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The Continuous Zone-Refining Method

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TRANSLATION OF

THE CONTINUOUS ZONE-REFINING METHOD

(Metod nepreryvnoi zonnoi perekristallizatsii)

by

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THE CONTINUOUS ZONE-REFINING METHOD

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In the past decade, the zone-refining process has been widely employed for maximum purification of the most diverse substances, from metals and semiconductor materials to organic and inorganic compounds. However, despite the considerable variety of design formulations, all known apparatuses have many substantial drawbacks.

In the zone-refining apparatus that has appeared to date, the distribution of impurities is that of a finite ingot and differs from the distribution in a hypothetical infinite ingot in that it has "contaminated" ends considerably enriched with impurities. The contaminated ends reduce the refining effect substantially. All practical methods of zone refining are based on the periodic (discontinuous) principle, by which the charging of the ingot is repeated over a specific number of time intervals corresponding to n passages of the molten zone from one end of the ingot to the other. The refining efficiency of each successive pass decreases with increasing numbers of passes, which points up the difficulty of attaining maximum distribution. This makes it practically impossible to separate the impurities with distribution coefficients close to unity.

Thus, development of new effective refining methods, particularly continuous zone methods, is one of the most important problems of the zone-refining technique.

The literature contains a number of reports on attempts to develop a continuous zone-refining process [1, 2], however, it would seem that no apparatus operating on the principles outlined in these reports has actually been built.[*] In our opinion, the trouble lies not so much in the difficulty of implementing the methods, as in the inadequacies of their theoretical foundation. As an example, let us

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[*] Apparatus of this type was described by Moates in 1960, see ref. [6] (Tr. note).

take the zone-void method proposed by Pfann [1], whereby the molten zone moves downward along a vertical tube, while the so-called voids have to pass upward, in steps, the length of the molten zone. The molten zone must lie between two stationary solid sections. In this case, considerable stresses occur even with relatively small unavoidable temperature fluctuations that increase the volume of the liquid zone because the melt is practically incompressible. Since the tube material is practically rigid and the plugs of solid material cannot move along the walls of the tube, an expansion invariably causes the tube to crack. Thus, we may conclude that there is no means of realizing the zone-void method [1]; analysis of the literature will also demonstrate this.

Of the other methods of normal zone refining, let us mention two [4, 5] aimed at removing the impure molten zone after the first pass through the ingot. In [4], an apparatus was proposed in which the material in the zone is replaced forcibly, whereby a system of pumps is used to exchange the material in the zone for a melt of the initial composition. An apparatus is proposed in [5] with which the molten zone may be drawn off into a special branch line after the first pass. However, none of these approaches has solved the problem of intensifying the process.

We have developed a continuous zone-refining method marked by effective separation of the components and high productivity, accomplished by diluting the molten zone in the last section of the separating part of the column with simultaneous tapping of the molten zone at the end of each pass. We studied the separation mechanism of continuous zone refining with an apparatus designed for that purpose. Further, we worked out several basic designs of continuous zone-refining apparatus.

Brief statement of the method and stages of the continuous process. Continuous zone refining is conducted in a vertical column (fig. 1) with a feeder, i.e., a tank with starting material, at the upper end.

Just below the feeder is a receiver and below it an opening for tapping the molten zone. In the lower, separating part of the column there is an outlet for releasing the refined product. On moving upward, the heater (or heater system) moves the molten zone together with a void which, in this case, acts as a pneumatic shock absorber and governs the rate of movement of material in the column.
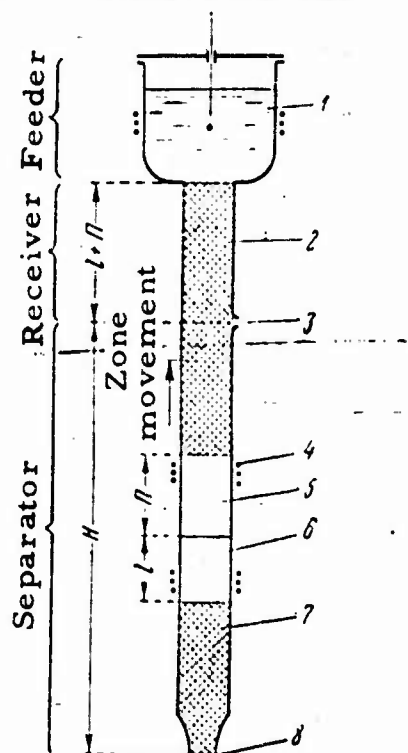

Figure 1

Apparatus for continuous zone refining;
1. starting material; 2. solid phase; 3. vent for
tapping the molten zone; 4. heater; 5. void; 6.
molten zone; 7. solid phase; 8. outlet.

The operating cycle of continuous zone refining may be divided into four stages: I. zone formation, consisting in melting out the refined material through the outlet, and formation of a void and a molten zone; II. zone refining (fig. 2a); III. tapping the molten zone (fig. 2 b, c, and d); IV. feeding the column (2 e, f).

Distribution of impurities. Basic equations. The column consists of two parts: the lower, or separating portion, where the material has already passed through one or several purifying cycles and

the upper, or receiving and feeder portion, which contains the material in its initial concentration.
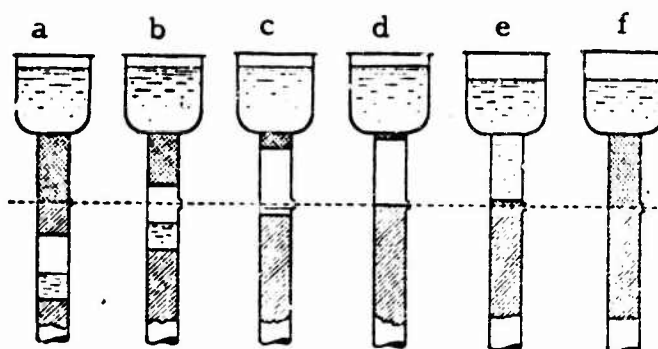

Figure 2

Diagram showing the tapping of the molten zone
and the feeding of the column in the continuous
zone-refining process.

The separating portion of the column consists of two parts: a lower part, from the outlet to a point one molten-zone length distant from the tap, and an upper part, which is a segment of the molten zone. Normal zone refining takes place in the lower part in conjunction with the movement of material in the column. In the upper part, the liquid zone is tapped (drawn off) and at the same time diluted with melt of the initial concentration.

Usually the following simplifying approximations are used for mathematical analysis of zone refining: The density of the material does not change during melting, the components do not vaporize, impurities are distributed evenly in the liquid zone, there is no diffusion in the solid phase, the distribution coefficient is in equilibrium and constant, and the length of the molten zone remains constant during the process. Several approximations made for the normal zone-refining process are quite rough and are superfluous for continuous zone refining, viz., that the density of the material be constant and

that there be no vaporization. Owing to the specific conditions of continuous zone melting, the demand for uniform impurity distribution in the molten zone is greater than in the case of normal zone refining.

For the first pass in section $0 \leq x \leq H - l$, the distribution of impurities along the length of the column is described by the familiar equation

$$C = C_0\left[1 - (1 - k)\exp\left(-k\,\frac{x}{l}\right)\right] \tag{1}$$

where x is the distance of an examined point from the outlet, H is the height of the separating part of the column, C is the impurity concentration at point x, C_0 is the impurity content of the starting material, k is the distribution coefficient, and l is the length of the molten zone.[*]

The following equation gives the solute distribution for the last molten zone $(H - l \leq x \leq H)$:

$$C = C_0 - (C_0 - kC_1)\left(\frac{H - x}{l}\right)^k \tag{2}$$

where kC_1 is the impurity concentration at the beginning of the last zone (where $x = H - l$). Equation (2) is of a universal nature, since it may be used to describe the impurity distribution not only after the first passage of the zone, but for any subsequent passage, for which one need only know the value of the impurity concentration at the initial point of the last zone $(x = H - l)$.

One should note the complex combined nature of the continuous zone-refining process in the last zone segment: Material of initial composition, characteristic of zone-refining processes is added, while the volume of the molten zone, characteristic of the processes of normal oriented crystallization, is reduced.

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[*] The area cross section of the separating part of the column is assumed to be unity, in which case the length of the molten zone instead of its volume may be used for purposes of simplification.

Comparison of continuous zone refining with zone refining of
finite and infinite ingots. The calculated curves of distribution for
three cases examined (H = 16, l = 1, k = 0.1, n = 1) show the simi-
larity of the distribution curve for continuous zone refining and the
ideal distribution curve for a hypothetical infinite ingot (fig. 3).
For example, at a distance of 0.01 mm from the end of the calculated
part (H = 16 cm), the impurity content is 0.900 versus 0.820 for an
infinite ingot, while for a finite ingot the value is 400 at that point.
The total impurity content in the final zone segment (0.826) also prac-
tically coincides with the value for an infinite ingot (0.809), while for
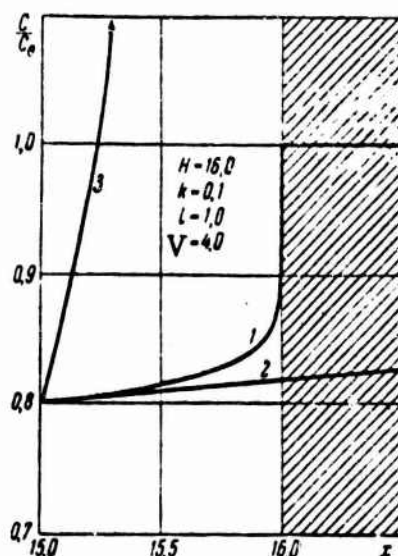a finite ingot the value is 8.18.

Figure 3

Impurity distribution in the last zone (H - l ≤ x ≤ H)
after the first pass: 1. continuous zone-refining
process; 2. hypothetical infinite ingot; 3. finite
ingot.

Distribution after n > 1 passes. There are no analytical meth-
ods for determining the impurity content in the lower segment of the
separating section, from the tap to the beginning of the last zone
(0 ≤ x ≤ H - l), after many passes of the molten zone. Serious diffi-
culties involving ratios are encountered in developing such methods
[2, 3] even for simple zone refining, since the solutions obtained
are very cumbersome without commensurate accuracy. In the case
of continuous zone refining, these difficulties are further aggravated
by the movement of the material along the column.

In the present paper, we have used as our basis a calculation method usually employed to verify analytical methods [3]. We have formulated the following expression for calculating the impurity distribution:

$$C_m^{(n+1)} = k \sum_{i=1}^{m} \overline{C}_i^n \, (1-k)^{m-i} \qquad (1 \leqslant m \leqslant p) \tag{3}$$

where p is the whole number of segments of length l in the ingot, C^{n+1} is the impurity concentration at the beginning of the m-th segment of the ingot after the (n+1)-th pass, $\overline{C}_i^{(n)}$ is the average impurity concentration in the i-th segment after n passes of the molten zone; m is the ordinal number of the segment in the direction of zone movement. Expression (3) may be used for the separating part of the column, except for the last zone segment (H - l ≤ x ≤ H). The value of $\overline{C}_p^{n+1}$ for the last zone can be determined from

$$\overline{C}_p^{(n+1)} = C_0 - \frac{1}{1+k} \, [C_0 - C_p^{(n+1)}] \tag{4}$$

which may be obtained by integrating eq. (2) over that segment. For small values of k, one may use a fictitious value for an infinite ingot at point x = H (H = pl) instead of calculating $\overline{C}_p^{(n+1)}$ by eq. (4), because in this case the values obtained from eqs. (1) and (4) (n = 1) agree. The error of this approximation may be determined from

$$c^k \approx 1 + k \tag{5}$$

which is equivalent to the condition k << 1. This method allows us to find the value of the impurity concentration along the length of the column over intervals l, except for the end of the column (H - l ≤ x ≤ H). In the last zone segment (upper segment of the separator), the impurity concentration is determined in conformity with eq. (2)

$$C^{(n)}(x) = C_0 - [C_0 - C^{(n)} \, (H-l)] \; \left(\frac{H-x}{l}\right)^k \tag{6}$$

We checked the method involving eq. (3) and found it to be sufficiently accurate. For example, the impurity concentration, 0.959, at the end of a sufficiently long column (H = 32 and x = 31) (n = 1, l = 1, k = 0.1) obtained from (1) differs but negligibly from the calculated value 0.966.

Startup period and minimum distribution.   If we take the uniform impurity distribution along the column with concentration C_0 as the initial position, we get a subsequent reduction of impurity content with an increasing number of passages of the molten zone, until a minimum impurity distribution (fig. 4) is reached after a sufficient number of passes (comprising the startup period).   This corresponds to the beginning of the operational period, when the refined material with a stable impurity concentration comes from the column.   With an operating cycle of this type, the column can function as long as starting material is supplied from the feeder.
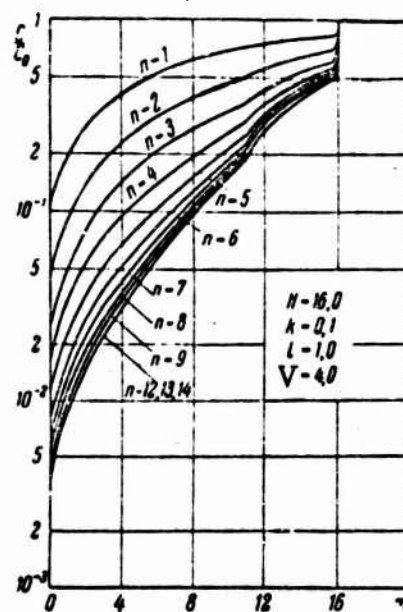

Figure 4

Impurity distribution (C) along the length of the
column (x) with different numbers of passes (n)
of the molten zone.

In the general case, the minimum distribution is established more rapidly, the smaller the height of the separator H, the longer the molten zone l, the longer the void V, and the smaller the distribution coefficient k. For example, the limiting distribution (H = 16, l = 1, V = 4, and k = 0.1) in the column is established after 12 passes, but if H is reduced to 8, the startup period reduces to 6 passes; if the length of the molten zone is increased to l = 2, the number of passes will be 9; and if the distribution coefficient is reduced to k = 0.01,

the startup period will comprise 7 passes; if the length of the void is reduced to V = 2, the startup period will comprise 20 passes.
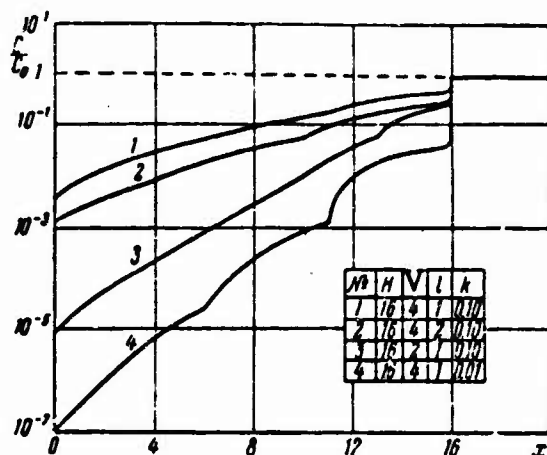

Figure 5

Typical lines of minimum impurity distribution
in the column for continuous zone refining.

The lines of minimum distribution (fig. 5) are more or less con-vex compared to those for a finite ingot and some of the curves have nearly straight sections. The curves clearly show the difference in the nature of impurity distribution between individual sections V + l long, into which the distribution curves are divided, beginning with the upper end of the separating part of the column (x = 16). The "waves" that form on the distribution curves are gradually damped with distance from the end of the separator, but at least the two first waves are well defined (in curves 1 and 4, the wave boundaries are at points x = 16, 11, and 6, V + l = 5; on curve 2, x = 16, 10, and 4, V + l = 6; on curve 3, x = 16, 13, and 10, V + l = 3). The waves on the distribution curves are explained by the characteristics of the continuous process. When the material moves down the column, beginning at x = H - (V + l) the zone is fed with starting material of concentration C_0, which substantially exceeds the impurity concentration in the lower part of the column. The first wave from the end of the column, the most clearly defined wave, forms directly in this manner. The second wave will be smaller in amplitude than the first, etc. Evidently, the amplitude is a function of the parameters of the process.

The magnitudes of the distribution coefficients k and the void length V have the strongest effect on the impurity distribution in the column. The abrupt change in the purification of material is illustrated graphically by the change in the slope of the lines of minimum distribution, since in first approximation they may be represented as emerging from a single point and may be replaced by equivalent straight lines. Thus, other conditions being equal, reduction of V by a factor of two increases the coefficient of purification of the column $(K = \log C_0/C)$ from K to 2K. A reduction of the distribution coefficient from 0.1 to 0.01 reduces the impurity content at the beginning of the column $(x = 0)$ from 3.6×10^{-3} to 1.0×10^{-7} (with $H = 16$, $l = 1$, $V = 4$). The effect of the length of the molten zone on the purification of the material is less pronounced. As fig. 5 shows, when the zone length was increased by a factor of two, additional purification was attained, not indicated by a change in slope, but by a shifting ("drop") of the entire distribution curve (curves 1 and 2).

The degree of purification may be increased sharply by reducing the void length V, but in this case, other conditions being equal, the column yield will decrease proportionately.

The ratio H/V, which determines the length of time the material remains in the column, is especially important for refining efficiency. When $V = 4$, a column $H = 16$ high has a coefficient of purification of 2.4. To double this coefficient, one must select a ratio H/V double the initial value, i.e., $H/V = 8$, whence $V = 2$. The impurity distribution found by the above numerical method confirms this calculation (curves 1 and 3 of fig. 5).

Comparison of the refining efficiency of the two processes. Other conditions being equal and with the same number of zone passes, the continuous zone method will produce purer material than the normal zone method, as is indicated by the calculations (see table).

The height of the column H is chosen equal to the length of the ingot. The figures for ordinary zone refining do not allow for the

effect of the impure end, thus the difference between the purity of the material in the two cases will actually be greater if this factor is taken into account. The data show that the continuous process yields more complete purification with the same number of passes than does normal zone refining, and this difference increases with an increase of ratio H/V. When n = 4, the impurity content of the material refined by the continuous method is half that of the material refined by the normal method, but when n = 16, the difference is a factor of 35.

Comparison of refining efficiency by the
continuous process and normal zone refining

Number of passes of molten zone	Average impurity content of material	
	Continuous	Normal [*]
4	$1.5 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$
8	$2.4 \cdot 10^{-6}$	$2.5 \cdot 10^{4}$
16	$6.0 \cdot 10^{-10}$	$2.0 \cdot 10^{-6}$

[*] The influence of the contaminated end is not con-
sidered. The impurity content is taken for the middle
of the ingot.

<u>Productivity of the process and yield of acceptable product.</u> If p heaters move simultaneously along the column at a speed v, the productivity W will be determined by the expression

$$W = \frac{vpS}{1 + H/V} \qquad (7)$$

W increases with increasing V; if V remains constant, W will increase with decreasing column length. Productivity cannot be increased by changing H and V simultaneously, if their ratio is kept constant. A comparison has shown that the continuous process is more productive than the normal process. However, if one considers that in normal zone refining part of the work time is lost on replacing the ingot, the ratio of these values will be still greater. The net yield of refined material η

$$\eta = \frac{1}{1 + l/V} \qquad (8)$$

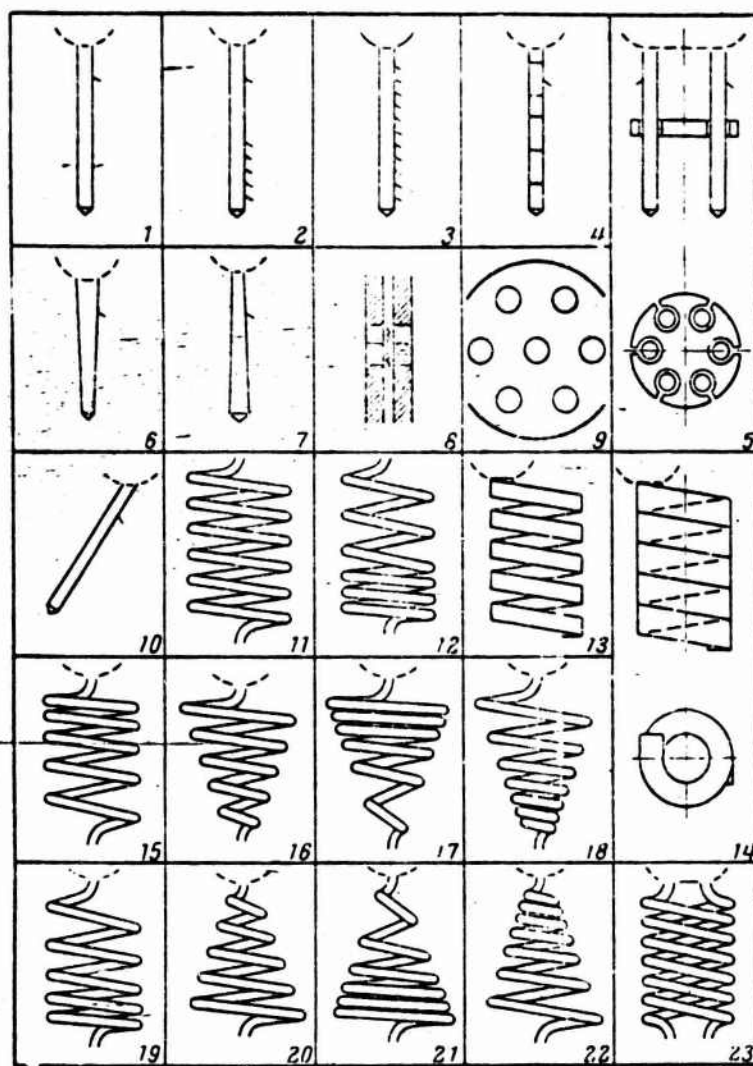is a function of the ratio l/V, which is analogous to the reflux ratio.

Figure 6

Some variants of the apparatus
for continuous zone melting.

On the basis of this analysis, one may recommend the following
system of calculating a continuous zone-refining column for the given
parameters (coefficient of purification K_2 and a reflux ratio l/V asso-
ciated with the yield of refined product):

1) Calculate the coefficient of purification K_1 of any column with
the required distribution coefficients k and zone length l numerically
or by selection from experimental data.

2) Determine the ratio H_2/V_2 from

$$\frac{H_2}{V_2} = \frac{H_1 \lg K_2}{V_1 \lg K_1}$$

(9)

3) Find the void size V_2 from the reflux number.

4) Find the height of the separator H_2 from the ratio H_2/V_2.

5) Determine the height of the receiver $(V_2 + l)$.

6) Select the number of heaters p on the basis of design.

7) Select the crystallization velocity v and the area cross section S from experimental data and determine the productivity of the column W.

Some variants of the zone-refining apparatus. Configuration of the apparatus. As analysis has shown, if one is to solve a specific problem of separation, one must select the optimum values of the main parameters of the process from a multitude of choices. These parameters are: the length of the molten zone l, the void length V, and the separator height H, the crystallization velocity v, and the size of the cross section of the column S.

Other conditions being equal, the coefficient of purification K is determined by the height of the separator H. In the simplest variant of the apparatus, a vertical column with two openings, one for removal of the refined product and the other for tapping the molten zone (fig. 6, 1), the possibilities for varying the parameters are limited: H = const, the values of $l + V$ = const (when $x \le H - l$) are determined by the size of the receiver, otherwise the operation of the column will be disrupted. However, this sum may not remain constant in the middle of the separator. If the heaters advance at a constant speed, the crystallization velocity will also be constant. If there are several openings at various heights along the column (fig. 6, 2 and 3), the possibilities of changing H, l, and V increase. A broader choice of effective parameters of the process (H, l, V) is also offered by a composite column (fig. 6, 4), assembled from a specific number of standard elements: a feeder, a receiver with a tubular drain, a separator, and outlet funnels.

The productivity can be increased considerably if the apparatus is designed as a vertical column of circular cross section and a group of columns is served by a single heater or by a series of rigidly connected heaters (fig. 6, 5). If the cross section of the column is not constant, the size of the molten zone will change, other conditions being equal (fig. 6, 6 and 7).

A better heater arrangement can be achieved in a vertical column with a coaxial channel (fig. 6, 8 and 9), in which case all the energy released by the heater is transmitted to the column. Special note should be made of the advantage of this variant over the circular vertical column with respect to area cross section.

The performance of the apparatus will not be disrupted if the column is tilted somewhat (fig. 6, 10). The extensive group of coil apparatuses (fig. 6, 11-23) is a development of this variant. These apparatuses are very compact. The one with a uniform cylindrical coil (fig. 6, 11) allows for great column height H, while the apparatus itself is small; H in this case corresponds to the coil line segment between the taps and outlet apertures. The spiral apparatus may have any cross-sectional coil shape: circular (fig. 6, 12), rectangular (fig. 6, 13), et al. The most compact variant has no gaps between the turns of the coil apparatus (fig. 6, 14).

The following relation

$$\tan a > \frac{d}{2l} \tag{10}$$

expresses the requirement for building the above apparatuses and any coil apparatus. Here a is the angle of inclination of a coil turn, d is the diameter or vertical dimension of the cross section, and l is the length of the molten zone. If condition (10) is fulfilled, the cross section of the coil will be completely occupied by the meniscus of the molten zone. In the cylindrical coil apparatuses, the molten zone moves at a constant speed (with a constant rate of advance of the heater). In contrast, the rate of movement of the molten zone is not constant in

helical apparatuses of other types, viz.: the cylindrical varying-
pitch coil apparatus (fig. 6, 12), those with a progressive variation
in pitch (fig. 6, 15, 19), those with conical spacing of the coils (fig.
6, 16, 20), those with a steadily increasing spacing of the coils (fig.
6, 18, 21), and those with a steadily decreasing spacing of the coils
in the direction of movement of the zone (fig. 6, 17, 22). The multi-
coil apparatus (fig. 6, 23) is one possibility for developing appara-
tuses of the coil type for continuous zone refining.

Heaters. The success of the separation process depends, to
a large extent, on the thermal distribution in the zone area, and in this
respect the heater design is decisive. One or several moving heat-
ers can be used to move a zone of specific length l and velocity v,
depending on the design and size of the column. In this case, the
values of l and v need not remain constant during the process, but
may change according to the solute distribution.

The use of various thermal agents to form the zone may be
demonstrated by the simplest ring heaters (or coolers), shown in
fig. 7, 1-7. A heater with an open electric coil (fig. 7, 1) has a
much less stable thermal distribution than a heater with a metal heat
regulator (fig. 7, 2). If the heating coil is located outside the col-
umn (fig. 7, 3), the regulation of the thermal regime will be even
better. Induction heating (fig. 7, 4) complicates the heat regulation
process. Heaters with liquid or gaseous heat conductors have con-
siderable advantages from this point of view (fig. 7, 5 and 6). The
basic types of heating indicated above may also be applied to heaters
other than the ring type. In what follows, we shall treat, basically,
electric heaters, but at appropriate points we shall also discuss
heaters of another type.

By proper choice of thermal agent and corresponding heater
design, one may apply a specific, appropriately stabilized heating
intensity to the zone, and the distribution of this intensity along the
heater length has a substantial effect on the thermal regime, and,

consequently, on the structure of the zone. For the simple, uniform arrangement of turns of the heater coil (fig. 7, 8), one may bunch coils opposite the upper part of the zone, at the leading edge of the molten zone (fig. 7, 9). Taking the zone structure into account, which requires application of energy to the leading edge and body of the molten zone, one may employ a heater with a more widely spaced middle part (fig. 7, 10) or a two-section heater (fig. 7, 11). For maximum versatility, one may employ a multi-section heater (fig. 7, 12), with which one may establish the required thermal distribution in zones with the most diverse parameters l and V.
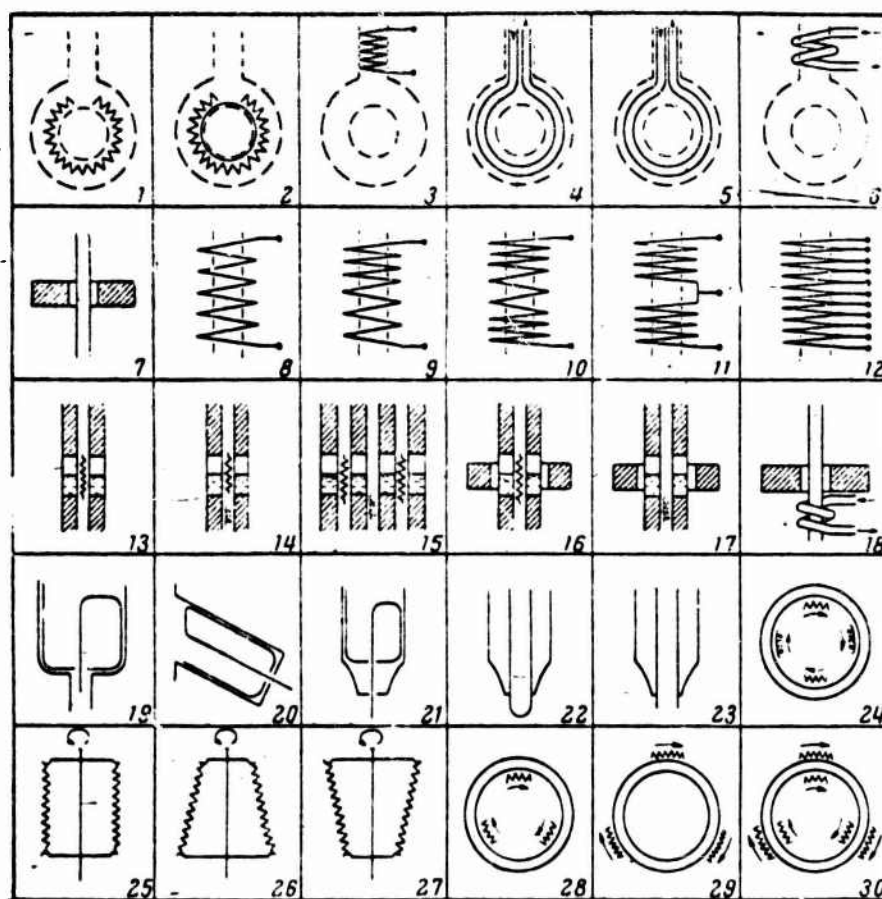

Figure 7

Sketches of thermal elements employed
in continuous zone-refining apparatuses.

Heaters (and also coolers) may be situated outside the zone (fig. 7, 1-7) or inside it (fig. 7 13-15), or both inside and outside (fig. 7,

16-17), depending on the type of heat exchange in the zone. The use of movable coolers in conjunction with heaters (fig. 7, 14, 15, 17, and 18), when individual heating units operate under various conditions and when several levels are required, helps establish the proper heat exchange and insure the required zone contours, primarily, a flat crystallization front.

In addition to these thermal elements, in some cases it is expedient to employ heat exchangers to alter the heat-exchange conditions within the column and also between the column and the ambient medium. These heat exchangers are cores situated inside the column. The heat conductivity of these cores differs somewhat from that of the material to be refined (fig. 7, 19-23).

The use of rotating heaters (fig. 7, 24-30) as coil apparatus offers broad possibilities for control of the process (varying l and v). In contrast to heaters that move back and forth, rotating heaters may move a zone at a variable speed while rotating at a constant speed, further they can vary the zone length, and move several zones simultaneously. Thus, when an apparatus having a uniform cylindrical coil (fig. 6, 11) and a rotating heater (fig. 7, 26) is used, the zone advances at a constant speed and the zone length is reduced in the direction of movement (with the heater inside, as in fig. 7, 28). When the heater is on the outside (fig. 7, 29), the zone length is increased. By combining the various types of spiral apparatuses (fig. 6, 11-23) with as few as three of the simplest types of rotating heaters (fig. 7 25-27), one may attain the most diverse operating regimes; e.g., the rate of advance of the zone can be increased with increasing zone length, the rate of movement can be increased with decreasing zone length, etc. It should be noted that the required thermal distribution may be attained by combining heater arrangements, and by using heaters and coolers (fig. 7, 25).

Separation during continuous zone refining. To study the characteristics of separation during continuous zone refining, we selected

a simple apparatus of the vertical type (fig. 6, 1 and fig. 7, 3) that allowed us to observe the process. We used naphthalene as our material, because of its low melting point (80.2°C), its transparency, and because it does not react with the transparent material of the column (molybdenum glass). We introduced small concentrations of impurities: alizarin, methyl red, and methylene blue (in doses of 0.2 to 0.5% by weight), which dyed the naphthalene intensively to allow better observation of the separation process.
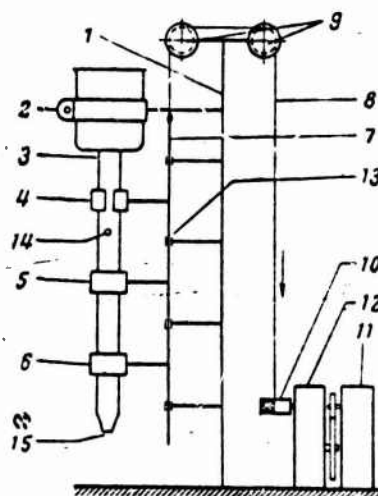

Figure 8

Diagram of continuous zone-refining apparatus:
1. support; 2. bracket; 3. column; 4-6. movable heaters; 7. support; 8. flexible cable; 9. blocks; 10. drum; 11. motor; 12. reduction gear box; 13. guide bearing; 14. hole for tapping molten zone; 15. outlet opening.

A sketch of the apparatus used in the continuous zone-refining experiments is shown in fig. 8. The separating column 3 is fastened to support 1 by bracket 2. The system of moving ring heaters 4-6 is rigidly fixed to support 7 and is moved on guide bearings 13 along the column by flexible cable 8. The cable moves along block 9 to drum 10, which is rotated at a certain speed by clock motor 11 through reduction gear box 12. The required number of heaters can be attached without changing the support because the heaters (4-6) are attached to support 7 by a bolted split coupling. The upper heater has a through slot along its axis to bypass tap 14. The rate of movement of support

7 is regulated by reduction gear box 12, which has the gear ratios 1:2, 1:8, 1:32, 1:128, and 1:512, by which speeds of 1.5, 6, 24, 96, and 192 mm/hr are attained at a constant motor speed of 6/7 rph. Support 7 returns to the lowest position under its own weight when drum 10 is released mechanically or by a magnetic clutch. When the magnetic clutch is used, the process can be completely automated: when the highest position is reached, a switch on the end of the support breaks the circuit of the electromagnet and releases drum 10. The cable 8 unwinds under the weight of support 7, which bears heaters 4-6, until the lowest position is reached, and again the end switch of the support breaks the circuit of the electromagnet.

Column 3 of the apparatus is made of transparent material (quartz or molybdenum glass 1.5 to 2 mm thick) that permits visual observation of the process and has an expanded part, a feeder (diameter 30 to 80 mm, height 50 to 100 mm). The entire lower part of the column consists of a receiver with a separator (diameter 10 to 15 mm, height 200 to 500 mm). The separator terminates in an opening for removal of the refined product. This opening is in the lower narrow part and allows the formation of a void in the column at the beginning of each passage of the molten zone.

The opening should be large enough so that the molten material can flow out unobstructed when heater 6 is opposite the opening and so that a solid "plug" of crystallized material can form rapidly and close the opening when it begins to cool [as the heater moves away]. The first requirement determines the surface tension of the molten material in contact with the wall of the opening. The optimum diameter employed with naphthalene is 7 to 9 mm; if the opening is smaller, the molten material cannot flow from the column spontaneously even though the molten zone is as much as 5 to 7 cm long. If the column is too wide in the outlet region, the solid plug will not form quickly enough because it will be too long and wide.

The molten zone is tapped through an inclined tube situated between the receiver and the separator and equipped with an electric

heater. The tube diameter is not critical for tapping the zone, because the void in the column promotes drainage which can take place with a tube diameter of 3 to 4 mm.

The distance from the tap hole to the feeder (height of the receiver) should be $V + l$; in which case the recever will not be filled with the molten material from the feeder until heater 4 has reciprocated and until the tap hole has been plugged with solid material.

The feeder replanishes the material in the column and maintains enough molten material to insure continuous operation of the column for a sufficient number of cycles (e.g., for 24 hours or more).

The thermal conditions of the column are regulated by laboratory autotransformers independently in each of five circuits: feeder, tap tube, and three moving resistance heaters (Nichrome, 0.7 mm).

The thermal distribution of the feeder was chosen such that the temperature of the molten material somewhat exceeded (by 3 to 5° C) the melting point of the starting material; thus, both solid and liquid material could be fed into the system.

The thermal distribution of the tap tube must satisfy two basic conditions: 1) During the period when the molten zone is being tapped, plugs of solid material must not form in the tube and cause blockage. 2) Once the zone has been tapped, the molten material arriving from the leading edge must crystallize immediately at the bottom of the void, closing the tap hole. In the simplest case, the system of moving heaters should insure uniform movement of the zones along the column with maximum stability of parameters V and l.

It should be noted that the zone stability increases with increasing l, since the molten zone acts as a heat damper: when the energy supplied to the zone is changed, the temperature of the melt changes,

weakening the effect of the change in heating intensity on crystalliza-
tion.

The effect of crystallization velocity on separation. The con-
figuration of the crystallization front. In the separation experiments,
it was found that the components did not separate in the column (length-
wise) at crystallization velocities $\geq$ 24 mm/hr, but at velocities $\leq$ 6
mm/hr, undyed transparent naphthalene was obtained throughout the
cross section of the column after one pass. Primarily, these were
single crystals which cracked with a characteristic sound shortly after
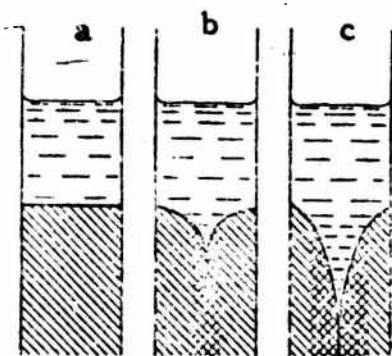crystallization, owing to thermal stresses.

Figure 9

Shape of the crystallization front for various rates
of movement of the molten zone: a. 6 mm/hr; b.
24 mm/hr; c. 96 mm/hr.

This difference in the behavior of the investigated systems is
closely related to the shape of the crystallization front: when v $\leq$ 6
mm/hr, the crystallization front is flat, without indentation, and
perpendicular to the axis of the column (fig. 9a). When v $\geq$ 24 mm/
hr, the front is shaped like a convex, conical funnel, which expands
upward before contact with the walls of the column (fig. 9b, c). A
column of opaque, contaminated material (a "channel") stretches
along the axis of the tube beneath the middle of the funnel, while
transparent colorless naphthalene crystals appear in the peripheral
regions at the walls of the column.

Thus, the naphthalene is not purified at v $\geq$ 24 mm/hr, because
of zone liquation that occurs in connection with the capture of con-
taminated melt by the walls of the highly convex crystallization front.

As the crystallization velocity increases, the peripheral region with the transparent naphthalene becomes smaller. The reason for the formation of a funnel-shaped crystallization front may be found by analyzing the heat-transfer conditions at the crystallization front. When the crystallization velocity is relatively small, the heat is transferred uniformly by the walls of the column and by the solid naphthalene; the isotherms are flat and conditions are favorable for equalizing the impurity concentration throughout the melt. When the crystallization velocity is increased, a substantial difference begins to appear in the heat conductivity values of the glass (1.4 to 1.8) and the naphthalene (~ 0.6 cal/cm sec deg), the heat of crystallization is transferred from the periphery sooner than from the middle of the cross section, the isotherms become convex with a downward trend, and a radial temperature gradient appears. The crystallization front becomes conical. In the extended part of this cone, conditions become unfavorable for equalizing the diffusion in the melt, whereby the melt becomes enriched with impurities, thus reducing the temperature of solidification. A comparatively long, narrow channel forms. It is filled with contaminated melt and includes the crystallization front. Evidently the difference in heat conductivities and the convexity of the funnel increase as the crystallization velocity increases.

Thus, naphthalene is not purified at high crystallization velocities, because of the distortion of the isotherms, which results in the funnel-shaped crystallization front and contamination of the axial channel. The maximum linear crystallization velocity (96 mm/hr) is not really the limiting rate for refining naphthalene, as indicated by the purified peripheral regions, and, apparently, this maximum could be realized by equalizing the isotherms in the region adjacent to the crystallization front.

Evidently the curving of the crystallization front, resulting from the difference in heat conduction of the material to be purified and the container, may produce the opposite result as well; if the heat conductivity of the material is higher than that of the container, the isotherms

at the crystallization front will be convex with an upward trend and the funnel of the front will be inverted, in which case the axial channel will be pure, while the material with impurities that lower the melting point of the main component will be situated on the periphery of the cross section and the radial temperature gradient will run in the opposite direction.

In analyzing the process, one must keep in mind the highly important role played by the cooling rate v_c as well as the described effect of the radial temperature gradient that affects the geometry of the crystallization front. To a considerable extent, the cooling rate determines the degree of phase balance and is proportional (in the case of a flat crystallization front) to the axial temperature gradient G_0 and the linear crystallization velocity v, which may be regarded as equal to the rate of advance of the heater, $v_c = vG_0$. Given identical values of the linear crystallization velocity, the degree of the phase balance may be improved by reducing the axial temperature gradient. Evidently, any variations of the heater speed (like temperature fluctuations) and, generally, of the linear crystallization velocity may have a harmful effect on crystallization, primarily on the cooling rate v_c.

This crystallization mechanism may be extended not only to the examined process of continuous zone refining, but to any case of crystallization in which there is a juxtaposition of melt, crystallized phase, and container; specifically, this mechanism is fully applicable to normal horizontal zone refining, although the change in shape of the crystallization front may differ substantially from that indicated above. In this case, the described mechanism is indicated by the radial concentration gradient and, if the separation conditions are chosen properly, the contaminated part of the material may be brought to a specific surface of the ingot, whence it may be removed comparatively easily.

Configuration of the leading edge of the molten zone. The shape of the leading edge, which is the upper limit of the void, is closely

associated with the described phenomena. During the first passage of the zone, the leading edge has a smooth surface that is convex downward (fig. 10, a). The isothermal surfaces are similar in shape to the leading edge, because the initial material is homogeneous and all points of the leading edge lie along the isotherm $T = T_1$, T_1 being the melting point of the starting material. During the second and subsequent passes of the zone, two situations are observed, depending on the regime of the preceding pass(es). If the preceding pass advanced at a rate $v \geq 24$ mm/hr, a crater corresponding to the impurity-enriched axial channel would form in the center of the leading edge (fig. 10, b). The peripheral regions of the leading edge, with the refined naphthalene, are situated on the isothermal surface $T = T_0$, T_0 being the melting point of the refined product.
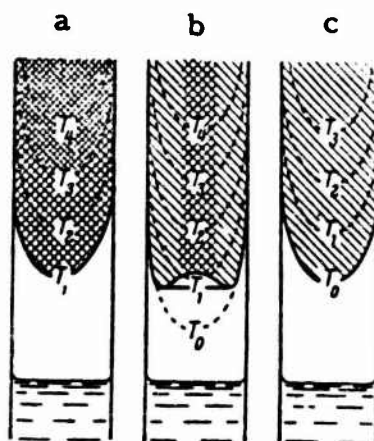

Figure 10

Shape of the leading edge of the molten zone for
various types of impurity distribution.

However, if the contaminated melt was not captured during the preceding pass ($v \leq 6$ mm/hr), the shape of the leading edge would coincide with the isothermal surface (fig. 10, c) and would be similar to the curve of the starting material (fig. 10, a), except that it would lie on the isotherm $T = T_0$, in which case $T_1 < T_0$. Thus, the shape of the leading edge is a criterion for determining the homogeneity of the material in the column.

Temperature distribution in the region of the zone. A thin copper-constantan thermocouple (diameter 30 μ) was used to investigate

the temperature distribution in the zone. To reduce the transfer of heat by the thermocouple material, the portion of the thermocouple next to the junction (about 2-cm long) was placed in an isothermal section. The thermocouple readings were recorded by an EPP-09 automatic potentiometer. The temperature distribution along the axis of the column is shown in fig. 11 ($v = 6$ mm/hr, $l = 15$ mm). The temperature reached 100°C at the surface of the melt, below which it decreased monotonically until the equilibrium temperature of crystallization (about 80°C with a gradient of 0.87°C/mm) was approached at the crystallization front.
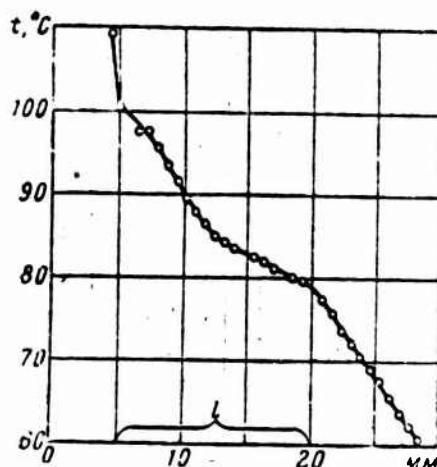

Figure 11

Temperature distribution along the column axis.

After the crystallization front has been crossed, the temperature variation can be described by a constant temperature gradient (2.05°C/mm). The temperature increases sharply in the void, beginning at the surface of the melt, reaching a maximum in the middle of the void (as much as 200°C) and then decreases abruptly to 80°C at the leading edge.

The experimental data show that the cooling rate near the crystallization front is $v_c = 5.2^{\circ}$C/hr, while it is 12.3°C/hr in the solid phase.

Mixing of the melt in the zone. The success of the zone-refining process depends, to a considerable extent, on the margin of

difference between the impurity concentration at the crystallization front and its average value in the zone. It should be noted that the axial concentration gradient becomes maximum at the crystallization front. Therefore, the problem of reducing the concentration gradient may be decisive for the separation process in some cases.

During continuous zone refining, two factors induce appreciable mixing of the melt: the kinetic energy of the drops of melt falling from the leading edge, and the high density of these drops. These drops, falling from the leading edge, quickly pass through the void, acquiring a velocity of $v_k = \sqrt{2gV}$ (of the order of 1 m/sec when $V = 4$ cm). When the drop strikes the surface of the melt, its meniscus quickly deforms, causing a clearly detectable movement of the melt, after which the falling drop loses a considerable part of its kinetic energy. Having broken the surface film, the drop, which still has a temperature of about $80^{\circ}C$, falls to the bottom of the zone (reaching the crystallization front), because of the kinetic energy it still retains and because it is denser than the heated upper layers of the molten zone. Consequently, the layer of melt next to the crystallization front is continually replenished, first, by mixing of the entire melt by the falling drops and, second, by the direct arrival of drops of fresh material which force impurity-enriched material out from the crystallization front.

The mixing process may be intensified by turning the column slightly (5 to 15°) and stopping it abruptly at the end points of the arc. Two rigidly fixed stops are used for this purpose. At the instant the column stops, the inertial forces overcome the adhesion of the layers of melt next to the crystallization front, tearing them from the front. Furthermore, the adhesion of the melt to the walls of the column also facilitates mixing of the melt.

One more characteristic of the continuous zone-refining process should be noted, where the crystallization front (at its appropriate velocity) is horizontal. In this case, there will be no concentration gradient along the crystallization front and the crystallizing

material will be uniform throughout the cross section even if the densities of the components differ considerably, i.e., even if the axial gradient of concentrations is large (fig. 12, a). In this case, the separation effect will be greater if the main component is heavier than the others (e.g., lead with impurities of light elements). However, when the crystallization front is vertical in normal (horizontal) zone refining, a vertical concentration gradient corresponds fully to a concentration gradient along the crystallization front and can lead to a substantial difference between the upper and lower parts of the ingot (fig. 12, b) and to a considerable inclination of the crystallization front, which increases the difference even more.
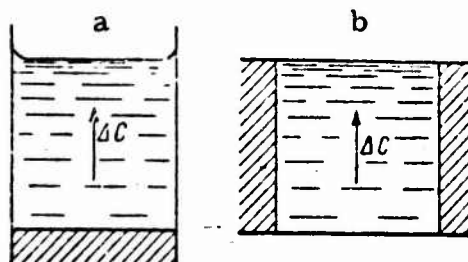

Figure 12

Relative position of the vertical concentration gradient:
a. continuous zone-refining process; b. horizontal
position of the boat during normal zone refining.

Deformation of the zone. Changes in external conditions cannot be completely neglected in any real process, i.e., such changes may affect the zone. Consequently, the stability of the zonal elements during a change in external conditions must be determined. For this purpose, we varied the applied heating intensity considerably.

The following were studied with this in mind: zone length, void length, and the position of the interface with respect to a heater moving at a constant speed. These remain constant when the conditions are stable. The experimental results showed that when the thermal distribution of the heaters was varied, the position of the crystallization front with respect to the heater remained practically constant. The zone length changed only when its meniscus rose or fell with respect to the heater moving at a constant speed. The leading edge moved

identically with the mensicus of the melt, and the void length remained practically constant.

Thus, when the external conditions were varied, the crystallization front remained comparatively stable and, in this respect, the conditions of crystallization probably changed comparatively little. On the other other hand, the volume of the molten zone responded fully to these changes, striving to weaken the external effect, as it were: when the heating intensity was increased, the molten zone expended the extra energy on increasing in size, when the heating intensity was reduced, it compensated the lack of heat by crystallizing to a considerable extent. This is a very important safety factor for the molten zone with respect to the crystallization front; consequently, a change in external conditions had comparatively little effect on the crystallization process. However, in this case the volume of the molten zone had to change. For example, a reduction of the zone volume increased the impurity content in the zone itself and in the crystallizing material.

With the arrangement described, one can insure reliable operating conditions and complete absence of cracks in the glass columns during the entire working period. Thus, it can be used for experiments in separating and refining metal systems.

Possible applications of the continuous zone-refining process. Continuous zone refining may be regarded as a process of continuous separation and purification of components and offers considerable advantages with regard to refining efficiency and productivity. The process is quite suitable for complete automation and may find future application in industry, particularly production-line application.

The degree of refinement, determined by the ratio H/V, as is the productivity of the system, may be varied within extremely broad limits, whereby the material may be refined with distribution coefficients approaching unity.

A specific feature of the method of continuous zone refining is the removal of impurities having a distribution coefficient k < 1. This

is not a serious limitation of the process, because it is not very likely that impurities with k > 1 will be present in the material to be refined and because the addition of the so-called "third components" to the feed may change the distribution coefficients of the impurities considerably, and an impurity that is difficult to remove may be transformed into one that is easy to remove.

A cascade of continuous zone-refining apparatuses might also be developed for various operations. In particular, a cascade for complete separation of a binary system may be based on a reciprocating operation, whereby partially-refined material, the refinate from the i-th column enters the feeder of the (i - 1)-th column, while the extract enters the feeder of the (i + 1)-th column; the material is removed from the end columns.

When multi-component systems are separated (main component with several impurities having distribution coefficients k < 1 and k > 1), partial separation of the impurities (a refinate with impurities k > 1 and extract enriched by impurities with k < 1) occurs when the material passes through the first column of the cascade. In this case, both the refinate and the extract may be sent into the subsequent columns of the cascade.

The continuous zone-refining method also opens broad possibilities for physicochemical investigations. In particular, this method may be used for studying the interaction of components by determining the distribution coefficients and by investigating the phase composition and sequence of phase changes during the crystallization of binary and more complex systems.

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