P = gas permeation constant defined in Equation (1) $\dfrac{\text{cm}^3\text{ (STP) cm}}{\text{s cm}^2\text{ cm Hg}}$
m = mass of the molecule
σ = collision diameter, cm
ϵ = energy parameter, erg
M = molecular weight, g/g-mole
T = temperature, °K
T_c = critical temperature, °K
T_g = glass transition temperature, °K
V_c = critical volume, cm^3/g-mole

LITERATURE CITED

Boyer, R. F., "$\Delta C_p T_g$ and Related Quantities for High Polymers," *J. Macromol. Sci-phys.*, **B7**(3), 487 (1973).

"General Electric Permselective Membranes," G. E. Medical Development Operation Chem. and Medical Div., General Electric Co., Schenectady, N. Y. 12305.

Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Ch. 9, Wiley, New York (1954).

Kobe, K. A., and R. E. Lynn, Jr., "The Critical Properties of Elements and Compounds," *Chem. Rev*, **52**, 117 (1953).

Michaels, A. S., and H. J. Bixler, "Flow of Gases through Polyethylene," *J. Polymer Sci.*, **50**, 413, 439 (1961).

Sharma, S. C., et al., "Relation Between Expansion Coefficients and Glass Temperature," *Polymer Letters*, **10**, 345 (1972).

Stannett, V., and M. Szarc, "The Permeability of Polymer Films to Gases—A Simple Relationship," *J. Polymer Sci.*, **46**, 89 (1955).

Stern, S. A., "Industrial Application of Membrane Processes—The Separation of Gas Mixtures," in *Membrane Processes for Industry, proc. of Symp.*, Southern Research Inst. p. 201 (1966).

Wolstenholme, W. F., "Correlation of Physical and Polymer Chain Properties," *Polymer Eng. Sci.*, **142** (1968).

Manuscript received June 21, 1973; revision received June 28 and accepted July 1, 1974.

Application of Khodorov's and Li's Entrainment Equations to Rotary Coke Calciners

KE WEN LI

Continental Oil Company, Ponca City, Oklahoma 74601

Two entrainment equations for rotary cylinders are available in the literature (Khodorove, 1961; Li, 1974). Pysiak (1965) has applied the equation of Khodorov (1961) to an aluminum salt rotary calciner. In this study the two equations were combined and used to derive a specific entrainment equation in order to predict the yield of petroleum coke from a rotary calciner. Entrainment is an important factor affecting the calcined coke yield, cost of elimination of entrained fines, and reactions occurring in the gas phase inside the kiln. Therefore, the entrainment equation is very important for studying the operation and design of a calciner. It is essential for the coke calciner simulation study (Li and Friday, 1974).

COMBINATION OF KHODOROV'S AND LI'S EQUATIONS

Khodorov (1961) presents an entrainment equation

$$\frac{C_g}{\rho} \propto \frac{U^3\mu^{3/2}}{d^{3/2}D^{3/4}\overline{D}_s^3\, n} \tag{1}$$

where n is obtained by fitting a linear equation, $\ln[\ln(1/m)] = a + n\ln(D_s)$. Equation (1) can be expressed as

$$W = \frac{\pi}{4} D^2(1-X)C_g U = K\frac{U^4\mu^{3/2}\rho D^2(1-X)}{d^{3/2}D^{3/4}\overline{D}_s^3\, n} \tag{2}$$

Li (1974) shows

$$dW/dL \propto ND\sqrt{V} \tag{3}$$

and

$$W = K_1 L (DNFS^{-1}\theta^{1/2})^{1/2} \tag{3a}$$

Khodorov conducted his experiment at constant rotation speed of 1.5 rev./min. and constant degree of fullness X of 0.1. When X is constant, $\sqrt{V}$ will be proportional to D. Under these conditions, Equation (3) can be written as

$$W = K_1 L D^2 \tag{4}$$

Equating Equations (2) and (4), and substituting $X = 0.1$, we obtain

$$K_1 = \frac{0.9KU^4\mu^{3/2}\rho}{Ld^{3/2}D^{3/4}\overline{D}_s^3\, n} \qquad (5)$$

Inserting Equation (5) into Equation (3a), we can obtain a combined entrainment equation:

$$W = K_2(DNFS^{-1}\theta^{1/2})^{1/2}\frac{U^4\mu^{3/2}\rho}{d^{3/2}D^{3/4}\overline{D}_s^3 nf(C_f)} \qquad (6)$$

where K_2 is a proportionality constant which varies with the roughness between the cylinder wall and feed solid or with the cylinder wall flight design. A modification function $f(C_f)$ is added to Equation (6) because of experimental data reported by Friedman and Marshall (1949) in their Figure 13, showing the effect of gas flow rate on entrainment. Their data plotted on log-log graph is shown in Figure 1. The slopes of the lines in this figure indicate that the entrainment rate does not consistently follow Khodorov's 4th power relation with the gas flow velocity but varies with the gas flow velocity with a power ranging from 0.5 to 4. This indicates that $f(C_f)$ is proportional to the gas flow velocity with a power ranging at least from 0 to 3.5 depending mainly on the entrainable fines concentration in the feed solid as will be discussed later.

CALCINER ENTRAINMENT EQUATION

Equation (6) was used to obtain an entrainment equation in order to predict the calcined coke yield data of Conoco's commercial calciner test runs. The entrainment

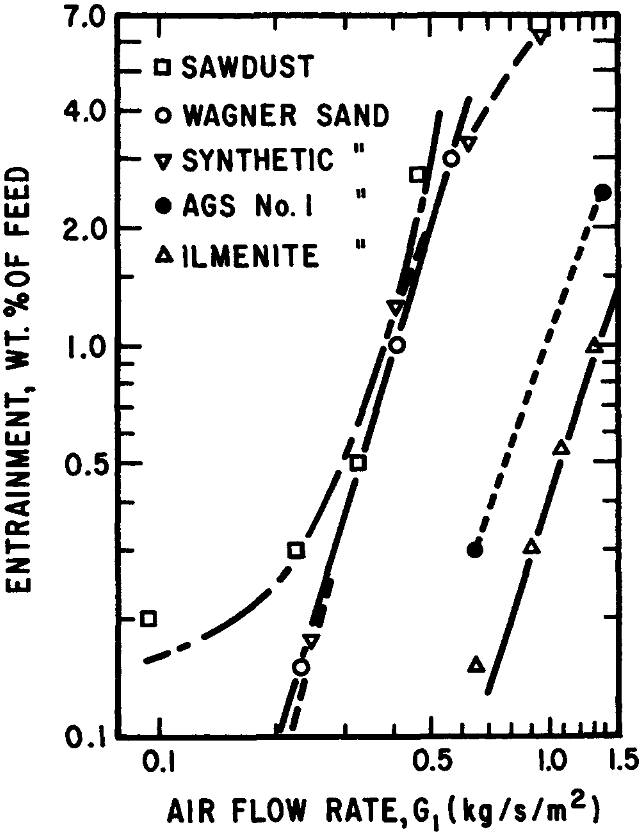

Fig. 1. Entrainment vs. gas flow rate. Feed rate = 2.84 × 10^{-4} m^2/s/m^2. Rotation speed = 1.047 rad/s.

in a coke calciner is complicated by the high temperature coke reactions occurring in the kiln so that some data required for Equation (6) cannot be obtained by direct measurement; therefore, the following assumptions were made:

1. The coke fines entrainment W is equivalent to the coke loss minus the volatile matter loss. Actually there is another loss due to the coke bed combustion with oxygen and carbon monoxide. This combustion is competing with the combustion of entrained fines in the gas. The fines combustion rate is much higher because the fines have a greater reaction surface area and better contact with the gas. Therefore, the coke bed combustion loss can be neglected. Furthermore, the coke bed combustion rate is controlled by gas diffusion which is a function of the same gas turbulence affecting the entrainment rate.
2. The viscosity of the gas stream μ is proportional to the square root of the average of the exit gas temperature and the maximum solid bed temperature $\sqrt{T}$.
3. The average gas mass velocity $U\rho$ is proportional to the exit gas mass flow rate G.

The available calciner test runs cover the following ranges of variables:

Coke feed rate, F	3.33-7.22 kg/s
Exit gas flow rate, G	6.80-17.6 kg/s
Average temperature, T	1388-1683 °K
Kiln rotation speed, N	0.126-0.147 rad/s
Kiln inside diameter, D	2.59 m for Coke A
	3.20 m for Coke B

Coke B had a higher volatile matter content than Coke A so that a kiln with larger diameter was used for Coke B. Under these conditions, Equation (6) can be expressed as

$$Z = \frac{W}{(DNF)^{1/2}T^{3/4}} \propto \frac{U^4\rho}{f(C_f)D^{3/4}} \qquad (7)$$

In order to find a correlation to describe the experimental data, Z was chosen to contain some well characterized variables. In Equation (7), $(NDF)^{1/2}$ represents the fines availability, that is, $ND\sqrt{V}$ shown in Equation (3) and $T^{3/4}$ for the Khodorov's viscosity shown in Equation (1). A good correlation was obtained as shown in Figure 2. The straight line in this figure indicates

$$Z = 4.6 \times 10^{-4}\left[\frac{\pi}{4}D^2(1-X)U\rho\right]^{1/2}$$

or

$$W = 3.61 \times 10^{-4}(NFD)^{1/2}T^{3/4}[U\rho D^2(1-X)]^{1/2} \qquad (8)$$

Equation (8) predicts Conoco's test run yields satisfactorily as shown in Table 1. Since the effect of kiln diameter is confounded by coke type, Equation (8) can be written

$$W = K_3[NF\mu^3U\rho(1-X)]^{1/2} \qquad (9)$$

Equation (9) is an entrainment equation for any petroleum coke calciner. The proportionality constant K_3 varies with coke type, kiln size, and the roughness between kiln wall and solid particles.

Although Equation (8) is obtained by an empirical correlation method, its validity is supported by the fact that entrainment is a function of fines availability $ND\sqrt{V}$,

TABLE 1. COMPARISON OF PREDICTED CALCINED COKE YIELDS WITH EXPERIMENTAL DATA

Run no.	1	2	3	4	5	6	7	8
Yield deviation, wt. % (Exp.-predicted)	−0.1	+0.5	−0.4	−0.4	−0.2	+0.2	+0.2	0.0

average particle terminal velocity U_t, and gas Reynolds number R_e. This fact is expressed in the following equation:

$$\frac{dW}{dL} \propto (NDFS^{-1}\theta^{1/2})^{1/2} \left(\frac{\mu}{\overline{D}_s^2 d}\right)^2 \left(\frac{DU\rho}{\mu}\right)^{1/2}$$
$$\propto ND\sqrt{V}\, U_t^{-2}\, R_e^{1/2} \qquad (10)$$

Equation (10) is obtained by inserting the fixed variables used in the test runs into Equation (9) and using Equations (3) and (3a). $(1 - X)$ is considered as a constant because it varied within 5% in the test runs. According to Stokes' Law the particle terminal velocity U_t is proportional to $\overline{D}_s^{-2}(d - \rho)/\mu$. Since $d - \rho \simeq d$, U_t will be proportional to $\overline{D}_s^2 d/\mu$.

DISCUSSION

The reason entrainment rate does not consistently follow Khodorov's 4th power relation with U can be explained as follows.

It is known that a particle can be entrained only when the terminal velocity of the particle is smaller than an eddy upward velocity. Therefore, the entrainable fines concentration C_f, that is, the concentration of the fines having sizes smaller than can be lifted up by the maximum eddy upward velocity is an important factor affecting entrainment. C_f can be expressed as the cumulative weight percentage of particles smaller than a given size. Figure 3 shows how C_f varies with D_f for some feed solids. A log-log plot is used in the figure so that the slope of the distribution line will indicate the power relation between C_f and D_f. Since the entrainment rate W is affected by C_f, and D_f by U, the slope of the distribution line will be closely related to the power relation between W and U. Slopes of the distribution lines may vary with feed solids. Therefore, the power relation of U to W will vary with the feed material.

Figure 3 contains lines of the two types of sand used by Khodorov (1961) in establishing the 4th power relation of U to W. It is seen that the two size distribution lines of the sand are linear in the entrainment region of C_f lower than 70%. The linearity and the steepness of the lines indicate that Khodorov's 4th power relation is reasonable for the sand he used.

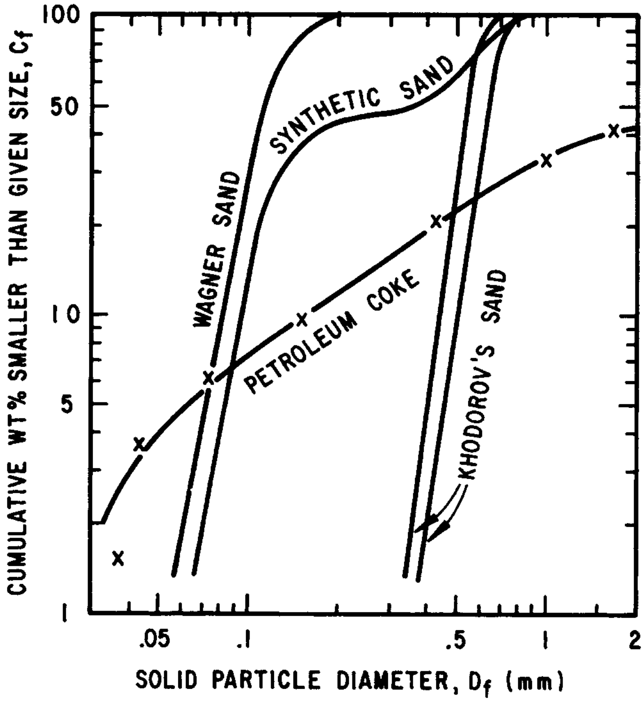

Fig. 3. Size distribution of feed solid.

Size distribution of the feed solids illustrated in Figure 1 are available in Figure 3 of Friedman and Marshall (1949), excepting that for the sawdust for the entrainment region of C_f lower than 25%. The distribution lines for the AGS, Ilmenite, and Wagner sands have similar shapes as those of Khodorov's sand. To demonstrate this, the distribution line of Wagner sand is plotted in Figure 3. The similarity of these distribution lines with those of Khodorov's sand explains why the slopes of the lines in Figure 1 for the sands are close to 4. The distribution of the synthetic sand is also plotted in Figure 3. The slope of this distribution line starts to decrease at a C_f of about 15% as D_f increases. This explains why the line for the synthetic sand in Figure 1 has a decrease of slope in the higher entrainment region.

Figure 3 also shows a typical size distribution line of petroleum coke feed to a calciner. The calciner test runs were operated within a C_f region from about 6 to 20%. In this region, the slope of the distribution line is fairly constant. This will cause a constant power relation of U to W. Since this slope having a value of 0.7 is so small compared to the average of those of Khodorov's sand, 7.7, the 0.5 power relation shown in Equation (8) for coke entrainment seems reasonable.

Based on the above discussion, by comparing the slope of a size distribution line with those in Figure 3, one may predict roughly the power relation of U to W for a certain solid feed. It is desirable to make more experiments to further investigate the power relation or $f(C_f)$ as a function of the slope of the size distribution line and other operation variables.

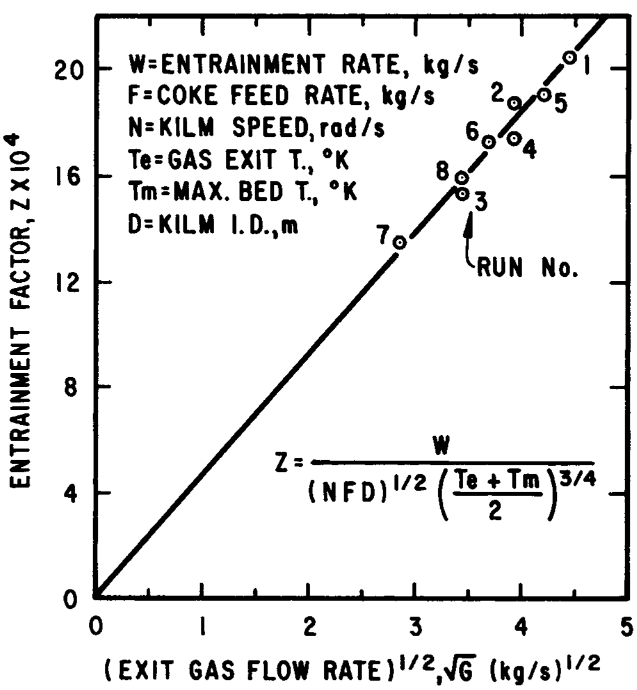

Fig. 2. Correlation of entrainment factor vs. exit gas flow rate for petroleum coke calciners.

CONCLUSION

An entrainment equation, Equation (8), is developed which predicts satisfactorily the available yield data of Conoco's commercial calciner test runs. The method used in developing the entrainment equation from Equation (6) is applicable to other rotary cylinders. Equation (9) or Equation (10) is useful in investigating the operation of a rotary petroleum coke calciner.

ACKNOWLEDGMENT

The author wishes to thank Drs. J. R. Friday and F. E. Sage for reviewing this article and Mr. G. A. Sweany for discussion on a portion of the study. Permission to publish this article given by Continental Oil Company is gratefully acknowledged.

NOTATION

a = constant
C_g = concentration of fines in the gas, kg/m^3
C_f = concentration of entrainable fines in solid, wt. %
d = density of solid, kg/m^3
D = inside diameter of cylinder, m
D_f = diameter of the largest fine particle which can be entrained, mm
D_s = diameter of feed solid particles, m
F = feed rate of solid, kg/s
F_1 = $D/d/(\pi D^2/4)$, m^3/s/m^2
G = gas flow rate, kg/s
G_1 = $G/(\pi D^2/4)$, kg/s/m^2
K, K_1, K_2, K_3 = proportionality constants
L = length of cylinder, m
m = weight fraction of feed particles with size larger than D_s
n = solid particle size distribution parameter
N = cylinder rotation speed, rad/s
Re = $DU\rho/\mu$
S = cylinder slope, m/m
T = average of gas exit temperature T_e and maximum bed temperature T_m, °K
U_t = average fines terminal velocity, m/s
U = gas velocity in the direction of cylinder axis, m/s
V = bed holdup volume per unit cylinder length, m^3/m
W = fines entrainment rate, kg/s
X = fraction of cylinder volume occupied by solid bed
Z = $W/(NFD)^{1/2}/T^{3/4}$
θ = dynamic angle of repose of solid, rad
ρ = density of gas, kg/m^3
μ = viscosity of gas, N · s/m^2

LITERATURE CITED

Friedman, S. J., and W. R. Marshall, Jr., "Studies in Rotary Drying, Part I, Holdup and Dusting," *Chem. Eng. Progr.*, **45**(8), 482 (1949).

Khodorov, E. I., "Entrainment of Materials from Rotary Kilns," *Khim. Prom.*, **416** (1961); *Chem. Abstr.*, **55**, 26560g (1961).

Li, K. W., "Entrainment in Rotary Cylinders," *AIChE J.*, **20**, 1031 (1974).

———., and J. R. Friday, "Simulation of Coke Calciners," *Carbon*, in press.

Pysiak, J., "Amount of Material Carried Off in the Form of Dust with Gases from a Rotary Kiln," *Przem. Chem.*, **44**(9), 497 (1965); *Chem. Abstr.*, **64**, 330a (1966).

Manuscript received April 22 and accepted April 24, 1974.

Optimal Performance of Equilibrium Parametric Pumps

H. T. CHEN and J. A. MANGANARO

Department of Chemical Engineering
Newark College of Engineering, Newark, New Jersey 07102

In previous papers (Chen et al., 1971, 1972, 1973), continuous and semicontinuous pumps have been analyzed in terms of an equilibrium theory of pump performance. Mathematical expressions for the concentration transients have been given for the region of infinite separation factors and two regions of finite separation factors. In addition, it has been shown that when the penetration distance of the cold cycle is less than or equal to that of the hot cycle and the height of the column, the pump with feed at the enriched end is capable, as a theoretical limit, of complete removal of solute from one product stream and, at the same time, gives arbitrarily large enrichment of solute in the other product stream. In this note we extend the mathematical models previously developed to determine the optimal pump performance. The model system used is sodium nitrate-water on an ion retardation resin adsorbent. Emphasis is given on the operating conditions necessary to achieve high separation factors with the maximum yield. Information in connection with such optimal values of operating parameters is essential for design or scale-up purposes.

THEORY

Let us assume that a dilute solution includes s adsorbable components in an inert solvent. Let us assume further that the solution may be treated as s pair of pseudo binary systems. Each system includes one solute and the common inert solvent, each with a dimensionless equilibrium parameter b_i and the corresponding values of L_{1i} and L_{2i}. Furthermore

$$b_1 > b_2 \ldots\ldots b_k \geqq \phi_B > b_{k+1} \ldots\ldots > b_s \qquad (1)$$

for the continuous pump, and

$$\left(\frac{2b}{1-b}\right)_1 > \left(\frac{2b}{1-b}\right)_2 \ldots\ldots\ldots \left(\frac{2b}{1-b}\right)_k \geqq \phi_B > \left(\frac{2b}{1-b}\right)_{k+1} \ldots\ldots > \left(\frac{2b}{1-b}\right)_s \qquad (2)$$

for the semicontinuous pump. Also

$$L_{2i} = \frac{v_0\,(1+\phi_B)}{(1+b_i)(1+m_0)}\left(\frac{\pi}{\omega}\right) \leqq h \qquad (3)$$

where $i = 1, 2, \ldots.\ k$.

At steady state $(n \rightarrow \infty)$ the components $i = 1, 2, \ldots$ k for which operations occur in region 1 would appear only in the top product stream, and the remaining components $(k + 1, \ldots.\ s)$ would appear in both top and bottom