A Bidisperse Porosity Approach to Dilution in Catalyst Pellets with Uniform Distribution of Active Material

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Catalysts that consist of active agents imbedded in inert or low-activity matrices are of considerable importance to the petroleum refining industry. Prominent examples are cracking and hydrocracking catalysts wherein highly active zeolitic components are dispersed in relatively inactive binders such as Al_2O_3. Although structural stability and reduction of reaction severity (for highly exothermic reactions) are often the primary goals of binder addition, it has been recognized in the literature that enhancement in catalytic activity can be effected as a consequence (Ruckenstein, 1970; Varghese and Wolf, 1980; Dadyburjor, 1982, 1985; Nandarpurkar and Ruckenstein, 1984).

Activity enhancement through diluent addition can be caused through either chemical modification or physical modification of transport characteristics in the pellet. As an example of chemical modification, migration of Al atoms from the binder to form an integral part of the intracrystalline zeolitic framework can cause substantial increases in pellet activity due to acidity enhancement (Chu et al., 1985). In this paper we examine only the physical modifications of the pellet caused by dilution. Earlier research has shown that for pellets wherein the reaction is severely diffusion-limited, dilution at certain levels can help sustain overall reaction rates that are higher than the rates obtained with pellets containing active material alone. From a physical perspective, this is due to improved access of the pellet interior to the reactant, resulting in a higher concentration of reactant within the pellet and subsequently higher reaction rates and better pellet utilization.

Earlier models of pellet dilution have considered the composite pellet to consist of a matrix of diluent containing embedded microspheres of the active particles, while the undiluted pellet is treated as containing active material alone and having a monomodal porosity. Varghese and Wolf (1980) showed that this conceptualization of a composite pellet reduces to the zero dilution case of a pellet with monodisperse porosity only if the Thiele modulus of the active microspheres in the composite is constrained to values less than unity. This is much too restrictive a constraint for zeolite-based catalysts where configurational diffusivities of 10^{-10} m^2/s or lower in the zeolitic particles, coupled with high intrinsic reaction rates (Weisz, 1973) lead to values of the Thiele modulus much greater than unity.

In this paper, the composite pellet is conceptualized as an aggregate consisting of particles of active material and diluent together with interparticle voids; the pellet then has bidisperse porosity with intraparticle micropores and interparticle macropores. The bidisperse porosity concept is particularly realistic for zeolite-based pellets where the intraparticle pore sizes are much smaller than interparticle pore sizes. The bidisperse pellet has been studied by several researchers, both experimentally (Wakao and Smith, 1962) and from an effectiveness factor point of view (Mingle and Smith, 1962; Carberry, 1962; Hashmimoto et al., 1976; Ors and Dogu, 1979; Namjoshi et al., 1984). In this work, we focus on the bidisperse concept as applied to a diluted pellet and show that this conceptualization yields generalized and theoretically rigorous expressions for the rate of reaction, applicable at all levels of dilution and all values of the Thiele modulus in the active particles. The model is used to determine criteria and design parameters to predict the desirability of dilution. In addition, the model yields insight into diffusion-based discrimination (shape selectivity) between molecular species reacting in a zeolite-based pellet.

Theory

In model development, we have assumed spherical geometry for the particles and slab geometry for the pellet. For simplicity, only an isothermal reaction is considered, with first-order kinetics; the model however enables easy visualization of the physical implications of dilution.

The pellet is considered to be made up of particles of type X (the active material) with radius R_X, and of type Y with radius R_Y (the diluent). For particles of type X, the intraparticle concentration derived from conventional diffusion-reaction theory is

$$\psi_x = \frac{\psi_x^0}{\eta_x} \frac{\sinh (h_x \eta_x)}{\sinh h_x} \tag{1}$$

where h_x is the particle Thiele modulus. The differential mass balance over the pellet, assuming complete inactivity in the diluent particles is,

$$D_e \frac{d^2C}{dz^2} = MF_x \left(D_x \frac{dC_x}{dr} \right) \bigg|_{r=R_x} 4\pi R_x^2 \tag{2}$$

and in dimensionless form

$$\begin{aligned} \frac{d^2\Psi}{d\xi^2} &= (4\pi MF_x L^2 R_x) \left(\frac{D_x}{D_e} \right) \left(\frac{d\psi_x}{d\eta_x} \bigg|_{\eta_x=1} \right) \\ &= \bar{h}^2 \Psi \end{aligned} \tag{3}$$

where,

$$\bar{h}^2 = (4\pi MF_x L^2 R_x) \left(\frac{D_x}{D_e} \right) (h_x \coth h_x - 1) \tag{4}$$

In deriving Eq. 3 it has been assumed that $\Psi = \psi_x^0$, i.e., there are no interparticle concentration gradients in the direction parallel to the pellet axis. With boundary conditions,

$$\Psi = \Psi_0 \text{ at } \xi = 1 \text{ and } \frac{d\Psi}{d\xi} = 0 \text{ at } \xi = 0 \tag{5}$$

the analytical solution,

$$\Psi = \Psi_0 \frac{\cosh (\bar{h}\xi)}{\cosh \bar{h}} \tag{6}$$

for the concentration profile in the pellet is obtained. The overall rate of reaction can be derived from the mass flux at the pellet surface. Thus,

$$R = \left(\frac{D_e C_{A\text{in}}}{L} \right) \bar{h} \Psi_0 \tanh \bar{h} \tag{7}$$

It is easily proved that Eq. 7 reduces to the case of the undiluted pellet simply by substituting $F_x = 1$; thus for the undiluted pellet,

$$R' = \left(\frac{D'_e C_{A\text{in}}}{L} \right) \bar{h}' \Psi_0 \tanh \bar{h}' \tag{8}$$

with,

$$\bar{h}'^2 = 4\pi M \left(\frac{D_x}{D'_e} \right) L^2 R_x (h_x \coth h_x - 1) \tag{9}$$

where the primes are used to denote quantities that are specific to the undiluted, single-component pellet. The ratio of the rate of reaction in the composite pellet to the rate in the undiluted pellet has the form,

$$R^* = \frac{D_e}{D'_e} \frac{\bar{h}}{\bar{h}'} \frac{\tanh \bar{h}}{\tanh \bar{h}'} \tag{10}$$

The effective diffusivities D_e and D'_e are averaged over the volume fractions of the active material (X), diluent (Y), void space (Z) as proposed by Delancey (1974). Thus,

$$\begin{aligned} D_e &= D_x \epsilon_x + D_y \epsilon_y + D_z \epsilon_z \\ D'_e &= D_x \epsilon'_x + D_z \epsilon_z \end{aligned} \tag{11}$$

with $\epsilon_z = 0.26$ for close packing in the pellet, and

$$\begin{aligned} \epsilon'_x &= \epsilon_x + \epsilon_y = 0.74 \\ F_x &= \epsilon_x / (\epsilon_x + \epsilon_y) \end{aligned} \tag{12}$$

In calculations based on the above equations, the parameters and pellet properties listed in Table 1 have been used. Thus diffusivities in the active particles are in the configurational diffusivity range (Weisz, 1973), while those in the diluent and interparticle voids are within the Knudsen range. The diluent is therefore considered typical of amorphous material such as SiO_2 or Al_2O_3. Particle sizes (0.1 μm) are typical of small zeolite crystallites, small crystal ZSM-5 for example. Intrinsic rate constants can vary by several orders of magnitude depending on the reactant and zeolite acid strength (Haag et al., 1982); a representative value of 10 s^{-1} is chosen in this work. Changes in parameter values are listed in the text and accompanying figures.

Figures 1a and 1b illustrate the concept that an improved utilization of the pellet ($R^* > 1$) can be obtained at certain levels of dilution. Additionally it is seen that at all levels of dilution there is an optimal value of the diffusivity through the active material. The result is significant for cases where the intrinsic activity of the catalytic sites is unchanged with time, but diffusivities within the active particles decrease with time, by partial pore blockage for example. Figure 1b thus illustrates the time trajectory of deactivation by pore blockage for diluted pellets;

Table 1. Pellet Properties Used in the Computations*

Intrinsic rate constant, k	$10\ s^{-1}$
Radius of active grain, R_x	10^{-7} m
Radius of inert grain, R_y	10^{-7} m
Diffusivity in inert grain, D_y	$10^{-6}\ m^2/s$
Diffusivity in active grain, D_x	$10^{-10}\ m^2/s$
Interparticle diffusivity, D_z	$10^{-6}\ m^2/s$
Interparticle void volume fraction	0.26
No. of particles per unit volume M	1.77×10^{20}
Pellet half-width, L	1.0×10^{-3} m

*Default values; changes are indicated in the text and figures.

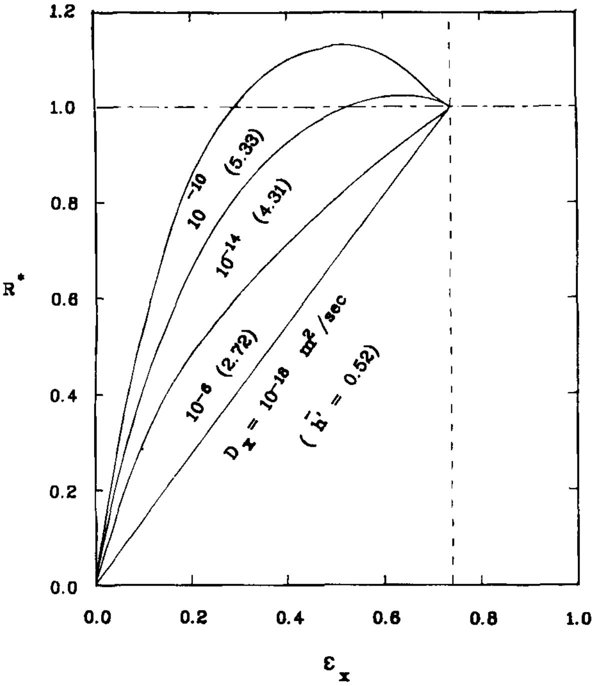

Figure 1a. Effect of dilution on R^*.

the curves indicate that although the performance (as measured by the overall rate of reaction in the pellet) of a fresh diluted pellet is inferior to that of a fresh undiluted pellet, the performance during deactivation improves relative to that of a similarly deactivated undiluted pellet, and for some levels of dilution (e.g., at $\epsilon_x = 0.5$) becomes superior to the undiluted pellet.

The above observations can be quantitatively rationalized as follows. For identical particle size ($R_x = R_y = R$), $\bar{h}$ and $\bar{h}'$ are simplified as

$$\bar{h}^2 = 3\epsilon_x(L^2/R^2)(D_x/D_e)(h_x \coth h_x - 1)$$

$$\bar{h}'^2 = 3\epsilon'_x(L^2/R^2)(D_x/D'_e)(h_x \coth h_x - 1) \qquad (13)$$

If we consider Eq. 13 for small $\bar{h}'$ (and hence small $\bar{h}$), R^* tends to its limiting value

$$R^* = \frac{D_e}{D'_e}\frac{\bar{h}^2}{\bar{h}'^2} = \frac{\epsilon_x}{\epsilon'_x} = 1.35\,\epsilon_x \qquad (14)$$

which does not indicate a maximum with ϵ_x. For large $\bar{h}'$ (and $\epsilon_x > 0$ such that $\bar{h}$ is also large), R^* has an asymptotic limit,

$$R^* = \frac{D_e}{D'_e}\frac{\bar{h}}{\bar{h}'} = \left(\frac{D_e}{D'_e}\right)^{1/2}\left(\frac{\epsilon_x}{\epsilon'_x}\right)^{1/2} \qquad (15)$$

and if $D_x \ll D_y, D_z$; $D_y = D_z$, as the parameter values in Table 1 imply, the expression can be simplified to,

$$R^* = \left(\frac{1-\epsilon_x}{\epsilon_z}\right)^{1/2}\left(\frac{\epsilon_x}{1-\epsilon_z}\right)^{1/2} \qquad (16)$$

which has a maximum at $\epsilon_x = 0.5$ of 1.14. Thus we have established the criterion that the modified Thiele modulus $\bar{h}'$ for the undiluted pellet must be greater than unity in order to justify dilution.

The functional form of $\bar{h}'$ is now examined to determine the parameters that lead to large values of the modified Thiele modulus. Equation 13 indicates that $\bar{h}'$ is dependent on h_x, the Thiele modulus of the active particles. For large h_x,

$$\bar{h}'^2 = 3\epsilon'_x\frac{L^2}{R}\frac{\sqrt{kD_x}}{D'_e} \qquad (17)$$

A few interesting observations can be inferred from Eq. 17. If reaction in the active particles is highly diffusion-controlled, this does not necessarily imply that dilution will enhance overall reaction in the pellet. For $D_x \rightarrow 0$, h_x is large; however $\bar{h}' \rightarrow 0$, implying that dilution does not benefit the pellet as shown in Figure 1 at $D_x = 10^{-18}$ m^2/s. Physically, this means that the reactant tends to bypass the active particles and to diffuse through the interparticle voids; dilution at any level will not therefore improve pellet performance. Equation 17 clearly implies that large intrinsic reaction rates k lead to high modified Thiele modulus values, indicating potential benefits in dilution. The effect of k on R^*, showing the asymptotic limit of R^* of 1.14, is illustrated in Figure 2. Equation 17 is of particular importance to zeolite-based pellets where low intraparticle configurational diffusivities coupled with high intrinsic rate constants at the acid sites lead to highly diffusion-controlled reaction in the active particles. The value of the modified Thiele modulus and the viability of dilution is then dependent on the product (kD_x).

For the case where the active particles are not transport-limited (small h_x), the modified Thiele modulus is simplified to

$$\bar{h}'^2 = \frac{L^2k\epsilon'_x}{D'_e} \qquad (18)$$

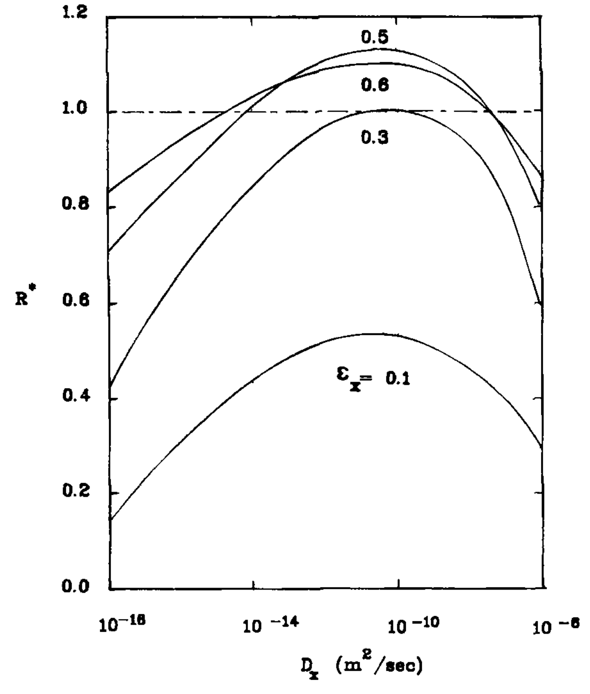

Figure 1b. Effect of intraparticle diffusivity D_x on R^*.

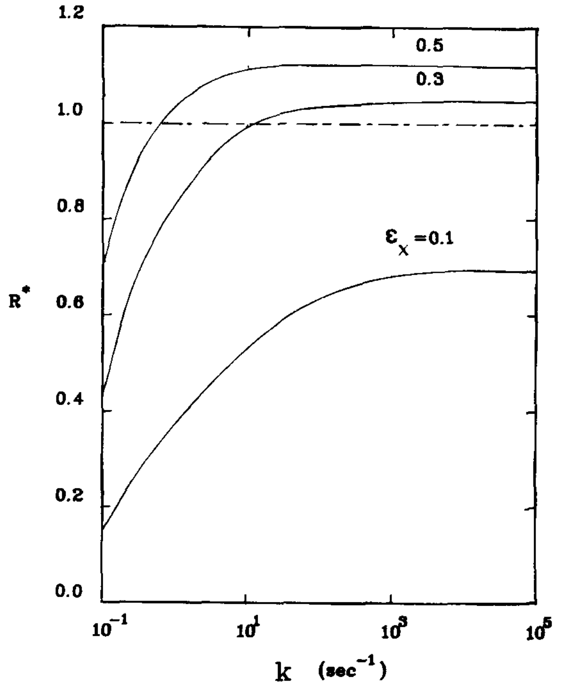

Figure 2. Effect of rate constant k on R^* at different various levels.

which is similar in form to the conventional Thiele modulus. Large $\bar{h}'$ values then imply that the pellet is effectively transport-limited while the particles are not. For example, at $D_x = 10^{-10}$ m²/s in Figure 1, $h_x = 0.032$ and $\bar{h}' = 5.34$, indicating a potential benefit in pellet dilution.

Figure 3 summarizes the trends in $\bar{h}'$ and illustrates the fact that the modified Thiele modulus exhibits a maximum with intraparticle diffusivity. Also shown in the figure is the Thiele modulus for the active particles. The distinctions between transport limitations in the active particles and transport limitations in the overall pellet can be clearly seen by comparing h_x and $\bar{h}'$ at identical values of k and D_x.

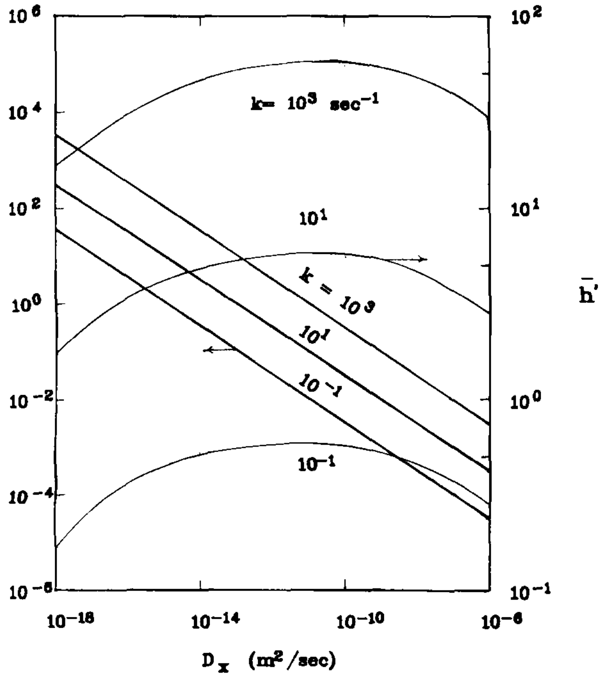

Figure 3. Variation of active particle Thiele modulus h_x and modified Thiele modulus $\bar{h}'$ with intraparticle diffusivity D_x.

The effect of diluent properties can be seen in Figure 4. Curve *a* in Figure 4 illustrates the effect of D_y and it is seen that D_y must be of the same order of magnitude as D_z in order for species Y to be used as a diluent. It can be easily shown, analogous to the development of Eq. 16, that for $D_y < 0.35D_z$ the maximum of R^* falls at physically unrealistic values of ϵ_x (i.e., $\epsilon_x > 0.74$). Curve *b* illustrates the effect caused by a diluent of particle size larger than the active particles ($R_y > R_x$) and which additionally serves to improve interparticle transport ($D_z > D_z'$).

The approach followed for the bidisperse pellet where both active medium and diluent are microporous can be used in analysis wherein the active particles and/or the diluent are nonporous. For the sake of brevity such analysis is not included, although it is mentioned that the case of nonporous active particles refers to a monodisperse undiluted pellet where the modified Thiele modulus is replaced by $h' = L(k\epsilon_x/D)^{1/2}$.

An interesting aspect of the modified Thiele modulus $\bar{h}'$ can be inferred from the solution form of the reactant concentration in the undiluted pellet, i.e.,

$$\Psi = \Psi_0 \frac{\cosh(\bar{h}'\xi)}{\cosh \bar{h}'} \qquad (19)$$

It is evident that fairly flat concentration profiles are obtained for small $\bar{h}'$; a consequence either of minimal diffusion resistance in the active particles ($D_x \longrightarrow D_y, D_z$) or of highly restricted diffusion in the active particles ($D_x \longrightarrow 0$). In the latter case, the flat concentration profile established is due to the reac-

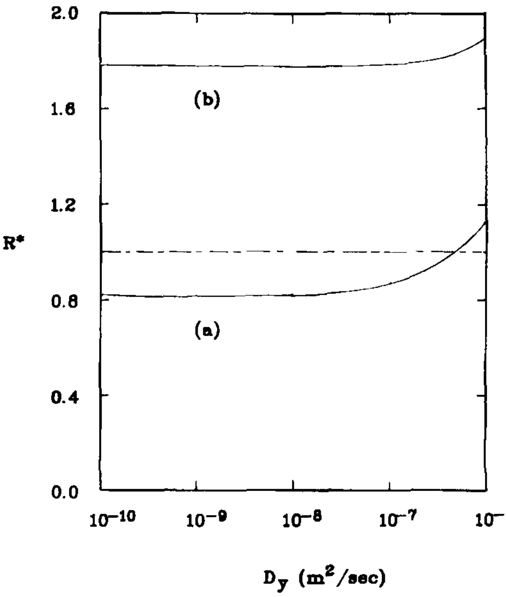

Figure 4. Effect of diluent characteristics on R^*.

a. $R_x = R_y = 10^{-7}$m; $D_z = 10^{-6}$m²; $M = 1.77 \times 10^{20}$
b. $R_x = 10^{-7}$m; $R_y = 0.5 \times 10^{-6}$m; $D_z = 0.5 \times 10\ {}^{5}$m²/s; $M = 1.198 \times 10^{20}$

Table 2. Effectiveness Factor Approach to Dilution

Case	Thiele Moduli	Effectiveness Factor	Observed Reaction Rate
	$\phi_x, \bar{h}'$	η	$\eta k C_o \epsilon_x$
i	$\phi_x, \bar{h}'$ large	$\frac{1}{\phi_x \bar{h}'}$	$\frac{k C_o \epsilon_x}{\phi_x \bar{h}'}$
ii	ϕ_x large $\bar{h}'$ small	$\frac{1}{\phi_x}$	$\frac{k C_o \epsilon_x}{\phi_x}$
iii	ϕ_x small $\bar{h}'$ small	1	$k C_o \epsilon_x$
iv	ϕ_x small $\bar{h}'$ large	$\frac{1}{\bar{h}'}$	$\frac{k C_o \epsilon_x}{\bar{h}'}$

tant bypassing the active particles. The observation has applications to shape selective hydrocracking wherein branched isomers bypass the active zeolitic particles, while straight chain hydrocarbons diffuse into the zeolitic structure and are cracked to smaller products.

The effectiveness factor approach can also be used to describe dilution in catalyst pellets of bidisperse porosity. From the conventional definition of the effectiveness factor, we have

$$\eta = \frac{D'_e}{L^2 k \epsilon_x} \bar{h}' \tanh \bar{h}' \qquad (20)$$

for an undiluted pellet. Following Carberry (1962), this expression can be rearranged to the form

$$\eta = \eta_\mu \eta_M \qquad (21)$$

where $\eta_\mu = (3/h_x^2)(h_x \coth h_x - 1)$ is a microeffectiveness factor and $\eta_M = \tanh \bar{h}'/\bar{h}'$ is a macroeffectiveness factor. Table 2 lists different limiting cases of the effectiveness factor. It is evident that the diluent can affect only the macroeffectiveness factor η_M; thus potential benefits in dilution can accrue in cases *i* and *iv* if the diluent helps decrease $\bar{h}'$ in the effectiveness factor expression. Case *ii* refers to the situation where reactant bypass of the active material occurs, and case *iii* to the situation of negligible diffusion resistance; in both situations dilution is not justified. From experimental considerations, $\bar{h}'$ can be obtained by the measurement centerline concentrations in a single-pellet reactor (Kunzru, 1984) and the application of Eq. 19. The magnitude of this experimentally obtained value of $\bar{h}'$ can thus serve as a criterion for dilution.

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Notation

C = concentration, kmol/m^3
C_{Ain} = reference concentration, kmol/m^3
D = diffusivity, m^2/s
F = number fraction
h = Thiele modulus
$\bar{h}$ = modified Thiele modulus
k = first-order rate constant, s^{-1}
L = pellet half-width (slab geometry), m
M = number of particles per unit volume
r = radial distance within particle, m
R_x = radius of particle x, m
R = overall rate of reaction in a pellet, kmol · s/m^3 cat
R^* = ratio of reaction rate for a diluted pellet to that for an undiluted pellet
z = distance from pellet center (slab geometry), m

Greek letters

ϵ = volume fraction
η = dimensionless radial distance in a particle, r/R_x
ξ = dimensionless distance in pellet, z/L
ψ = dimensionless interparticle concentration
Ψ = dimensionless interparticle concentration
$\phi_x = h_x/3$

Subscripts

e = "effective"
x = particles of type X (active particles)
y = particles of type Y (diluent)
z = interparticle voids
0 = pellet external surface

Superscripts

0 = particle external surface
$'$ = properties specific to an undiluted pellet

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