

MATHEMATICAL MODELLING OF SALT PURIFICATION BY RECRYSTALLIZATION. COUNTERCURRENT ARRANGEMENT

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The paper presents a simple model of recrystallization with countercurrent flows of the solution and the crystals being purified. The model assumes steady-state operating conditions, an equilibrium between the outlet streams of each stage, and the same equilibrium temperature and distribution coefficient for all stages. With these assumptions, the model provides the basis for analyzing the variation in the degree of purity as a function of the number of recrystallization stages. The analysis is facilitated by the use of a diagram constructed for the limiting case of perfect removal of the mother liquor from the crystals between the stages.

In crystallization of salts from multicomponent systems, microadmixture are practically always entrained into the macrocomponent crystals. This is an undesirable phenomenon when high-purity products are required. Crystal contamination can arise from a number of causes. Surface contamination may occur as a result of the adherence of the mother liquor to the crystal surface or impurities may be entrained into the bulk of the crystals. Although there are different mechanisms of the entrainment^{1,2}, the distribution of a microcomponent at equilibrium can frequently be approximated by the so-called homogeneous distribution law

$$Y = k_H X, \quad (1)$$

where X and Y are the masses** of the microcomponent per unit mass of the macrocomponent in the liquid (sol) and solid (c) phases, respectively.

We assume that the equilibrium macrocomponent concentration in solution is

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** When the relative mole fractions are substituted for X and Y in Eq. (1), the coefficient k_H has the same numerical value.

independent of the microcomponent concentration and that

$$W_{\text{eq}} = W_{\text{eq}}(t), \quad (2)$$

where W_{eq} is the equilibrium mass of the macrocomponent per unit mass of solvent, and t is the temperature.

THEORETICAL

We assume that steady-state countercurrent recrystallization is carried out in an n -stage cascade (Fig. 1). We consider a batchwise operation, but the derivation is also valid for the continuous arrangement. The mass streams of macrocomponent m with microcomponent concentrations X and Y leaving the k -th stage are denoted by the superscript k , *i.e.* $m^{(k)}$, $X^{(k)}$, $Y^{(k)}$. The temperature is the same at all stages. We assume that the streams leaving each stage are in equilibrium, so that Eqs (1) and (2) are valid. The solution entering the k -th stage contains $m_{\text{sol}}^{(k+1)}$ of macrocomponent, and after recrystallization the amount of the macrocomponent is $m_{\text{sol}}^{(k)}$. The crystals (solid phase) entering and leaving the k -th stage contain, respectively, $m_{\text{c}}^{(k-1)}$ and $m_{\text{c}}^{(k)}$ of the macrocomponent. The crystals entrain the mother liquor, which contains $m_{\text{m}}^{(k-1)}$ of the macrocomponent at the inlet and $m_{\text{m}}^{(k)}$ at the outlet of the k -th stage. The relative concentrations of the microcomponent in the liquid streams of the k -th member are $X^{(k-1)}$, $X^{(k)}$, and $X^{(k+1)}$, and in the solid phase they are $Y^{(k-1)}$ and $Y^{(k)}$.

The crystals are dissolved and recrystallized at each stage. The relative mass fraction of the macrocomponent in solution (based on the mass of solvent) is W on crystal dissolution and W_{eq} on recrystallization. The model assumes that the crystals generated at each stage are separated from the major portion of the mother liquor but are not washed and pass on together with the adhering solution to the next stage. The relative amount of the macrocomponent in the mother liquor entrained by the crystals, $m_{\text{m}}^{(k)}/m_{\text{c}}^{(k)}$, remains the same at all stages. Since the equilibrium temperature is the same at all stages and the ratio $m_{\text{m}}^{(k)}/m_{\text{c}}^{(k)}$ is constant, we also have

$$m_{\text{m}}^{(o)} = m_{\text{m}}^{(k)} = m_{\text{m}} = \text{constant} \quad (3a)$$

$$m_{\text{c}}^{(o)} = m_{\text{c}}^{(k)} = m_{\text{c}} = \text{constant} \quad (3b)$$

$$m_{\text{sol}}^{(n+1)} = m_{\text{sol}}^{(k)} = m_{\text{sol}} = \text{constant} . \quad (3c)$$

This also implies a constant moisture content of crystals leaving the individual stages. The moisture content U is defined as the ratio of the amount of solvent to the total amount of crystals. The fresh solution fed to the n -th stage is prepared from the pure solvent in which part of the crystal product from the n -th stage freed

from any mother liquor has been dissolved at the equilibrium temperature. Then

$$X^{(n+1)} = Y^{(n)}. \quad (4)$$

With these assumptions, we can write a mass balance for the microcomponent on the k -th stage in the form

$$\begin{aligned} & m_c Y^{(k-1)} + m_m X^{(k-1)} + m_{sol} X^{(k+1)} = \\ & = m_c Y^{(k)} + (m_m + m_{sol}) X^{(k)}, \quad [k = 1, 2, \dots, n]. \end{aligned} \quad (5)$$

The mass balance for the microcomponent over the whole n -stage recrystallization system can be written as

$$\begin{aligned} & m_c Y^{(0)} + m_m X^{(0)} + m_{sol} X^{(n+1)} = \\ & = m_c Y^{(n)} + m_n X^{(n)} + m_{sol} X^{(1)}. \end{aligned} \quad (6)$$

The aim in solving Eq. (6) is to find the composition, *i.e.* the microcomponent contents of the product, $Y^{(n)}$, and of the exit mother liquor, $X^{(1)}$, for given process conditions. Besides Eqs (5) and (6), we can write, on the basis of Eq. (1), the following relation between the streams leaving the k -th stage

$$Y^{(k)} = k_H X^{(k)}, \quad [k = 1, 2, \dots, n]. \quad (7)$$

To solve Eqs (5) and (6), we need a formal expression for $X^{(n+1)}$ as a function of $Y^{(n+1)}$. From Eqs (1) and (4) it follows that

$$Y^{(n+1)} \equiv k_H X^{(n+1)} = k_H Y^{(n)}. \quad (8)$$

Let us introduce the dimensionless concentration parameters

$$Z^{(k)} \equiv Y^{(k)}/Y^{(0)}, \quad [k = 1, 2, \dots, n] \quad (9)$$

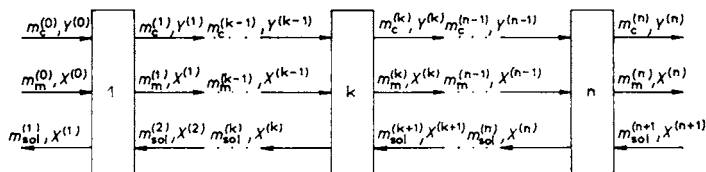


FIG. 1

Model of stagewise countercurrent recrystallization

and the recrystallization factor

$$K \equiv \frac{m_{\text{sol}}/m_c}{k_H + m_m/m_c} \quad (10a)$$

Equation (10a) can be rewritten as

$$K = \frac{W_{\text{eq}}(W - W_{\text{eq}}) - UW_{\text{eq}}/(1 - UW_{\text{eq}})}{k_H + UW_{\text{eq}}/(1 - UW_{\text{eq}})} \quad (10b)$$

In the special (ideal) case where the crystals are entirely free from the mother liquor, *i.e.* for $U = 0$, Eq. (10b) simplifies to

$$K^* \equiv W_{\text{eq}}/[(W - W_{\text{eq}})k_H] \quad (10c)$$

The product UW_{eq} in Eq. (10b) is usually much smaller than unity.

We shall denote the microcomponent content of the final product by

$$Z_c^{(n)} \equiv Z^{(n)} \quad (11)$$

Using Eqs (4), (7) to (10a), and (11), the balance equations (5) and (6) can be rewritten in the form

for the k -th stage

$$Z^{(k-1)} - (1 + K)Z^{(k)} + KZ^{(k+1)} = 0, \quad [k = 1, 2, \dots, n] \quad (12)$$

for the whole system

$$X^{(1)}/Y^{(0)} = [1 - Z_c^{(n)}(1 - k_H K)]/k_H K \quad (13)$$

Using Eqs (8) and (9) in solving the set of equations (12), we obtain (see Appendix)

$$Z_c^{(1)} = (1 + K - k_H K)^{-1} \quad (14a)$$

$$Z_c^{(2)} = [(1 + K - k_H K)(1 + K) - K]^{-1} \quad (14b)$$

$$1/Z_c^{(n)} = (1 + K)/Z_c^{(n-1)} - K/Z_c^{(n-2)}, \quad n \geq 3 \quad (14c)$$

DISCUSSION

From Eqs (13) and (14) we can determine the required parameters $Z_c^{(n)}$ and $X^{(1)}$ for given conditions (n, K, k_H) of countercurrent crystallization. The variation in $Z^{(k)}$ for $k = 1, 2, \dots, n - 1$ is determined on the basis of a known value of $Z_c^{(n)}$ by solving the set of equations (12) successively for $k = n - 1, n - 2, \dots, 2, 1$.

For the purpose of a simulation analysis, it is convenient to treat the relation $Z_e^{(n)} = Z_e^{(n)}(n, K, k_H)$ in tabular form. In the special case where $U = 0$ and $(1 + K) \gg \gg k_H K$ or $X^{(n+1)} = 0$, Eqs (14a,b,c) reduce to the two-parameter (n, K^*) relationships

$$Z_e^{(1)} = (1 + K^*)^{-1} \quad (15a)$$

$$Z_e^{(2)} = [(1 + K^*)^2 - K]^{-1} \quad (15b)$$

$$1/Z_e^{(n)} = (1 + K^*)/Z_e^{(n-1)} - K^*/Z_e^{(n-2)}, \quad n \geq 3. \quad (15c)$$

Equations (15a,b,c) can be used instead of (14a,b,c) for preliminary calculations provided that the crystals leaving each cascade member are low in moisture content.

The variation in $Z_e^{(n)}$ obtained from Eqs (15a,b,c) is shown in Fig. 2 for chosen values of K^* . We can use the figure to establish the dependence of K^* on n for a desired purity $Z_e^{(n)}$ of the product. For example, if we require a 1000-fold decrease in the microcomponent content, i.e. $Z_e^{(n)} = 0.001$, we obtain the numerical results given in Table I.

TABLE I
Variation in K^* with n for $Z_e^{(n)} = 0.001$

| n | 9 | 6 | 5 | 4 | 3 | 2 | 1 |
|-------|---|---|-----|-----|-----|----|-----|
| K^* | 2 | 3 | 3.9 | 5.4 | 9.7 | 30 | 999 |

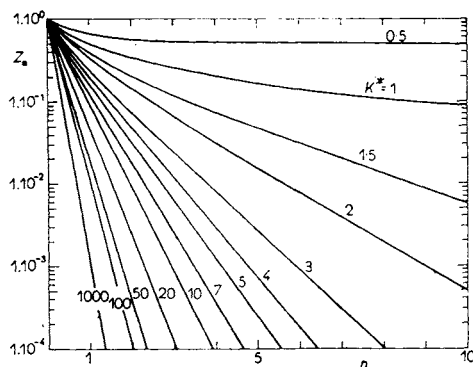


FIG. 2
A plot of Z_e vs n for various values of K^* according to Eq. (15)

For low moisture contents, we can assume, as a first approximation, that $K^* = K$. On the basis of Eq. (10b) we can decide whether a required value of K can be achieved with a given number of crystallization stages. The value of K then represents a technically important quantity, the relative yield or the relative amount of the effluent solution. In accord with the assumption included in the model, the usual practice in preparing a fresh saturated solution is to use the product from the n -th member. The difference $(W - W_{\text{eq}})$ appearing in Eq. (10c) represents the amount of macrocomponent produced per unit mass of solvent. If a non-zero production is to be obtained after dissolving part of the product, it is necessary that $W > 2W_{\text{eq}}$.

APPENDIX

Derivation of Eqs (14a,b,c):

In matrix notation, the set of equations (12) is

$$\mathbf{D}_n \mathbf{Z} = \mathbf{A} \quad (16)$$

where \mathbf{D}_n is a tridiagonal matrix of order $n \times n$,

$$\mathbf{D}_n = \begin{bmatrix} -(1+K), & K, & 0, & \dots, & 0, & 0, & 0 \\ 1, & -(1+K), & K, & \dots, & 0, & 0, & 0 \\ 0, & 1, & -(1+K), & K, & \dots, & 0, & 0 \\ \vdots & & & & & & \\ 0, & 0, & \dots, & 0, & 1, & -(1+K), & K \\ 0, & 0, & \dots, & 0, & 0, & 1, & -(1+K - Kk_{11}) \end{bmatrix}$$

The matrices \mathbf{Z} and \mathbf{A} are of order $1 \times n$:

$$\mathbf{Z} = \begin{bmatrix} Z^{(1)} \\ Z^{(2)} \\ \vdots \\ Z^{(n-1)} \\ Z_e \end{bmatrix} \quad \mathbf{A} = \begin{bmatrix} -1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

Solving the set of equations (16) by means of determinants gives

$$Z_e^{(n)} = \frac{\det(\mathcal{D}_n)}{\det(\mathbf{D}_n)}, \quad (17)$$

where matrix \mathcal{D}_n is obtained from matrix \mathbf{D}_n by replacing the last column in matrix \mathbf{D}_n by the elements of matrix \mathbf{A} .

By expanding $\det(\mathcal{D}_n)$ about the last column, we find

$$\det(\mathcal{D}_n) = (-1)^n. \quad (18)$$

Expansion of $\det(\mathbf{D}_n)$ about the first row yields

$$\det(\mathbf{D}_n) = -(1 + K) \det(\mathbf{D}_{n-1}) - K \det(\mathbf{D}_{n-2}), \quad (19)$$

where matrices \mathbf{D}_{n-1} and \mathbf{D}_{n-2} are similar in structure to matrix \mathbf{D}_n , but are of orders $(n-1) \times (n-1)$ and $(n-2) \times (n-2)$, respectively.

Using Eqs (17) and (18) and considering the identity

$$(-1)^n = (-1)^{n-2} = -(-1)^{n-1},$$

we can transform Eq. (19) for $n \geq 3$ into Eq. (14c). Equations (14a) and (14b) are obtained directly by solving the set of equations (12). This completes the proof of Eqs (14a,b,c).

LIST OF SYMBOLS

| | |
|---|---|
| A | matrix in Eq. (16) |
| \mathcal{D}_n | matrix in Eq. (17) |
| D _n | matrix in Eq. (16) |
| <i>K</i> | recrystallization factor defined by Eq. (10a) |
| <i>k</i> _H | homogeneous distribution coefficient |
| <i>k</i> | <i>k</i> -th stage of crystallization |
| <i>m</i> _c ^(<i>k</i>) | amount of macrocomponent in crystals leaving the <i>k</i> -th stage |
| <i>m</i> _m ^(<i>k</i>) | amount of macrocomponent in adhering mother liquor leaving the <i>k</i> -th stage |
| <i>m</i> _{sol} ^(<i>k</i>) | amount of macrocomponent in solution leaving the <i>k</i> -th stage |
| <i>n</i> | number of recrystallization stages |
| <i>t</i> | temperature of crystallization |
| <i>U</i> | relative mass fraction of moisture in crystal product |
| <i>W</i> _{eq} | equilibrium mass of macrocomponent per unit mass of solvent at temperature <i>t</i> |
| <i>W</i> | mass of macrocomponent per unit mass of solvent |
| <i>X</i> ^(<i>k</i>) | mass of microcomponent in the liquid phase per unit mass of macrocomponent in the <i>k</i> -th stage |
| <i>Y</i> ^(<i>k</i>) | mass of microcomponent in the solid phase per unit mass of macrocomponent in the <i>k</i> -th stage |
| Z | matrix in Eq. (16) |
| <i>Z</i> ^(<i>k</i>) | relative concentration of microcomponent in crystals, defined by Eq. (9) |
| <i>Z</i> _c ^(<i>n</i>) | relative concentration of microcomponent in crystal product from <i>n</i> -stage countercurrent recrystallization |

Superscripts

| | |
|--------------|--------------------|
| (o) | input value |
| (<i>k</i>) | <i>k</i> -th stage |
| (<i>n</i>) | <i>n</i> -th stage |
| * | ideal state |

Subscripts

| | |
|-----|---|
| e | cascade output |
| eq | equilibrium |
| c | macrocomponent in crystals |
| sol | macrocomponent in solution |
| m | macrocomponent in solution adhering to crystals |

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