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Modification of TOUGH2 to Include the Dusty Gas Model for Gas Diffusion

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Modification of TOUGH2 to Include the Dusty Gas Model for Gas Diffusion

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Abstract

The GEO-SEQ Project is investigating methods for geological sequestration of CO_2. This project, which is directed by LBNL and includes a number of other industrial, university, and national laboratory partners, is evaluating computer simulation methods including TOUGH2 for this problem. The TOUGH2 code, which is a widely used code for flow and transport in porous and fractured media, includes simplified methods for gas diffusion based on a direct application of Fick's law. As shown by Webb (1998) and others, the Dusty Gas Model (DGM) is better than Fick's Law for modeling gas-phase diffusion in porous media. In order to improve gas-phase diffusion modeling for the GEO-SEQ Project, the EOS7R module in the TOUGH2 code has been modified to include the Dusty Gas Model as documented in this report. In addition, the liquid diffusion model has been changed from a mass-based formulation to a mole-based model. Modifications for separate and coupled diffusion in the gas and liquid phases have also been completed. The results from the DGM are compared to the Fick's law behavior for TCE and PCE diffusion across a capillary fringe. The differences are small due to the relatively high permeability ($k=10^{-11}$ m^2) of the problem and the small mole fraction of the gases. Additional comparisons for lower permeabilities and higher mole fractions may be useful.

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Nomenclature

b	Klinkenberg parameter (Pa)
c	molar concentration (mol/m^3)
d	distance to the interface (m)
D_i^K	Knudsen diffusion coefficient for component i (m^2/s)
D_{ij}	binary diffusion coefficient for components i and j (m^2/s)
g	gravity (m/s^2)
J^M	molar diffusive flux relative to relative to the molar-average velocity (mol/m^2-s)
k	permeability (m^2)
K_H	Henry's constant (-)
m	molecular weight (g/mol)
N^D	molar diffusive flux relative to stationary coordinates (mol/m^2-s)
P	pressure (Pa)
R	gas constant (J/mol-K)
T	temperature (K)
x	mole fraction (-)

Greek

τ	tortuosity (-)
ϕ	porosity (-)
θ	exponent on temperature correction factor (-)
μ	viscosity (Pa-s)
ρ	density (kg/m^3)

Subscripts

1,2,…	component number
air	air
d	downstream
eff	effective value
g	gas value
i	interface
ℓ	liquid value
P	value at P
T	value at T
u	upstream
0	reference conditions, all-gas value for the porous medium
β	saturation

Superscripts

g	gas value
i	interface
ℓ	liquid value
*	effective value

Acknowledgments

I want to thank the Nick Francis of SNL and Karsten Pruess and Curt Oldenburg of LBNL for their thorough reviews. This work was sponsored through the GEO-SEQ Project at Lawrence Berkeley National Laboratory by Dr. Curtis M. Oldenburg. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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1.0 Introduction

The GEO-SEQ Project is investigating methods for geological sequestration of CO_2. This project, which is directed by LBNL and includes a number of other industrial, university, and national laboratory partners, is evaluating computer simulation methods including TOUGH2 for this problem. The TOUGH2 code, which is a widely used code for flow and transport in porous and fractured media, includes simplified methods for gas diffusion based on a direct application of Fick's law.

Application of Fick's law to gas diffusion in porous media has recently been questioned by a number of investigators including Thorstenson and Pollock (1989), Abriola et al. (1992), and Webb (1998). The Dusty Gas Model (DGM), which is a more fundamental approach to gas diffusion in porous media, is preferable to Fick's law. In contrast to Fick's law, the DGM considers the diffusive flux relative to the mixture, not to stationary coordinates. In addition, gas-wall interactions are included in the DGM, and momentum transfer between the gases, similar to the Stefan-Maxwell equations, is considered. The DGM is discussed in great detail by Mason and Malinauskas (1983) and Cunningham and Williams (1980).

Webb (1998) compared Fick's law and the DGM to comprehensive gas diffusion data in low-permeability graphite ($k=2.13 \times 10^{-18}$ m^2) obtained by Evans et al. (1962, 1963). The DGM predictions compared very well with the experimental data and to Graham's laws, which are fundamental gas diffusion relationships for porous media. In contrast, the Fick's law predictions did not obey Graham's laws and did not compare well to the data.

Webb (1998) and Webb and Pruess (2001) showed that for a binary mixture, the DGM model can be rewritten similar to Fick's law. However, the coefficient in front of the mass fraction gradient is not a constant but is a function of the mass fractions of the components. Webb and Pruess (2001) showed that for trace gas diffusion, a simple modification of Fick's law can be performed that will produce the same results as the DGM. However, for gas diffusion involving other than trace gases, the two approaches cannot be made equivalent.

Due to the fact that gas diffusion can be an important physical process in geologic CO_2 sequestration, TOUGH2 (Pruess et al., 1999) has been modified to include the DGM for gas diffusion. The EOS7R equation-of-state module has been chosen for this modification because it includes five components (water, brine, radionuclide 1, radionuclide 2, air) and has been selected for modification for use in the GEO-SEQ Project. In addition to the DGM, a model for the diffusion of gases dissolved in the aqueous phase has also been included. This brief report consists of a summary of the DGM along with discussion of coupling for a two-phase system and the corresponding solution approach as implemented in TOUGH2. The new TOUGH2 input for invoking the DGM in TOUGH2 is discussed in Appendix A, along with a sample input file. The results from the DGM are compared to Fick's law behavior for diffusion across a capillary fringe.

A comment on Fick’s law is in order. There are various forms of Fick’s law as shown in detail by Bird, Stewart, and Lightfoot (1960), which are discussed in Appendix B. The form that is almost universally used is that the molar flux from Fick's law is relative to stationary coordinates; when Fick’s law is mentioned in this report, it refers to this form. Implicit in this equation is that there is equimolar counter-diffusion such that the total molar flux relative to stationary coordinates is zero. Note that this assumption is not generally true as mentioned in Appendix B.

2.0 Model Description

2.1 Diffusion Equations

The general form of the Dusty Gas Model for the diffusion of component i is given by (Thorstenson and Pollack, 1989)

$$\sum_{j=1,\, j\neq i}^{n} \frac{x_i N_j^D - x_j N_i^D}{D_{ij}^*} - \frac{N_i^D}{D_i^{K*}} = \frac{\left(\nabla P_i - r_g g\right)}{RT} \tag{1}$$

where N^D is the molar diffusive flux, x is the mole fraction, D_{ij}^* is the effective binary diffusion coefficient, D^{K*} is the effective Knudsen diffusion coefficient, P is the pressure, R is the gas constant, and T is the temperature. The summation is over all components in the system except itself.

For a 3-component system and ignoring gravity, the set of equations becomes

$$-\left[\frac{1}{D_1^{K*}} + \frac{x_2}{D_{12}^*} + \frac{x_3}{D_{13}^*}\right] N_1^{D,g} + \frac{x_1}{D_{12}^*} N_2^{D,g} + \frac{x_1}{D_{13}^*} N_3^{D,g} = \frac{\nabla P_1}{RT} = \frac{P\nabla x_1}{RT} + \frac{x_1 \nabla P}{RT} \tag{2a}$$

$$\frac{x_2}{D_{21}^*} N_1^{D,g} - \left[\frac{x_1}{D_{21}^*} + \frac{1}{D_2^{K*}} + \frac{x_3}{D_{23}^*}\right] N_2^{D,g} + \frac{x_{21}}{D_{23}^*} N_3^{D,g} = \frac{\nabla P_2}{RT} = \frac{P\nabla x_2}{RT} + \frac{x_2 \nabla P}{RT} \tag{2b}$$

$$\frac{x_3}{D_{31}^*} N_1^{D,g} + \frac{x_3}{D_{32}^*} N_2^{D,g} - \left[\frac{x_1}{D_{31}^*} + \frac{x_2}{D_{32}^*} + \frac{1}{D_3^{K*}}\right] N_3^{D,g} = \frac{\nabla P_3}{RT} = \frac{P\nabla x_3}{RT} + \frac{x_3 \nabla P}{RT} \tag{2c}$$

where the two terms on the right-hand side represent ordinary and Knudsen diffusion driving forces, respectively. Note that self diffusion, D_{11}^*, is not explicitly included in the equation set. Self diffusion in gases is expressed by the Knudsen diffusion coefficient, D_i^{K*}, which is operative even if the gas only has a single component.

For a single component, the DGM equation reduces to

$$N_1^{D,g} = -D_1^{K^*} \frac{\nabla P_1}{RT} \tag{3}$$

where the Knudsen diffusion coefficient models the “slip” of the gas, or the Klinkenberg effect.

As can be seen from equation (2), the diffusion of any single component may be strongly coupled with the diffusion of the other components. Therefore, in general, a single equation for the diffusion of a given component cannot be developed. Two exceptions are binary gas diffusion, where equations can be developed as given by Thorstenson and Pollock (1989), and trace gas diffusion, where an effective tortuosity can be defined for use with Fick’s law (Webb and Pruess, 2001) that will give the same results as the DGM.

For diffusion of dissolved components in the liquid phase, a simpler model has been used. There is no model equivalent to the DGM that is applicable to liquids. Therefore, a simple Fick’s law model has been implemented for liquids in the present study. The model is different from that of Pruess et al. (1999), however, in that the present formulation is in terms of mole fractions rather than mass fractions. The present model gives equimolar diffusion in the liquid, while the model used by Pruess et al. (1999) gives equal and opposite mass fluxes. The diffusion fluxes for each dissolved component (including water) are given by

$$N_i^{D,\ell} = -c_\ell D_{i\ell}^{*} \nabla x_i \tag{4}$$

where i applies to all the components including water.

2.2 Coupling of Diffusive Fluxes

The above equations predict gas and liquid diffusion for uniform properties and under single-phase conditions. For nonuniform properties and multiphase conditions, the solution of the above equations becomes much more complicated. Pruess and Webb (1999) developed a multiphase diffusion scheme by invoking conservation of total flux across the interface, which leads to harmonic weighting of the strength coefficient. However, their diffusion equations were based on Fick’s law, such that coupling between components in a given phase was not included; only the coupling between phases was considered.

The general concept of a weighting scheme for diffusion is that the fluxes to and from an “interface” condition are equal. This “interface” condition is defined by this equality of fluxes. For simple cases, harmonic weighting is the correct scheme as discussed by Tsang and Pruess (1990) for example. The same principle of conservation of mass flux, or diffusive flux, will be used in this case based on the combined gas and liquid rates. As discussed by Pruess and Webb (1999), the weighting scheme must consider the combined fluxes rather than each one individually.

For example, the DGM equation for component 1 can be written in terms of the unspecified interface conditions (mole fraction and pressure) as follows

$$-\left[\frac{1}{D_1^{K*}}+\frac{x_2}{D_{12}^*}+\frac{x_3}{D_{13}^*}\right]N_1^{D,g}+\frac{x_1}{D_{12}^*}N_2^{D,g}+\frac{x_1}{D_{13}^*}N_3^{D,g}=\frac{P}{RT}\frac{x_{1,i}-x_{1,u}}{d_u}+\frac{x_1}{RT}\frac{P_i-P_u}{d_u} \qquad (5)$$

where subscript i denotes the interface condition, and d_u is the distance from element 1 to the interface, or the upstream length. Naturally, the properties of element 1 are used for the coefficients. Similarly, the downstream equation is

$$-\left[\frac{1}{D_1^{K*}}+\frac{x_2}{D_{12}^*}+\frac{x_3}{D_{13}^*}\right]N_1^{D,g}+\frac{x_1}{D_{12}^*}N_2^{D,g}+\frac{x_1}{D_{13}^*}N_3^{D,g}=\frac{P}{RT}\frac{x_{1,d}-x_{1,i}}{d_d}+\frac{x_1}{RT}\frac{P_d-P_i}{d_d} \qquad (6)$$

where d_d is the downstream length from the interface to element 2, and the properties of element 2 are used. Similar sets of equations can be written for each gas phase component and each liquid phase component.

The gas equations specify the interfacial mole fraction in terms of the gas mole fraction, while the liquid equations use the liquid mole fraction for the interface. The difference between the mole fractions is resolved by defining an effective value of Henry's constant, which is defined as

$$K_{H,i,eff}=K_{H,i}\frac{c_\ell}{c_g}=\frac{x_{g,i}}{x_{\ell,i}} \qquad (7)$$

so the liquid interfacial mole fractions can be converted to gas interfacial mole fractions. $K_{H,i,eff}$ for the interface is calculated from the upstream and downstream elements based on the element mole fractions. Only elements with gas in them are considered. The value at the interface is estimated by harmonic weighting of the element values.

The values of the interfacial mole fractions and total interfacial pressure are calculated in the present procedure by invoking equal upstream and downstream total molar fluxes (gas plus liquid) to and from the interface for each component, as well as the requirement that the mole fractions sum to 1.0.

For 3 components, the following relationships are calculated for each connection:

diffusive gas flux from the upstream element to the interface (3 eqns)
diffusive gas flux from the interface to the downstream element (3 eqns)
diffusive liquid flux from the upstream element to the interface (3 eqns)
diffusive liquid flux from the interface to the downstream element (3 eqns)
gas + liquid flux to interface = gas + liquid flux away from interface
for each component (3 eqns)
sum of interface mole fractions in gas phase equals 1.0 (1 eqn)

where the flux equations are the DGM or liquid diffusion equations.

The unknowns are:

- diffusive gas flux from the upstream element to the interface (3 unk)
- diffusive gas flux from the interface to the downstream element (3 unk)
- diffusive liquid flux from the upstream element to the interface (3 unk)
- diffusive liquid flux from the interface to the downstream element (3 unk)
- interface mole fractions (3 unk)
- interface pressure (1 unk)

where the gas and liquid diffusive fluxes for each component are unknowns. Therefore, for a 3-component system, there are 16 equations and 16 unknowns. For a 5-component system such as in EOS7R, there are 26 equations and 26 unknowns for the fully coupled solution.

Separate gas and liquid diffusion calculations are available as an option similar to the original implementation in Pruess et al. (1999). Separate calculations are also performed if the fully coupled option is selected but there is no diffusion in a given phase for all components. In this case, gas diffusion and liquid diffusion are calculated separately using the DGM for the gas phase and Fick's law for the liquid phase. For a 5-component system, the separate gas diffusion equation set involves 16 equations and 16 unknowns. For liquid diffusion, the equation set includes 15 equations and 15 unknowns. There is no interface pressure unknown, and the mole fraction sum equation is deleted.

Solution of the diffusion equations is easily accomplished with standard matrix solvers. Checks are made that the upstream and downstream fluxes for each component have a relative error < 10^{-3} (typical values are 10^{-10} or less) and that the sum of the interface mole fractions is equal to 1.0 with the same relative error as the mass fluxes.

Some numerical roundoff problems were encountered in the matrix inversion when the difference in magnitude of the various fluxes was too large. In order to overcome this difficulty, if the ratio of the mole diffusive flux of a given component to the largest diffusive flux is less than 10^{-8}, the component diffusive flux is zeroed out. This limitation must be kept in mind when attempting to analyze diffusion of components with small concentrations.

2.3 Gas Diffusion Coefficients

For ordinary diffusion, the effective diffusion coefficients are the binary gas values, such as those calculated by Fuller (see Reid et al., 1987), multiplied by the medium tortuosity, τ_0, and the saturation-dependent tortuosity, τ_β, as well as pressure and temperature correction factors. These parameters are the same as used by Pruess et al. (1999), or

$$D_{ij,PT} = D_{ij}\left(P_0, T_0\right)\frac{P_0}{P}\left(\frac{T + 273.15}{273.15}\right)^q \tag{8}$$

where P_0 and T_0 are 10^5 Pa and 0^oC, respectively, and

$$D_{ij}^* = D_{ij,PT} f t_0 t_b \tag{9}$$

For Knudsen diffusion, the coefficient is often calculated from the Klinkenberg coefficient, b_i, (Klinkenberg, 1941) using the following relationship (Thorstenson and Pollock, 1989)

$$D_i^K = \frac{k b_i}{m_i} \tag{10}$$

The Knudsen diffusion coefficients for different gases are related by

$$D_j^K = D_i^K \left(\frac{m_i}{m_j} \right)^{1/2} \tag{11}$$

where m is the molecular weight.

The Klinkenberg coefficient for air at 25°C has been correlated with the liquid permeability by Heid et al. (1950) using numerous samples from oil-field cores and can be written as follows

$$b_{air} = 0.11 k_\ell^{-0.39} \tag{12}$$

where b_{air} is the Klinkenberg coefficient for air in Pascals, and k_ℓ is the liquid-phase permeability in m^2. Note that the data used in this correlation were based on permeability values in the range 10^{-12} to 10^{-17} m^2. Subsequently, Jones and Owens (1980) measured permeabilities on low-permeability gas sands in the range 10^{-14} to 10^{-19} m^2; their correlation is

$$b_{air} = k_\ell^{-0.33} \tag{13}$$

Between 10^{-14} and 10^{-17} m^2, where the permeability data overlap, the values from both correlations are quite similar. Each correlation gives lower values than the other in the region it is most applicable. Therefore, a reasonable approach is to take the minimum Klinkenberg coefficient from the two correlations.

The Knudsen diffusion coefficient input into the code is assumed to be at 25°C similar to the Heid et al. (1950) correlation. The temperature correction to other conditions is given by

$$D_{i,T}^K = D_i^K (T_0) \left(\frac{T + 273.15}{298.15} \right)^{0.5} \tag{14}$$

Note that there is no pressure correction because the Knudsen diffusion coefficient is independent of pressure (Mason and Malinauskas, 1983).

Because the Klinkenberg coefficient, and therefore the Knudsen diffusion coefficient, has been correlated in a porous medium, the porosity and tortuosity, τ_0, effects are already included in the value as discussed by Thorstenson and Pollock (1989). Therefore, only the saturation-dependent tortuosity, τ_β, is used to modify the Knudsen diffusion coefficient, or

$$D_i^{K*} = D_{i,T}^{K}\, t_{b} \tag{15}$$

The same equations and relationships for τ_0 and τ_β presented by Pruess et al. (1999) are used in the present model implementation, including the various options for the tortuosity coefficients. Because the tortuosity values τ_0 and τ_β have to be separately stored due to the Knudsen diffusion coefficient, the value of NB (see Pruess et al., 1999) for diffusion was increased from 8 to 9.

2.4 Liquid Diffusion Coefficients

Methods for calculating liquid diffusion coefficients in a non-porous system are given by Reid, et al. (1987), where typical values for water as the solvent are about 10^{-9} m^2/s at infinite dilution for room temperature conditions. Unlike gases, no pressure or temperature correction is applied. However, the tortuosity factors as given in equation (9) above are employed. When the Millington-Quirk relationship is selected for the saturation-dependent tortuosity, τ_β, the gas saturation is simply replaced by the liquid saturation; Jury et al. (1983) also used this approach to estimate the tortuosity for liquids.

2.5 Model Applicability

Note that there is a lower limit for Knudsen diffusion. The assumption in the above equations is that “slip” flow occurs, which can be modeled by the Klinkenberg factor. However, at very low permeabilities, other diffusion mechanisms become important such as configurational diffusion, where the pore size and the gas molecule diameter are approximately equal, and the configuration of the molecules and molecule-surface effects become important (Xiao and Wei, 1992a). The diffusion coefficient drops off dramatically in the configurational diffusion range to values of 10^{-13} m^2/s or below (Xiao and Wei, 1992b). The approximate transition between Knudsen diffusion and configurational diffusion occurs at a Knudsen diffusion coefficient of 10^{-8} m^2/s (Xiao and Wei, 1992a). Based on the Jones and Owens (1980) correlation, this transition occurs at a permeability of approximately 10^{-19} m^2. Therefore, the applicability of the above Klinkenberg correction should be limited to media with permeabilities of 10^{-19} m^2 and greater. If the porous medium has a lower value, the diffusion regime is probably configurational, and additional model modifications are required.

3.0 Verification

The above model has been verified by comparison to a number of problems with known or hand-calculated solutions. Most of the verification problems involve the Dusty Gas Model and the solution in terms of unknown interfacial conditions.

3.1 Single Gas

A simple two-volume problem with a single gas (air) was modeled to check the Knudsen diffusion coefficient case. Conditions were a permeability of 10^{-12} m^2 (Knudsen diffusion coefficient of 2.88 x 10^{-4} m^2/s at 25°C), a temperature of 20°C, and a pressure gradient of 0.1 Pa/m. The diffusion of air was evaluated by equation (3) as 3.394 x 10^{-10} kg/s, which agrees with the program output to within 0.03%.

3.2 Binary Gases

The DGM has been compared to the experimental data of Evans et al. (1962, 1963) for a low permeability (2.13 x 10^{-18} m^2) graphite by Webb (1998), which showed that the DGM compares well to the data while Fick’s law does not. Some of these same data have been used in the present verification exercise. The trace gases were specified to be Argon and Helium as in the experiments. Two situations were considered, zero pressure difference diffusion (Knudsen and ordinary diffusion only) and combined advection and diffusion.

a. Zero Pressure Difference

For the zero pressure difference case, Mason and Malinauskas (1983) give a relationship for the mole flux of both gases as a function of total pressure, which assumes a linear variation in the mole fraction of both gases in the graphite. The experimental data compare well to the relationship. Figure 1 compares the results of the present modified version of TOUGH2 with the relationship of Mason and Malinauskas; the agreement is excellent.

b. Combined Advection and Diffusion

For this more general case, Mason et al. (1967) performed an integration of the DGM assuming a linear variation for the mole fraction as above. Iteration is required to obtain the desired fluxes. The experimental data compare very well to the integrated equation. Explicit equations describing the various curves were not presented, so the curve was extracted from the original figures of Mason and Malinauskas (1983).

Comparison of the present modified version of TOUGH2 to these curves is given in Figure 2. Note that the viscosity of the fluid was not altered. The He-Ar mixture has a viscosity of about 2.26 x 10^{-5} $Pa \cdot s$ at 25°C compared to an air value of 1.85 x 10^{-5} $Pa \cdot s$.

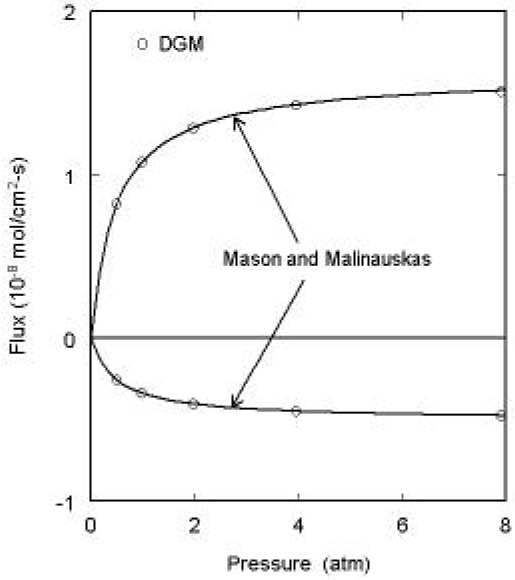

Figure 1. Verification for Zero Pressure Difference Diffusion

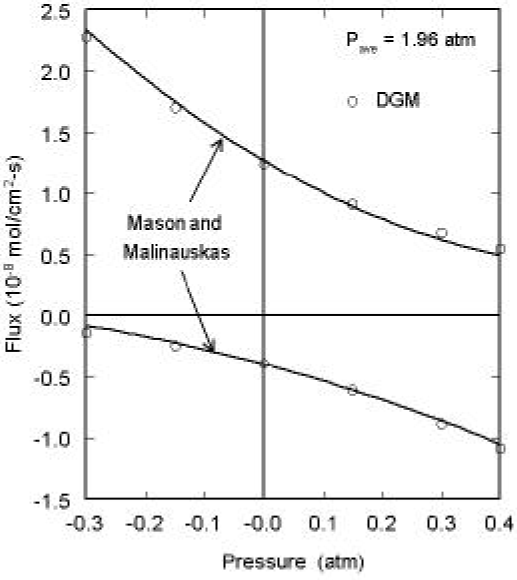

Figure 2. Verification for Combined Advection Plus Diffusion

Nevertheless, the program results and the curves compare very well. As mentioned above, the authors have made a number of assumptions in their derivation, so the agreement is not expected to be perfect.

3.3 Separate Diffusion

A simple two-volume problem was formulated such that both volumes were unsaturated. Volume 1 had a pressure of 99995 Pa and a liquid saturation of 0.3, while the volume 2 had a pressure of 100005 Pa and a liquid saturation of 0.4. The permeability of both volumes was 10^{-14} m^2.

For simplicity, hand calculations were performed for separate gas and liquid diffusion where the liquid saturation in both volumes was 0.3; equal pressures were also assumed for the evaluation of properties and diffusion coefficients. The hand calculations for the air and water vapor diffusion rates in the air phase, which used a closed form equation for the DGM applicable to binary gas mixtures (Thorstenson and Pollock, 1989), agreed to within 1%. The liquid diffusion rates agreed to within 0.5% of hand calculations.

3.4 Coupled Diffusion

Coupled hand calculations were not explicitly performed. All of the elements of the matrix were explicitly checked and found to be accurate. The resulting solution for the interfacial pressure and mole fractions was approximately the arithmetic average of that of the two volumes, and the resulting total diffusion fluxes were within a few percent of the total gas and liquid rates from the separate calculations, which was expected because the gas diffusion rates were much larger than the liquid diffusion rates. The matrix solutions for the individual gas and liquid diffusion rates to and from the interface were close to the separate calculations.

3.5 Discontinuous Diffusion

A special two-volume problem involving an all-liquid volume and an all-gas volume was considered. This problem evaluated the harmonic weighting of the effective value of Henry’s constant, as well as the formulation of equal total (gas plus liquid) diffusion to and from the interface. Naturally, the separate diffusion option resulted in zero diffusion, while the coupled calculations gave a value that agreed to within 1% of hand calculations.

3.6 Diffusion Across a Capillary Fringe

Pruess et al. (1999) presented a sample problem involving TCE and PCE diffusion across a capillary fringe. The problem consists of TCE and PCE in the gas phase at the solubility limits above the water table, which diffuses through the capillary fringe into the water table below. The original TOUGH2 results in Pruess et al. (1999) show considerable differences between the separate and coupled diffusion models. The calculation has been redone with the modified code to check the original implementation as well as to ascertain the differences between the previous Fick's law model and the present Dusty Gas Model for this problem.

Figures 3 and 4 show the results from the original Fick's law approach and the DGM. The differences between the results are minimal. As discussed by Webb (1998) and

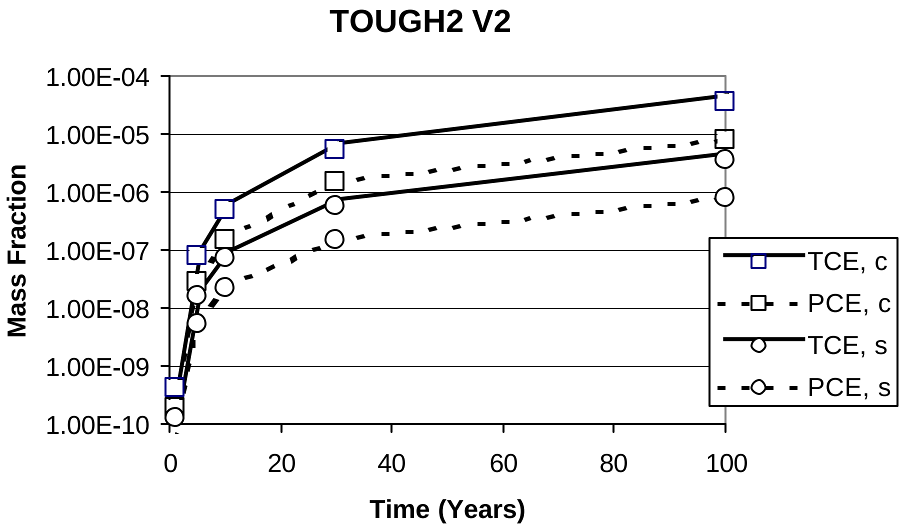

Figure 3. Original TOUGH2 Fick's Law Results for Coupled (c) and Separate (s) Diffusion

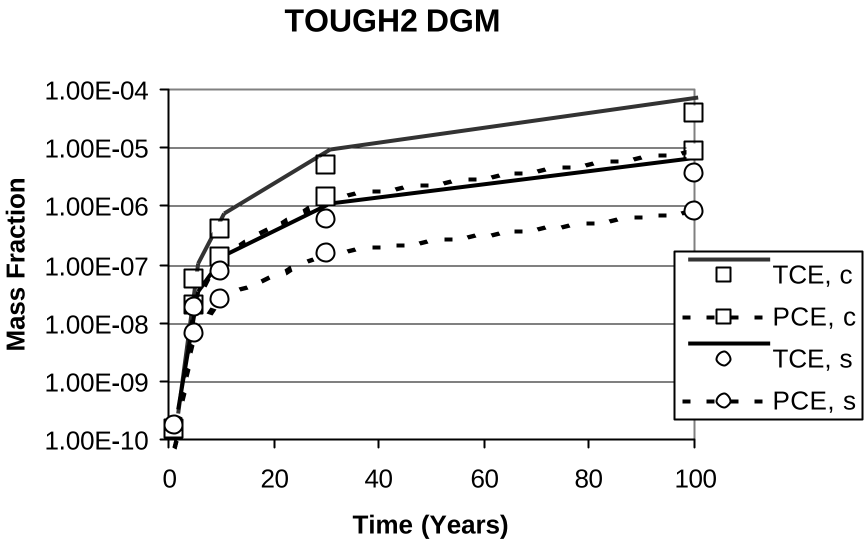

Figure 4. TOUGH2 DGM Results for Coupled (c) and Separate (s) Diffusion

Webb and Pruess (2001), the difference between Fick's law and the DGM are minimal for trace gases at higher permeabilities (k > 10^{-13} m^2), but may become orders of magnitude at lower values (k ~ 10^{-18} m^2). Note that the present problem involves small mole fractions of TCE and PCE (~7 mol% for TCE, 1.8 mol% for PCE). Therefore, the present problem is not a definitive test of the possible differences between Fick's law and the DGM. Additional comparisons for lower permeabilities and higher mole fractions may be useful.

4.0 Discussion

The Dusty Gas Model (DGM) has been added to TOUGH2 (Pruess et al, 1999). This gas diffusion model, as well as a modified liquid diffusion model, includes options for separate and coupled gas-liquid diffusion. The original Fick's law options have been retained. The DGM implementation, as well as the liquid diffusion model, has been verified for separate and coupled calculations. This new model has been compared to the original Fick's law model results for the sample problem involving diffusion across a capillary fringe. The differences are small due to the relatively high permeability considered and the small mole fraction of the gases. Additional tests would be useful for lower permeability media and higher mole fractions.

The input for the Dusty Gas Model is given in Appendix A including the input deck for the capillary fringe problem. The new model is triggered by additional options in MOP(24) while retaining the original models. The Knudsen diffusion coefficient for air at 25^oC is input in the ROCKS Block in the location of the Klinkenberg coefficient. If a Knudsen diffusion coefficient is not input and the DGM is selected, the value is calculated as the minimum value from the Heid et al. (1950) and the Jones and Owens (1980) correlations as discussed earlier.

Note that the DGM options take considerably more computer time than Fick's law. The difference is due to the fact that the DGM solves a series of matrices, which may be up to (26x26), for all the components and for the evaluation of the derivatives while the Fick's law options simply solves algebraic equations. It may be possible to speed up the DGM model by compressing the matrices by eliminating zero mole fraction components or by optimizing the solvers.

If the permeability of the porous media is less than about 10^{-19} m^2, the present model may not be appropriate. In this low permeability regime, configurational diffusion may be important as the pore size is approximately equal to the molecular diameter. In this case, a gas diffusion model for the configurational regime needs to be included.

5.0 References

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Appendix A

Input for Dusty Gas Model

Changes to the input to TOUGH2 are needed for the Dusty Gas Model. A change to the NB parameter in the MULTI block from 8 to 9 was made in order to separate out the tortuosity terms into their saturation and porous medium components as discussed in the main report.

The value of MOP(24) triggers the different gas diffusion options as follows:

= 0 – Fully-coupled Fick's law Model
= 1 – Separate Fick's law Model
= 2 – Fully-coupled DGM
= 3 – Separate DGM

Knudsen diffusion coefficients for air are entered in the ROCKS BLOCK in the location reserved for the Klinkenberg parameter, b, in units of m^2/s at $25^{o}C$. The MOP(24) value determines whether the input parameter is the Klinkenberg parameter or the Knudsen diffusion coefficient. If the input is a Knudsen diffusion coefficient, the correction to the gas permeability for slip effects is not performed. If a Knudsen diffusion coefficient is not input and the DGM is selected, the value is calculated based on the minimum value from the Heid et al. (1950) and the Jones and Owens (1980) correlations as discussed earlier.

The major addition is the DGM BLOCK, which specifies the Knudsen and ordinary diffusion coefficients. The liquid diffusion coefficients specified in the DIFFU BLOCK in the original implementation of Pruess et al. (1999) are used in the modified model. The DGM BLOCK format is as follows:

DGM – diffusion coefficients for DGM – DIFFU or SELEC BLOCK values not used
Format (8E10.4)

diffusivity values for DGM are input as follows (assumes $D_{j-i} = D_{i-j}$) (m^2/s):
first row: Ratio of Knudsen Diffusion Coefficients for component i over that for air followed by binary diffusion coefficients at P_0 and T_0 for components 1 through 5:
second row: D_{1-2}, D_{1-3}, D_{1-4}, D_{1-5}
third row: D_{2-3}, D_{2-4}, D_{2-5}
fourth row: D_{3-4}, D_{3-5}
fifth row: D_{4-5}

Example input

```
DGM
   1.268     1.268    0.4696   0.4180      1.0
   1.0e-6    1.0e-6    1.0e-6    1.0e-6
   1.0e-6    1.0e-6    1.0e-6
   1.0e-6    1.0e-6
   1.0e-6
```

The Knudsen diffusion coefficients should be related by the square root of the inverse of the molecular weight ratio such that the value is smaller for a higher molecular weight. The binary diffusion coefficients ($D_{1\text{-}2}$, etc) should be calculated for each gas pair using a model such as the Fuller method or the Wilke and Lee approach as discussed by Reid et al. (1987). For the example given above, constant values for the binary diffusion coefficients were assumed for comparison with the sample problem in Pruess et al. (1999).

The abbreviated input deck for the TOUGH2 capillary fringe sample problem is shown in Figure A-1 similar to that given by Pruess et al.(1999). The only differences are the input of the Knudsen diffusion coefficient in the ROCKS Block, a change in the value of MOP(24), and the addition of the DGM Block. Note that the value of NB is equal to 8 in the MULTI Block, even though the appropriate value is 9 as discussed in the main report. Changes were made in the code such that if an NB value of 8 is read, it is changed internally to be equal to 9.

```
*rdica* ... diffusion in a 1-D column across a capillary fringe
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
vados    2  2600.e00       .35    1.e-11   1.0e-11    1.e-11      2.51      920.
                                    0.25   1.17e-3
    7           .457       .15        1.       .10
    7           .457       .00  5.105e-4      1.e7        1.
...

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5    5    2    8
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   32000     99910 0 0000020000400 00  2
           3.15576e9        1.                          9.81
     1.e-5
             1.013e5                  0.                  0.                  0.
               10.50                 20.
TIMES----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6
        1. 31.5576e6 157.788e6 315.576e6 946.728e6 3.15576e9
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6
     -1.e5

     0.e-0     0.e-1
     0.e-6     0.e-6     0.e-6    -1.e-6    -1.e-6     0.e-6
     1.e50   131.389     0.e-6    -1.e-6                      2.10e-08
     1.e50   165.834    -1.e-6     0.e-6                      1.18e-08
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     1.e-6    1.e-10
     0.e-6    1.e-10
     1.e-6    1.e-10
     1.e-6    1.e-10
     1.e-6    1.e-10

     diffusivity values for DGM are input as follows (assumes Dj-i = Di-j):
     first row:  Knudsen Diffusion Coefficient Ratios for components 1-5
     second row: D1-2, D1-3, D1-4, D1-5
     third row:  D2-3, D2-4, D2-5
     fourth row: D3-4, D3-5
     fifth row:  D4-5
DGM
     1.268     1.268    0.4696    0.4180       1.0
    1.0e-6    1.0e-6    1.0e-6    1.0e-6
    1.0e-6    1.0e-6    1.0e-6
    1.0e-6    1.0e-6
    1.0e-6
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1          vados .1000E+01 .1000E+01           .5000E+00 .5000E+00-.5000E+00
...
AF1 1          aquif .1000E+01 .1000E+01           .5000E+00 .5000E+00-.1450E+02
ina 0
con 0          trapp
top 0          atmos        1.
bot 0          aquif        1.

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
con 0A51 1                   1     1.e-9        .5     1.e-1
top 0A11 1                   3     1.e-9        .5        1.        1.
A11 1A21 1                   3 .5000E+00 .5000E+00 .1000E+01 .1000E+01
...
AE1 1AF1 1                   3 .5000E+00 .5000E+00 .1000E+01 .1000E+01
AF1 1bot 0                   3        .5     1.e-9        1.        1.

INCON -- INITIAL CONDITIONS FOR   19 ELEMENTS AT TIME   .100000E-08
A11 1            .35000000E+00
  .1011830232536E+06  .0000000000000E+00  .0000000000000E+00  .0000000000000E+00
  .1084703339434E+02  .2000000000000E+02
...
con 0            .35000000E+00
  .1012297975914E+06  .0000000000000E+00           1.0998e-3           2.0063e-4
  .1084567823274E+02  .2000000000000E+02
bot 0            .35000000E+00
  .1438478256741E+06  .0000000000000E+00  .0000000000000E+00  .0000000000000E+00
  .9999999999008E-12  .2000000000000E+02

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure A-1. Abbreviated TOUGH2 DGM Input File for Capillary Fringe Problem.

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Appendix B

Various Forms of Fick's Law

Fick's first law of diffusion for a binary mixture is (Bird, Stewart, and Lightfoot, 1960)

$$J_A^M = -cD_{AB}^{*}\nabla x_A \qquad \text{(B-1)}$$

where J_A^M is the mole flux of component A relative to the molar-average velocity. Bird, Stewart, and Lightfoot (1960) present Fick's first law in numerous equivalent forms. The equivalent flux relative to stationary coordinates is

$$N_A = x_A(N_A + N_B) - cD_{AB}^{*}\nabla x_A \qquad \text{(B-2)}$$

where N_i is the mole flux of component i relative to stationary coordinates. The flux relative to stationary coordinates is a combination of the molar flux of the bulk fluid (first term) and the diffusive flux. If equimolar counter-diffusion occurs, $N_A = -N_B$, the molar-average velocity is zero, and the two fluxes are equivalent, or

$$N_A = -cD_{AB}^{*}\nabla x_A \qquad \text{(B-3)}$$

As discussed by Webb (1998), this popular assumption is generally not correct. Nevertheless, equation (B-3) is commonly used.

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