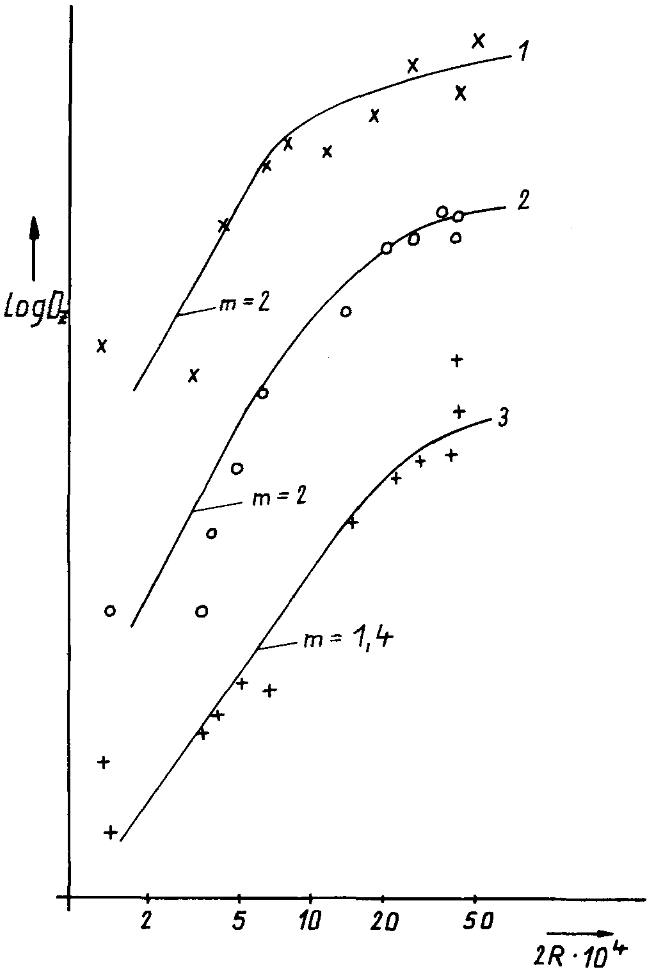

Fig. 2. Intracrystalline diffusion coefficients as a function of crystal size. Data from Kärger et al. (1976) and Caro (1977). 1. Ethane/NaCaA/—80°C; 2. propane/NaCaA/+23°C; 3. *n*-butane/NaCaA/+23°C.

5A zeolites, with respect to varying degree and type of cation introduced into the lattice, and with respect to increasing adsorbate concentration. From this point of view, they do not appear to be measuring completely different phenomena. Finally, the adsorption rate experiments are adequately described during an extended initial phase by the $\sqrt{t}$ law valid for diffusion; initial uptakes are not directly proportional to t as should be expected from the barrier resistance model.

In conclusion, there are differences of some orders of magnitude between NMR and adsorption rate diffusivities, and diffusion coefficients reported on the basis of adsorption rate experiments increase with crystal size. However, the barrier resistance theory does not give a satisfactory explanation of the observed phenomena.

NOTATION

D_a = intercrystalline diffusion coefficient, cm^2/s
D_{NMR} = diffusion coefficient measured by NMR, cm^2/s
D_z = intracrystalline diffusion coefficient, cm^2/s
K_A = adsorption equilibrium constant
m = slope of log-log plot
R = crystal radius, cm
t = time, s
$\mathcal{B}$ = barrier transfer coefficient, cm/s

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Nonisothermal Fouling of Catalyst Pellets Using Langmuir-Hinshelwood Fouling Kinetics

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Catalyst deactivation by fouling is often an unavoidable process, since it is linked with the chemical reactions employed. Its effect may be minimized, however, and this has led to a number of theoretical linvestigations. An early analysis of the problem of poisoning and fouling coupled with intraparticle temperature gradients was made by Wheeler (1955). Most subsequent analytical studies of catalyst fouling have assumed integral or zero order rate expressions for both the main and fouling reactions. Thus, Masamune and Smith (1966) assumed both reactions to be first order and isothermal; subsequently, an extension to nonisothermal fouling using the same first-order expressions was made by Sagara et al. (1967). Greco et al. (1973) also assumed first-order fouling in a study of the dehydration of alcohols. Kam et al. (1975, 1977*a*, *b*, *c*) have given a number of analyses for catalyst fouling under isothermal and nonisothermal conditions accompanied by interphase and intraparticle resistances; in every case, however, the models were developed on the assumption of the fouling kinetics being first order.

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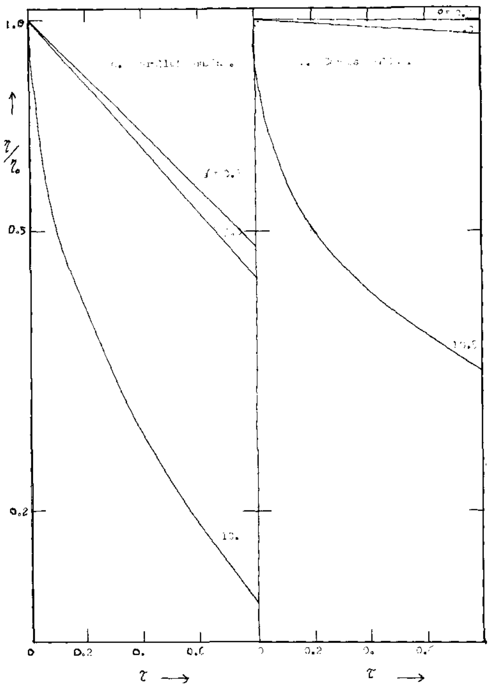

Fig. 1. Effect of Thiele modulus on relative effectiveness factor for parallel and series fouling. $K_A = K_B = 10$.

If the main reaction rate is of complex form such as is given by Langmuir-Hinshelwood kinetics, then it is most logical to assume that the fouling reaction will proceed by a similar mechanism. An analysis of this form has been made by Chu (1968) using Langmuir-Hinshelwood rate expressions for both main and deactivating reactions, but he assumed isothermal conditions throughout. In this note, some results of a study of nonisothermal fouling employing Langmuir-Hinshelwood kinetics for both the main and fouling reactions are presented. Previous studies by the authors (Kam et al., 1977*a*) have investigated the influence of a number of parameters. In this note, attention will be concentrated on the effect of the Thiele modulus ϕ for the main reaction and the adsorption equilibrium constants K_A and K_B for reactants and products, respectively, as these have been shown by us to be important parameters. The process considered is exothermic, with the activation energy for fouling being greater than that for the main reaction. This has been quoted as being applicable for steam reforming processes by Rostrup-Nielsen (1974).

A general reaction scheme for parallel and series fouling may be assumed as follows:

$$A \xrightarrow{k_0} B \qquad \text{(main reaction)}$$

$$A \xrightarrow{k_{f1}} \text{Coke} \quad \text{(parallel fouling)}$$

TABLE 1. PARAMETER VALUES

Sh^*	Nu^*	β	γ	γ_f	h_{KA}, h_{KB}
250	1.5	0.02	20	40	5

$$B \xrightarrow{k_{f2}} \text{Coke} \quad \text{(series fouling)}$$

The dimensionless form of the continuity equations for the mass and energy balances under pseudo steady state conditions are

$$\frac{d^2a}{d\delta^2} + \frac{(\alpha - 1)}{\delta}\frac{da}{d\delta} = \phi^2 f_0(a, \theta, S) \tag{1}$$

$$\frac{d^2\theta}{d\delta^2} + \frac{(\alpha - 1)}{\delta}\frac{d\theta}{d\delta} = -\beta\phi^2 f_0(a, \theta, S) \tag{2}$$

where S is equal to one at time zero, α is three for spherical particles, and $f_0(a, \theta, S)$ takes the form of the usual Langmuir-Hinshelwood expression for the main reaction; that is

$$f_0(a, \theta, S) = \frac{K_A\, a \exp[(\gamma - h_{KA})(1 - 1/\theta)]S}{1 + K_A \exp[-h_{KA}(1 - 1/\theta)]a + K_B \exp[-h_{KB}(1 - 1/\theta)]b} \tag{3}$$

The general deactivation expression when both parallel and series fouling may be present can be written in dimensionless form as

$$-\frac{dS}{d\tau} = f_1(a, \theta, S) + \frac{k_{f2}}{k_{f1}} \cdot f_2(b, \theta, S) \tag{4}$$

where τ is defined as $k_{f1}\, C_{A0}t$ for parallel fouling and $k_{f2}\, C_{A0}t$ for series fouling, and

$$f_1(a, \theta, S) = \frac{K_A\, a \exp[(\gamma_{f1} - h_{KA})(1 - 1/\theta)]S}{1 + K_A \exp[-h_{KA}(1 - 1/\theta)]a + K_B \exp[-h_{KB}\,(1 - 1/\theta)]b} \tag{5}$$

$$f_2(b, \theta, S) = \frac{K_B\, b \exp[(\gamma_{f2} - h_{KB})(1 - 1/\theta)]S}{1 + K_A \exp[-h_{KA}(1 - 1/\theta)]a + K_B \exp[-h_{KB}\,(1 - 1/\theta)]b} \tag{6}$$

In the following discussion, when the type of fouling is obvious, the numerical suffix is dropped.

Values of the parameters employed for the simulation are within the limits quoted by Aris (1975) as typical for most reactions, the values of γ and γ_f being those suggested by Rostrup-Nielson (1974) for steam reforming catalyst deactivation. The actual parameter values employed are listed in Table 1.

The values of other parameters will be given as they arise in the following paragraphs.

Results are plotted in terms of the relative effectiveness factor η/η_0 against process time τ. The relative effectiveness factor is defined as the ratio of catalyst effectiveness at any time τ to that at $\tau = 0$. Figure 1 shows the decrease in η/η_0 with τ for three values of the Thiele modulus ($\phi = 0.3$, 3 and 10.5) for both parallel and series fouling. For both types of fouling, an increase in ϕ increases the rate of catalyst deactivation, but the severity of fouling is much more pronounced for parallel fouling than for series particularly at low values of ϕ. Thus, as the curves for $\phi = 0.3$ and 3.0 for series fouling in Figure 1 demonstrate, even after a time on stream corresponding to $\tau =$

Table 2. Values of η/η_0 at $\tau = 0.8$

ϕ	Parallel fouling	Series fouling	Difference
0.3	0.474	0.999	0.525
3.0	0.430	0.950	0.520
5.5	0.229	0.546	0.317
9.5	0.187	0.457	0.270
10.5	0.150	0.320	0.170

0.8, there is very little drop in catalyst activity. The corresponding curves for parallel fouling at the same time show, however, that the catalyst activity is now about 50% of the initial value. This difference in behavior is explainable as follows. At low values of ϕ, the reaction is under chemical control, since the reaction rate is slow compared to diffusional processes, and the product concentration, which is the fouling precursor for series fouling, will be very low. As ϕ is increased, deactivation by either fouling process will be more severe, for now the reaction is under diffusion control. Conversion will be higher as will be the particle temperature. For parallel fouling, since the ratio γ_f/γ is two, the increase in temperature will favor the deactivation reaction. In the case of series fouling, a faster rate of deactivation is now attained, since the concentration of product within the pellet is much higher compared to lower values of the Thiele modulus. Of the two effects, the temperature seems more important, but with increasing Thiele modulus the deactivation due to series fouling approaches that for parallel fouling. This is illustrated in Table 2, where the difference in loss of activity is given in the final column, and the decreasing value of this quantity with increasing ϕ is apparent.

An important factor in Langmuir-Hinshelwood mechanisms is the magnitude of the adsorption constants. Chu (1968) suggested that an increase in the value of the appropriate adsorption constants would increase the rates of deactivation. This has been confirmed in the present work for values of ϕ equal to 0.3 and 3.0 for both fouling mechanisms because under these conditions, the catalyst pellet operates at temperatures almost identical to those of the bulk gas. It was found, for example, that maximum temperature rises were less than 1.001 dimensionless temperature units with respect to the bulk gas at these low values of ϕ. The thermal effect is thus negligible.

At higher values of ϕ, however, an opposite trend has been observed in this work. This is shown in Figures 2*a* and 2*b* for parallel and series fouling for a Thiele modulus of 10.5. At this value of ϕ, the main reaction is under diffusion control, and the reaction rate depends on the combined effects of adsorption equilibrium constant, concentrations, temperature, and activity of the catalyst. For the case of parallel fouling, K_B is fixed at 10, and K_A varied in the range 10 and 20 to 30, while for series fouling, K_A was fixed at 10 and K_B took values of 10, 20, and 30. Corresponding values of the surface temperature of the pellet θ_s are given in Table 3 for these combinations of K_A and K_B. Intraparticle temperatures were slightly higher than these surface values but were not sufficiently different to influence the following argument. Since γ_f is greater than γ, fouling is favored at higher temperatures.

The results in Table 3 show that for parallel fouling an increase in K_A is accompanied by a corresponding decrease in θ_s at this value of ϕ. This reduces the extent of fouling as shown in Figure 2*a*. For series fouling, the surface temperatures are also reduced but to a lesser extent than for parallel fouling. This would be expected to lead to more severe fouling in the series case, but the situation is complicated by the additional effect of K_B on the main reaction. A high value of K_B will hinder the adsorption of A, resulting in lower conversion of A to B which will, in turn, reduce the extent of fouling compared to the parallel case as shown in Figure 2*b*. It is interesting to note, however, that the greatest deactivation occurs when the surface temperature is greatest. Similar effects occur at values of ϕ greater than 10.5.

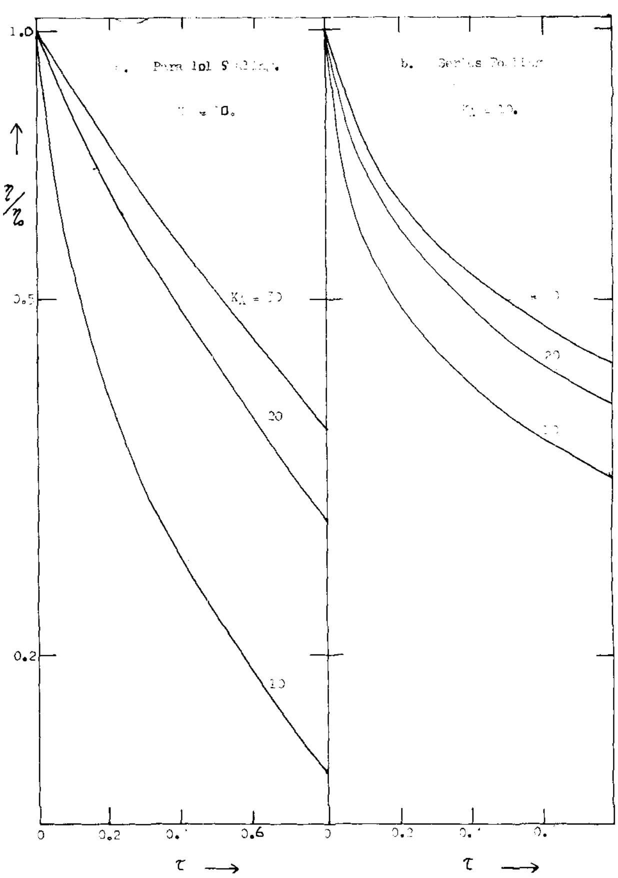

Fig. 2. Effect of K_A and K_B on relative effectiveness factor for parallel and series fouling. $\phi = 10 \cdot 5$.

Table 3. Particle Surface Temperatures

Parallel fouling			Series fouling		
K_A	K_B	θ_s	K_A	K_B	θ_s
10	10	1.07081	10	10	1.07081
20	10	1.01560	10	20	1.05039
30	10	1.00648	10	30	1.04178

Thus, the conclusions of Chu (1968) on the influence of adsorption equilibrium constants on deactivation are modified when nonisothermal behavior is considered. The example considered of simple single species reactions in series or parallel is somewhat basic. For more complex adsorption mechanisms, different behavior may be obtained, but this would require more extensive studies.

NOTATION

A = reactant species
a = dimensionless concentration of A
B = product species
b = dimensionless concentration of B
C_{A0} = bulk concentration of A
De_A = effective diffusivity of A
$f_0(\ ), f_1(\ ), f_2(\ )$ = function of ( )

h = heat transfer coefficient
h_{KA}, h_{KB} = heat of adsorption for A and B, dimensionless
K_A, K_B = dimensionless adsorption equilibrium constant for A and B
k_0 = main reaction rate constant
k_{f1}, k_{f2} = fouling reaction rate constant for parallel and series fouling, respectively
km = mass transfer coefficient
Nu^* = modified Nusselt number, $Rh/\kappa e$
R = radius of pellet
S = activity
Sh^* = modified Sherwood number, $R\,k_m/De_A$
t = process time

Greek Letters

α = geometric factor
β = thermicity factor
γ, γ_{f1}, γ_{f2} = dimensionless activation energy parameter for the main, parallel fouling and series fouling reaction
δ = dimensionless particle radial coordinate
η = effectiveness factor
η_0 = effectiveness factor at $\tau = 0$
κe = effective conductivity of particle
τ = dimensionless time
ϕ = Thiele modulus
θ = dimensionless particle temperature
θ_s = dimensionless particle surface temperature

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A Note on the Upper and Lower Solutions of a Mass Transfer Problem with Chemical Kinetics

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There has recently been great interest in applying the Nagumo Lemma (Walter, 1970) to construct upper and lower solutions to practical physical problems (Tam, 1976; McDaniel and Murthy, 1976, 1977). It has already been pointed out by Tam and Ng (1977) that the Nagumo Lemma can be employed to construct upper and lower solutions to problems which can be described by a nonlinear, parabolic, partial-differential equation. The object of this note is to expand the family of problems to which the Nagumo Lemma can be successfully applied to give upper and lower solutions to problems in chemical engineering.

In this note we construct upper and lower solutions to a system of weakly coupled parabolic equations arising from the study of a mass transfer problem with chemical kinetics (Brian et al., 1961). The problem to be considered is that in which a gaseous species A dissolves into the liquid phase and then reacts irreversibly with species B according to a second-order chemical reaction equation. Species B is a nonvolatile solute which has been dissolved into the liquid phase prior to its introduction into the gas absorber. It is assumed that the gas phase resistance to absorption is negligible, and thus the concentration of species A at the gas-liquid interface corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

The governing equations of this physical phenomenon can be expressed in terms of the following dimensionless variables (Brian et al., 1961):

$$\frac{\partial \alpha}{\partial \theta} = \frac{\partial^2 \alpha}{\partial \xi^2} - \Gamma \alpha \beta \tag{1}$$

$$\frac{\partial \beta}{\partial \theta} = \Delta \frac{\partial^2 \beta}{\partial \xi^2} - \alpha \beta \tag{2}$$

subject to

$$\alpha(\xi, 0) = 0, \quad \alpha(0, \theta) = 1, \quad \alpha(\infty, \theta) = 0 \tag{3}$$

$$\beta(\xi, 0) = 1, \quad \frac{\partial \beta}{\partial \xi}(0, \theta) = 0, \quad \beta(\infty, \theta) = 1 \tag{4}$$

The asymptotic solutions of the above systems of equations have been obtained by Pearson (1963), where he examined the following cases.

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