R = tube radius
r = radial variable
S = axial energy flow function, Equation (9)
T = temperature of the fluid
T_b = bulk temperature of the fluid, Equation (57)
T_0 = temperature of the fluid at $z = -\infty$
T_w = temperature of the fluid at $r=R$, Equation (58)
v_z = fluid velocity, Equation (1)
v = dimensionless fluid velocity identified below Equation (8)
V = some characteristic velocity, identified below Equation (8)
z = axial variable
z_1 = length of heating or mass exchange section, Equation (4)
Z_1 = dimensionless z_1, identified below Equation (8)

Greek Letters

ζ = dimensionless z, identified below Equation (8)
η = dimensionless r, identified below Equation (8)
θ = dimensionless T, identified below Equation (8)
θ_b, θ_w = dimensionless T_b, T_w respectively, Equations (59) and (60)
$\lambda_j, \lambda^+_j, \lambda^-_j$ = eigenvalues, positive and negative eigenvalues, Equations (30) and (33)
μ_j, μ^+_j, μ^-_j = square roots of the absolute values of λ_j, λ^+_j and λ^-_j, respectively, Equation (47)
ρ = density of the fluid
Σ = dimensionless S, Equation (19)
ϕ = vector element of $\mathcal{H}$
$\underset{\sim}{\phi}_j, \underset{\sim}{\phi}^+_j, \underset{\sim}{\phi}^-_j$ = eigenvectors corresponding to λ_j, λ^+_j and λ^-_j, Equation (30)
ψ = vector element of $\mathcal{H}$
$\tilde{\Psi}$ = function of η, equation (C13)
$<\,,\,>$ = inner product of Equation (28)
$\|\;\|$ = norm that corresponds to $<\,,\,>$, identified in Equation (35)

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Transport Phenomena in Solids with Bidispersed Pores

Existing analyses for transport phenomena in bidisperse porous media assume that the microparticles act as uniformly distributed point sinks. This article provides an analysis which determines under what conditions the point sink approximation is valid. For random packing, the concentration field inside a pellet is described by its ensemble average, i.e., the average over all possible ways in which the microparticles can be packed into the pellet. For these averaged quantities, we formulate the transport equations for a solid with bidisperse pores which provide the criteria of validity of the point sink approximation.

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SCOPE

Transient response in bidisperse porous media are conventionally analyzed by assuming that individual particles act as point sinks. With the formalism provided here, one can identify the conditions under which such an assumption can be used. The proposed formalism can be used to analyze cases in which the above approximation is not valid.

CONCLUSIONS AND SIGNIFICANCE

Transport equations for a bidispersed system based on an ensemble average have been derived. The concentrations involved in these equations provide a mean performance or response of a large number of pellets in which the microspheres are randomly distributed.

The transient response of bidisperse porous pellets can be classified into two groups.

First, only diffusion takes place, and the steady state or equilibrium profiles of concentrations are respectively linear or uniform in the macropores. The point sink approximation is valid in these cases, if, ω, the ratio between the radius of a microsphere and the major dimension of a pellet, remains below some value, say 1/20. Experimental data obtained previously had been analyzed through the point sink approximation.

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As in those systems $\omega << 1/20$, the diffusion coefficients so obtained are free of errors due to the point sink approximation.

For the second case, the steady state concentration profile in the macroparticle is nonlinear. This happens for instance when reaction takes place along with diffusion. The conditions under which the point sink approximation is valid depend as strongly on the transport coefficients and the reaction rate constant, as they do on the radius of the microspheres.

Small catalyst particles containing micropores are compacted into pellets for practical applications. This method of catalyst preparation gives rise to two widely differing pore sizes in the pellet. The pores between microparticles (macropores) are considerably larger than the micropores. As a consequence of this bidispersity in pore size, the transport rates in the pellet occur at two different levels; the rates in the macropores being much larger than the ones in the micropores. The transient response of a bidispersed system shows in some cases two steps. In the first step, the macropores attain a quasi-steady state or equilibrium. The second step is characterized by the uptake from the macropores into micropores. This has been observed experimentally by Layton and Youngquist (1969), and Ruckenstein, et al. (1971).

Various other systems besides catalyst pellets or ion-exchange resins fall under this category. A striking example is the diffusion through a mosaic of small crystals discussed by Aifantis (1979). Here the diffusion is much faster along the grain boundaries than through the grains themselves.

Ruckenstein, Vaidyanathan, and Youngquist (1971) have proposed a model for the bidisperse porous media. This model was used to analyze the transient response of a spherical pellet, composed of a large number of microspheres assumed to act as uniformly distributed point sinks. A conservation equation was written for the macropore accounting for the additional term due to the point sinks. This term was set equal to the flux to the microspheres. The conservation equation for a microsphere was then solved, subject to the boundary condition of a constant concentration on the surface. This constant concentration was identified as the local macrosphere concentration, in accordance with the point sink assumption. The microsphere concentration now being known in terms of the macrosphere concentration, the flux to a microsphere could be evaluated and the conservation equation for the macrosphere solved. This basic scheme has been adapted for specific systems by Ma and Lee (1974), Ma and Ho (1974), Lee and Ruthven (1979), and Lee, Yucel, and Ruthven (1979).

The point sink approximation appears to be a reasonable one, when the length scale over which the concentration changes significantly inside the macrosphere is large compared to the diameter of a microsphere. Although in the transient response of a macrosphere, large concentration gradients occur only for very short times and over very short distances from the surface where the step change is applied, this is not true in general. For instance, to a slab containing microspheres, a step change can be applied on one of its faces, and the initial concentration maintained on the other. If this applied concentration difference is very high, large concentration gradients will exist at all times throughout the slab.

Thus, it is possible that the point sink approximation is unsuitable under certain conditions. Consequently, it is necessary to know under what conditions this approximation cannot hold as well as to provide a method for analyzing such cases. In order to do this, it is necessary to derive a more general conservation equation, which obviously should contain the point sink approximation as a special case.

To provide such a model, we note that in principle at least, one should solve N-conservation equations for N-microspheres and one for the macropores, subject to relevant initial and boundary conditions. This being a difficult task, we try instead to obtain an overall description for a random distribution of microspheres. The problem encountered is that the detailed concentration field depends on the way in which the N-microspheres are placed in the pellet. There are a large number of arrangements compatible with randomness; instead of the detailed concentration field corresponding to one of these, we will try to obtain the overall concentration field, that is, the *mean* over all such possibilities.

Consider a large number of pellets of equal dimensions, and each containing N-microspheres randomly distributed. Each pellet, however, differs from others in that the microspheres are arranged differently. The same step change is applied to every pellet. Then the ensemble average of the concentration inside a pellet at location $\mathbf{r}$, is its average over all pellets. It is assumed that the total number of pellets is sufficiently large and represent all possible arrangements of microspheres. Formally, if there are N-particles (microspheres) with centers at $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$, the concentration is a function of position $\mathbf{r}$, as well as of $\{\mathbf{r}_i\}$. If $p_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ denotes the probability density function of such an arrangement of N-particles, the ensemble average is defined as:

$$<C>_N(\mathbf{r}) = \underset{\substack{N \text{ volume} \\ \text{integrals}}}{\int\int\int} p_N(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)C(\mathbf{r};\mathbf{r}_1\ldots\mathbf{r}_N)d\mathbf{r}_1\, d\mathbf{r}_2\ldots d\mathbf{r}_N \tag{1}$$

where $d\mathbf{r}_i$ is the differential volume element containing the point $\mathbf{r}_i$. We also define here for future reference, the conditional average $<C>_{N-1}(\mathbf{r},\mathbf{r}_N)$:

$$<C>_N = \int <C>_{N-1}\, p(\mathbf{r}_N)d\mathbf{r}_N \tag{2}$$

where p is the probability density function of finding the N^{th} particle in the volume V_T, when the remaining $(N-1)$ particles are already present. In other words, $<C>_{N-1}$ is the ensemble average concentration, when one particle is fixed and the averaging is carried out over $N-1$ particles.

For sufficiently small void volume fractions, ϵ_o, the number of ways of arranging the microspheres becomes restricted; at $\epsilon_o = 0.2595$, there is only one way of arranging the particles, that is, rhombohedral packing. At very low dilutions, once again the ensemble average loses its meaning.

Typical values of ϵ_o in bidisperse systems quoted by Ruckenstein, et al. (1971) are of the order of 0.4. We also observe that ϵ_o for random packing falls in this range (see Happel and Brenner, 1965). Hence, our assumption that microspheres are packed randomly into the pellet is consistent with these observations. We conclude here that ensemble averaging is both appropriate and convenient for bidisperse porous media.

In the next sections, we first start with a basic integral transport equation for the macropores. To this, we apply the ensemble average. The two sets of volume integrals (due to the integral mass balance and the ensemble average) can be interchanged to obtain a conservation equation for the ensemble averaged quantities, which holds pointwise in the pellet. No restrictions on the size of the pellet or its shape appear. The conservation equation contains a term involving the concentration inside a microsphere besides the terms involving the macropore concentration. To evaluate this term, we solve the transport equations in the microspheres under very general conditions and thus express this term in terms of the macropore concentration. The resulting equation, provides the *averaged* transport equation for an effectively homogeneous medium, that is, made homogeneous through averaging.

Transient response to several systems are analyzed next. It is shown that when the asymptotic behavior for large times is equilibrium or a linear steady state profile, under mild restrictions, the point sink approximation is valid. Depending on the values of the physical constants that appear, the point sink approximation can become inapplicable when the steady state profile is nonlinear. The more general method suggested here can be used to analyze the latter cases.

AVERAGED CONSERVATION EQUATION IN A PELLET

The integral conservation equation for a macroparticle is:

$$\frac{\partial}{\partial t}\int_{V_o} C_o\,dV = \mathscr{D}_o \int_{S_o} (\mathbf{n}_o \cdot \nabla C_o)dS + \sum_{j=1}^{N} \mathscr{D}_o \int_{S_j} (\mathbf{n}_j \cdot \nabla C_o)dS \tag{3}$$

The first surface integral is converted to volume integral with the divergence theorem. Together with the boundary conditions:

$$\mathscr{D}_o(\mathbf{n}_o \cdot \nabla C_o) = \epsilon_j \mathscr{D}_j(\mathbf{n}_j \cdot \nabla C_j) \text{ on } S_j \tag{4}$$

Eq. 3 becomes:

$$\frac{\partial}{\partial t}\int_{V_o} C_o\,dV = \mathscr{D}_o \int_{V_o} \nabla^2 C_o\,dV + \sum_{j=1}^{N} \epsilon_j \mathscr{D}_j \int_{S_j} (\mathbf{n}_j \cdot \nabla C_j)dS \tag{5}$$

Here, C_o and C_j are functions of $\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N$. Taking the ensemble average of Eq. 5, we get:

$$\frac{\partial}{\partial t}\int_{V_o} <C_o>_N dV = \mathscr{D}_o \int_{V_o} \nabla^2 <C_o>_N dV + \sum_{j=1}^{N} \epsilon_j \mathscr{D}_j \int_{S_j} (\mathbf{n}_j \cdot \nabla <C_j>_N)dS \tag{6}$$

In order to convert the global Eq. 6 to a local equation, we use the relation (Eq. 2) between the ensemble average concentrations averaged over N and $N-1$ microspheres, respectively. If all spheres are identical, Eq. 6 together with Eq. 2 reduces to:

$$\frac{\partial}{\partial t}\int_{V_o} <C_o>_N dV = \mathscr{D}_o \int_{V_o} \nabla^2 <C_o>_N dV + N\,\epsilon_i \mathscr{D}_i \int_{V_o+V} d\mathbf{r}\; p(\mathbf{r}) \int_S \mathbf{n}_i \cdot \nabla <C_i>_{N-1}\,dS \tag{7}$$

where $<C_i>_{N-1}$ is the ensemble averaged concentration inside the microsphere where the averaging has been performed with respect to all particles *other* than itself. The point $\mathbf{r}$ inside the volume integral on the right represents the center of the microsphere. Since the volume V_o is arbitrary:

$$\frac{\partial}{\partial t} <C_o>_N = \mathscr{D}_o \nabla^2 <C_o>_N + N\,\epsilon_i \mathscr{D}_i\, p(\mathbf{r}) \int_S \mathbf{n}_i \cdot \nabla <C_i>_{N-1}\,dS \tag{8}$$

holds pointwise. Eq. 8 is an approximate one, obtained by changing the volume of integration for the second term on the right in Eq. 7 from $V_o + V$ to V_o. Since $V << V_o$, such an approximation is reasonable. It is now necessary to evaluate $p(\mathbf{r})$. We note that point $\mathbf{r}$ belongs to the volume V_o. The simplest approximation for p is $1/V_o$ which constitutes a lower bound, because not the entire volume V_o is available to the *center* of the microsphere. Eq. 8 becomes

$$\frac{\partial}{\partial t} <C_o>_N = \mathscr{D}_o \nabla^2 <C_o>_N + \frac{n}{\epsilon_o} \mathscr{D}_i\, \epsilon_i \int_S \mathbf{n}_i \cdot \nabla <C_i>_{N-1}\,dS \tag{9}$$

where n is the number of microspheres per unit volume of the pellet. If N is sufficiently large, it is reasonable to assume that $<C_i>_{N-1} \approx <C_i>_N$.

Tam (1969) has used a similar averaging procedure for dispersions to obtain an averaged momentum transport equation and has made a similar assumption relating the two averages. Dropping the subscripts N and $N-1$, Eq. 9 can be rewritten as:

$$\frac{\partial}{\partial t} <C_o> = \mathscr{D}_o \nabla^2 <C_o> + \frac{n}{\epsilon_o} \mathscr{D}_i\, \epsilon_i \int_S \mathbf{n} \cdot \nabla <C_i> dS \tag{10}$$

$<C_o>$ and $<C_i>$ in Eq. 10 describe the mean concentration fields. If n, the number of particles per unit volume, is large, a small volume, δV_T, will contain many such particles. As the microspheres are packed randomly, all possible arrangements will show up in δV_T. Consequently under these conditions, the response of δV_T from pellet to pellet will not differ greatly. This leads us to conclude that the performance of one pellet is very close to the mean described by Eq. 10, when n is reasonably large.

In Eq. 10, one may also include the adsorption on the pore walls, by adding an accumulation term on the walls of the macropores in Eq. 4 which becomes:

$$\frac{\partial \mathscr{S}_o}{\partial t} + \epsilon_i \mathscr{D}_i(\mathbf{n}_i \cdot \nabla C_i) = \mathscr{D}_o(\mathbf{n}_o \cdot \nabla C_o) \text{ on } S_i \tag{11}$$

It follows that:

$$\frac{\partial}{\partial t} <C_o> = \mathscr{D}_o \nabla^2 <C_o> + \frac{n}{\epsilon_o} \epsilon_i \mathscr{D}_i \int_S \mathbf{n} \cdot \nabla <C_i> dS + \frac{1}{V_o}\frac{\partial}{\partial t}\int_{S_{\text{wall}}} <\mathscr{S}_o> dS \tag{12}$$

An averaged Henry's law is assumed to hold between the bulk and the surface concentrations, which can be written as:

$$\frac{1}{V_o}\int_{S_{\text{wall}}} <\mathscr{S}_o> dS = H_o\, s_o <C_o> \tag{13}$$

where H_o is the Henry's constant and s_o is the external surface of the microparticles per unit void volume of the macroparticle.

We write the final equation in dimensionless form,

$$\frac{\partial}{\partial \tau}\theta_o = \nabla^{*2}\theta_o - \frac{\beta}{4\pi}\int_0^{2\pi} d\phi \int_{-1}^{1} d\mu \left(\frac{\partial \theta_i}{\partial \gamma}\right)_{\gamma=1} \tag{14}$$

where

$$\theta_o = \frac{<C_o>-C^*}{C_\infty - C^*}, \quad \tau = \frac{\mathscr{D}_o\, t}{(1+s_oH_o)R_o^{\,2}}, \quad \gamma = \frac{r_i}{R_i}$$

$$\theta_i = \frac{<C_i>-C^*}{C_\infty - C^*}, \quad \beta = \frac{3(1-\epsilon_o)\epsilon_i}{\epsilon_o}\,\frac{\mathscr{D}_i\, R_o^{\,2}}{\mathscr{D}_o\, R_i^{\,2}}$$

and $\nabla^{*2} = R_o^{\,2}\nabla^2$, μ is the cosine of the polar angle θ, ϕ is the azimuthal angle. R_o is the representative dimension of the pellet. The microparticles are spheres of radius R_i, and r_i is the radial coordinate in the microspheres. To a system initially at C^*, a step change is applied on an outer surface to C_∞ at $t = 0$. The initial condition to Eq. 14 becomes:

$$\theta_o|_{\tau=0} = 0 \tag{15}$$

We note that θ_i is a function of $\mathbf{r}$, the interior points of the microsphere, and $\mathbf{r}_i$ the center of the microsphere. However, $\mathbf{r}_i$ corresponds to the independent variable (position) of θ_o.

CONSERVATION EQUATION FOR SINGLE MICROSPHERE

The ensemble averaged conservation equation in a microsphere can be derived in a similar fashion. We get:

$$\frac{\partial <C_i>}{\partial t} = \mathscr{D}_i \nabla^2 <C_i> + \frac{1}{\epsilon_i V}\int_{S_{\text{wall}}} \frac{\partial}{\partial t} <\mathscr{S}_i> dS \tag{16}$$

which, together with Henry's law:

$$\frac{1}{\epsilon_i V}\int_{S_{\text{wall}}} <\mathscr{S}_i> dS = H_i\, s_i <C_i> \tag{17}$$

where H_i and s_i are Henry's constant and the surface area per unit void volume, yields in dimensionless form:

$$\frac{\partial\theta_i}{\partial\tau} = \alpha\,\tilde{\nabla}^2\theta_i \tag{18}$$

where

$$\alpha = \frac{R_o^2\,\mathscr{D}_i(1 + s_o H_o)}{R_i^2\,\mathscr{D}_o(1 + s_i H_i)} \text{ and } \tilde{\nabla}^2 = R_i^2\nabla^2\cdot$$

Since Eq. 18 is subject to the initial condition:

$$\theta_i|_{\tau=0} = 0 \tag{19}$$

taking the Laplace transform of Eq. 18 we get:

$$p\,\bar{\theta}_i = \alpha\tilde{\nabla}^2\bar{\theta}_i \tag{20}$$

$\bar{\theta}_i$ is subject to the continuity condition:

$$\bar{\theta}_i = \bar{\theta}_o \text{ on } S_i \tag{21}$$

Jury (1977) expanded the right hand side of Eq. 21 with a Taylor series expansion about the center of the particle. Condition Eq. 21 was then accommodated by comparing the expansion term by term with a similar expansion for $\bar{\theta}_i$. This scheme is based on strong conditions of symmetry and the unidirectional nature of θ_o and cannot be extended to systems other than the case of a rectangular slab for which it has been derived. $\bar{\theta}_o$ is expanded in Taylor series about the center of the microsphere in terms of x_s, the coordinate of the axis of symmetry. First, this method can only apply if the concentration θ_o is unidirectional, that is, function of x_s alone. Secondly, it will lead to terms $\partial^2/\partial x_s^2$ instead of the Laplacian ∇^2, the two being the same only when the pellet is a rectangular slab. Thus, to adapt the basic scheme of Jury to the general case where θ_o and θ_i are three dimensional, it is necessary to obtain a Taylor series expansion in three dimensions. This is conveniently expressed through a symbolic operator, leading to:

$$\bar{\theta}_i|_{\gamma=1} = \exp\,(\mathbf{R}_i\cdot\nabla_Q)\bar{\theta}_{oQ} \tag{22}$$

The symbolic operator, $\exp(\mathbf{R}_i\cdot\nabla_Q)$, is explained in the following way. First, ∇_Q has relevance only when it operates on $\bar{\theta}_{oQ}$, for instance $\nabla_Q\bar{\theta}_{oQ} = \nabla\bar{\theta}_o$ evaluated at the point Q which is obviously the center of the microsphere. Secondly, on expanding the exponential, we obtain the Taylor's series on the surface S_i, expanded about point Q.

The advantage in the symbolic operator representation lies in the fact that ∇_Q can be treated as a constant vector in subsequent integrations. Consequently, we define the polar angle θ and azimuthal angle ϕ with ∇_Q as the reference. From the symmetry of a sphere, $\mathbf{R}_i\cdot\nabla_Q = \mu R_i\nabla_Q$, where μ is the cosine of the polar angle. It is this last simplification together with the nature of the solution to Eq. 20 that enormously cuts down the required calculations. Great simplification is achieved over the detailed procedure used by Jury which is already laborious when $\bar{\theta}_o$ is unidimensional. We note that ultimately we are required to interpret the scalar operator ∇_Q^2 which is the Laplacian operator. Solution to Eq. 20 subject to boundedness is:

$$\bar{\theta}_i = \sum_{k=0}^{\infty} a_k i_k\left(\gamma\sqrt{\frac{p}{\alpha}}\right) V_k(\theta,\phi) \tag{23}$$

where i_k is the modified spherical Bessel function of order k (Abramowitz and Stegun, 1972) and V_k are surface spherical harmonics (Hobson, 1931),

$$V_k = P_k(\mu) + \sum_{m=1}^{k}(c_m\sin m\phi + b_m\cos m\phi)\times P_k^m(\mu) \tag{24}$$

where P_k^m are Legendre polynomials of degree k and order m (Abramowitz and Stegun, 1972) and a_k, c_m, b_m are constants. It is seen that $\bar{\theta}_i$ appears in Eq. 14 only as a surface integral $\int_S \mathbf{n}\cdot\nabla\bar{\theta}_i dS$. This integral can be reduced to integrals of type $\int_{-1}^{1} V_k\,P_o(\mu)d\mu$, where $P_o(\mu) = 1$. Since

$$\int_0^{2\pi} d\phi\int_{-1}^{1} d\mu\, P_n^m(\mu)\,{}^{\cos}_{\sin}(m\phi)\cdot P_{n'}^{m'}(\mu)\,{}^{\cos}_{\sin}(m'\,\phi) = 0 \tag{25}$$

whenever $n \neq n'$ or $m \neq m'$, only the $k = 0$ term in Eq. 23 survives this surface integration, the rest are zeros. The method for evaluating a_o and the surface integral is given in Appendix. We provide here the final result,

$$\int_0^{2\pi} d\phi\int_{-1}^{1} d\mu\left(\frac{\partial\bar{\theta}_i}{\partial\gamma}\right)_{\gamma=1} = 4\pi\left[\frac{\sinh(R_i\nabla)}{(R_i\nabla)}\right]\bar{\theta}_o\,Y \tag{26}$$

where

$$Y = \sqrt{\frac{p}{\alpha}}\coth\left(\sqrt{\frac{p}{\alpha}}\right) - 1 \tag{27}$$

and the subscript Q has been dropped.

BASIC CONSERVATION EQUATION FOR THE PELLET

Eq. 14 is the governing equation for conservation in the pellet. The last term in Eq. 14 can be obtained from Eq. 26. Taking the Laplace transform of Eq. 14 subject to Eq. 15 and substituting from Eq. 26, we get:

$$p\bar{\theta}_o = \nabla^{*2}\bar{\theta}_o - \beta Y\frac{\sinh(\omega\nabla^*)}{(\omega\nabla^*)}\bar{\theta}_o \tag{28}$$

Noting (Abramowitz and Stegun, 1972) that

$$\frac{\sinh(\omega\nabla^*)}{(\omega\nabla^*)} = 1 + \frac{\omega^2\nabla^{*2}}{3!} + \frac{\omega^4\nabla^{*4}}{5!} + \ldots, \tag{29}$$

we observe that it is not necessary to evaluate ∇^* as it occurs only in even powers and ∇^{*2} is the Laplacian operator. At least in principle Eq. 28 can be solved exactly. If $\bar{\theta}_\lambda$ satisfies the equation:

$$\nabla^{*2}\bar{\theta}_\lambda = \lambda\bar{\theta}_\lambda \tag{30}$$

then $\bar{\theta}_\lambda$ is a solution of Eq. 28 with λ satisfying

$$p = \lambda - \beta Y\frac{\sinh(\omega\lambda)}{(\omega\lambda)} \tag{31}$$

The expansion (Eq. 29) has been used to obtain the above form. We also know that there are only two boundary conditions for Eq. 28. However, it is through Eq. 30 that one can realize that these boundary conditions are sufficient for Eq. 28 and that the problem is well posed. In principle, Eq. 30 can be solved subject to the relevant boundary conditions. However, the inversion of the Laplace transform, $\bar{\theta}_\lambda$, becomes torturous. In an effort to simplify the problem and maintain a correspondence with the point sink approximation of Ruckenstein, et al. (1971), we cut off the series on the right in Eq. 29 after the first two terms since $\omega << 1$. The resulting approximate equation remains second order and therefore the problem is also well posed. Eq. 28 becomes

$$\nabla^{*2}\bar{\theta}_o = \frac{p + \beta Y}{1 - \dfrac{\omega^2\beta Y}{6}}\bar{\theta}_o \tag{32}$$

which reduces to the point sink approximation of Ruckenstein, et al. (1971), if $\omega^2\beta Y/6 << 1$.

Eq. 32 still needs boundary conditions. These will depend on the geometry of the pellet and the nature of the step change. We analyze few important cases next.

(a) Transient Response in a Macrosphere. In this problem the concentration inside all the pores is initially at C^*. At time $t = 0$,

a step change to a concentration, C_∞, is applied on the outer surface of the macrosphere. This problem has been analyzed under the point sink approximation by Ruckenstein, et al. (1971). In dimensionless form, the conservation equation for the macrosphere can be obtained from Eq. 32:

$$\frac{1}{\eta^2}\frac{\partial}{\partial\eta}\left[\eta^2\frac{\partial}{\partial\eta}\overline{\theta}_o\right] = \frac{p+\beta Y}{1-\dfrac{\omega^2\beta Y}{6}}\overline{\theta}_o \tag{33}$$

where $\eta = r_o/R_o$, r_o is the radial position from the center of the macrosphere and R_0 is its radius. The boundary conditions, under Laplace transform become

$$\overline{\theta}_o = \frac{1}{p} \text{ at } \eta = 1 \tag{34}$$

together with the condition of boundedness on $\overline{\theta}_o$. The method of solution of Eq. 33 and its inversion follow exactly the procedure given by Ruckenstein, et al. (1971), in the Appendix. We skip the details here to give the final solution, which is:

$$\theta_o = 1 + \frac{4\pi}{\beta\eta}\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k(-1)^k\sin(k\pi\,\eta)e^{-\alpha\xi^2{qk}\,\tau}}{J_{qk}} \tag{35}$$

where

$$J_{qk} = \xi_{qk}^2\left[\frac{\alpha}{\beta} + \left\{\operatorname{cosec}^2\xi_{qk} - \frac{1}{\xi_{qk}^2}\left(1 - \frac{k^2\pi^2/\beta}{1-k^2\pi^2\omega^2/6}\right)\right\}\times (1 - k^2\pi^2\omega^2/6)\right] \times \left\{1 + \frac{\omega^2\beta}{6}(1-\xi_{qk}\cot\xi_{qk})\right\}^{-1} \tag{36}$$

and ξ_{qk} are the roots of

$$\alpha\xi^2 + \beta\left(1 - \frac{k^2\pi^2\omega^2}{6}\right)(1-\xi\cot\xi) = k^2\pi^2 \tag{37}$$

The fractional uptake at time τ, is:

$$\frac{M_t}{M_\infty} = \frac{\displaystyle\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k^2[1-\exp(-\alpha\xi_{qk}^2\tau)]}{\xi_{qk}^2J_{qk}}}{\displaystyle\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k^2}{\xi_{qk}^2J_{qk}}} \tag{38}$$

We note that ξ_{qk} for $q > 1$ have negligible contributions in Eq. 38. Now, the maximum value of k for which ξ_{qk} is significant in Eq. 38 is determined by α and β, both of which are proportional to $\mathscr{D}_i/\mathscr{D}_o\omega^2$. This dependence of k_{max} on $\mathscr{D}_i/\mathscr{D}_o$ and ω is however very weak. For instance, for $\mathscr{D}_i/\mathscr{D}_o \sim 10^{-8}$, $k_{max} \sim 6$, for ω between 10^{-3} to 0.05. For $\mathscr{D}_i/\mathscr{D}_o \sim 1$, k_{max} drops to 1. If the point sink approximation is to hold, $k_{max}^2\pi^2\omega^2/6 << 1$ in Eq. 37. If $k^2_{max}\pi^2\omega^2/6 \sim 0.1$, this translates to $\omega \sim 0.05$ for $\mathscr{D}_i/\mathscr{D}_o \sim 10^{-8}$ and $\omega \sim 1/3$ for $\mathscr{D}_i/\mathscr{D}_o \sim 1$. These conditions are easily satisfied in the usual bidisperse porous media. However, since these results indicate the mean, pellets with large ω; for example, $\sim 1/3$ may show large fluctuations about this mean.

(b) Transient Response in a Macroslab. This system was analyzed by Jury (1977). In this problem, a rectangular slab is initially at a concentration C^*. At time $t = 0$, a step change to a concentration C_∞, is applied on one face of the slab; that is, at $x = R_o$ and, the concentration C^* is maintained on the other face, $x = 0$. In dimensionless terms, the conservation equation can be obtained from Eq. 32 as:

$$\frac{\partial^2}{\partial\eta^2}\overline{\theta}_o = \frac{p+\beta Y}{1-\dfrac{\omega^2\beta Y}{6}}\overline{\theta}_0 \tag{39}$$

where $\eta = x/R_o$, R_o is the thickness of the slab and x is the coordinate in that direction. Together with the boundedness of $\overline{\theta}_o$, the boundary conditions are:

$$\overline{\theta}_o = \frac{1}{p} \text{ at } \eta = 1 \tag{40}$$

$$\overline{\theta}_o = 0 \text{ at } \eta = 0 \tag{41}$$

Eq. 39 can be solved to obtain:

$$\theta_o = \eta + \frac{4\pi}{\beta}\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k(-1)^k\sin(k\pi\,\eta)}{J_{qk}} \times \exp\{-\alpha\xi_{qk}^2\tau\} \tag{42}$$

ξ_{qk} and J_{qk} are given by Eqs. 36 and 37. The uptake M_t/M_∞ is given by Eq. 38, except that only the odd values of k are summed. The results do not differ significantly from the case of a macrosphere discussed earlier, even though very large concentration gradients can occur. The reasons will be discussed later in detail. Eqs. 39 and 42 have been previously obtained by Jury (1977).

(c) Transient Response in a Finite Cylinder. Here we analyze the case of a cylinder with one end at the axial position $z = 0$ and the other end at $z = L$. The surface at the radial position $r = R_o$ is insulated. The system is initially at a concentration C^*. At time $t = 0$, a step change to a concentration, C_∞, is applied on one end of the cylinder, that is, at $z = 0$. The concentration field $\overline{\theta}_o$ is expected to vary in two directions: axial and radial. The conservation equation is obtained from Eq. 32 as:

$$\frac{1}{\eta}\frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\overline{\theta}_o\right) + \frac{\partial^2}{\partial\zeta^2}\overline{\theta}_o = \frac{p+\beta Y}{1-\dfrac{\omega^2\beta Y}{6}}\overline{\theta}_o \tag{43}$$

where $\eta = r/L$, $\zeta = z/L$ and L is the length of the cylinder. Eq. 43 is subject to the condition of symmetry as:

$$\frac{\partial}{\partial\eta}\overline{\theta}_o = 0 \text{ at } \eta = 0, \tag{44}$$

of insulation on the surface,

$$\frac{\partial}{\partial\eta}\overline{\theta}_o = 0 \text{ at } \eta = R_o/L \tag{45}$$

$$\overline{\theta}_o = \frac{1}{p} \text{ at } \zeta = 0 \tag{46}$$

and

$$\overline{\theta}_o = 0 \text{ at } \zeta = 1 \tag{47}$$

We obtain the solution in terms of a cross-section averaged concentration $<\overline{\theta}_o> = 2\int_0^1\overline{\theta}_o\,\eta d\eta$. Eq. 44 becomes:

$$\frac{\partial^2<\overline{\theta}_o>}{\partial\zeta^2} = \frac{p+\beta Y}{1-\omega^2\beta Y}<\overline{\theta}_o> \tag{48}$$

where Eqs. 44 and 45 have been used to obtain Eq. 48. The solution to Eq. 48 is:

$$<\theta_o> = (1-\zeta) - \sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{2\sin(k\pi\zeta)\exp\{-\alpha\xi_{qk}^2\tau\}}{\xi_{qk}\left[\dfrac{d}{d\xi}\sin(M^{\frac{1}{2}})\right]_{\xi=\xi_{qk}}} \tag{49}$$

where

$$M(x) = \frac{\alpha x^2+\beta(1-x\cot x)}{1-\dfrac{\omega^2\beta}{6}(1-x\cot x)} \tag{50}$$

and ξ_{qk} is given by Eq. 37

We analyze here briefly, the results of problems (*a*)-(*c*). It is seen in Eq. 37 that if $k^2\pi^2\omega^2/6 << 1$ the point sink approximation applies. The effect of the diffusivity ratio enters only indirectly, that is, in determining the value of k which enters into the inequality.

Although in problem (*a*) near $\tau = 0$ the concentration gradients are large, they also last for a very short time. Consequently, it is not surprising that these effects are not felt and the point sink approximation holds. However in (*b*) and (*c*), the gradients are always large but the results obtained do not differ in nature from the other case studied. The reason becomes clear on examining Eqs. 26 and 29. The point sink approximation (obtained by taking the first term on the right in Eq. 29) is not *just proportional to the concentration* $\bar{\theta}_o$ at the center of the microsphere, but takes into account the linear variations in $\bar{\theta}_o$ with position. This can be checked from Eq. 29, where only *even* powers of ∇^* appear. Consequently, the two cases (linear steady state profile or equilibrium) are of the same nature. This implies that in both cases the point sink approximation applies under the *same restrictions on the ratio* ω, discussed in problem (*a*). The conclusion leads us to the case where the point sink approximation may not apply, when the steady state profile is *both* nonlinear and steep. We look into one such problem in (*d*).

(*d*) *Steady State Profile in a Macrosphere with a First Order Reaction on the Pore Walls.* We look into the case where the reactant diffuses into the macrosphere from its surface which is maintained at concentration C_∞. The concentration fields are at steady state both in the macro and microspheres, the diffusing reactant being adsorbed on the solid and then consumed by a first order chemical reaction on the surface. At steady state, the rate of adsorption is equal to the rate of reaction; that is, in terms of per unit void volume the rates of reaction in the micro and macrospheres are given by $s_iK_i(C_i/H_i - \mathscr{S}_i) = s_ik\mathscr{S}_i$ and $s_oK_o(C_o/H_o - \mathscr{S}_o) = s_ok\mathscr{S}_o$, respectively. Eliminating $\mathscr{S}_i$ and $\mathscr{S}_o$, we obtain the rates in terms of C_i and C_o respectively. Taking the ensemble average, we get the conservation equations for the micro and macrospheres as:

$$\mathscr{D}_i \nabla^2 <C_i> = \frac{s_ikK_i<C_i>}{H_i(k + K_i)} \tag{51a}$$

and

$$\mathscr{D}_o \nabla^2 <C_o> = \frac{s_okK_o<C_o>}{H_o(k + K_o)} + \frac{\mathscr{D}_iR_i^2n\epsilon_i}{\epsilon_o} \int_0^{2\pi} d\phi \int_{-1}^{1} \left[\frac{\partial}{\partial r} <C_i>\right]_{r=R_i} \times d\mu \tag{51b}$$

The *second term* on the right hand side of Eq. 51b remains as in Eq. 10. Nondimensionalizing, we get:

$$\tilde{\nabla}^2\theta_i = \delta_i^{-1}\theta_i \tag{52}$$

for the microsphere, and

$$\nabla^{*2}\theta_o = \delta_o^{-1}\theta_o + \frac{\beta}{4\pi}\int_0^{2\pi} d\phi \int_{-1}^{1} d\mu \left(\frac{\partial\theta_i}{\partial r}\right)_{r=1} \tag{53}$$

for the macrosphere, where

$$\delta_i = \frac{\mathscr{D}_iH_i(k + K_i)}{kK_is_iR_i^2}, \tag{54}$$

$$\delta_o = \frac{\mathscr{D}_oH_o(k + K_o)}{kK_os_oR_o^2}, \tag{55}$$

$\theta_o = <C_o>/C_\infty$ and $\theta_i = <C_i>/C_\infty$. The other symbols are as before. In solving Eq. 52, we note that it is identical to the previously obtained Eq. 20 for the unsteady state case with δ_i replacing α/p. The boundary conditions of boundedness on θ_i and continuity of θ_o and θ_i at the microsphere interface, are also as before. Thus, the solution to Eq. 52 is similar to that of Eq. 20, Eq. 23 with p/α replaced with δ_i^{-1}. Finally, the integral

$$\int_0^{2\pi} d\phi \int_{-1}^{1} d\mu \left(\frac{\partial\theta_i}{\partial r}\right)_{r=1} = 4\pi\frac{\sinh(R_i\nabla)}{(R_i\nabla)}\,\theta_o \times (\delta_i^{-\frac{1}{2}}\coth \delta_i^{-\frac{1}{2}} - 1) \tag{56}$$

is obtained by replacing p/α with δ_i^{-1} in Eq. 26.

With Eq. 56, Eq. 53 becomes

$$\frac{1}{\eta}\frac{\partial}{\partial\eta}\left[\eta\frac{\partial}{\partial\eta}\theta_o\right] = \chi\,\theta_o \tag{57}$$

where

$$\chi = \frac{\delta_o^{-1} + \beta\left[\frac{1}{\sqrt{\delta_i}}\coth\frac{1}{\sqrt{\delta_i}} - 1\right]}{1 - \frac{\omega^2\beta}{6}\left[\frac{1}{\sqrt{\delta_i}}\coth\frac{1}{\sqrt{\delta_i}} - 1\right]} \tag{58}$$

Eq. 57 was obtained by taking only the first two terms in the expansion of $\sinh(R_i\nabla)/(R_i\nabla)$, as before. Eq. 57 is subject to the boundary condition of

$$\theta_o = 1 \text{ at } \eta = 1 \tag{59}$$

besides the condition of boundedness of θ_o. The solution is:

$$\theta_o = \frac{1}{\eta}\,\frac{\sinh(\eta\sqrt{\chi})}{\sinh(\sqrt{\chi})} \tag{60}$$

Comparing Eqs. 57 to 60 to the previously treated unsteady state case for a macrosphere [problem(a)], the point sink approximation is seen to be valid if

$$\frac{\omega^2\beta}{6}\left[\frac{1}{\sqrt{\delta_i}}\coth\frac{1}{\sqrt{\delta_i}} - 1\right] << 1.$$

This always holds when $\delta_i^{-\frac{1}{2}}$ is small; if $\delta_i^{-\frac{1}{2}}$ is large, it should satisfy the inequality

$$\delta_i^{-\frac{1}{2}} << \frac{\mathscr{D}_o}{\mathscr{D}_i}$$

for the point sink approximation to be valid. Here, $\delta_i^{-\frac{1}{2}}$ is the Thiele modulus of the microsphere.

Thus, as the steady state profile is nonlinear, it can give rise to cases where the point sink approximation is not valid. This range is sensitive to the values of $\mathscr{D}_i$, $\mathscr{D}_o$, k, etc.

DISCUSSION

The ensemble averaged conservation equation for a pellet that has been obtained here essentially replaces the many-particle problem with a single equivalent conservation relation. The averaging gives rise to an effective homogeneous system that takes into account the different transport rates in the two phases and a measure of heterogeneity, that is, the ratio ω. The governing Eq. 28 has the advantage that it can be applied to pellets of any shape.

The validity of the point sink approximation rests on the value of ω and the ratio $\mathscr{D}_i/\mathscr{D}_o$. For $\mathscr{D}_i/\mathscr{D}_o$ from 10^{-8} to 10^0, it is shown that if ω is 1/20 or less, the point sink approximation is valid when the steady state profile is linear or when the asymptotic equilibrium profile is uniform. It is shown that the point sink approximation can also take into account the linear variations in concentration profiles in the macropores surrounding the microspheres. This has led us to conclude that the cases where the steady state profile is nonlinear and steep, impose stronger conditions for the point sink approximation to be valid. Problem (d) illustrates such a case.

We note that for cases where only diffusive transport occurs [problems (a)-(c)], all constraints are directed towards providing an upper limit on ω below which the point sink approximation is valid. This limit does not change appreciably in the wide range of the ratio $\mathscr{D}_i/\mathscr{D}_o \sim 10^{-8}$ to 10^0. Here the steady state or equilibrium profiles are uniform or linear. On the other hand when the steady state profile is nonlinear as in (d), the case of diffusion with reaction, the limits of the validity of the point sink approximation are strongly affected by transport quantities and kinetic rate constants.

For the cases where the point sink approximation is not valid, it is necessary to include at least the second term on the right in Eq. 29 to be substituted into Eq. 28.

SUMMARY

Bidisperse catalyst pellets are made up of microspheres. Conventionally these microspheres are modeled as uniformly distributed point sinks. The applicability of such a model has been investigated through a more methodical approach.

We use statistical average to consider the random nature in which microspheres are packed into a pellet. A symbolic operator representation is used to evaluate the flux to the microspheres of finite size. Analyses of the transient response to pellets in the shape of a sphere, slab, and cylinder, show that in the range of usual values of transport coefficients encountered, the point sink approximation is valid. These values are $\mathcal{D}_i/\mathcal{D}_o \sim 10^{-8}$ to 10^{-4} and $\omega \sim 1/20$ to $1/100$.

We are also able to show that in general the point sink approximation will be valid if the steady state concentration field is given by a constant or by a linear function of position. However, in the case of steady state diffusion with reaction the concentration field is nonlinear. It is shown that depending on the values of transport coefficients and reaction rates, the point sink approximation may be invalid. A criterion has been provided to determine the applicability of the point sink approximation in this case.

The general formalism that we have provided can be used to include the size effects to any required degree of approximation.

APPENDIX

One important theorem in potential theory (Hobson, 1931) is the following integration on the surface of a sphere of radius R_i,

$$\int dS\, Y_k(x,y,z) f(x,y,z) = 4\pi R_i^{2k+2} \left[\left\{ \frac{1}{(R_i\nabla_Q)} \frac{d}{d(R_i\nabla_Q)} \right\}^k \frac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)} \right] Y_k\left(\frac{\partial}{\partial x_Q}, \frac{\partial}{\partial y_Q}, \frac{\partial}{\partial z_Q} \right) \times f(x_Q, y_Q, z_Q) \qquad \text{(i)}$$

where x,y,z are rectangular coordinates and Y_k is a solid spherical harmonic, $Y_k = r^k V_k(\theta,\phi)$, where Y_k satisfies the Laplace equation $\nabla^2 Y_k = 0$. Brenner (1966) noted that $f(x,y,z) = \exp\{\mathbf{r} \cdot \nabla_Q\} f(x_Q, y_Q, z_Q)$ and substituted this in the first expression and thus obtained:

$$\int dS \exp(\mathbf{r}\cdot\nabla_Q) = 4\pi R_i^2 \frac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)} \qquad \text{(ii)}$$

for $k = 0$ and $Y_o = 1$.

If $i_k V_k$ is the k^{th} solution in Eq. 23, then

$$\{\int dS \exp(\mathbf{r}\cdot\nabla_Q)\}\, \bar{\theta}_{oQ} = a_o\{\int dS\, Y_o i_o V_o\} \qquad \text{(iii)}$$

since $\int dS\, Y_o V_k = 0$ for $k \neq 0$.

The left hand side in Eq. iii is given by Eq. ii and the right hand side by setting $k = 0$ in Eq. i, we get

$$a_o = \frac{\dfrac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)}\, \bar{\theta}_{oQ}}{\dfrac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)}\, i_o V_o} \qquad \text{(iv)}$$

Since $i_o V_o$ is a solution to Eq. 20, that is, $R_i^2 \nabla^2 i_o V_o = p/\alpha\, i_o V_o$, if we expand $\sinh(R_i\nabla_Q)/R_i\nabla_Q$ in series, we obtain

$$\frac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)} i_o V_o = \frac{\sinh\left(\sqrt{\dfrac{p}{\alpha}}\right)}{\sqrt{\dfrac{p}{\alpha}}} i_{oQ}$$

as $V_o = 1$. i_{oQ} is i_o evaluated at the center or at $r = 0$, and $i_o(0) = 1$. Eq. iv becomes

$$a_o = \frac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)} \bar{\theta}_{oQ} \Bigg/ \left\{ \frac{\sinh\left(\sqrt{\dfrac{p}{\alpha}}\right)}{\sqrt{\dfrac{p}{\alpha}}} \right\}$$

Through straightforward calculations, the integral in Eq. 14 is obtained as:

$$\int_0^{2\pi} d\phi \int_{-1}^{1} d\mu\, a_{o0} \frac{di_o}{d\gamma}\bigg|_{\gamma=1} = 4\pi \left[\sqrt{\frac{p}{\alpha}} \coth\left(\sqrt{\frac{p}{\alpha}}\right) - 1 \right] \times \frac{\sinh(R_i\nabla_Q)}{(R_i\nabla_Q)} \bar{\theta}_{oQ} \qquad \text{(v)}$$

where the relation (Abramowitz and Stegun, 1972)

$$\frac{d}{dx} i_o(x) = i_1(x) = -\frac{\sinh(x)}{x^2} + \frac{\cosh(x)}{x}$$

has been used.

NOTATION

C = concentration
C_∞ = stepped-up concentration
C^* = initial concentration
$\mathcal{D}$ = diffusion coefficient
H = Henry's constant
i_k = modified spherical Bessel function of first kind and order k
J_{qk} = defined by Eq. 36
k = surface reaction rate constant
K = surface adsorption rate constant
M_t, M_∞
= mass uptake at time t and at $t = \infty$
M = defined by Eq. 50
N = total number of microspheres in the system
$\mathbf{n}$ = unit normal vector to a sphere surface
n = number of microparticles per unit volume
$p_N(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N)$, $p(\mathbf{r}_i)$ = probability density functions defined before Eq. 1 and after Eq. 2
p = Laplace transform corresponding to t
P_k^m = Legendre polynomial of degree k and order m
R = characteristic length or radius
r = radial coordinate
s = area per unit void volume
$\mathcal{S}$ = surface concentration
S = surface area
t = time
V_o, V_i, V = volumes of macropores, of the i^{th} microsphere and of any microsphere when they are all equal
V_k = surface spherical harmonic
∇^2, ∇^{*2}, $\tilde{\nabla}^2$ = Laplacian operators, dimensional and dimensionless defined after Eq. 14 and Eq. 18
∇_Q, ∇^* = symbolic operators and dimensionless symbolic operator defined after Eq. 22
$\langle\rangle_N$, $\langle\rangle_{N-1}$ = ensemble average and conditional average defined in Eqs. 1 and 2
α = defined after Eq. 18
β = defined after Eq. 14
γ = defined after Eq. 14
δ_o, δ_i = defined by Eqs. 54 and 55
ϵ = void volume fraction
η = dimensionless radius in macroparticle
ϕ = azimuthal angle in microsphere from ∇_Q
μ = cosine of θ
θ_o, θ_i = dimensionless concentrations in the macro and microspheres
θ = polar angle in a microsphere between ∇_Q and $\mathbf{R}_i$
θ_λ = defined in Eq. 30
ω = R_i/R_o
τ = dimensionless time defined after Eq. 14
ξ, ξ_{qk} = roots of Eq. 37
χ = defined in Eq. 58
λ = defined in Eq. 30

Subscripts

i = microsphere
o = macroparticle

T = total
j = refers to j^{th} microsphere

Superscripts

$-$ = Laplace transformed quantity

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Fundamental Investigations and Electrochemical Engineering Aspects Concerning an Advanced Concept for Alkaline Water Electrolysis

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A thorough search for electrocatalysts for anodic oxygen evolution from caustic potash solution together with an investigation for the main reasons of ohmic potential drops in the interelectrode gap has lead to a new concept for an advanced medium temperature (150° to 200°C), medium pressure (30 to 100 bars) alkaline water electrolysis. The new concept will allow electrolytic water decomposition at temperatures between 160° and 200°C with current densities of 1 to 1.5 A/cm² and cell voltages between 1.55 and 1.65 V.

SCOPE

Mixed oxides known to catalyze cathodic oxygen reduction were tested under technical working conditions (current densities 0.5 to 1.5 A/cm², 80° to 260°C, 30 to 60 bars) and judged for their ability to catalyze anodic oxygen evolution from concentrated (30 to 50 wt %) potash solutions in order to reduce cell voltages for electrolytic water decomposition.

The problem of the detrimental gas accumulation which causes waste of electrical energy at gas evolving electrodes was investigated in order to find electrode/diaphragm configurations which minimize or eliminate the voltage drop caused by this bubble curtain effect.

A search for new diaphragms was performed in order to supply a diaphragm for a medium temperature (150° to 250°C) alkaline water electrolysis which would be superior to the classical asbestos diaphragm with respect to corrosion stability and electrical resistance.

Material and corrosion research was performed in order to find an economically attractive construction concept for MT-MP-water electrolyzers.

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