

**MATHEMATICAL MODELLING OF SALT PURIFICATION
BY RECRYSTALLIZATION.
ESTIMATION OF THE RECRYSTALLIZATION FACTOR
FOR COUNTERCURRENT ARRANGEMENT**

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In a previous paper a simple model was developed for salt purification by countercurrent recrystallization. Analysis of mass balances for a microcomponent provided a relation for the composition (purity) of the product as a function of the number of recrystallization stages and of recrystallization conditions reduced to a single parameter called the recrystallization factor. The problem can be readily solved if the dependence of the product purity on the number of recrystallization stages is to be established for a given recrystallization factor. Some difficulties arise when the product purity and maximum number of stages are fixed. For this variant, relations are derived from which the upper and lower limits for the recrystallization factor can be estimated. For recrystallization factors $K > 2$, this method is more accurate than the use of diagrams published previously. An example is given to illustrate the proposed method.

In previous papers^{1,2} we presented simple models for salt purification by countercurrent and cross-current recrystallization. The aim in developing the models was to establish, on the basis of mass balances for a microcomponent, the dependence of the product composition (purity) on the number of recrystallization stages and on process conditions reduced to a single parameter called the recrystallization factor. The problem is readily solved for a cross-current arrangement. For the technologically more important countercurrent arrangement, numerical difficulties may be encountered if the product purity and maximum number of recrystallization stages are specified and the necessary conditions of recrystallization (the recrystallization factor) are to be established.

The aim of the present work is to derive an algorithm for estimating the upper and lower limits for the recrystallization factor. These estimates give a basis for deciding whether the process is technologically feasible and if so, they allow the crystallization conditions to be determined.

Figs 1 and 2 show diagrams of n -stage countercurrent and cross-current recrystal-

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lization processes, respectively. The streams are designated as follows: 1 – crystal input; 2 – output of purified crystals; 3 – fresh solution feed; 4 – withdrawal of effluent solution.

The model for the countercurrent arrangement was developed¹ on the following assumptions: steady-state operating conditions; the same moisture of crystals leaving each stage; the same equilibrium temperature of crystallization for all stages; preparation of fresh saturated solution by dissolving part of the product at the equilibrium temperature of crystallization.

In the case of the cross-current flow, we assumed additionally that the fresh solution was distributed equally among the recrystallization stages². The equilibrium relation between the amounts of the microcomponent in the crystals and in the liquid phase was considered in the form

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

where k_H is the distribution coefficient, and Y and X are the masses of the microcomponent per unit mass of macrocomponent in the solid and liquid phases, respectively. The parameter k_H was assumed to be the same at all stages. A macrocomponent can be purified by recrystallization if $k_H < 1$.

Subject to these assumptions, mass balances for the microcomponent were used to derive relations for the composition (purity) of the product leaving the n -th stage as a function of the number of recrystallization stages and the recrystallization factor in countercurrent and cross-current arrangements.

Let us introduce the dimensionless concentration of microcomponent in the product

$$Z_e^{(n)} \equiv Y^{(n)}/Y^{(0)}, \quad (2)$$

where $Y^{(n)}$ and $Y^{(0)}$ are the relative mass fractions of microcomponent in the crystals from the n -th stage and in the original crystals, respectively. The recrystallization factor is given by

$$K = [W_{eq}/(W - W_{eq}) - \phi]/(k_H + \phi) \quad (3)$$

$$\phi = UW_{eq}/(1 - UW_{eq}),$$

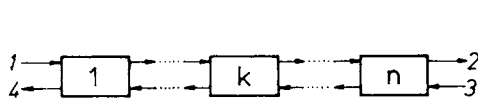


FIG. 1

Countercurrent recrystallization. 1 – crystal input; 2 – output of purified crystals; 3 – fresh solution; 4 – effluent solution

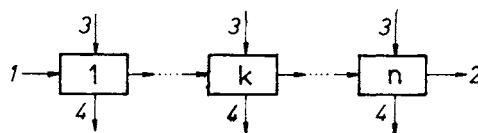


FIG. 2

Cross-current recrystallization. 1 – crystal input; 2 – output of purified crystals; 3 – fresh solution; 4 – effluent solution

where W_{eq} and W are the masses of the macrocomponent per unit mass of solvent in the liquid phase at equilibrium temperature and after dissolution of all the crystals in a given stage before their recrystallization, respectively, and U is the relative mass of moisture in the product. Usually, it can be assumed that $1 \gg UW_{\text{eq}}$. In the special case where the mother liquor is completely removed from the crystals, Eq. (3) simplifies to

$$K^* = W/[k_{\text{H}}(W - W_{\text{eq}})], \quad [U = 0]. \quad (4)$$

From Eqs (3) and (4), it follows that $K^* > K$ for identical values of k_{H} , W , and W_{eq} .

The solution of the mass balance equation for the microcomponent in the counter-current arrangement was obtained in the form¹

$$Z_{\text{e}}^{(0)} = 1 \quad (5a)$$

$$Z_{\text{e}}^{(1)} = (1 + K - k_{\text{H}}K)^{-1} \quad (5b)$$

$$1/Z_{\text{e}}^{(n)} = (1 + K)/Z_{\text{e}}^{(n-1)} - K/Z_{\text{e}}^{(n-2)}, \quad n \geq 2. \quad (5c)$$

The model for the countercurrent arrangement formulated by Eqs (5a,b,c) has a physical meaning² for

$$k_{\text{H}}K < 1. \quad (6)$$

Similarly, for the cross-current flow we have the equation²

$$Z_{\text{e}}^{(n)} = (1 + K)^{-n} \{1 - k_{\text{H}}[1 - (1 + K)^{-n}]\} \quad (7)$$

which has a physical meaning² for

$$nk_{\text{H}}K < 1, \quad (8)$$

where n is the number of recrystallization stages.

Analytical solution of Eq. (7) for the cross-current flow presents no difficulties. Numerical complications arise in solving Eqs (5a,b,c) for the countercurrent arrangement if the recrystallization conditions*, *i.e.* the recrystallization factor K , are to be determined from these equations for a given final value of $Z_{\text{e}}^{(n)}$ and maximum number of recrystallization stages $n \geq 3$ (for $n \leq 2$, the solution is straightforward).

* Knowing K , we can use Eq. (3) or (4) to calculate the conditions of recrystallization, *i.e.* the functional relationship between W and W_{eq} .

We shall now derive a method for estimating the upper and lower limits for the value of K . The use of these estimates substantially simplifies the solution of the problem. It can be shown that

$$K_{\min} < K < K_{\max}. \quad (9)$$

From condition (6) it follows that

$$K < 1/k_H. \quad (10)$$

It will be shown in the Appendix that the K_{\max} appearing in condition (9) is given by

$$K_{\max} = \text{MIN} \{ \sqrt[n]{1/Z_e^{(n)}}, 1/k_H \}. \quad (11)$$

We have shown in previous papers^{1,2} that a required final value of $Z_e^{(n)}$ can be achieved in cross-current recrystallization at a value of K lower than that needed in the countercurrent arrangement with the same n . Thus, the parameter K obtained by solving Eq. (7) can be taken as K_{\min} for the countercurrent arrangement. The expression for K_{\min} is, therefore,

$$K_{\min} = \sqrt[n]{\left(\frac{1 - k_H Z_e^{(n)}}{Z_e^{(n)}(1 - k_H)} \right)} - 1. \quad (12)$$

From conditions (9) and (10) it follows that

$$K_{\min} < 1/k_H. \quad (13)$$

If condition (13) is not satisfied, the problem has no physical meaning and a new choice of the input parameters $Z_e^{(n)}$ and n must be made. By comparing Eqs (11) and (12), we find that

$$K_{\min} > K_{\max} - 1. \quad (14)$$

Hence, the difference between the upper and lower estimates of K does not exceed unity. Thus, the relative error in the estimates decreases with increasing K . For $K > 2$, the estimates K_{\min} and K_{\max} are more accurate than the value of K determined from diagrams presented in previous papers^{1,2}.

The estimates K_{\min} and K_{\max} facilitate the numerical calculation of K from Eqs (5a,b,c) and this parameter, in turn, allows the conditions of crystallization to be determined from Eq. (3) or (4).

Let us consider an example to illustrate the proposed method. $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ containing Na^+ as the microcomponent is to be purified by countercurrent recrystallization in water. Measurements with a laboratory crystallizer³ have established that the distribution coefficient k_H assumes the following values:

for rapid cooling

$$k_H = 0.082, \quad [\text{conditions } A]$$

for slow cooling

$$k_H = 0.035, \quad [\text{conditions } B].$$

It is required that $Z_c^{(3)} < 2 \cdot 10^{-4}$ for $n = 3$. The relative moisture content of the crystals is assumed to be $U = 0.03$, and the equilibrium temperature of crystallization is 20°C . Solution: For conditions $[A]$ and $[B]$ we calculate K_{\min} from Eq. (12) and check whether condition (13) is satisfied. If not, the problem has no physical meaning. If it is satisfied, we determine K_{\max} from Eq. (11). The sought-for solution K of Eqs (5a,b,c) for $Z_c^{(3)} = 2 \cdot 10^{-4}$ and $n = 3$ is determined numerically. According to relation (9), it lies between K_{\min} and K_{\max} . The crystallization conditions, *i.e.* W , are obtained by solving Eq. (3). In the present case, $W_{\text{eq}} = W(20^\circ\text{C})$. From the calculated value of W , we can determine the minimum temperature required for the homogeneous phase to form in the crystallizer. If $U = 0$, we can use the simpler equation (4). The data for the dependence $W(t)$ are available in published tables⁴. Numerical calculation: From Eq. (12), we obtain

$$K_{\min} = 15.59, \quad [A],$$

$$K_{\min} = 16.30, \quad [B].$$

A check reveals that criterion (13) is not met for condition $[A]$. Thus, three-stage recrystallization with rapid cooling will not provide the required purity, but slow cooling can accomplish the task. By solving Eq. (11), we obtain

$$K_{\max} = 17.10.$$

Thus,

$$16.30 < K < 17.10.$$

Numerical solution of Eqs (5a,b,c) yields

$$K = 16.957.$$

In solubility tables⁴ we find that

$$W_{\text{eq}} = W(20^\circ\text{C}) = 0.1127.$$

Equation (3) gives

$$W = 0.2849.$$

According to the solubility tables⁴, this value corresponds to $t > 44^\circ\text{C}$.

APPENDIX

Proof of Eq. (11)

Let us consider the series

$$1 = Z_e^{(0)}, Z_e^{(1)}, \dots, Z_e^{(j-1)}, Z_e^{(j)}, \dots, Z_e^{(m)} \quad (A-1)$$

representing the variation in $Z_e^{(j)}$, the dimensionless outlet concentration of a microcomponent in the solid phase of j -th stage in countercurrent arrangement of a crystallizer. In this series

$$Z_e^{(j-1)}/Z_e^{(j)} > 1, \quad [j \geq 1], \quad (A-2)$$

and we shall show that

$$Z_e^{(j-2)}/Z_e^{(j-1)} > Z_e^{(j-1)}/Z_e^{(j)}, \quad [j \geq 2]. \quad (A-3)$$

For $j \geq 2$, Eq. (5c) can be rewritten as

$$Z_e^{(j-1)}/Z_e^{(j)} = 1 + K - K/[Z_e^{(j-2)}/Z_e^{(j-1)}]. \quad (A-4)$$

Dividing Eq. (5a) by (5b), we obtain

$$Z_e^{(0)}/Z_e^{(1)} = 1 + K - k_H K, \quad (A-5)$$

where, according to (6), $0 < k_H K < 1$. Relations (A-2), (A-4), and (A-5) imply the validity of (A-3), and this inequality will now be used as a starting point in proving Eq. (11).

Let us introduce, for brevity,

$$Z_e^{(j-2)}/Z_e^{(j-1)} \equiv x > 1 \quad (A-6)$$

and substitute for $Z_e^{(j-1)}/Z_e^{(j)}$ in Eq. (A-3) in terms of Eq. (A-4). After rearrangement, we obtain

$$(x - 1)(x - K) > 0. \quad (A-7)$$

From relations (A-6) and (A-7) it follows that

$$Z_e^{(j-2)}/Z_e^{(j-1)} > K. \quad (A-8)$$

Condition (A-3) implies that the series

$$Z_e^{(0)}/Z_e^{(1)}, Z_e^{(1)}/Z_e^{(2)}, \dots, Z_e^{(j-2)}/Z_e^{(j-1)}, \dots, Z_e^{(m-1)}/Z_e^{(m)} \quad (A-9)$$

is monotonically decreasing. Therefore,

$$1 < Z_e^{(j-2)}/Z_e^{(j-1)} < (j-1)\sqrt[j-1]{\prod_{k=0}^{j-1} Z_e^{(k-1)}/Z_e^{(k)}} = (j-1)\sqrt[j-1]{(1/Z_e^{(j-1)})}, \quad [j \geq 2]. \quad (A-10)$$

The expression $(j-1)\sqrt[j-1]{(1/Z_e^{(j-1)})}$ represents the geometric mean value of the first $(j-1)$ terms of series (A-9). Let

$$j = n + 1. \quad (A-11)$$

On the basis of (A-8), we can write, using (A-10) and (A-11),

$$K_{\max} = n\sqrt[n]{(1/Z_e^{(n)})} > K. \quad (A-12)$$

In order to have a physical meaning, the parameter K must satisfy condition (10). The same constraint can be imposed on K_{\max} .

$$K_{\max} \leq 1/k_H. \quad (A-13)$$

By the intersection of relations (A-12) and (A-13) we obtain Eq. (11), which is thus proved.

LIST OF SYMBOLS

| | |
|-------------|--|
| k_H | equilibrium coefficient defined by Eq. (1) |
| K | recrystallization factor defined by Eq. (3) |
| K^* | recrystallization factor defined by Eq. (4) |
| t | temperature |
| U | relative mass fraction of moisture in the product |
| W | mass of macrocomponent per unit mass of solvent in the liquid phase |
| X | mass of microcomponent per unit mass of macrocomponent in the liquid phase |
| \dot{Y} | mass of microcomponent per unit mass of macrocomponent in the solid phase |
| $Z_e^{(n)}$ | relative concentration of microcomponent in the product leaving an n -stage cascade, Eq. (2) |
| ϕ | parameter in Eq. (3) |

Superscripts

| | |
|-----|----------------|
| x | ideal state |
| j | j -th member |
| m | m -th member |
| n | n -th member |
| 0 | zeroth member |

Subscripts

| | |
|-------|-------------------|
| e | outlet |
| eq | equilibrium state |
| max | maximum |
| min | minimum |

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