

DROP BREAKUP DURING MECHANICAL STIRRING IN ABSENCE OF COALESCENCE

L. N. Braginskii and M. A. Belevitskaya

UDC 532.517.4:66.063.8

This paper proposes a mathematical model for the kinetics of drop dispersion during mechanical stirring under turbulent conditions in the absence of coalescence. Expressions are obtained for the local energy and the time required for drop breakup to a specified diameter. The calculated drop diameters are compared with experimental figures.

Formation of a liquid-liquid dispersion in equipment fitted with stirrers under turbulent conditions is a traditional area of research on stirring. The fundamental results of numerous studies in this area are generalized in [1-5]. The basis for theoretical interpretation of experimental results is generally the breakup model proposed by Kolmogorov [6, 7], which is based on the assumption that the condition for stability of a drop of radius r in a turbulent stream is equality of the capillary pressure within the drop and the fluctuation pressure corresponding to the mean square fluctuation velocity of scale r . For a stream with energy dissipation ϵ_0 in the scale region corresponding to the conditions under which the "two-thirds" rule is applicable, this model leads [6] to the following expression for the diameter of the largest stable drops:

$$d_m \sim (\sigma/\rho)^{0.6} \epsilon_0^{-0.4} \quad (1)$$

with a proportionality factor of the order of 2 [8].

The authors of [9-11] assumed that there is a direct proportionality between d_m and the mean surface bulk drop diameter, and it was suggested [10] that the energy dissipation ϵ_0 be determined as

$$\epsilon_{av} = N/(\rho V_{ap}) \quad (2)$$

However, the results of a number of experimental studies have shown that mean drop size is far less (usually by an order of magnitude) than that predicted by Eqs. (1) and (2) even in the absence of surfactants, i.e., in instances where coalescence occurs [1, 12], and that it is smaller by factors of 100 or more when emulsification takes place in the absence of coalescence. This discrepancy is scarcely reduced at all if one utilizes the sharpened equation given in [13], in whose derivation the fluctuation pressure acting to deform a drop is assumed to correspond to three times the mean square fluctuation velocity. Measurement results have also shown that there is a one-to-one correspondence between mean drop diameter and average energy dissipation in the apparatus only when geometric similarity is preserved, with a change in the ratio D/d_p or the type of stirrer leading to significant deviations from relations (1) and (2) [4, 14]. Moreover, experimental data on drop breakup in the absence of coalescence [2] indicate that the duration of the breakup process has a significant influence, which is not reflected in (1).

Analysis of experimental data and the information in [15-17] indicating an inhomogeneous energy dissipation distribution in stirrer-equipped units provided the basis for the hypothesis [8, 5] that drop breakup takes place only in the zone of high local dissipation levels rather than throughout the entire apparatus volume. However, this hypothesis has not as yet been verified experimentally; the literature accessible to us gives no interpretation of experimental data on the change in drop size with time.

The present investigation was therefore undertaken as an attempt to utilize the results obtained in fluid dynamic studies in equipment fitted with stirrers and baffles as a basis for examination and quantitative estimation of the influence of stirrer and apparatus design and size on drop-dispersion kinetics under turbulent conditions in the absence of coalescence.

LenNIKhimmash Leningrad Scientific-Commercial Association. Translated from *Teoreticheskie Osnovy Khimicheskoi Tekhnologii*, Vol. 24, No. 4, pp. 509-516, July-August, 1990. Original article submitted December 27, 1988.

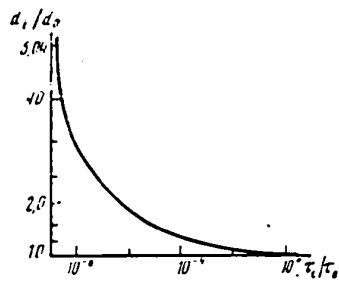


Fig. 1

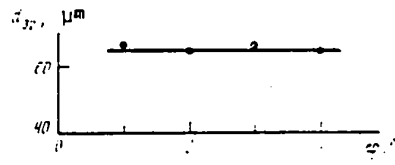


Fig. 2

Fig. 1. Calculated dependence of diameter on breakup time.

Fig. 2. Dependence of drop size on dispersed phase concentration with $\tau = 3600$ sec.

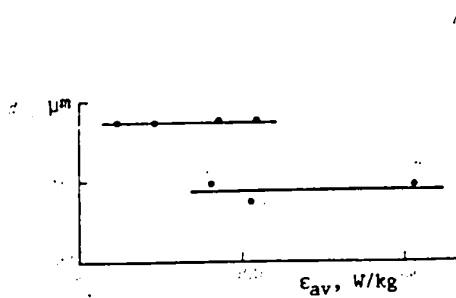


Fig. 3

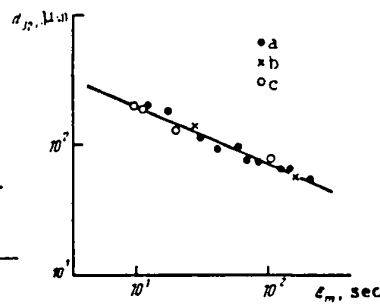


Fig. 4

Fig. 3. Dependence of drop size on specific power with $\tau = 3600$ sec.

Fig. 4. Dependence of drop size on local specific power determined from (9) with $\tau = 3600$ sec. a) $D/d_s = 3.0$, open impeller stirrer; b) 2.27, two-blade stirrer; c) $D/d_s = 1.7$, open impeller stirrer; line represents calculation.

Number of drop	d_s , mm	h/d_s	V_{ap}/dm^3	n , rpm	ϵ_m , W/kg	ϵ_{av} , W/kg
1	100	0,2	16	150	30,3	0,06
2			8		25,7	0,12
3			4,5		21,9	0,213
4		0,4	16	200	30,4	0,27
5		0,3	16		53,7	0,20
6		0,2	8		60,9	0,27
7		0,4	16	250	59,4	0,53

Proceeding from the results obtained in filming drop breakup [18], we will assume that a spherical drop of diameter d_0 assumes the form of an elongated ellipsoid under the action of a turbulent pressure fluctuation and is then transformed into a "dumbbell" shape, subsequently dividing into two equal-sized drops of diameter

$$d \approx d_0 / (2)^{1/2}.$$

The approximate equality sign is used here because a certain number of small drops having a diameter of the order of $(0.1-0.2)d_0$ is also formed as the "dumbbell" cross-piece disintegrates. Since the minimum ellipsoid radius of curvature cannot be greater than the radius of the two drops formed, the fluctuation pressure should satisfy the condition

$$P_d' = \rho \frac{v_d^n}{2} \geq 4 \cdot (2)^{1/2} \frac{\sigma}{d_0}.$$

Hence the minimum fluctuation velocity necessary for drop breakup is:

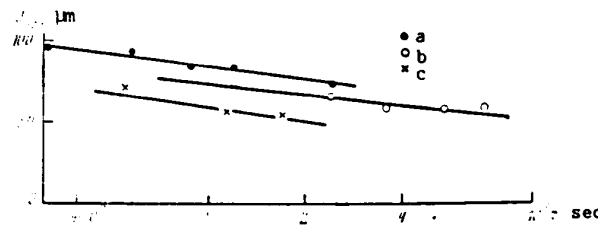


Fig. 5. Change in drop size with time. a, b) Open impeller stirrer, $d_s = 100$ mm, $h_b = 20$ mm; a) $n = 250$ rpm; b) 300 rpm; c) two-blade stirrer, $d_s = 180$ mm, $h_b = 18$ mm, $n = 200$ rpm; line represents calculation.

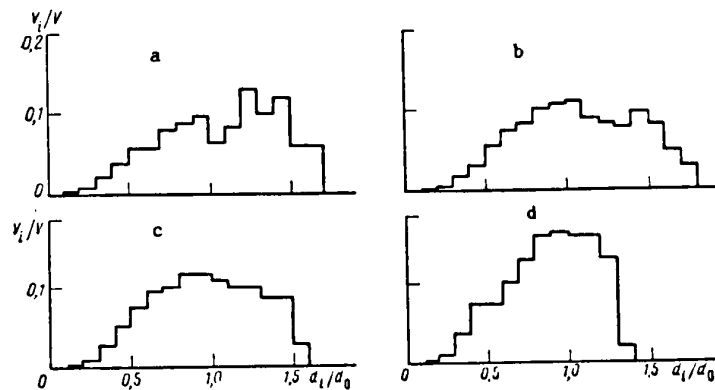


Fig. 6. Change in drop size distribution function with time; open impeller stirrer, $d_s = 100$ mm, $h_b = 20$ mm, $n = 250$ rpm, $V_{ap} = 4.5$ dm³. a) $t = 300$ sec; b) 600 sec; c) 900 sec; d) 2400 sec; value of d_0 determined by computation.

$$v_d' = \left(\frac{8 \cdot (2)^{1/2} \sigma / \rho}{d_0} \right)^{1/2} \approx \left(\frac{10 \sigma / \rho}{d_0} \right)^{1/2} \quad (3)$$

In making such an estimate, the fluctuation scale λ should evidently be assumed to equal the length of the ellipsoid's longitudinal axis. Since the analysis is approximate, we will simplify the problem by replacing the ellipsoid with a cylinder having two hemispheres at its two ends. If we assume the volume of this body of revolution to equal that of the original drop:

$$\frac{\pi d_0^3}{6} = \frac{\pi d_c^2 (L - d_c)}{4} + \frac{\pi d_c^3}{6},$$

where d_c is the cylinder diameter (m) and L is the total length of the body of revolution (m), and take into account the fact that its surface area cannot be less than the total surface area of the two drops formed on its disintegration:

$$2\pi d^2 \leq \pi d_c (L - d_c) + \pi d_c^2,$$

and appropriate transformation gives us the greatest linear dimension:

$$L = \lambda_m = 2.17 d_0. \quad (4)$$

Thus, a drop of diameter d_0 can be broken down when it is acted upon by velocity fluctuations of scale $2.17 d_0$ and amplitude no less than the b_d' determined from (3).

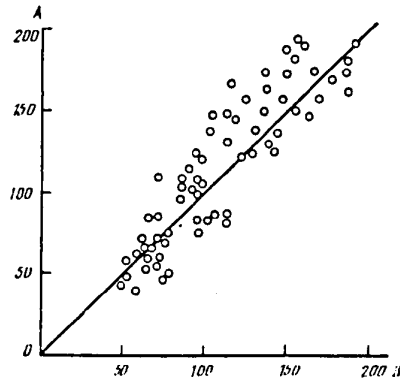


Fig. 7. Comparison of experimental and calculated drop diameters. A) Drop diameters calculated from (5)-(10), μm ; B) experimental Sauter mean drop diameter, μm .

According to [19], the instantaneous fluctuation velocities of scale λ can be assumed to have a normal distribution. Hence the proportional fluctuations responsible for breakup of a drop of diameter d_0 is:

$$P(U) = 1 - \frac{2}{\sqrt{\pi}} \int_0^U \exp\left(-\frac{U^2}{2}\right) dU,$$

where $U = v_d' / \bar{v}_\lambda'$, with \bar{v}_λ' being the mean square fluctuation velocity of scale $\lambda = 2.17 d_0$ (m/sec).
When we express \bar{v}_λ' as

$$\bar{v}_\lambda' \approx \epsilon_m^{1/4} \lambda^{1/4}$$

in conformity with the Kolmogorov-Obukhov "two-thirds" rule and take (3) and (4) into account, we obtain

$$U_0 = \frac{2.45}{\epsilon_m^{1/4} d_0^{3/4}} \sqrt{\nu \sigma / \rho}, \quad (5)$$

where ϵ_m is the energy-dissipation in the breakup zone (W/kg). In accordance with the "two-thirds" rule, the frequency of fluctuations of scale $2.17 d_0$ is

$$\nu \approx \epsilon_m^{1/4} / (2.17 d_0)^{3/4} \approx 0.6 \epsilon_m^{1/4} / d_0^{3/4}, \quad (6)$$

whence the mean frequency of fluctuations of scale $2.17 d_0$ with amplitude $v' \geq v_d'$ is

$$\nu_0 \approx 0.6 \epsilon_m^{1/4} P(U_0) / d_0^{3/4}, \quad (7)$$

and the mean time for which a drop of diameter d_0 must reside in the zone with dissipation ϵ_m in order for it to be broken up is:

$$\theta_{br} = \nu_0^{-1} = d_0^{3/4} / [0.6 \epsilon_m^{1/4} P(U_0)]. \quad (8)$$

Equations (5) and (6) characterize the dependence of drop diameter on energy dissipation and time. It can easily be seen that, when $\tau_{br} = \text{const}$, they lead to an expression wholly analogous to (1), the only difference being the fact that the coefficient of the equation is a function of time.

When utilizing the equations obtained above for computations, one estimates the greatest local energy dissipation levels that can be realized in a stirrer-equipped unit.

Analysis at the most general level and the results of numerous experimental studies of turbulent flow past bodies [20, 21] lead to the assumption that the energy dissipation maximum is localized in the breakup formation zones near the ends of the stirrer blades, i.e., in the region where the velocity difference between the blades and medium is greatest. If we assume the scale of the vortices formed beyond the blade to be close to the maximum linear blade

dimension and the flow speed to be close to the difference between the circumferential blade speed and medium velocity at radius r_0 , we obtain

$$\epsilon_m \approx \frac{2(\omega_0 r_0 - v_0)^2}{l_b} = \frac{2\omega_0^2 r_0^2}{l_b} (1 - \bar{v}_0)^2. \quad (9)$$

The volume of the zone with energy dissipation ϵ_m for a stirrer having Z_b blades is:

$$V_m \approx 2Z_b (1/2 h_b)^2 l_b = 0.25 Z_b h_b^2 l_b \quad (10)$$

The quantity v_0 is the circumferential liquid velocity at the blade edge radius r_0 from (9) and does not require experimental determination for equipment of standard design; it is calculated from the equations in [8], proceeding from data on the nominal dimensions of the apparatus, stirrer, and internal systems and the properties of the medium.

As follows from the results of a circulation study [13], the frequency distribution for passage of volume elements through a stirrer in a baffle-equipped unit at $Re_c > 1000$ corresponds to the simplest fluctuation distribution. With a stirring time τ , the average emulsion residence time in region V_m under these conditions is

$$\tau_m = \tau \frac{V_m}{V_{ap}} \approx 0.25 Z_b \frac{h_b^2}{V_{ap}} \tau. \quad (11)$$

If we assume τ_m to equal θ_{br} , Eqs. (8) and (9) give us r_0 , i.e., the stirring time corresponding to the average time required for breakup of a drop of diameter d_0 :

$$\tau_0 \approx 6.7 \frac{d_0^{3/2} V_{ap}}{\epsilon_m^{1/2} P(U_0) h_b^2 Z_b}. \quad (12)$$

When we consider drop dispersion to be a sequence of divisions of a drop having some initial size d_i at the start of stirring ($\tau = 0$) to diameter d_0 , the required stirring time must be found as the sum of the τ_i determined from (8) and (12) for each successive division. However, computations show that, with actual values for the energy dissipation and mean drop diameter, the breakup time for drop d_i is roughly 5-10 times that for the drop d_{i-1} from which it was formed (Fig. 1). The total emulsification time can therefore be estimated with sufficient accuracy from the time of the last breakup, which is determined from (12).

The mean emulsion residence time in the dispersion zone τ_m , determined from (11), is realized as a result of a certain number of passes of the stirred medium through the stirrer during circulation. By (11), the average number of circulation cycles through the zone with dissipation ϵ_m is

$$Z_0 = \tau_0 \frac{q}{V_{ap}} \frac{V_m}{V_{ap}} = \tau_m \frac{q}{V_{ap}}, \quad (13)$$

where q is the circulation flow rate (m^3/sec).

Since the pass frequency distribution follows the very simple Poisson rule, the proportion of the emulsion that goes through no less than Z_0 cycles over time τ_0 and is in the dispersion zone for a time τ_m or more amounts to

$$\bar{V} = 1 - e^{-1} = 0.637.$$

The development of velocity fluctuations $\bar{v}' > v$ can also be regarded as a very simple steady random flow of events with an average frequency ν_0 , whereupon the probability that a particular drop will break up after Z_0 cycles is

$$P_0 = 1 - e^{-1}.$$

Since some proportion of the drops breaks up over a time shorter than τ_0 , the proportion of drops with a diameter less than d_0 after a stirring time that equals the mean breakup time for drops of this diameter should be more than $\eta = (1 - e^{-1})^2 \approx 0.4$. The value of d_0 should therefore be close to the mean surface bulk drop diameter d_{s2} .

Our approximate analysis thus leads to equations that, in combination with the fluid-dynamic equations in [8], relate the degree of dispersion of an emulsion formed in the absence of coalescence to apparatus and stirrer characteristics and to stirring time.

We verified the above results by measuring drop sizes in units with diameters of 0.17 and 0.29 m equipped with six-blade, open impeller, and two-blade stirrers. Stirrer diameter was 100-180 mm, blade height was 18-40 mm, and

ratio of blade width to stirrer diameter was 0.1-0.4. Stirrer speed ranged from 125 to 800 rpm. The equipment was fitted with four baffles having a width equivalent to 0.1 times the apparatus diameter. Liquid volume was 4.5 dm³ in the apparatus with a diameter of 0.17 m and 8 and 16 dm³ in the apparatus with a diameter of 0.29 m.

The experiments were conducted with an emulsion consisting of a mixture of kerosene and carbon tetrachloride in tap water. The dispersed phase viscosity at the experimental temperature (18-25°C) was ~2.5 mPa/sec, and its density was ~1050 kg/m³. In order to preclude the influence of coalescence on drop size, the experiments were conducted in the presence of SEK emulsifier. The interface surface tension was 0.01 N/m. The drop sizes were measured by counting samples with an MBS-9 microscope fitted with an MFN-5 photoadapter. That coalescence had no effect was confirmed by a special series of experiments conducted under identical conditions with emulsion concentrations of 1-4 vol.% (Fig. 2). Most of the experiments were performed with a dispersed phase concentration of 2 vol.%.

One of the basic objectives of these experiments was to test our original assumptions regarding the influence of the energy distribution in the apparatus and the stirring time on degree of emulsion dispersion. Figure 3 shows the results of experiments conducted to check the influence of the average energy dissipation ϵ_{av} (specific power) with slightly different values of ϵ_m . Figure 4 shows d_{32} as a function of the maximum dissipation ϵ_m calculated from (9) with constant specific power. It follows from these experimental data that drop breakup actually takes place mainly in the zones with maximum dissipation rather than throughout the unit. These graphs can also be regarded as confirming that Eq. (9) can be employed to estimate the maximum local energy dissipation levels.

We conducted a series of experiments lasting up to 2.5 h in order to study the manner in which drop size depended on stirring time. Our results showed (Fig. 5) that drop size decreased with time, but the character of the relationship was nearly logarithmic, which was in good agreement with [2]. However, average drop diameter proved to be considerably greater (by a factor of 2-3) than the calculated figure during the initial period, when the average number of emulsion passes through the dispersion zone was small [see (13)]. Analysis of the drop size distribution histograms showed this discrepancy to be due to the fact that there were more large drops, which produced a second maximum in the distribution curve (Fig. 6). One possible explanation might be that, when Z_0 was small, a considerable proportion of the drops did not have time to break up in zone ϵ_m , so that their size was determined by the dispersion conditions in areas with lower energy dissipation levels. As follows from the graphs given here, the proportion of such drops decreased as the number of cycles increased, and the second maximum disappeared*.

It follows from analysis of the histograms that, with sufficiently long stirring times (10-20 min or more), the average proportion of the dispersed phase in drops having a diameter smaller than $d_0 = 0.5$, i.e., conforms to the theoretical estimate made above.

The experimental validation results thus enable us to conclude that, over the range investigated, Eqs. (5)-(10) describe drop breakup with an adequate degree of approximation and reflect the dependence of degree of emulsion dispersion on the design features of stirrer-equipped units and on stirring time. The results obtained in comparing the calculated values of d_0 with the experimental Sauter mean drop diameter (Fig. 7) can also be considered satisfactory.

LITERATURE CITED

1. R. T. Treybal, *Mass Transfer Operations*, 3rd Edition, McGraw, 1979.
2. M. Stamatoudis and L. L. Tavlarides, "The effect of continuous phase viscosity on the unsteady state behavior of liquid-liquid agitated dispersions," *Chem. Engng. J.*, **35**, 137 (1987).
3. J. J. Oldshue, D. O. Mechler, and D. W. Grinnell, "Fluid mixing variables in suspension and emulsion polymerization," *AIChE Journal*, **2**, 68 (1982).
4. R. R. Rounsley, "Oil dispersion with a turbine mixer," *Ibid.*, **29**, No. 4, 597 (1983).
5. B. Platzer and G. Noll, *Chem. Techn.*, No. 8, 430 (1981).
6. A. N. Kolmogorov, "Drop breakup in a turbulent flow," *Dokl. Akad. Nauk SSSR*, **66**, No. 5, 825 (1949).
7. M. K. Baranaev, E. N. Teverovskii, and É. L. Tregubova, "Minimum fluctuation size in a turbulent flow," *Ibid.*, **66**, No. 5, 821 (1949).
8. L. N. Braginskii, V. M. Barabash, and V. I. Begachev, *Stirring in Liquid Media* [in Russian], Khimiya, Leningrad (1984).
9. G. P. Piperskikh and E. R. Valashek, "Extraction in turbulent flows," *Khim. Prom.*, No. 1, 35 (1956).
10. J. M. Church and R. Shinnar, "Stabilizing liquid-liquid dispersions by agitation," *Ind. Engng. Chem.*, **53**, No. 6, 479 (1961).

*Appearance of a second maximum in the drop size distribution curves in stirrer-equipped units was reported in [2, 22].

11. P. H. Calderbank, "Physical rate processes in industrial fermentation. Pt. 1: The interfacial area in gas-liquid contacting with mechanical agitation," *Trans. Inst. Chem. Engrs.*, **36**, 443 (1958).
12. L. N. Braginskii and V. I. Begachev, "Retention capacity of throughflow stirring equipment for liquid-liquid systems," *Teor. Osn. Khim. Tekhnol.*, **3**, No. 1, 103 (1969).
13. I. O. Protod'yakonov and S. V. Ul'yanov, *Fluid Dynamics and Mass Transfer in Dispersed Liquid-Liquid Systems* [in Russian], Nauka, Moscow (1986).
14. Yu. N. Kobalev, S. Z. Kagan, and M. I. Molochkova, "Phase interface during stirring of immiscible liquids," in: *Second All-Union Conference on Theory and Practice of Agitation in Liquid Media* [in Russian], Cherkassy (1973), p. 185.
15. L. A. Cutter, "Flow and turbulence in a stirred tank," *AIChE Journal*, **12**, No. 1, 35 (1966).
16. A. A. Günkel and M. E. Weber, *Chem. Techn.*, **21**, No. 5, 931 (1969).
17. F. Liepe, H.-O. Möckel, and H. Winkler, *Ibid.*, **23**, No. 415, 231 (1971).
18. S. Noro, "Studies on liquid-liquid dispersion by mechanical agitation," *Progr. Organic Coatings*, **6**, 271 (1978).
19. I. O. Khintse, *Turbulence* [in Russian], Fizmatgiz, Moscow (1963).
20. J. E. A. Komasaawa, "Fluid and particle motion in turbulent dispersion. I. Measurement of turbulence of liquid by continual pursuit of tracer particle motion," *Chem. Engng. Sci.*, **29**, No. 3, 641 (1974).
21. B. Platzer and G. Nool, *Maschinenbautechnik*, **36**, No. 5, 221 (1984).

MATHEMATICAL MODEL OF PRODUCTION OF DEFLUORINATED PHOSPHATES

V. I. Bodrov, Yu. Yu. Gromov, and V. G. Matveikin

UDC 62.501.72

This paper gives a mathematical description of dynamic operating regimes for a rotary drum kiln used in producing defluorinated phosphates.

Defluorinated phosphates are produced for use in feed additives and are finding increasingly broad application in the economy.

Defluorination is carried out in a rotary kiln, of the type shown diagrammatically in Fig. 1, through contact between the stack gases formed as a fuel oil spray burns and the initial feedstock (charge). The process takes place at high temperature, and some variable states are not observable in Kalman's sense [1]. It is consequently very difficult to conduct active experimental studies on nonoperating systems, and it is best to employ mathematical modeling methods to describe the process.

A multifaceted systems-analysis approach was taken in devising a mathematical process model [2]. The proposed model was built up from individual modules describing elementary events of the process under consideration; Figure 2 is a diagram of their interaction.

The kinetic model cannot be described at the traditional deterministic level, since there is no standard interpretation of the mechanism underlying the chemical transformations [3] and the kinetic constants and coefficients cannot be determined. It is therefore suggested that final product quality be assessed on the basis of a logical-semantic model that generalizes qualitative and quantitative information.

We will consider each module of the mathematical model. Heat removal processes are segregated in a separate module and are formalized by utilizing boundary conditions of the fourth kind, a consequence of the fact that the local heat removal coefficients cannot be determined experimentally. One therefore cannot use Newton's law to describe the heat removal process [4, 5]. Attempts at iterative refinement of these coefficients result in considerable expenditure of computer time, so that iterative studies are not practicable.

We will consider heat removal at the wall of the roasting kiln. In design terms, the apparatus wall consists of three layers: the luting, lining, and steel shell. However, because the luting gradually ages during furnace operation and

Tambov Institute of Chemical Machine Building. Translated from *Teoreticheskie Osnovy Khimicheskoi Tekhnologii*, Vol. 24, No. 4, pp. 517-522, July-August, 1990. Original article submitted December 5, 1988.

DokumentenlieferungTel. +41 44 632 21 52
Fax +41 44 632 10 87
docdel@library.ethz.ch**Kundeninformation / Customer information**Sehr geehrte Kundin, sehr geehrter Kunde
Dear Customer**Qualitätseinbusse / Loss of quality**Die Qualität des Scans kann im besten Fall nur so gut wie die Originalvorlage sein.
The quality of the scan can only be as good as the original itself.Das Dokument weist leider folgenden Mangel auf:
The document has the following insufficiency:

- | | |
|---|--|
| <input type="checkbox"/> Papier vergilbt/ dünn (störende Punkte)
Paper yellowed/ thin (Visual noise) | <input type="checkbox"/> Dokument sehr eng gebunden
Binding of document very tight |
| <input type="checkbox"/> Schrift/ Tabellen sehr klein (verfließt)
Font size/ chart too small | <input checked="" type="checkbox"/> Mässige Bildwiedergabe (Textscanner)
Insufficient picture quality |
| <input type="checkbox"/> | |

Auftragsannullierung / Cancellation

-
- 1 Auftrag – mehrere Artikel (pro Auftrag wird nur ein Artikel erledigt)
-
- 1 order – more than one article (only one article per order is being processed)

Bitte folgende Seiten neu bestellen
Please reorder the following pages: _____**Fehlende Seiten / Missing pages**

-
- Im Artikel ist ganzseitige Werbung enthalten. Wurde nicht kopiert und mitgeliefert.
-
- This paper contains full-page advertisement which has not been scanned.

Vielen Dank für Ihr Verständnis / Thank you for your understanding.

Bei Rückfragen wenden Sie sich bitte an das Team Dokumentenlieferung.
If you have any questions please contact the team Document Delivery.Mit freundlichen Grüßen / Sincerely
ETH-Bibliothek