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Comparison of refining by distillation and crystallization

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The equations for comparison of refining efficiency by distillation and Czochralski crystallization have been derived. It has been shown that for some systems being purified (for example, at purification of cadmium from zinc, cadmium from arsenic, sulfur from arsenic) distillation may be either more effective or less effective than Czochralski crystallization, depending on the product yield.

Выведены уравнения для сравнения эффективности дистилляционного и кристаллизационного (по Чохральскому) рафинирования. Показано, что для некоторых рафинируемых систем (например, для очистки кадмия от цинка, кадмия от мышьяка, серы от мышьяка) дистилляция может быть более эффективной или менее эффективной, чем кристаллизация по Чохральскому, в зависимости от выхода продукта.

Properties of modern functional materials are defined by their purity to a great extent. Distillation and crystallization are the main methods in production of high purity substances, and to combine those methods is reasonable for achievement of best results [1]. There is a selection problem of one or another method for effective purification of a specific system. The aim of this investigation is to compare the efficiency of distillation and Czochralski crystallization purification methods.

To solve that problem, let us use the simplified equations for calculation of distillation at low impurity concentration [2] and conclusion from the work [3] that distillation and Czochralski crystallization are described by identical equations (at corresponding substitution in equations the separation factor α at distillation by distribution coefficient k at crystallisation and vice versa) at low impurity concentration if interphase distribution coefficients are not differing from unity strongly.

For distillation:

— the impurity concentration in condensate, C_d:

$$\frac{C_d}{C_0} = \frac{1 - \left(1 - \frac{G_d}{G_0}\right)^{\alpha}}{\frac{G_d}{G_0}}, \qquad (1)$$

where C_0 is the initial impurity concentration; G_d and G_0, the condensate mass and the initial material mass, respectively;

— the impurity concentration in the crucible residue, C_1:

$$\frac{C_1}{C_0} = \left(\frac{G_1}{G_0}\right)^{\alpha - 1}, \qquad (2)$$

where G_1 is the crucible residue mass.

For Czochralski crystallization:

— the impurity concentration in the crystal, C_c:

$$\frac{C_c}{C_0} = \frac{1 - \left(1 - \frac{G_c}{G_0}\right)^{k}}{\frac{G_c}{G_0}}, \qquad (3)$$

where G_c is the crystal mass;

— the impurity concentration in the crucible residue, C_2:

$$\frac{C_2}{C_0} = \left(\frac{G_2}{G_0}\right)^{k-1}, \tag{4}$$

where G_2 is the crucible residue mass.

Depending on the values of coefficients α and k, the condensate (at $\alpha < 1$), crystal (at $k < 1$) or crucible residue (at $\alpha > 1$ and $k > 1$) may form the purified product. To compare the efficiency of distillation and Czochralski crystallization purification, let the ratios below be considered:

$$\left(\frac{C_d}{C_0} \Big/ \frac{C_c}{C_0}\right)^{-1}, \left(\frac{C_d}{C_0} \Big/ \frac{C_2}{C_0}\right)^{-1}, \left(\frac{C_1}{C_0} \Big/ \frac{C_c}{C_0}\right)^{-1}, \left(\frac{C_1}{C_0} \Big/ \frac{C_2}{C_0}\right)^{-1}$$

(selecting one thereof depending on what is the purification product) or, in the generalized form, the ratio:

$$\left(\frac{C_\alpha}{C_0} \Big/ \frac{C_k}{C_0}\right)^{-1} = \frac{C_k}{C_\alpha},$$

where C_α and C_k are the impurity concentration in the distillation or crystallization product, respectively. This ratio shows how many times the impurity concentration in the distillation product is lower than that in the crystallization product.

Let the processes be compared at the same product yield G/G_0: $G = G_d$, if the product is a condensate; $G = G_1$, if the product is the crucible residue at distillation; $G = G_c$, if the product is a crystal; $G = G_2$, if the product is the crucible residue at crystallization. Combining formulas (1)–(4), we get formulas for calculation of relative efficiency:

1) at $\alpha < 1$ and $k < 1$ (the distillation product is a condensate, the crystallization product is a crystal)

$$\frac{C_k}{C_\alpha} = \frac{1 - \left(1 - \frac{G}{G_0}\right)^k}{1 - \left(1 - \frac{G}{G_0}\right)^\alpha}; \tag{5}$$

2) at $\alpha > 1$ and $k > 1$ (the refining products are crucible residues)

$$\frac{C_k}{C_\alpha} = \left(\frac{G}{G_0}\right)^{k-\alpha}, \tag{6}$$

3) at $\alpha < 1$ and $k > 1$ (the distillation product is a condensate, the crystallization product is the crucible residue)

$$\frac{C_k}{C_\alpha} = \frac{\left(\frac{G}{G_0}\right)^k}{1 - \left(1 - \frac{G}{G_0}\right)^\alpha}; \tag{7}$$

4) at $\alpha > 1$ and $k < 1$ (the distillation product is the crucible residue, the crystallization product is a crystal)

$$\frac{C_k}{C_\alpha} = \frac{1 - \left(1 - \frac{G}{G_0}\right)^k}{\left(\frac{G}{G_0}\right)^\alpha}. \tag{8}$$

Table 1. Relative efficiency C_k/C_α depending on α and k

α and k values	C_k/C_α
$\alpha < 1$, $k < 1$, $\alpha < k$	>1
$\alpha < 1$, $k < 1$, $\alpha > k$	<1
$\alpha > 1$, $k > 1$, $\alpha < k$	<1
$\alpha > 1$, $k > 1$, $\alpha > k$	>1
$\alpha < 1$, $k > 1$	>1 or <1, depending on G/G_0
$\alpha > 1$, $k < 1$	>1 or <1, depending on G/G_0

The consideration results of equations (5)–(8) are summarized in Table 1 (at $C_k/C_\alpha > 1$, the distillation is more effective than crystallization).

It is to note the conditions $\alpha < 1$, $k > 1$ and $\alpha > 1$, $k < 1$ when distillation is more efficient or less efficient than crystallization, depending on G/G_0. Tables 2 and 3 that relate to some values of α and k (at $\alpha < 1$, $k > 1$ and $\alpha > 1$, $k < 1$, respectively) illustrate the nature of this dependence (values $C_k/C_\alpha > 1$ are in bold). It is seen that an interval of G/G_0 values may exist in the systems to be refined where distillation is more efficient than crystallization.

The calculation results of relative efficiency C_k/C_α for some real systems using the reference data [4] are shown in Table 4.

Table 2. Relative efficiency C_k/C_α depending on yield G/G_0 at $\alpha < 1$, $k > 1$

G/G_0	C_k/C_α at different α and k			
	$\alpha = 1/4$, $k = 2$	$\alpha = 1/2$ $k = 2$	$\alpha = 1/4$, $k = 4$	$\alpha = 1/2$ k = 4
0.1	0.4	0.2	0.004	0.002
0.2	0.7	0.4	0.03	0.02
0.3	**1.1**	0.6	0.1	0.05
0.4	**1.3**	0.7	0.2	0.1
0.5	**1.6**	0.9	0.4	0.2
0.6	**1.8**	1.0	0.6	0.4
0.7	**1.9**	**1.1**	0.9	0.5
0.8	**1.9**	**1.2**	**1.2**	0.7
0.9	**1.9**	**1.2**	**1.5**	1.0

Table 3. Relative efficiency C_k/C_α depending on yield G/G_0 at $\alpha > 1$, $k < 1$

G/G_0	C_k/C_α at different α and k			
	$k = 1/4$, $\alpha = 2$	$k = 1/2$, $\alpha = 2$	$k = 1/4$, $\alpha = 4$	$k = 1/2$, $\alpha = 4$
0.1	**2.6**	**5**	**250**	**500**
0.2	**1.4**	**2.3**	**35**	**67**
0.3	0.9	**1.8**	**11**	**20**
0.4	0.8	**1.4**	**5**	**9**
0.5	0.6	**1.2**	**2.5**	**4.6**
0.6	0.6	1.0	**1.6**	**2.9**
0.7	0.5	0.9	**1.1**	**1.9**
0.8	0.5	0.9	0.8	**1.3**
0.9	0.5	0.8	0.7	1.0

Table 4. Relative efficiency C_k/C_α for some systems

G/G_0	C_k/C_α at different α and k		
	Based substance: Cd, Impurity: Zn $\alpha = 2$, $k = 0.22$ [4]	Based substance: Cd, Impurity: As $\alpha = 25$, $k = 0.002$ [4]	Based substance: S, Impurity: As $\alpha = 30$, $k = 0.4$ [4]
0.1	2.6	$\sim 10^{21}$	$\sim 10^{30}$
0.3	0.9	$\sim 10^{11}$	$\sim 10^{15}$
0.8	0.5	0.8	396
0.9	0.5	0.06	1.0
0.95	0.5	0.02	0.5

It is seen that for cadmium refining from zinc, cadmium from arsenic, sulfur from arsenic, the using of distillation is reasonable with yield not more than ≈0.3, ≈0.8 and ≈0.9, respectively. If higher yield values are desirable, the crystallization purification is reasonable.

So, using the developed equations, it is shown that for some systems to be refined, distillation may be either more effective or less effective than Czochralski crystallization, depending on product yield. It is reasonable to take into account the results obtained when designing the refining technologies based on distillation and Czochralski crystallization.

References

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Порівняння дистиляційного та кристалізаційного рафінування

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Виведено рівняння для порівняння ефективності дистиляційного та кристалізаційного (за Чохральським) рафінування. Показано, що для деяких систем, що рафінуються (наприклад, при очищенні кадмію від цинку, кадмію від миш'яку, сірки від миш'яку), дистиляція може бути більш ефективною чи менш ефективною, ніж кристалізація за Чохральським, залежно від виходу продукту.