need to maintain strict supervision over the handling of the radioactive materials. The added precautions necessary in the tunnel operation are tolerable in view of the measurements which are made possible.

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NOTATION

Any consistent set of units may be employed. Those listed are merely illustrative.

D = distance above grids, ft.
$F(n)$ = spectral density
L_y = Eulerian macroscale, ft.
n = frequency
N_o = average number of zero values of u' per second
R_y = Eulerian correlation coefficient, dimensionless
u' = fluctuating component of fluid velocity in axial direction, ft./sec.
U = mean fluid velocity measured at any radial distance from duct axis, ft./sec.
U_c = mean fluid velocity measured at duct axis, ft./sec.
U_p = absolute particle velocity, ft./sec.
v' = fluctuating component of fluid velocity in radial direction ft./sec.
x = longitudinal distance along duct axis, ft.
y = radial distance from duct axis, ft.
λ_x = Eulerian microscale in x direction, ft.
λ_y = Eulerian microscale in y direction, ft.
θ = time, sec.

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Adsorption Kinetics of a Nonflow System with Nonlinear Equilibrium Relationship

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The kinetics of adsorption in a nonflow system with nonlinear equilibrium relationship and negligible liquid-phase resistance has been studied, and the numerical solutions corresponding to different initial conditions are presented. The concentration ratio is found to be a function of two dimensionless groups. Consideration is also given to the problem of convergence in connection with the numerical calculation.

The study of the problem on the adsorption rate in a nonflow system is an old one. Analytical solutions for cases with linear adsorption isotherms have been obtained by Berthier (*1*), Carman and Haul (*2*), and Grober (*4*), respectively. Edeskuty and Amundson (*3*) considered the effect of intraparticle diffusion and assumed that the concentration of the liquid solution in the interior of the particles is different from that in the exterior liquid, with a linear equilibrium relationship. For cases where a nonlinear equilibrium relationship is observed, it has been found highly unlikely to obtain the solution analytically.

The object of this investigation is to treat this problem by a numerical method and present results which can be used in industrial design work. Some of the treatments involved in this work parallel closely those of a previous paper by this author (*6*) in which the adsorption kinetics for cases with nonlinear equilibrium relationship in a flow system were studied.

MATHEMATICAL DEVELOPMENT

A simple model for the adsorption process is postulated as follows. A vessel containing a definite amount of solution of known concentration is brought into contact with a known quantity of solute-free solid particles. These particles are spherical and their sizes identical. Rigorous agitation is provided which eliminates completely the film resistance of mass transfer in the liquid phase. In other words this is tantamount to assuming that solid-phase diffusion is the controlling mechanism. Furthermore it is assumed that the particles are quasihomogeneous in structure and equilibrium exists everywhere at the surface of the particle. Adsorption will take place and continue until the concentration throughout the particle becomes uniform and in equilibrium with the liquid solution. The following equations can be used to describe the physical situation:

$$V\frac{dC}{dt} + M\frac{dq}{dt} = 0 \qquad (1)$$

$$\nabla^2 q_i = \frac{1}{D}\frac{\partial q_i}{\partial t} \qquad (2)$$

$$q_s(t) = q_i(R, t) \qquad (3)$$

$$q(t) = \frac{3}{4\pi R^3}\int_0^R q_i(r, t)\pi r^2 \cdot dr \qquad (4)$$

$$q_s(t) = f(c) = A\,c^a \qquad (5)$$

Combining Equations (2), (3), (4), and (5) as shown in reference (6) one obtains

$$\frac{dq}{dt} = \frac{6D}{R^2}\int_0^t \sum_{n=1}^{\infty} \frac{\partial q_s}{\partial \lambda} e^{-D\left(\frac{n\pi}{R}\right)^2 (t-\lambda)} \cdot d\lambda \qquad (6)$$

For the summation of the infinite series one first writes

$$\sum_{n=1}^{\infty} e^{-D\left(\frac{n\pi}{R}\right)^2 (t-\lambda)} = \sum_{n=0}^{\infty} e^{-B^2 n^2 \pi^2} - 1 \qquad (7)$$

$$B^2 = \frac{D(t-\lambda)}{R^2}$$

By the Gaussian Summation formula it can be shown that

$$\sum_{n=0}^{\infty} e^{-B^2 n^2 \pi^2} = \frac{\sqrt{\pi}}{2B\pi} + \frac{1}{2} = \frac{R}{2\sqrt{\pi D(t-\lambda)}} + \frac{1}{2} \qquad (8)$$

and

$$\sum_{n=1}^{\infty} e^{-D\left(\frac{n\pi}{R}\right)^2 (t-\lambda)} = \frac{\sqrt{\pi}}{2}\,\frac{R}{\sqrt{D(t-\lambda)\,\pi}} + \frac{1}{2} - 1 = \frac{R}{2\sqrt{\pi D(t-\lambda)}} - \frac{1}{2} \qquad (9)$$

Combining Equations (9) and (6) one gets

$$\frac{dq}{dt} = \frac{6D}{R^2}\int_0^t \frac{dq_s}{d\lambda}\left[\frac{R}{2\sqrt{\pi D(t-\lambda)}} - \frac{1}{2}\right] \cdot d\lambda \qquad (10)$$

Equations (1), (5), and (11) constitute systems of integro-differential equations for the description of the adsorption kinetics for cases with the Freundlich type of adsorption isotherm. The object of the present investigation is to present numerical solutions when the exponent a in Equation (5) is equal to ½.

Equations (1), (5), and (10) can be written in the following dimensionless forms:

$$\frac{d\beta}{d\theta} + \frac{d\alpha}{d\theta} = 0 \qquad (11)$$

$$\frac{d\beta}{d\theta} = \frac{3}{2\pi}\int_0^\theta \frac{d\beta_s}{d\lambda}\left[\frac{1}{\sqrt{\theta-\lambda}} - \frac{1}{2}\right] \cdot d\lambda \qquad (12)$$

$$\beta_s = \alpha^a \qquad (13)$$

where

$$\alpha = \left(\frac{MA}{V}\right)^{\frac{1}{a-1}} \cdot C \qquad (14)$$

$$\beta = \left(\frac{M}{V}\right)\left(\frac{MA}{V}\right)^{\frac{1}{a-1}} q \qquad (15)$$

$$\theta = \frac{4\pi D}{R^2}\,t \qquad (16)$$

For numerical computation the following approximations are used:

$$\left.\frac{d\beta}{d\theta}\right|_j = -\left.\frac{d\alpha}{d\theta}\right|_j \simeq -\frac{\alpha_j - \alpha_{j-1}}{\Delta\theta} \qquad (17)$$

By a similar technique described before (6, 7) the following expression is obtained by combining (11), (12), and (13):

$$\alpha_{j-1} - \alpha_j = \left[\frac{3}{\pi}\sqrt{\Delta\theta} - \frac{3}{4\pi}\Delta\theta\right]\alpha_j^{\,a} - \frac{3}{\pi}\sqrt{\Delta\theta}\sum_{k=1}^{j-1} K_{j-k}\,\alpha_k^{\,a} \qquad (18)$$

where

$$K_{j-k} = 2\sqrt{K-j} - \sqrt{K-(j-1)} - \sqrt{K-(j+1)} \qquad (19)$$

Equation (18) provides the basis for computing α at different intervals of θ. For $a = ½$ the realistic root of the quadratic equation is given by

$$\alpha_j^{\,1/2} = -C_1 + \sqrt{C_1^2 + \left[\alpha_{j-1} + C_2\sum_{k=1}^{j-1} K_{j-k} \cdot \alpha_k^{\,1/2}\right]} \qquad (20)$$

$$C_1 = \frac{\frac{3}{\pi}\sqrt{\Delta\theta} - \frac{3}{4\pi}\Delta\theta}{2} \qquad (21)$$

$$C_2 = \frac{3}{\pi}\sqrt{\Delta\theta} \qquad (22)$$

As an indication of the degree of separation which has been reached it is convenient to express the results in terms of the ratio of concentration differences defined as $(C_0 - C)/(C_0 - C_\infty)$, when C_∞ is the ultimate concentration of the liquid solution after infinite contact time with the solid particles. Note by the definition of α one has

$$\frac{C_0 - C}{C_0 - C_\infty} = \frac{\alpha_0 - \alpha}{\alpha_0 - \alpha_\infty} \qquad (23)$$

where

$$\alpha_0 = \left(\frac{MA}{V}\right)^{\frac{1}{a-1}} \cdot C_0$$

The ultimate concentration parameter of solution α_∞ can be found from a consideration of material balance and equilibrium relationship. For $a = ½$, α_∞ is given as

$$\alpha_\infty^{\,1/2} = \left(\frac{1}{2}\right)\left[-1 + \sqrt{1 + 4\alpha_0}\right] \qquad (24)$$

Numerical values of $C_0 - C/C_0 - C_\infty$ with exponent $a = ½$ for cases $\alpha_0 = 1$, 4, 25, and 400 have been obtained, and a few selected values are given in Table 1. The actual computation was carried out in accordance with Equations (20), (23), and (24). The increment $\Delta\theta$ was so chosen as to insure a maximum error of less than 2% from the limiting value. This will be discussed in detail in the next section.

DISCUSSION OF RESULTS

One of the most pertinent questions involved in the numerical solution with finite-difference approximation is convergence. Although there are several recently published treatises on this subject, the application of the general theory to a specific problem often encounters difficulty. For this particular problem this question can be examined from a different angle. Suppose one approximates Equation (11) in a different way, such as

$$\frac{d\beta}{d\theta} = -\frac{d\alpha}{d\theta} \cong -\frac{\alpha_{j+1} - \alpha_j}{\Delta\theta} \qquad (17a)$$

Combining Equation (17*a*) and (12) and (13) one obtains a different expression for α:

$$\alpha_{j+1} = \alpha_j - \left[\frac{3}{\pi}\sqrt{\Delta\theta} - \frac{3}{4\pi}\Delta\theta\right]\alpha_j^{\,a} + \frac{3}{\pi}\sqrt{\Delta\theta}\sum_{k=1}^{j-1} K_{j-k}\,\alpha_k^{\,a} = \alpha_j - 2C_1\alpha_j^{\,a} + C_2\sum_{k=1}^{j-1} K_{j-k}\,\alpha_k^{\,a} \qquad (25)$$

with C_1 and C_2 defined as before and

$$\alpha_1 = \alpha_0 - 2\,C_1\,\alpha_0^{\,a} \qquad (26)$$

$$\alpha_2 = \alpha_1 - 2\,C_2\,\alpha_1^{\,a} \qquad (27)$$

For the case $a = ½$ one has

$$\alpha_{j+1} = \alpha_j - 2\,C_1\,\alpha_j^{\,1/2} + C_2\sum_{k=1}^{j-1} K_{j-k}\,\alpha_k^{\,1/2} \qquad (28)$$

Equation (28) can be considered as a counterpart of Equation (20) based on the approximation given by Equation (17*a*).

From the consideration of the physical situation it is reasonable to assume that the adsorption rate is maximum at the beginning and becomes diminishing as time increases. Therefore it is conceivable to claim that $d\alpha/d\theta$ is a monotonically decreasing function of θ. Under this reasoning one should have

$$\frac{\alpha_j - \alpha_{j+1}}{\Delta\theta} \leqq \left|\frac{d\alpha}{d\theta}\right|_j \leqq \frac{\alpha_{j-1} - \alpha_j}{\Delta\theta} \tag{29}$$

This results in the following inequality: $(\alpha)_{\text{from Equation (28)}} \leqq (\alpha)_{\text{limiting value}} \leqq (\alpha)_{\text{from Equation (20)}}$

In other words Equations (28) and (20) provide an upper and lower bound for the limiting value of α and should approach the same value as the increment $\Delta\theta$ approaches zero, thus enabling the estimation of the value of α. This point is verified in actual calculation. Values of α for the same initial conditions have been obtained in accordance with Equations (20) and (28), respectively, with the same value of $\Delta\theta$ used. The values of α, obtained from Equation (20), have been consistently greater than those obtained from (28).

One interesting feature which has been observed is that the value of α as obtained from Equation (20) decreases as the magnitude of $\Delta\theta$ decreases, while the opposite trend is observed if Equation (28) is employed for computation. Furthermore the rate of decrease in the former case is much smaller in comparison with the rate of increase in the latter case. One may therefore conclude that Equation (20) is less sensitive to the effect of the magnitude of $\Delta\theta$ because Equation (20) was used as the basis of computation. A typical example is shown in Figure 1.

TABLE 1. NUMERICAL VALUE OF $C_o - C/C_o - C$ FOR SYSTEM WITH ADSORPTION ISOTHERM CHARACTERIZED BY $a = A \cdot C^{12}$

$$\frac{C_o - C}{C_o - C}$$

θ	$\alpha_o = 1$	$\alpha_o = 4$	$\alpha_o = 25$	$\alpha_o = 400$
0.001	0.0479	0.0379	0.0331	0.0307
0.005	0.1044	0.0838	0.0729	0.0678
0.01	0.1448	0.1170	0.1021	0.0952
0.02	0.1998	0.1626	0.1425	0.1333
0.03	0.2400	0.1061	0.1726	0.1617
0.04	0.2725	0.2236	0.1976	0.1854
0.05	0.3005	0.2475	0.2190	0.2060
0.06	—	0.2687	0.2383	0.2241
0.08	0.3650	0.3051	0.2717	0.2559
0.10	0.3998	0.3362	0.3003	0.2834
0.15	0.4693	0.3990	0.3591	0.3402
0.20	0.5227	0.4489	0.4062	0.3859
0.30	0.6026	0.5254	0.4804	0.4586
0.40	0.6617	0.5846	0.5383	0.5157
0.50	0.7079	0.6322	0.5860	0.5631
0.60	0.7422	0.6704	0.6058	0.6037
0.70	0.7736	0.7046	0.6607	0.6390
0.80	0.8020	0.7340	0.6919	0.6701
1.00	0.8426	0.7827	0.7431	0.7229
1.40	—	—	0.8178	0.8016
1.50	0.9100	0.8654	—	—
1.80	—	—	0.8710	0.8564
2.00	0.9472	0.9172	0.8908	0.8775
3.00	0.9777	0.9603	0.9474	0.9393
3.80	—	—	0.9584	0.9533

From the development discussed above it becomes possible to estimate the error of these numerical solutions due to the approximation of time derivations. For a given value α_0 values of α at different θ are obtained by employing both Equations (20) and (28) with various magnitudes. The values of α for any given θ are then plotted against the magnitude of the increment $\Delta\theta$, and the limiting value is obtained by extrapolation as shown in Figure 1. Although the errors vary depending upon values of α_0 and θ, in no case does the value as presented in Table 1 give an error greater than 2%.

Another question which has to be considered is the stability of the difference scheme used in the computation. O'Brien suggested a criterion which can be used for this purpose. The scheme used in the present investigation has been found to be stable in a previous work (7).

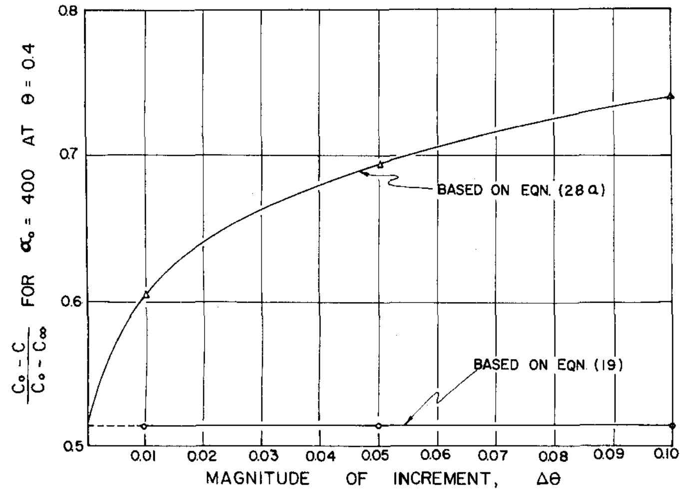

Fig. 1. Effect of increment size on numerical results.

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NOTATION

A = constant in Equation (5)
a = exponent in Equation (5)
C = concentration of liquid solution
D = diffusion coefficient
K_{j-h} = constant defined for $\sqrt{j-h} - \sqrt{j-(h-1)} - \sqrt{j-(h+1)}$
M = total mass of solid particles
q = concentration of solid particles expressed on mass basis
q = average concentration of solid particles
q = surface concentration of solid particles
R = radius of spherical particles
r = radial distance from center of particle
t = time
V = volume of liquid solution
α = dimensionless group defined as $(MA/V)^{1/a-1}\,C$
β = dimensionless group defined as $(M/V)\ (MA/V)^{1/a-1}\,q$
θ = dimensionless group defined as $4\pi D/R^2\ t$

Subscript

0 = initial state
s = surface
∞ = equilibrium state
j = jth increment of θ

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