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Memorandum

Date: August 19, 2002

From: Christopher J. Neville

To: File

SSPA Project: -

Subject: **Notes on dual domain parameters for solute transport: Mass transfer coefficients for fractured rock**

Genuchten and Dalton (1986) and Sudicky (1990) have shown that the dual-domain modeling approach with a first-order mass transfer coefficient can approximate solute transport in idealized fractured rock settings consisting of uniform slabs and spheres.

The expressions for the first-order mass transfer coefficients

1. For parallel slabs:

$$\varsigma = \frac{3\theta_{im} D^*_{im}}{B^2}$$

2. For spheres:

$$\varsigma = \frac{15\theta_{im} D^*_{im}}{r_o^{\ 2}}$$

Here:

θ_{im}	:	porosity of the immobile zone (porosity that is occupied by the matrix slabs) [-];
D^*_{im}	:	effective diffusion coefficient for the immobile zone [L^2T^{-1}];
B	:	slab-thickness [L]; and
r_0	:	sphere radius [L].

The attached notes present detailed developments of the physically-based expressions for the mass transfer coefficients for slabs and spheres.

References

Sudicky, E.A., 1990: The Laplace transform Galerkin technique for efficient time-continuous solute of solute transport in double-porosity media, *Geoderma*, *46*, pp. 209-232.

van Genuchten, M.T., and F.N. Dalton, 1986: Models for simulating salt movement in aggregated field soils, *Geoderma*, *48*, pp. 165-183.

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MARCH 6, 2002

NOTES ON DOUBLE POROSITY TRANSPORT:

DEVELOPMENT OF EXPRESSIONS FOR THE DOUBLE POROSITY TERM

1. GOVERNING EQUATION
2. INITIAL AND BOUNDARY CONDITIONS
3. LAPLACE-TRANSFORMED GOVERNING EQUATION
4. TREATMENT OF THE DOUBLE POROSITY TERM
   A. SLAB MODEL
   B. SPHERE MODEL
   C. FIRST-ORDER MASS TRANSFER COEFFICIENT APPROACH
   D. RELATIONS BETWEEN PHYSICAL DUAL POROSITY MODELS (SLABS AND SPHERES) AND THE MASS TRANSFER COEFFICIENT APPROACH
5. EXAMPLE

1. GOVERNING EQUATION

CONSIDER 3^D ADVECTIVE-DISPERSIVE TRANSPORT OF A REACTIVE SOLUTE. FOR STEADY FLOW, THE GOVERNING EQUATION FOR THE CONCENTRATION IN THE MOBILE ZONE IS:

$$\frac{\partial(\theta_m R_m c)}{\partial t} = \underbrace{-\frac{\partial(q_i c)}{\partial x_i}}_{\text{ADVECTIVE FLUX}} + \underbrace{\frac{\partial}{\partial x_i}\left(\theta_m D_{ij}\frac{\partial c}{\partial x_j}\right)}_{\text{DISPERSIVE FLUX}} \underbrace{- \theta_m R_m \lambda c}_{\text{FIRST ORDER DECAY}} - \underbrace{\phi \gamma}_{\text{DOUBLE POROSITY TERM}} + \underbrace{Q^* c^*}_{\text{SOURCE}}$$

where:

(i) θ_m = POROSITY OF THE MOBILE ZONE = $\dfrac{\text{VOLUME OF MOBILE WATER}}{\text{VOLUME OF ENTIRE POROUS MEDIUM}}$

(ii) R_m = RETARDATION FACTOR FOR THE MOBILE ZONE

- FOR A SOLUTE UNDERGOING EQUILIBRIUM PARTITIONING ONTO THE SOLID PHASE:

$$R_m = 1 + \frac{\rho_m}{\theta_m} K_{d_m}$$

(iii) θ_{im} = POROSITY OF THE IMMOBILE ZONE = $\dfrac{\text{VOLUME OF IMMOBILE ZONE}}{\text{TOTAL VOLUME OF POROUS MEDIUM}}$

(iv) γ = DOUBLE POROSITY TERM = TOTAL MASS THAT DIFFUSES INTO THE IMMOBILE ZONE, PER UNIT VOLUME OF IMMOBILE ZONE

ϕ = GEOMETRIC FACTOR

= POROSITY OF THE IMMOBILE ZONE = $\dfrac{\text{VOLUME OF IMMOBILE WATER}}{\text{VOLUME OF POROUS MEDIUM}}$

2. INITIAL AND BOUNDARY CONDITIONS

1. $c(t=0) = f(x_i)$

   — USUALLY WE WILL ASSUME $c(x,z,0) = 0$

2. a) $c = c_o(t)$ ON Γ_1

   b) $\left[\theta_m D_m^* \frac{\partial c}{\partial x_j} \right] n_i = u(t)$ ON Γ_2

   c) $\left[q_i c - \theta_m D_{ij} \frac{\partial c}{\partial x_j} \right] n_i = q_o c_o(t)$ ON Γ_3

3. LAPLACE-TRANSFORMED GOVERNING EQUATION

APPLY THE LAPLACE TRANSFORM W.R.T. TIME :

$$\theta_m R_m \left[p\bar{c} - c(t=0) \right] = -\frac{\partial (q_i \bar{c})}{\partial x_i} + \frac{\partial}{\partial x_i}\left(\theta_m D_{ij} \frac{\partial \bar{c}}{\partial x_j}\right)$$

$$- \theta_m R_m \lambda \bar{c} - \phi \bar{\gamma} + Q^* \bar{c}^*$$

WE MUST ALSO APPLY THE LAPLACE TRANSFORM TO THE BOUNDARY CONDITIONS :

a) $\bar{c}(x_i, p) = \bar{c}_o(p)$ ON Γ_1

b) $\left[\theta_m D_m^* \frac{\partial \bar{c}}{\partial x_j} \right] n_i = \bar{u}(p)$ on Γ_2

c) $\left[q_i \bar{c} - \theta_m D_{ij} \frac{\partial \bar{c}}{\partial x_j} \right] n_i = q_o \bar{c}_o(p)$ on Γ_3

4. TREATMENT OF THE DOUBLE POROSITY TERM

THE DOUBLE POROSITY TERM REPRESENTS THE TOTAL MASS THAT DIFFUSES INTO THE IMMOBILE ZONE PER UNIT VOLUME OF IMMOBILE ZONE. THE DOUBLE POROSITY TERM IS REPRESENTED BY THE FOLLOWING CONVOLUTION INTEGRAL:

$$\gamma = \int_0^t c(x_i, \tau)\, g(t-\tau)\, d\tau$$

where: $g(t)$ = 'INFLUENCE FUNCTION'

→ REPRESENTING THE DIFFUSIVE FLUX TO THE IMMOBILE ZONE AS A CONVOLUTION INTEGRAL POSES PROBLEMS FOR CONVENTIONAL TIME-MARCHING SCHEMES. THIS IS BECAUSE THE ANALYSIS MUST KEEP TRACK OF THE HISTORY OF THE CONCENTRATION AT THE INTERFACE OF THE MOBILE AND IMMOBILE ZONES. COMPUTATIONALLY, THIS MEANS THAT THE F.E. COEFFICIENT MATRIX MUST BE RE-ASSEMBLED FOR EVERY TIME STEP, EVEN FOR CONSTANT TIME STEPS.

APPLYING THE LAPLACE TRANSFORM TO THE DOUBLE POROSITY TERM:

$$\bar{\gamma} = \bar{c}(x_i, p)\, \bar{g}(p)$$

→ IN LAPLACE SPACE THE CONVOLUTION INTEGRAL REDUCES TO THE PRODUCT OF TWO FUNCTIONS. THERE IS NO HISTORY TO KEEP TRACK OF.

IN ORDER TO COMPLETE THE DOUBLE POROSITY FORMULATION, IT IS NECESSARY TO :

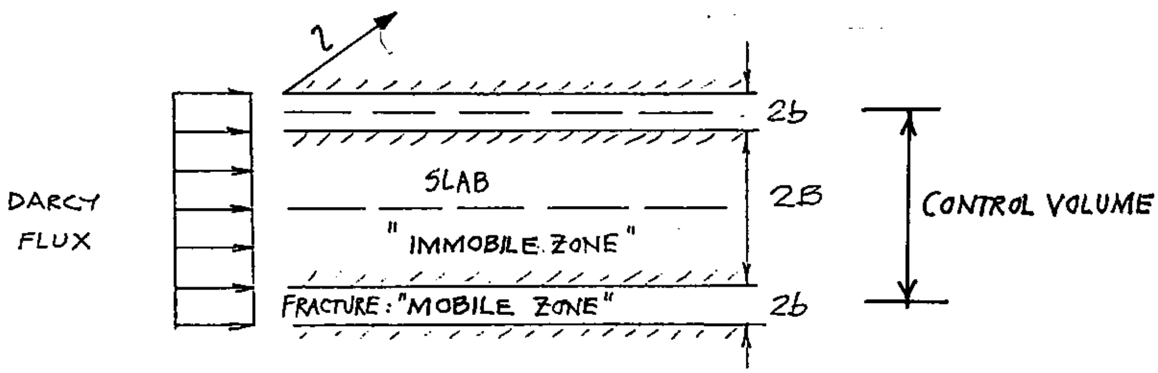
(i) DEFINE THE EFFECTIVE POROSITY OF THE MOBILE REGION
(ii) DEFINE THE DOUBLE POROSITY TERM γ
(iii) DEFINE THE GEOMETRIC FACTOR ϕ

WE WILL CONSIDER THREE MODELS :

- SLABS;
- SPHERES ; and
- FIRST-ORDER MASS TRANSFER COEFFICIENT APPROACH.

A. SLABS

CONSIDER A FRACTURED SYSTEM COMPOSED OF SLABS:
FOR A FRACTURED SYSTEM THE MOBILE POROSITY IS THE FRACTURE POROSITY.



— DEFINE MOBILE POROSITY θ_m

$$\theta_m = \frac{\text{VOLUME FRACTURE}}{\text{CONTROL VOLUME}} = \frac{b \cdot l}{(B+b)\,l}$$

$$\therefore \quad \theta_m = \frac{b}{B+b}$$

— DEFINE MASS TRANSFORM TERM, γ

Diffusive flux from immobile region per unit volume of immobile region

• APPLYING FICK'S LAW FOR SLAB:

$$\gamma = \theta_{im} D_{im}^{*} \left.\frac{\partial c'}{\partial z'}\right|_{z'=B} * \left(\frac{SA}{\forall_{im}}\right)$$

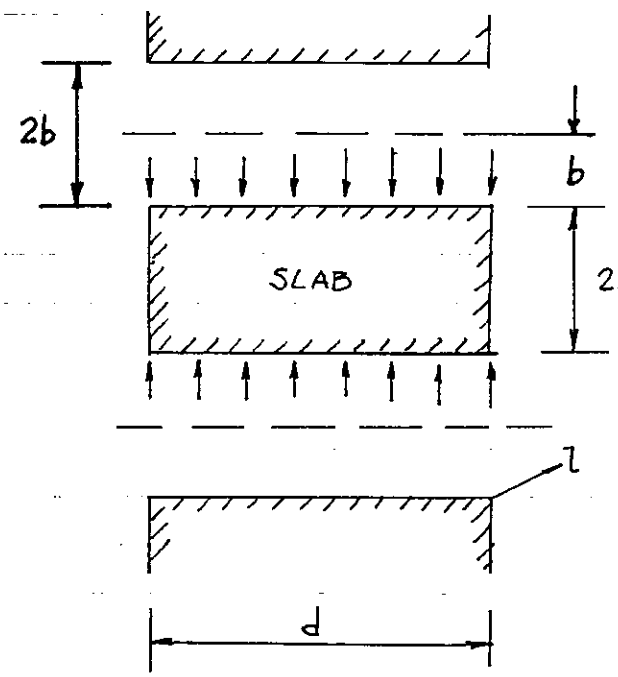
where $(SA/\forall_{im})$ is the surface area per unit volume of porous medium

NB: The negative sign is omitted because a gain of mass in the immobile zone corresponds to a loss in the mobile zone

The Laplace transform of γ is given by:

$$\overline{\gamma} = \theta_{im} D_{im}^{*} \left.\frac{d\bar{c}'}{dz}\right|_{z'=B} * \left(\frac{SA}{\forall_{im}}\right)$$

• Define $\left(\frac{SA}{\forall_{im}}\right)$, the surface area per unit volume of porous medium:



FOR A SLAB THERE ARE TWO FACES ACROSS WHICH MASS DIFFUSES FROM THE MOBILE TO THE IMMOBILE ZONE. THEREFORE, THE SURFACE AREA AVAILABLE FOR DIFFUSION IS:

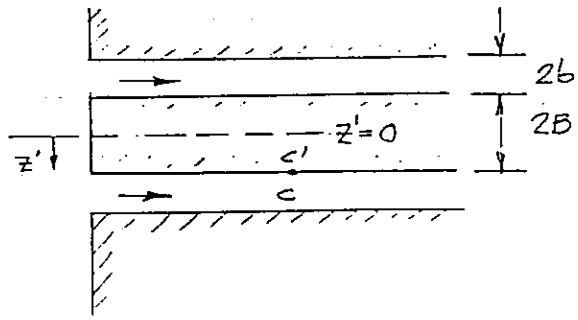
$$SA = 2\left(l \cdot d\right)$$

THE VOLUME OF A SLAB IS:

$$\forall_{im} = (2B)(l \cdot d)$$

$$\therefore \quad \frac{SA}{\forall_{im}} = \frac{2\,(l \cdot d)}{(2B)(l \cdot d)} = \frac{1}{B}$$

- DERIVE EXPRESSION FOR CONCENTRATION GRADIENT



BECAUSE OF SYMMETRY WE NEED TO CONSIDER ONLY HALF OF THE BLOCK.

FOR 1D DIFFUSION INTO THE BLOCKS, THE CONCENTRATION IS GOVERNED BY FICK'S SECOND LAW:

$$R'\frac{\partial(\theta_{im}c')}{\partial t}-\frac{\partial}{\partial z'}\left(\theta_{im}D_{im}^{*}\frac{\partial c'}{\partial z'}\right)+\theta_{im}R'\lambda c'=0 \quad ; \quad 0\le z'\le B$$

SUBJECT TO:
$$\frac{\partial c'}{\partial z'}(0,t) = 0$$
$$c'(B,t) = c(t)$$
$$c'(z',0) = 0$$

ASSUMING THAT EACH SLAB HAS A UNIFORM POROSITY θ_{im} THE GOVERNING EQUATION CAN BE SIMPLIFIED TO:

$$R'\frac{\partial c'}{\partial t} - D_{im}^{*}\frac{\partial^2 c'}{\partial z'^2} + R'\lambda c' = 0$$

APPLYING THE LAPLACE TRANSFORMATION YIELDS:

$$R'p\bar{c}' - D_{im}^{*}\frac{d^2\bar{c}'}{dz'^2} + R'\lambda\bar{c}' = 0$$

RE-ARRANGING :

$$\bar{c}'(PR') - D_{im}^* \frac{d^2\bar{c}'}{dz^2} = 0$$

where , $P = p + \lambda$

SUBJECT TO : $\frac{d\bar{c}'}{dz}(0, P) = 0$

$$\bar{c}'(B, P) = c(P)$$

RE-WRITING THE TRANSFORMED GOVERNING EQUATION :

$$\frac{d^2\bar{c}'}{dz^2} - \frac{PR'}{D_{im}^*}\bar{c} = 0$$

THIS HAS AS ITS GENERAL SOLUTION :

$$\bar{c}' = A \,\mathrm{EXP}\left\{\left(\frac{PR'}{D_{im}^*}\right)^{1/2} z\right\} + B \,\mathrm{EXP}\left\{-\left(\frac{PR'}{D_{im}^*}\right)^{1/2} z\right\}$$

AND $$\frac{d\bar{c}'}{dz} = \left(\frac{PR'}{D_{im}^*}\right)^{1/2} A \,\mathrm{EXP}\left\{\left(\frac{PR'}{D_{im}^*}\right)^{1/2} z\right\}$$

$$- \left(\frac{PR'}{D_{im}^*}\right)^{1/2} B \,\mathrm{EXP}\left\{-\left(\frac{PR'}{D_{im}^*}\right)^{1/2} z\right\}$$

EVALUATING THE CONSTANTS A AND B BY INVOKING THE BOUNDARY CONDITIONS :

$$\frac{d\bar{c}'}{dz}(0) = 0 = A - B \longrightarrow A = B$$

$$\therefore \quad \bar{c}'(B) = \bar{c} = A \, \text{EXP}\left\{ \left(\frac{PR'}{D_{im}^*}\right)^{1/2} B \right\} + A \, \text{EXP}\left\{ -\left(\frac{PR'}{D_{im}^*}\right)^{1/2} B \right\}$$

LETTING $\beta = \left(\frac{PR'}{D_{im}^*}\right)^{1/2}$

THE SECOND BOUNDARY CONDITION SIMPLIFIES TO :

$$\bar{c} = A \cdot \cosh(\beta B)$$

$$\therefore \quad A = \frac{\bar{c}}{\cosh(\beta B)}$$

$\therefore$ SUBSTITUTING INTO THE GENERAL SOLUTION FOR $\bar{c}'$:

$$\bar{c}' = \frac{\bar{c}}{\cosh(\beta B)} \left[\text{EXP}\{\beta z'\} + \text{EXP}\{-\beta z'\} \right]$$

$$\therefore \quad \bar{c}' = \bar{c} \, \frac{\cosh(\beta z')}{\cosh(\beta B)}$$

DIFFERENTIATING W.R.T. z' :

$$\frac{d\bar{c}'}{dz'} = \bar{c}\,\beta \, \frac{\sinh(\beta z')}{\cosh(\beta B)}$$

$$\therefore \quad \left.\frac{d\bar{c}'}{dz'}\right|_{z'=B} = \bar{c}\,\beta \, \frac{\sinh(\beta B)}{\cosh(\beta B)}$$

$$= \bar{c}\,\beta \tanh(\beta B)$$

SUBSTITUTING FOR $\left(\frac{SA}{\forall_{im}}\right)$ IN THE EXPRESSION FOR $\overline{\gamma}$ YIELDS:

$$\overline{\gamma} = \theta_{im} D_{im}^* \left.\frac{d\bar{c}'}{dz'}\right|_{z'=B} \cdot \frac{1}{B}$$

SUBSTITUTING FOR $\left.\frac{d\bar{c}'}{dz'}\right|_{z'=B}$ WE OBTAIN:

$$\overline{\gamma} = \frac{\theta_{im} D_{im}^* \left(\bar{c}\,\beta \tanh(\beta B)\right)}{B}$$

SIMPLIFYING:

$$\overline{\gamma} = \bar{c} \cdot \frac{\theta_{im} D_{im}^*}{B} \beta \tanh(\beta B)$$

HOWEVER, FROM THE DEFINITION OF THE DOUBLE POROSITY TERM WE HAD :

$$\bar{\gamma} = \bar{c}\,\bar{g}$$

THEREFORE, COMPARING THE TWO EXPRESSIONS FOR $\bar{\gamma}$ WE DEDUCE :

$$\boxed{\bar{g} = \frac{\theta_{im} D_{im}^{*}}{B} \beta \, \mathrm{TANH}(\beta B)}$$

FOR SLABS

— GEOMETRIC FACTOR ϕ

$$\phi = \frac{\forall_{immobile}}{\forall_{PM}}$$

For slabs :

$$\phi = \frac{2B\,l\,d}{(b+B+b)\,l\,d}$$

$$= \frac{2B}{2(B+b)} = \frac{B}{B+b}$$

$$= 1 - \theta_m$$

B. SPHERES

FOR DIFFUSION INTO SPHERES THE DIFFUSION EQUATION IN SPHERICAL COORDINATES IS :

$$R'\frac{\partial(\theta_{im}c')}{\partial t} - \frac{1}{r^2}\frac{\partial}{\partial r^2}\left(r^2\theta_{im}D_{im}^*\frac{\partial c'}{\partial r}\right) + \theta_{im}R'\lambda c' = 0 \qquad ;\ 0 \le r \le r_o$$

SUBJECT TO : $\frac{\partial c'}{\partial r}(0,t) = 0$

$$c'(r_o, t) = c$$

$$c'(r, 0) = 0$$

WHERE $r_o \equiv$ RADIUS OF A SPHERE

ASSUMING CONSTANT POROSITY θ_{im} THE GOVERNING EQUATION SIMPLIFIES TO :

$$R'\frac{\partial c'}{\partial t} - D_{im}^*\frac{1}{r^2}\frac{\partial}{\partial r^2}\left(r^2\frac{\partial c'}{\partial r}\right) + R'\lambda c' = 0$$

APPLYING THE LAPLACE TRANSFORMATION :

$$R'p\bar{c}' - D_{im}^*\frac{1}{r^2}\frac{\partial}{\partial r^2}\left(r^2\frac{\partial\bar{c}'}{\partial r}\right) + R'\lambda c' = 0$$

RE-ARRANGING :

$$\bar{c}'(PR') - D_{im}^*\frac{1}{r^2}\frac{\partial}{\partial r^2}\left(r^2\frac{\partial\bar{c}'}{\partial r}\right) = 0$$

THE SOLUTION IS GIVEN BY :

$$\bar{c}' = \bar{c}\,\frac{r_o\ \sinh(\beta r)}{r\ \sinh(\beta r_o)}$$

where : $\beta = \left(\frac{PR'}{D_{im}^*}\right)^{1/2}$

DIFFERENTIATING W.R.T. r :

$$\frac{d\bar{c}'}{dr} = \bar{c}\left[\frac{(r \sinh(\beta r_o))(r_o \beta \cosh(\beta r)) - (r_o \sinh(\beta r))(\sinh(\beta r_o))}{(r \sinh(\beta r_o))^2}\right]$$

$$= \bar{c}\left[\frac{r \cdot r_o \beta \cosh(\beta r) - r_o \sinh(\beta r)}{r^2 \sinh(\beta r_o)}\right]$$

EVALUATING THE DERIVATIVE AT THE SPHERE SURFACE, $r = r_o$

$$\left.\frac{d\bar{c}'}{dr}\right|_{r=r_o} = \bar{c}\left[\frac{r_o^2 \beta \cosh(\beta r_o) - r_o \sinh(\beta r_o)}{r_o^2 \sinh(\beta r_o)}\right]$$

$$= \bar{c}\left[\beta \coth(\beta r_o) - \frac{1}{r_o}\right]$$

— NOW, CONSIDERING THE GEOMETRY OF A SPHERE :

i. SURFACE AREA : $4\pi r_o^2$

ii. VOLUME : $\frac{4}{3}\pi r_o^3$

THUS, ACCORDING TO FICK'S LAW, THE DIFFUSIVE FLUX PER UNIT VOLUME OF IMMOBILE ZONE IS :

$$\gamma = \theta_{im} D_{im}^{*} \left.\frac{\partial c'}{\partial r}\right|_{r=r_0} \left(\frac{4\pi r_0^{2}}{\frac{4}{3}\pi r_0^{3}} \right)$$

AND $$\bar{\gamma} = \theta_{im} D_{im}^{*} \left.\frac{d\bar{c}'}{dr}\right|_{r=r_0} \left(\frac{4\pi r_0^{2}}{\frac{4}{3}\pi r_0^{3}} \right)$$

SUBSTITUTING FOR $\left.\frac{d\bar{c}'}{dr}\right|_{r=r_0}$ AND SIMPLIFYING :

$$\bar{\gamma} = \theta_{im} D_{im}^{*} \bar{c} \left[\beta \coth(\beta r_0) - \frac{1}{r_0} \right] \cdot \frac{3}{r_0}$$

SIMPLIFYING :

$$\bar{\gamma} = \bar{c} \cdot \frac{3\theta_{im} D_{im}^{*}}{r_0} \left[\beta \coth(\beta r_0) - \frac{1}{r_0} \right]$$

COMPARING THIS EXPRESSION FOR $\bar{\gamma}$ WITH THE DEFINITION OF $\bar{\gamma}$, WE OBTAIN:

$$\boxed{\bar{g} = \frac{3\theta_{im} D_{im}^*}{r_0}\left[\beta \coth(\beta r_0) - \frac{1}{r_0}\right]}$$

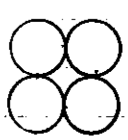
FOR SPHERES

→ NOTE: BOTH OF THE LAPLACE-TRANSFORMED INFLUENCE FUNCTIONS, $\bar{g}$, CAN BE INVERTED ANALYTICALLY. THE 'REAL TIME' EXPRESSIONS FOR g ARE CONVOLUTION INTEGRALS INVOLVING INFINITE SERIES. THEREFORE, CONVENTIONAL TIME-MARCHING SCHEMES NEED TO EVALUATE THE INFINITE SERIES AS WELL AS RETAIN THE CONCENTRATION HISTORY IN THE MOBILE ZONE.

— GEOMETRIC FACTOR FOR SPHERES:

ϕ = depends upon the packing of the spheres

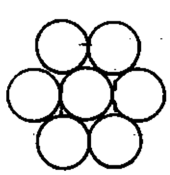
$\theta_m = 0.47$



$\rightarrow \phi = \theta_{im} = 1 - \theta_m \doteq 0.53$

CUBIC

$\theta_m = 0.26$



$\rightarrow \phi = \theta_{im} = 1 - \theta_m = 0.74$

RHOMBOHEDRAL

C. FIRST ORDER APPROACH

THE DIFFUSIVE FLUX TO THE IMMOBILE ZONE CAN ALSO BE MODELLED AS A FIRST ORDER REACTION. THIS APPROACH DOES NOT INVOKE FICK'S LAW, INSTEAD SPECIFYING THAT THE FLUX IS LINEARLY PROPORTIONAL TO THE CONCENTRATION DIFFERENCE BETWEEN THE MOBILE AND IMMOBILE ZONES.

— THE ADVECTION-DISPERSION EQUATION FOR THE MOBILE ZONE IS WRITTEN AS :

$$\frac{\partial(\theta_m R_m c)}{\partial t} = -\frac{\partial(q_i c)}{\partial x_i} + \frac{\partial}{\partial x_i}\left(\theta_m D_{ij}\frac{\partial c}{\partial x_j}\right) - \theta_m R_m \lambda c$$

$$- \alpha\,(c - c')$$

where : $\alpha(c-c')$ = FLUX TO THE IMMOBILE ZONE $= \phi\gamma$

α = MASS TRANSFER COEFFICIENT

THE INITIAL CONDITIONS ARE :

$$c(x_i, 0) = f(x_i)$$

APPLYING THE LAPLACE TRANSFORM WE OBTAIN :

$$\theta_m R_m\left[p\bar{c} - f(x_i)\right]$$

$$= -\frac{\partial(q_i\bar{c})}{\partial x_i} + \frac{\partial}{\partial x_i}\left(\theta_m D_{ij}\frac{\partial\bar{c}}{\partial x_j}\right) - \theta_m R_m \lambda\bar{c} - \alpha\left(\bar{c} - \bar{c}'\right)$$

SETTING $P = p + \lambda$ WE OBTAIN :

$$\theta_m R_m P \bar{c} + \frac{\partial (q_i \bar{c})}{\partial x_i} - \frac{\partial}{\partial x_i}\left(\theta_m D_{ij} \frac{\partial \bar{c}}{\partial x_j}\right) + \alpha(\bar{c} - \bar{c}') = \theta_m R_m f(x_i)$$

— THE GOVERNING EQUATION FOR THE IMMOBILE ZONE CONCENTRATION IS :

$$\theta_{im} R' \frac{\partial c'}{\partial t} = -\theta_{im} R' \lambda c' + \alpha(c - c')$$

→ THE SIGN ON THE DIFFUSIVE FLUX IS REVERSED BECAUSE A LOSS FROM THE MOBILE ZONE CORRESPONDS TO A GAIN IN THE IMMOBILE ZONE.

INITIAL CONDITIONS :

$$c'(0) = 0$$

APPLYING THE LAPLACE TRANSFORM YIELDS :

$$\theta_{im} R' p \bar{c}' = -\theta_{im} R' \lambda \bar{c}' + \alpha(\bar{c} - \bar{c}')$$

OR ,

$$\bar{c}' \theta_{im} R' P = \alpha(\bar{c} - \bar{c}')$$

SOLVING FOR $\bar{c}'$ YIELDS:

$$\bar{c}' = \bar{c}\,\frac{\alpha}{\theta_{im} R' P + \alpha}$$

$$\therefore \quad \bar{\gamma} = \frac{\alpha}{\phi}(\bar{c} - \bar{c}')$$

$$= \frac{\alpha}{\phi}\left[\bar{c} - \bar{c}\,\frac{\alpha}{\theta_{im} R' P + \alpha}\right]$$

$$= \bar{c} \cdot \frac{\alpha}{\phi}\left[\frac{\theta_{im} R' P + \alpha - \alpha}{\theta_{im} R' P + \alpha}\right]$$

$$= \bar{c} \cdot \frac{1}{\phi}\left[\frac{\alpha\,\theta_{im} R' P}{\theta_{im} R' P + \alpha}\right]$$

$$\therefore \quad \bar{g} = \frac{1}{\phi}\left[\frac{\alpha\,\theta_{im} R' P}{\theta_{im} R' P + \alpha}\right]$$

NOW, IN THIS FORMULATION THE IMMOBILE ZONE IS UBIQUITOUS, HENCE $\phi = 1$.

$$\therefore \quad \boxed{\bar{g} = \frac{\alpha\,\theta_{im} R' P}{\theta_{im} R' P + \alpha}}$$

D. RELATIONS BETWEEN PHYSICAL DUAL POROSITY MODELS AND THE MASS TRANSFER COEFFICIENT APPROACH

It is possible to derive approximate relations between the slab and sphere models and the first-order approaches, and thereby attach some physical significance of the mass transfer coefficient.

1. First, let us recall the expression for the first-order mass transfer coefficient approach:

$$\bar{g} = \frac{\alpha\,\theta_{im} R' P}{\theta_{im} R' P + \alpha}$$

Re-arranging:

$$\bar{g} = \theta_{im} R' P \cdot \frac{\alpha}{\theta_{im} R' P + \alpha} = \theta_{im} R' P \cdot \frac{1}{\frac{\theta_{im} R' P}{\alpha} + 1}$$

Now, using the approximation:

$$\frac{1}{1+x} \approx 1 - x \quad , \quad \text{valid for } x \lesssim 0.1$$

with $x = \dfrac{\theta_{im} R' P}{\alpha}$

we write:

$$\bar{g} \cong \theta_{im} R' P \left(1 - \frac{\theta_{im} R' P}{\alpha}\right) \qquad \text{——(A)}$$

2. Recalling the solution for slabs:

$$\bar{g} = \frac{\theta_{im} D_{im}^*}{B} \beta \,\mathrm{TANH}\{\beta B\}$$

Now, using the approximation:

$$\mathrm{TANH}\{x\} \cong x - \frac{x^3}{3}$$

with $x = \beta B$

we write:

$$\bar{g} \cong \frac{\theta_{im} D_{im}^*}{B} \beta \left(\beta B - \frac{(\beta B)^3}{3}\right)$$
$$= \frac{\theta_{im} D_{im}^*}{B} \beta \; \beta B \left(1 - \frac{(\beta B)^2}{3}\right)$$
$$= \theta_{im} D_{im}^* \; \beta^2 \left(1 - \frac{(\beta B)^2}{3}\right)$$

Substituting for β $\left(= \left(\frac{PR'}{D_{im}^*}\right)^{1/2}\right)$:

$$\bar{g} \cong \theta_{im} D_{im}^* \left(\frac{PR'}{D_{im}^*}\right) \left(1 - \frac{B^2}{3}\left(\frac{PR'}{D_{im}^*}\right)\right)$$

$$= \theta_{im} R'P \left(1 - \frac{R'P B^2}{3 D_{im}^*}\right) \qquad \text{—— (B)}$$

→ If we equate (A) and (B) we can derive an expression for α that is approximately consistent with the slab model.

$$\bar{g} = \theta_{im} R'P \left(1 - \frac{\theta_{im} R'P}{\alpha}\right) = \theta_{im} R'P \left(1 - \frac{R'PB^2}{3D_{im}^*}\right)$$

These two expressions will be equivalent if:

$$\frac{\theta_{im} R'P}{\alpha} = \frac{R'PB^2}{3D_{im}^*}$$

Solving for α:

$$\boxed{\alpha = \frac{3\theta_{im} D_{im}^*}{B^2}} \quad \longleftarrow \text{FOR SLABS}$$

3. Recalling the solution for spheres:

$$\bar{g} = \frac{3\,\theta_{im} D_{im}^*}{r_o}\left[\beta \coth\{\beta r_o\} - \frac{1}{r_o}\right]$$

Now, using the approximation:

$$\coth\{x\} \cong \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45}$$

with $x = \beta r_o$

we write:

$$\bar{g} \cong \frac{3\,\theta_{im} D_{im}^*}{r_o}\left[\beta\left(\frac{1}{\beta r_o} + \frac{\beta r_o}{3} - \frac{(\beta r_o)^3}{45}\right) - \frac{1}{r_o}\right]$$

$$= \frac{3\,\theta_{im} D_{im}^*}{r_o}\left[\beta^2 \frac{r_o}{3} - \beta^4 \frac{r_o^3}{45}\right]$$

Substituting for β

$$\bar{g} = \frac{3\,\theta_{im} D_{im}^*}{r_o}\left[\left(\frac{PR'}{D_{im}^*}\right)\frac{r_o}{3} - \left(\frac{PR'}{D_{im}^*}\right)^2 \frac{r_o^3}{45}\right]$$

$$= \theta_{im} R' P \left[1 - \left(\frac{PR'}{D_{im}^*}\right)\frac{r_o^2}{15}\right] \qquad \text{(C)}$$

→ If we equate (A) and (C) we can derive an expression for α that is approximately consistent with the slab model:

$$\bar{g} = \theta_{im} R'P \left(1 - \frac{\theta_{im} R'P}{\alpha}\right) = \theta_{im} RP' \left[1 - \left(\frac{R'P}{D_{im}^*}\right)\frac{r_o^2}{15}\right]$$

These two expressions will be equivalent if:

$$\frac{\theta_{im} R'P}{\alpha} = \left(\frac{R'P}{D_{im}^*}\right)\frac{r_o^2}{15}$$

Solving for α:

$$\boxed{\alpha = \frac{15\,\theta_{im} D_{im}^*}{r_o^2}}$$

← for SPHERES

5. EXAMPLE ANALYSIS

ref: SUDICKY (1990)

1. This problem is concerned with transport in a system comprised of closely-spaced, parallel fractures for which the analytical solution by Sudicky and Frind (1982) is available. The thickness of each rock slab is $2B=0.1$ m and the aperture of each fracture is 10^{-4} m which yields a fracture porosity θ_m, equal to 10^{-3} (Table II). For the given values of the Darcy flux, q and fracture porosity, the groundwater velocity in each fracture is 0.1 m/d.

Fracture aperture, $2b=10^{-4}$ m
Fracture spacing, $2B=10^{-1}$ m
Darcy flux, $q=10^{-4}$ m/d
Fracture porosity, $\theta_m=0.5\times10^{-1}/5\times10^{-1}=10^{-3}$
Rock matrix porosity, $\theta_{im}=10^{-2}$
Longitudinal dispersivity, $\alpha_l=0.1$ m
Fracture diffusion coefficient, $D^*_m=1.38\times10^{-4}$ m^2/d
Matrix diffusion coefficient, $D^*_{im}=1.38\times10^{-5}$ m^2/d
Solute decay coefficient, $\lambda=1.54\times10^{-4}$ d^{-1}
Retardation factors, $R=R'=1.0$

2. CHECK ON SUDICKY (1990) CALCULATIONS:

Sudicky (1990) Verification problem 2

$$\theta_{im} = 0.01$$
$$D_m^* = 1.38\times10^{-5}\ m^2/d$$
$$B = 0.05\ m$$

We calculate a first order mass transfer coefficient of:

$$\alpha = 3\,\frac{(0.01)(1.38\times10^{-5}\,m^2/d)}{(0.05\,m)^2}$$

$$= 1.656\times10^{-4}\ /d$$

[NOT 1.56×10^{-4}/d REPORTED ON SUDICKY (1990) p. 226]

$$\theta_m = \frac{2b}{2B+2b}$$

$$= \frac{10^{-4}\ m}{10^{-1}m + 10^{-4}m} = 9.990 \times 10^{-4}\ ,\ \text{say } 10^{-3} \quad \checkmark$$

$$V_f = 0.1\ m/d \stackrel{?}{=} \frac{q}{\theta_m} = \frac{(10^{-4}\ m/d)}{(10^{-3})} = 0.100\ m/d \quad \checkmark$$

$$\phi = \frac{\theta_m}{\theta_T} = \frac{9.990 \times 10^{-4}}{1.100 \times 10^{-2}} = 9.082 \times 10^{-2}$$

3. MODEL

The 300 m long grid was subdivided into 30 rectangular elements, each of length $\Delta x = 10$ m (31 by 2 node grid). Considering the small value of the longitudinal dispersivity for a fracture ($\alpha_l = 0.1$ m), the spatial discretization is considered to be coarse. As in Problem 1, the source condition is constant with $c = c_0$ at $x = 0$.

The LTG results are presented in Fig. 3 where they are compared to the analytical solution. Again the LTG results are essentially exact with no evidence of numerical dispersion being present. For example, the LTG simulation at $t = 100$ days correctly predicts a negligible concentration for $x = 10$ m although no nodes are located in the interval $0 < x < 10$. Even at $t = 1000$ days, only a single node is located in the region of significant concentrations yet it agrees with the analytical solution.

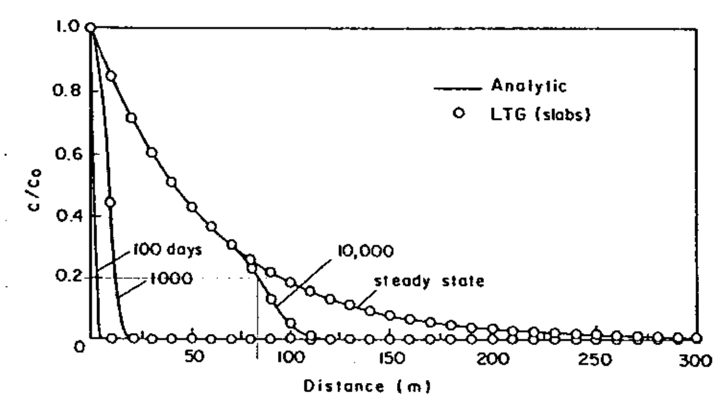


Fig. 3. Comparison of LTG solution with exact analytic solution for verification problem 2 (parallel-fracture case).

4. RESULTS WITH FIRST-ORDER MASS TRANSFER COEFFICIENT APPROACH

Figure 4 is used to demonstrate that Problem 2 can be solved without significant loss of accuracy by representing the diffusive exchange between the fracture and the rock matrix using either spheres instead of slabs or first-order theory instead of either slabs or spheres. The value of the mass transfer coefficient, $\alpha = 1.56 \times 10^{-4}$/d, used in Fig. 4a is based on that for equivalent slab behaviour according to (31) and is seen to yield identical results compared to the exact slab formation. In Fig. 4b, the sphere radius is chosen such that the surface-area-to-volume ratio is identical to that for the slabs ($r_0 = 1.5B$) and the value of the mass transfer coefficient, $\alpha = 3.68 \times 10^{-4}$/d, for the first-order approximation was calculated according to (32). Again, the first order theory closely approximates the more rigorous theory based on Fick's second law of diffusion. Also, comparison of Fig. 4b with Fig. 4a indicates that different immobile-zone geometries will produce similar mobile-zone concentrations as long as the surface-area-to-volume ratio remains identical (Rasmuson, 1984; Van Genuchten and Dalton, 1986).

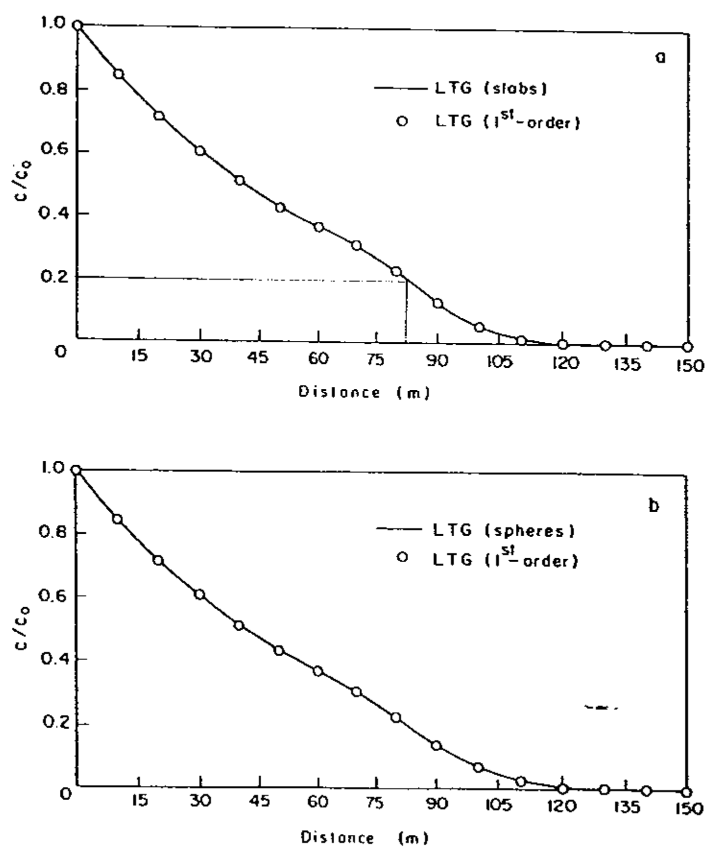


Fig. 4. LTG solution at $t = 10{,}000$ days for problem 2 comparing: (a) slabs with equivalent first-order theory and (b) spheres with equivalent first-order theory.