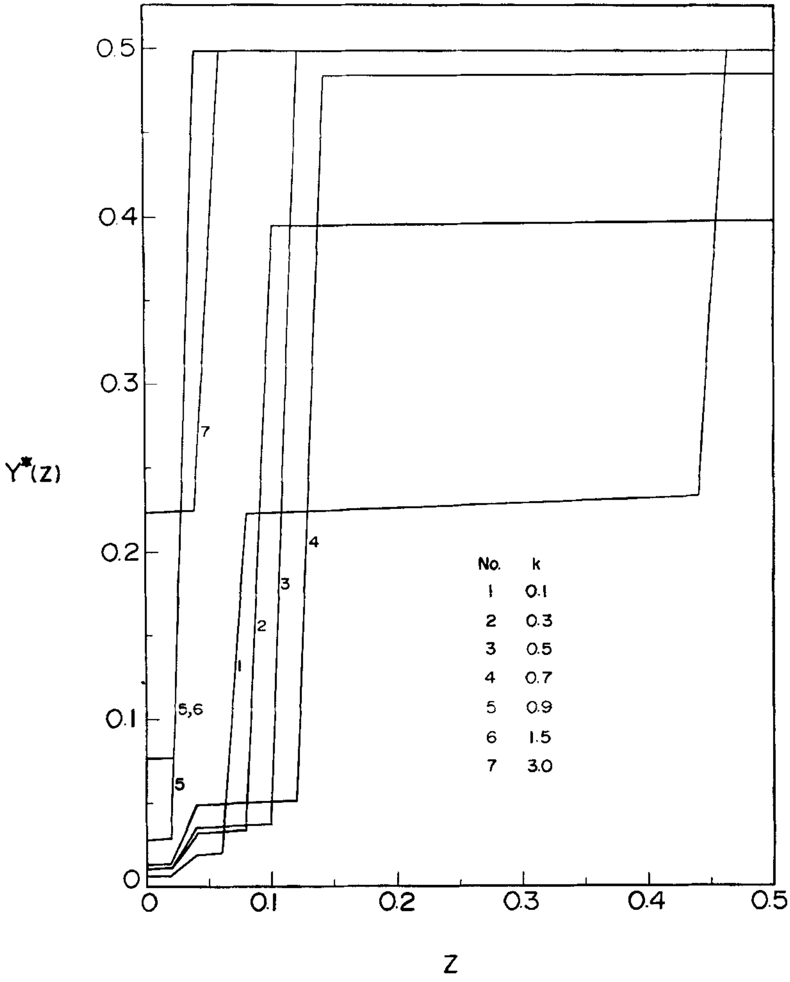

FIG. 2. The optimal functions of zone length for the second pass.

For the second pass

$$\frac{d\bar{C}_2(Z)}{dZ} + \frac{k}{Y_2}\bar{C}_2(Z) = \frac{k^2(1 - Z - Y_2)^{k-1}}{Y_2}, \qquad 0 \leqslant Z \leqslant 1 - Y_2 \tag{19}$$

$$\bar{C}_2(0) = \frac{k}{Y_2}\int_0^{Y_2} \bar{C}_1^*(Z)\,dZ \tag{20}$$

Similarly, the optimal zone length $\dot{Y}_2$ and the corresponding values of minimum or maximum $\dot{I}_2$ have been calculated numerically from Eqs. (11), (12), (19), and (20). The results are presented in Tables 1 and 2, respectively.

DISCUSSION AND CONCLUSION

It has been shown that a substantial increase in separation can be obtained by continuously adjusting the zone length during zone refining. The maximum separation with the first pass is achieved when the zone length l_1 is equal to L, the length of the ingot, i.e., normal freezing for all values of k. Following a normal freeze, the optimal functions of zone length for the second pass depend on k, and the results are presented in Fig. 2.

The values of minimum (for $k < 1$) or maximum (for $k > 1$) I_2 have been calculated for comparison with I_0 (= 0.5), and the results are

TABLE 1

Optimal Zone Length for the Second Pass with Constant Zone Length

k	0.1	0.3	0.5	0.7	0.9	1.5	3.0
$\dot{Y}_2$	0.342	0.345	0.345	0.345	0.345	0.351	0.380

TABLE 2

Comparison of Separations after Second Pass in Processes with Adjustable Zone Length

k	I_0	$\dot{I}_2$	I_2^*
0.1	0.5	0.012522	0.007902
0.3	0.5	0.091006	0.043781
0.5	0.5	0.205231	0.091708
0.7	0.5	0.328430	0.144005
0.9	0.5	0.445883	0.191917
1.5	0.5	0.712102	0.998191
3.0	0.5	0.916480	0.999154

presented in Table 2. It was found from this table that $I_0 > \dot{I}_2 > I_2^*$ for $k < 1$ and $I_0 < \dot{I}_2 < I_2^*$ for $k > 1$. Consequently, we conclude that the separations obtained in the process with adjustable zone length are much better than those in the process with constant zone length for all values of k. Therefore, in order to obtain a higher degree of separation in zone refining, the process with optimal function of zone length is recommended.

There are some experimental problems caused by changing the zone size. However, for the material whose density changes between melt and solid, the inclined boat is recommended. In this case the explosion and gas bubble will not happen, and the uniform cross section of the boat can be obtained with the optimal angle of inclination (*6*).

Practically, sudden changes in zone size would be very difficult to accomplish. However, this may be overcome, more or less, by having the heaters or the ingot travel as slowly as possible.

SYMBOLS

C	solute concentration in the freezing solid at solid–liquid interface
C_L	solute concentration in the main body of the liquid zone
$C_n(x)$	solute concentration freezing out of the zone at distance x in the nth pass
$\bar{C}_n(Z)$	dimensionless concentration $C_n(x)/C_0$
$\bar{C}_n^*$	$\bar{C}_n$ obtained in the process with optimal function of zone length
C_0	uniform solute concentration
I_n	separation defined by Eq. (15) or (16)
$\dot{I}_n$	I_n obtained in the process with optimal zone length
I_n^*	I_n obtained in the process with optimal function of zone length
k	distribution coefficient defined by C/C_L
L	ingot length
	zone length
n	zone length in the nth pass
x	distance from the starting end of the ingot
Y_n	dimensionless zone length, l_n/L
$\dot{Y}_n$	optimal value of Y_n in the constant zone length process
Y_n^*	optimal function of Y_n in the adjustable zone length process
Z	x/L

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