On Vertical Diffusion of Gases in a Horizontal Reservoir

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Abstract. Exact and approximate solutions to vertical diffusion in gravity-stable, ideal gas mixtures in gas reservoirs, depleted oil reservoirs, or drained aquifers are presented, and characteristic times of diffusion are obtained. Our solutions also can be used to test numerical simulators that model diffusion after gas injection. First, we consider isothermal, countercurrent vertical diffusion of carbon dioxide and methane in a horizontally homogeneous reservoir. Initially, the bottom part of the reservoir, with no flow boundaries at the top and bottom, is filled with CO_2 and the upper part with CH_4. At time equal zero, the two gases begin to diffuse. We obtain the exact solution to the initial and boundary-value problem using Fourier series method. For the same problem, we also obtain an approximate solution using the integrated mass balance method. The latter solution has a particularly simple structure, provides a good approximation and retains the important features of the exact solution. Its simplicity allows one to perform calculations that are difficult and non-transparent with the Fourier series method. It also can be used to test numerical algorithms. Furthermore, we consider diffusion of CO_2 with partitioning into connate water. We show that at reservoir pressures the CO_2 retardation by water cannot be neglected. The diffusion-retardation problem is modelled by a non-linear diffusion equation whose self-similar solution is obtained. Finally, we obtain a self-similar solution to a nonlinear diffusion problem. This solution is a good approximation at early times, before the diffusing gases reach considerable concentrations at the top and bottom boundaries of the reservoir.

Key words: diffusion, ideal gas, reservoir, approximate solution, connate water, retardation, self-similar solution.

1. Introduction

This work has been motivated by the evaluation of the possibility of carbon sequestration enhanced natural gas recovery, CSEGR, proposed in Oldenburg *et al.* (2001). CSEGR involves injection of CO_2 into a depleted natural gas reservoir and simultaneous or sequential enhanced production of natural gas. Much like a number of approaches to enhanced oil recovery, reservoir simulation has shown that CO_2 injection can repressurize a depleted natural gas reservoir and consequently lead to increased natural gas production. Revenues from enhanced natural gas production can then offset the cost of capture and separation of the injected CO_2.

One of the critical issues that will determine the feasibility of **CSEGR** is the rate and extent of mixing between injected CO_2 and resident natural gas. Mixing will occur because of the combined influence of molecular diffusion, gravity-driven buoyancy flow and advective dispersion caused by local and macroscopic variations in flow velocity (Oldenburg *et al.*, 2001).

Similar issues are encountered with cushion gases for natural gas storage and more generally, with mixing among different gases in underground reservoirs. The use of cushion gases, particularly N_2, to improve the efficiency of gas storage in aquifers and depleted natural gas reservoirs, can improve deliverability and reduce the working gas requirements (Carriére *et al.*, 1985; Laille and Coulomb, 1986; Laille *et al.*, 1988).

In this paper, we focus on developing a better understanding of and predictive capability for the countercurrent diffusion of CO_2 and CH_4. Our analysis is extended to include the dissolution of the diffusing CO_2 into connate water, which has the potential to slow down the rate of mixing of CO_2 and CH_4.

In addition to the aforementioned applications, the analytical solutions presented here can be used to verify numerical solutions dominated by gas diffusion, for example Oldenburg *et al.* (2001).

2. Problem Formulation

In this section, we formulate a model of isothermal diffusion of constituents of a gaseous mixture in mechanical equilibrium in a large horizontal reservoir. More specifically, we estimate the evolution of vertical concentration profiles of the gas constituents.

Consider a uniform and homogeneous horizontal reservoir of thickness L. We focus our attention on diffusion far enough from the lateral boundaries of the reservoir so that we can neglect the horizontal components of gas fluxes. Initially, an upper part of the reservoir is filled with pure methane and a lower one with pure carbon dioxide. Both gases are at the same constant temperature. At time $t = 0$, the gases begin to diffuse into each other. The gas mixture is considered ideal, and the thermodynamic activities (Abbott and Van Ness, 1972) of both gases are equal to their mole fractions. We assume that the reservoir thickness and pressure are not too large and, therefore, we can neglect the change of hydrostatic pressure in the gas column and the vertical gradation of equilibrium mixture composition caused by gravity.

At a given temperature and pressure, the density of carbon dioxide is higher than that of methane; therefore, diffusion is gravity-stable and its characteristic time scale, τ can be simply estimated as

$$\tau \propto \frac{L^2}{D_{12}}, \tag{1}$$

where D_{12} is the mean effective binary diffusion coefficient in a mixture of two constituents. We call the diffusion coefficient 'effective' because the process is

strongly affected by the structure of the pore space and the actual diffusion rate may be different from the one measured in a diffusion cell. In general, the effective diffusion coefficient depends also on the temperature, the pressure, and the composition of the gas mixture. As we neglect changes of pressure and temperature and consider a homogeneous reservoir, we assume that the coefficient D_{12} in Equation (1) is constant. Equation (1) allows us to make rough estimates. For example, if, at a given pressure and temperature, the effective binary diffusion coefficient of CO_2 in methane is assumed to be 0.001 cm^2/s, and the reservoir thickness is of the order of 100 m, then, from Equation (1), it will take hundreds of years to reach a practically uniform mixture of CO_2 and CH_4, when the bottom half of the reservoir is initially filled with CO_2.

3. Background

The principal equations of gas diffusion are listed in this section. A full derivation may be found in, for example Bird *et al.* (1960). For convenience, we use the following indexing convention: carbon dioxide is the mixture constituent 1 and methane is 2.

The mass or molar flux of constituent $B = 1, 2$ of a fluid mixture with respect to a reference frame is defined as a vector whose magnitude is equal to the mass or moles of constituent B that pass through a unit area per unit time.

One may define the *mass* diffusive flux in a binary system 1, 2 as

$$\boldsymbol{j}_{(m|v^*)1} = -\mathcal{D}_{12}\nabla\rho_1 \quad \text{(Fick's law)}, \tag{2}$$

where $\boldsymbol{j}_{(m|v^*)1}$ should be read as 'the mass flux of constituent 1 relative to the molar-average mixture velocity $\boldsymbol{v}^*$', ρ_1 is the mass density of constituent 1, and $\mathcal{D}_{12}$ is the binary diffusion coefficient based on the mass flux. The total mass density of the mixture, ρ, is uniform in Equation (2), that is, it is constant given a constant temperature.

If the fluid density is not uniform, one defines the mass diffusivity $D_{12} = D_{21}$ in a binary system using the *molar* diffusive flux:

$$\boldsymbol{j}_{(n|v^*)1} = -cD_{12}\nabla x_1. \tag{3}$$

Here c is the total molar concentration of both constituents of the gas, and x_1 is the molar fraction of constituent 1.

It may easily be shown (Hirschfelder *et al.*, 1954; Bird *et al.*, 1960) that the molar diffusion fluxes can be expressed by the respective fluxes relative to a stationary frame of reference as

$$\boldsymbol{j}_{(n|v^*)1} = \boldsymbol{j}_{(n)1} - x_1\sum_{B=1}^{2}\boldsymbol{j}_{(n)B} = -cD_{12}\nabla x_1, \tag{4}$$

where $\boldsymbol{j}_{(n)1}$ is the molar flux of constituent 1 relative to a stationary frame of reference, and so on.

The binary diffusion coefficients of equimolar mixtures of gaseous CO_2 and several other gases are listed in the CRC Handbook of Chemistry and Physics at 1 atm and temperatures ranging from 273.15 to 573.15 K. At 293.15 K and 1 atm, the diffusion coefficient of CO_2 in propane is 0.084 cm²/s and at 373.15 K, it is 0.133 cm²/s. If one assumes that the diffusion coefficient is 0.1 cm²/s at atmospheric pressure and the reservoir temperature, then at the reservoir pressure of 30 atm, this coefficient is approximately equal to 0.003 cm²/s. If one also assumes the pore tortuosity factor of three, the effective binary diffusion coefficient of CO_2 in CH_4 at reservoir conditions might be 0.001 cm²/s. This particular value has been used here.

In a 100 m thick reservoir subject to the geothermal gradient of 0.02 K/m, the temperature difference between the reservoir top and bottom is just 2 K, the reservoir temperature variation is about 2K/340 K, or 0.7%, and we assume a uniform reservoir temperature.

With gravity, mixture constituents separate in proportion to their molecular weights. For an ideal mixture of two constituents, one obtains (Gibbs, 1961):

$$x_B(z)P(z) = x_B(0)P(0)\exp\left(-\frac{M_B g}{RT}z\right), \qquad B = 1, 2$$

$$P(z)/P(0) = \left[x_1(0)\exp\left(-\frac{M_1 g}{RT}z\right) + x_2(0)\exp\left(-\frac{M_2 g}{RT}z\right)\right], \qquad (5)$$

where M_1 and M_2 are the molecular weights of CO_2 and CH_4, $P(0)$ is the pressure at the reservoir bottom, R is the universal gas constant, and g is the acceleration of gravity. In an equimolar mixture of CO_2 and CH_4, $x_1(0) = 0.5$, at the reservoir temperature $T = 340$ K, the mixture pressure at the top of the reservoir ($L = 100$ m) is

$$P(100) \approx 0.99 P(0). \qquad (6)$$

Thus, the reservoir pressure is uniform to within 1%. The equilibrium mole fraction of CO_2 at the top of the reservoir is

$$x_1(100)/x_1(0) = \frac{P(0)}{P(z)}\exp\left(-\frac{M_1 g}{RT}z\right) \approx 0.99. \qquad (7)$$

The equilibrium mole fraction of CO_2 is vertically uniform to within 1%.

4. Model Formulation

We assume that the positive flow is upwards in the vertical z-direction. In one-dimensional vertical flow with no chemical reactions, the mole balance equation of each gas is

$$\frac{\partial c_i}{\partial t} + \frac{\partial j_{(n)i}}{\partial z} = 0, \qquad i = 1, 2. \qquad (8)$$

From Equation (4) we now have

$$j_{(n)i} = x_i(j_{(n)1} + j_{(n)2}) - cD_{12}\frac{\partial x_i}{\partial z}, \qquad i = 1, 2, \tag{9}$$

that is, the molar flux of component i in stationary coordinates is the sum of the flux resulting from total molar bulk flow and from the diffusion flux.

At each reservoir cross-section and at any given time, one gas replaces an equal volume of the other

$$\bar{V}_1 j_{(n)1} + \bar{V}_2 j_{(n)2} = 0, \tag{10}$$

where $\bar{V}_i(x_1, P, T)$ is the partial molar volume of constituent i. Substitution of Equation (10) into Equation (9) yields

$$j_{(n)1} = \frac{-cD_{12}(\partial x_1/\partial z)}{1 - x_1(1 - \bar{V}_1/\bar{V}_2)}, \qquad j_{(n)2} = \frac{cD_{12}(\partial x_1/\partial z)}{x_1 + (1 - x_1)\bar{V}_2/\bar{V}_1}, \tag{11}$$

and the mole balance equations (8) are two coupled nonlinear PDE's in c and x_1

$$\frac{\partial(x_1 c)}{\partial t} - \frac{\partial}{\partial z}\left[\frac{cD_{12}\frac{\partial x_1}{\partial z}}{1 - x_1(1 - \bar{V}_1/\bar{V}_2)}\right] = 0,$$

$$\frac{\partial[(1 - x_1)c]}{\partial t} + \frac{\partial}{\partial z}\left[\frac{cD_{12}\frac{\partial x_1}{\partial z}}{x_1 + (1 - x_1)\bar{V}_2/\bar{V}_1}\right] = 0. \tag{12}$$

In an ideal gas mixture, however, the partial molar volumes are constant

$$\bar{V}_i \equiv \left.\frac{\partial V}{\partial n_i}\right|_{T,P,n_{j\neq i}} = \frac{RT}{P}, \qquad i = 1, 2, \tag{13}$$

and

$$j_{(n)1} = -j_{(n)2}. \tag{14}$$

Note that for a non-ideal gas mixture Equations (13) and (14) are invalid because the partial molar volumes are functions of composition, pressure and temperature, and they can be negative (Abbott and Van Ness, 1972). Thus, for a non-ideal gas mixture, the mass flux equations (12) are coupled and no simplification is possible. Note that in some numerical models that use an equation of state to calculate the fluid properties, for example Adenekan *et al.* (1993), the partial molar volumes are still assumed constant, leading in effect to an ideal mixture approximation.

For an ideal gas mixture, Equation (14) can be inserted into Equation (9) with the following result:

$$j_{(n)i} = -cD_{12}\frac{\partial x_i}{\partial z}, \qquad i = 1, 2. \tag{15}$$

Because the fluxes are equimolar, the total concentration $c = c_1(z, t) + c_2(z, t)$ is constant. Therefore, Equation (15) is equivalent to

$$j_{(n)i} = -D_{12}\frac{\partial c_i}{\partial z}, \qquad c_i = x_i c, \qquad i = 1, 2, \tag{16}$$

and Equation (8) simplifies to

$$\frac{\partial c_i}{\partial t} - \frac{\partial}{\partial z}\left(D_{12}\frac{\partial c_i}{\partial z}\right) = 0, \qquad i = 1, 2. \tag{17}$$

In dimensionless variables,

$$\tilde{c}_i = c_i/c, \qquad i = 1, 2, \qquad \tilde{z} = z/L, \qquad \tilde{t} = tD/L^2, \tag{18}$$

Equation (17), and appropriate initial and boundary conditions, take the following form:

$$\frac{\partial \tilde{c}_i}{\partial \tilde{t}} = \frac{\partial^2 \tilde{c}_i}{\partial \tilde{z}^2}, \qquad i = 1, 2, \tag{19}$$

$$\tilde{c}_1(\tilde{z}, 0) = \begin{cases} 1 & \text{for } 0 \leqslant \tilde{z} \leqslant \tilde{z}_0 \\ 0 & \text{for } \tilde{z}_0 < \tilde{z} \leqslant 1 \end{cases}, \qquad \tilde{c}_2(\tilde{z}, 0) = \begin{cases} 1 & \text{for } \tilde{z}_0 \leqslant \tilde{z} \leqslant 1, \\ 0 & \text{for } 0 \leqslant \tilde{z} < \tilde{z}_0, \end{cases}$$

$$\left.\frac{\partial \tilde{c}_1}{\partial \tilde{z}}\right|_{z=0,1} = \left.\frac{\partial \tilde{c}_2}{\partial \tilde{z}}\right|_{z=0,1} = 0. \tag{20}$$

Here $\tilde{z}_0 = z_0/L$, z_0 is the initial reservoir thickness filled with constituent 1, the initial dimensional concentration of 1 is $c_1(z, 0) = P/RT$, $0 \leqslant z \leqslant z_0$, etc.

5. Solution to Initial and Boundary Value Problem (19)–(20)

5.1. FOURIER SERIES SOLUTION

Solution to the initial and boundary-value problem (19)–(20) can be obtained using standard Fourier series technique, see, for example, Carslaw and Jaeger (1959) and Tikhonov and Samarskii (1963):

$$\tilde{c}_1(t, z) = \tilde{z}_0 + \sum_{n=1}^{\infty} \frac{1}{\pi n} \exp(-\pi^2 n^2 \tilde{t}) \sin \pi n \tilde{z}_0 \cos \pi n \tilde{z}. \tag{21}$$
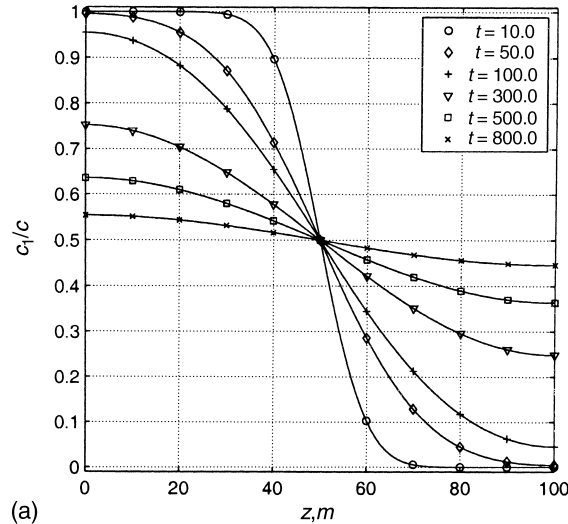
In particular, if $\tilde{z}_0 = 0.5$ ($z_0 = L/2$), we obtain in original variables

$$\frac{c_1(t, z)}{c} = \frac{1}{2} + \frac{2}{\pi} \times$$

$$\times \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left[-\pi^2(2n+1)^2\frac{D_{12}t}{L^2}\right] \cos\left[\frac{(2n+1)\pi z}{L}\right]. \tag{22}$$
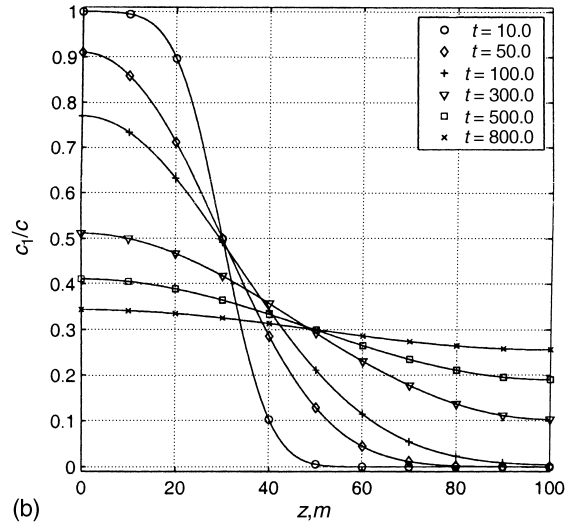
The results are plotted in dimensionless coordinates in Figure 1 for $\tilde{z}_0 = 0.5$ and 0.3, respectively. In agreement with Equation (1), in 800 years almost all of the CO_2 in the lower half of the reservoir diffuses into the upper half, and the diffusion is practically over.

The Fourier series solution (21) can be rewritten in the following form:

$$\tilde{c}_1(\tilde{t}, \tilde{z}) = \tilde{z}_0 + \frac{1}{\pi} \exp(-\pi^2 \tilde{t}) \sin \pi \tilde{z}_0 \cos \pi \tilde{z} + R(\tilde{t}, \tilde{z}), \tag{23}$$

Figure 1. Dimensionless concentration of CO_2 as a function of time in years ((a) $\tilde{z}_0 = 0.5$. (b) $\tilde{z}_0 = 0.3$.) Initially, CO_2 is in the lower part of the reservoir. The CH_4 concentration profiles are the mirror images.

where

$$R(\tilde{t}, \tilde{z}) = \exp(-4\pi^2\tilde{t}) \sum_{n=2}^{\infty} \frac{1}{\pi n} \exp(-\pi^2(n^2 - 4)\tilde{t}) \sin \pi n \tilde{z}_0 \cos \pi n \tilde{z}. \quad (24)$$

The quadratic mean of remainder term (24) can be roughly estimated in the following way:

$$\sqrt{\int_0^1 R(\tilde{t}, \tilde{z})^2 d\tilde{z}} \leqslant \frac{1}{\pi\sqrt{2}} \exp(-4\pi^2\tilde{t})\sqrt{\frac{\pi^2}{6} - 1} \approx 0.18 \exp(-4\pi^2\tilde{t}). \quad (25)$$

Therefore, for large t, the solution (21) can be approximated by the first two terms:

$$\tilde{c}_1(\tilde{t}, \tilde{z}) \approx \tilde{z}_0 + \frac{1}{\pi} \exp(-\pi^2\tilde{t}) \sin \pi \tilde{z}_0 \cos \pi \tilde{z}. \quad (26)$$

5.2. APPROXIMATE SOLUTION

In Figure 1, the early time concentrations of CO_2 near the upper boundary and of CH_4 near the lower boundary are essentially zero. This observation allows one to construct an approximate but analytic solution that is much simpler than the full Fourier series solution.

We consider Equation (19) in integral form. The approximate method used here is described in Barenblatt *et al.* (1990). Since all the equations are already dimensionless, we skip the tilde in the notations throughout this section.

First, note that the solution (22) is symmetric with respect to $z = 0.5$, and $c(0.5, t) = 0.5$. Therefore, let us consider an auxiliary problem:

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2}, \qquad 0 \leqslant z \leqslant 1, \qquad t > 0, \quad (27)$$

with the zero initial conditions and the following boundary conditions:

$$c(z, 0) = 0; \qquad c(0, t) = c_0, \qquad \frac{\partial c(1, t)}{\partial z} = 0. \quad (28)$$

Clearly, at $c_0 = 0.5$, the change of variables, $z \rightarrow 0.5 + 0.5z$ and $t \rightarrow 0.25t$, transforms the solution of Equations (27)–(28) to the solution of Equations (19)–(20) restricted to the values of $\tilde{z}$ between 0.5 and 1.

Integration of Equation (27) with respect to z from 0 to 1 yields

$$\frac{du(t)}{dt} = -\left.\frac{\partial c}{\partial z}\right|_{z=0}, \qquad u(t) = \int_0^1 c(z, t) dz. \quad (29)$$

We search a solution to Equation (29) in the form

$$c(z, t) = \begin{cases} a_0(t)z^2 + a_1(t)z + a_2(t), & 0, \leqslant z \leqslant b(t), \\ 0, & b(t) < z \leqslant 1 \end{cases} \quad (30)$$

with

$$\left. \frac{\partial c}{\partial z} \right|_{z=b(t)} = 0. \quad (31)$$

Here $a_i(t)$, $i = 0, 1, 2$, and $b_i(t)$ are the functions of time to be determined. Straightforward calculations lead to the following solution:

$$c(z, t) = \begin{cases} \dfrac{c_0}{12t}z^2 - \dfrac{c_0\sqrt{3}}{3\sqrt{t}}z + c_0, & 0 \leqslant z \leqslant 2\sqrt{3t}, \\ 0, & 2\sqrt{3t} < z \leqslant 1. \end{cases} \quad (32)$$

Clearly, this solution is valid only for $t \leqslant 1/12$, when diffusion has not altered the concentrations at the top of the reservoir. The Fourier solution (22) and solution (32) are very close for short times (here up to 50 years), but the solution (32) is much simpler. It also allows one to calculate the rate of propagation of CO_2 at a given concentration. For example, from Equation (32), the coordinate $z(t)$ of the concentration level $c/c_0 = 0.1$ is given by the following equation:

$$z(t) = \sqrt{12}(1 - \sqrt{0.1})\sqrt{t} \approx 2.4\sqrt{t}. \quad (33)$$

Solution (32) can be extended to dimensionless times exceeding $1/12$. Indeed, at $t \geqslant 1/12$, let us replace the condition (31) with the original boundary condition (28) and let us look for a solution to the integrated mass balance equation (29) in the form

$$c(z, t) = a_0(t)z^2 + a_1(t)z + a_2(t). \quad (34)$$

Again, $a_i(t)$, $i = 1, 2$, and $b_i(t)$ are the functions to be determined. Cumbersome, but straightforward calculations yield

$$c(z, t) = c_0 \exp\left[-3\left(t - \frac{1}{12}\right)\right]z^2 - 2c_0 \exp\left[-3\left(t - \frac{1}{12}\right)\right]z + c_0. \quad (35)$$

For larger times, the solution given by Equation (35) produces not as good an approximation to the exact solution as the solution given by Equation (32). However, at larger t, the estimate (25) suggests to look for an approximate solution in the form of a trigonometric polynomial. Let us look for a solution of the form

$$c(z, t) = -a(t)\sin\frac{\pi z}{2} + c_0. \quad (36)$$

Then, using an integrated equation similar to Eq. (29), we obtain

$$c(z, t) = c_0 - c_0 \exp\left[-\pi^2(t - 1/12)/4\right]\sin\frac{\pi z}{2}. \quad (37)$$

6. CO₂ Diffusion in Presence of Connate Water

Suppose now that the gas reservoir has immovable ('connate') water saturation S_{wc}. Methane does not dissolve in connate water, but CO_2 does. Hence, the mass balance equation for CO_2 must be augmented by a term that reflects its partitioning into the water

$$
\left[1 + \frac{\phi S_{wc} K_1}{\phi (1 - S_{wc})}\right] \frac{\partial c_1}{\partial t} = \frac{\partial j_{(n)1}}{\partial z},
$$
$$
\frac{\partial c_2}{\partial t} = \frac{\partial j_{(n)2}}{\partial z},
$$
$$
j_{(n)i} = x_i (j_{(n)1} + j_{(n)2}) -
$$
$$
- c D_{12} \frac{\partial x_i}{\partial z}, \qquad i = 1, 2, \tag{38}
$$

where ϕ is the rock porosity, $K_1 = c_{1,w}/c_1$ is the equilibrium solubility of CO_2 in water, $c_{1,w}$ being the concentration of CO_2 dissolved in water. The coefficient in front of the time derivative in Equation $(38)_1$, is easily recognized as the CO_2 retardation factor

$$
R_1 \equiv 1 + \frac{S_{wc} K_1}{(1 - S_{wc})}. \tag{39}
$$

The solubility of CO_2 in water at $T = 340$ K and $P = 50$ atm is about 10 Nm³ CO_2/kg H_2O. At constant temperature, this solubility increases almost linearly with pressure. At 125 atm, some 25 Nm³ CO_2 dissolves in 1 kg of water. At these two pressures the respective equilibrium constants are K_1 (340 K, 50 atm) ≈ 0.25, K_1 (340 K, 125 atm) ≈ 1.2.

At $S_{wc} = 0.37$, the CO_2 retardation factors are, respectively,

$$
R_1(340 \text{ K}, 50 \text{ atm}) \approx 1.15, \qquad R_1(340 \text{ K}, 125 \text{ atm}) \approx 1.73. \tag{40}
$$

Therefore, at moderate reservoir pressures and geothermal temperatures, the CO_2 partitioning into the connate water cannot be neglected.

With retardation, the CO_2 and CH_4 fluxes are no longer equimolar, because CO_2 partitions into the water while it also diffuses

$$
\bar{V}_1 \frac{j_{(n)1}}{R_1} + \bar{V}_2 j_{(n)2} = 0. \tag{41}
$$

We assume that the CO_2-filled portion of the reservoir is initially in gas–water equilibrium. With these assumptions, and for an ideal gas mixture, Equations (12) become

$$
\frac{\partial (x_1 c)}{\partial t} = \frac{\partial}{\partial z} \left[\frac{c D_{12}}{R_1 + x_1 (1 - R_1)} \frac{\partial x_1}{\partial z} \right],
$$
$$
\frac{\partial [(1 - x_1) c]}{\partial t} = - \frac{\partial}{\partial z} \left[\frac{c D_{12}}{R_1 + x_1 (1 - R_1)} \frac{\partial x_1}{\partial z} \right]. \tag{42}
$$

The flow constant is again the total concentration in the gaseous phase

$$c = x_1 c + (1 - x_1)c = \frac{P}{RT} = \text{const.} \tag{43}$$

The gas pressure is still practically constant because initially CO_2 is in equilibrium with water in the bottom part of the reservoir, $\tilde{z}_0$, in which it resides

$$
\begin{aligned}
n_1 &= R_1 \frac{P_i(\tilde{z}_0 V)}{RT} = R_1 \frac{p_{1\tilde{z}_0} V}{RT} \Rightarrow p_{1\tilde{z}_0} = P_i \tilde{z}_0, \\
n_2 &= \frac{P_i[(1 - \tilde{z}_0)V]}{RT} = \frac{p_{2\tilde{z}_0} V}{RT} \Rightarrow p_{2\tilde{z}_0} = P_i(1 - \tilde{z}_0), \\
P_{\tilde{z}_0} &= p_{1\tilde{z}_0} + p_{2\tilde{z}_0} = P_i,
\end{aligned}
\tag{44}
$$

where n_1 and n_2 are the total numbers of moles of CO_2 and CH_4 in the reservoir, respectively; P_i is the initial reservoir pressure; and $P_{\tilde{z}_0}$ is the sum of the partial pressures of CO_2 and CH_4, $p_{1\tilde{z}_0}$ and $p_{2\tilde{z}_0}$, respectively, after the final mixture equilibrium has been reached. Because initially the CO_2 is in equilibrium with the connate water, its diffusion does not change the total gas pressure.

With Equation (43), the governing equation for the mole fraction of CO_2 is simply

$$\frac{\partial x_1}{\partial t} = D_{12} \frac{\partial}{\partial z} \left[\frac{1}{R_1 + (1 - R_1)x_1} \frac{\partial x_1}{\partial z} \right]. \tag{45}$$

If we put $u = R_1 + (1 - R_1)x_1$, the following nonlinear diffusion equation in u is obtained:

$$\frac{\partial u}{\partial t} = D_{12} \frac{\partial}{\partial z} \left(u^{-1} \frac{\partial u}{\partial z} \right). \tag{46}$$

We seek a self-similar solution to Equation (46) subject to the following initial and boundary conditions:

$$
\begin{aligned}
u(z < 0, t = 0) &= 1, \quad u(z > 0, t = 0) = R_1, \\
u(z \to -\infty, t) &= 1, \quad u(z \to +\infty, t) = R_1, \qquad t > 0.
\end{aligned}
\tag{47}
$$

Let us choose the following similarity variable:

$$\xi = \frac{z}{\sqrt{D_{12}t}}. \tag{48}$$

Then Equation (46) transforms to

$$\frac{d^2(\ln u)}{d\xi^2} + \frac{1}{2}\xi \frac{du}{d\xi} = 0, \tag{49}$$

with the following boundary conditions:

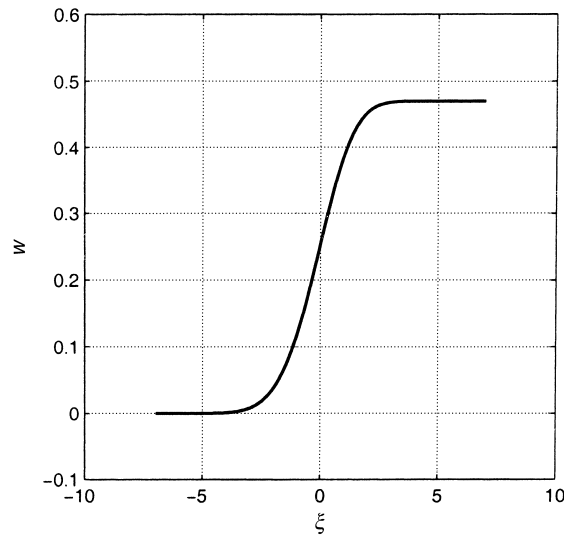$$u(\xi \to -\infty) = 1, \qquad u(\xi \to +\infty) = R_1. \tag{50}$$

Figure 2. Solution to problem (51)–(52).

Put $w(\xi) = \ln u(\xi)$, then for the function $w(\xi)$ we obtain the following boundary-value problem:

$$\frac{d^2 w}{d\xi^2} + \frac{1}{2}\xi \exp(w)\frac{dw}{d\xi} = 0, \tag{51}$$

$$w(\xi)|_{\xi \to -\infty} = 0, \qquad w(\xi)|_{\xi \to +\infty} = \ln R_1. \tag{52}$$

The solution to the boundary problem (51)–(52), Figure 2, can be obtained numerically with a Runge–Kutta method combined with shooting. The corresponding profiles of the CO_2 mole fraction are shown in Figure 3 for several different times.

7. Solution to a Nonlinear Diffusion Equation

In the next two sections, we analyze other possible ways of solving Equation (18) along with the initial and boundary conditions (19).

Solution (22) has been obtained by assuming a constant diffusion coefficient. If this assumption does not hold, the solution must be found using a different technique. In this section, we find a self-similar solution to equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D(c)\frac{\partial c}{\partial z}\right), \qquad z \in -\infty, +\infty, \tag{53}$$

subject to the following initial and boundary conditions:

$$c(0, z) = \begin{cases} 1, & z < 0 \\ 0, & z \geqslant 0 \end{cases}; \qquad c(t, -\infty) = 1, \qquad c(t, \infty) = 0. \tag{54}$$
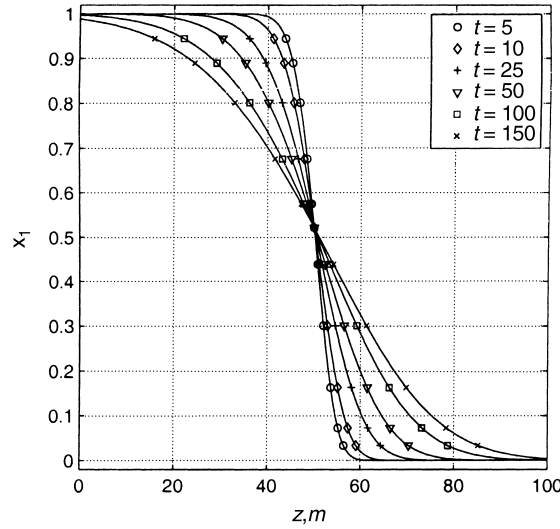
Figure 3. The self-similar profiles of mole fraction of CO_2 with $\tilde{z}_0 = 0.5$. When compared with Figure 1, the CO_2 diffusion is significantly retarded by the connate water.

The initial and boundary-value problem (53–54) models the diffusion process considered in the previous sections at intermediate times when diffusion has not changed noticeably the respective gas concentrations at the upper and lower boundaries of the reservoir.

Let us assume that

$$D = D_0 \, \Psi \left(c/c_0 \right), \tag{55}$$

where D_0 is the value of the diffusion coefficient at a reference concentration c_0, and Ψ is a *known function* of c/c_0. Then solution to the nonlinear IBV problem (53–54) depends on the following variables: $c = f(D_0, t, z, c_0)$, whose dimensions are, respectively: $\frac{L^2}{T}$, T, L, $[C]$.

Dimensional analysis, [3, 4], then tells us that the self-similar solution of the initial and boundary-value problem (53–54) must have the form:

$$\tilde{c} = \frac{c}{c_0} = F(\xi), \qquad \xi = \frac{z}{\sqrt{D_0 t}}, \tag{56}$$

and the partial differential equation (53) reduces to the following ordinary differential equation:

$$-\frac{\xi}{2} \frac{\mathrm{d}\tilde{c}(\xi)}{\mathrm{d}\xi} = \frac{\mathrm{d}}{\mathrm{d}\xi} \left(\Psi \left(\tilde{c}(\xi) \right) \frac{\mathrm{d}\tilde{c}(\xi)}{\mathrm{d}\xi} \right). \tag{57}$$

We need to find the solution to Equation (57) satisfying the following boundary conditions:

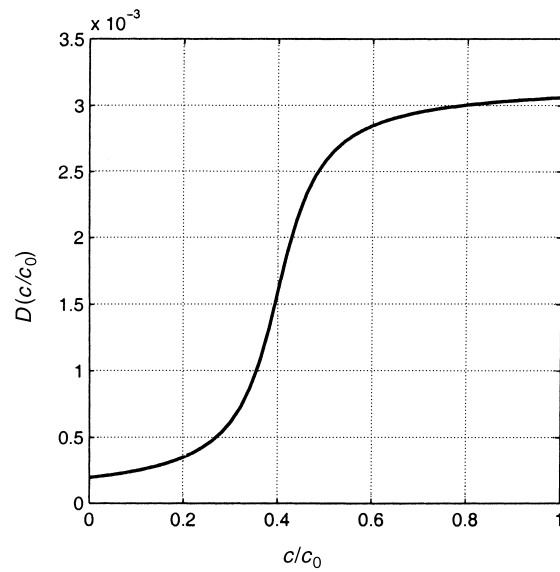$$\tilde{c}(-\infty) = 1, \quad \tilde{c}(\infty) = 0. \tag{58}$$

Figure 4. A nonlinear diffusion coefficient in cm^2/s.

The boundary-value problem (57)–(58) is formulated for an ordinary differential equation. The solution to Equations (57)–(58) is computed using the method of shooting. Equation (57) itself can be solved with a high-accuracy Runge–Kutta method with automatic discretization.

For example, let $D(\tilde{c}) = 0.001[1 + \arctan(15\tilde{c} - 6)]$, Figure 4. The resulting concentration profiles are non-symmetric, Figure 5. The upper boundary of the
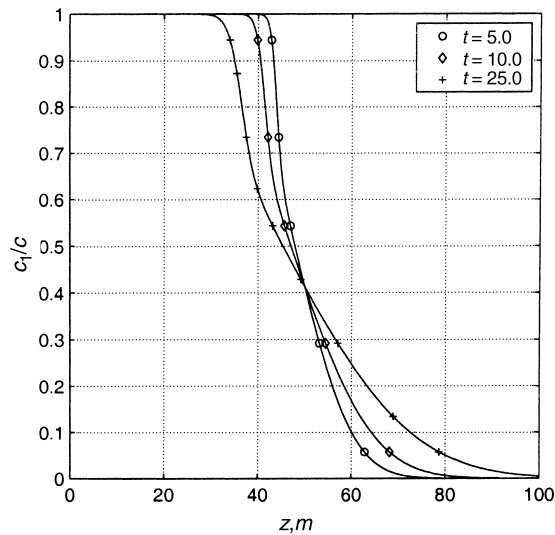

Figure 5. Dimensionless concentration of CO_2 as a function of time, in years.

reservoir ($z = 100$ m) is reached considerably earlier than the lower one. The self-similar solution provides a reasonable approximation to the solution satisfying zero-flow boundary conditions at the bottom and the top of the reservoir. As we see in Figure 5, in this particular example, the flux through the top boundary becomes noticeably non-zero after approximately 30 years. Therefore, for larger times the solution plotted in Figure 5 needs modifications.

8. Conclusions

A model of counter-current, one-dimensional vertical diffusion of CO_2 and CH_4 in a uniform horizontal reservoir has been developed. The model assumes isothermal diffusion under constant pressure and no flow through the upper and lower boundaries of the reservoir. Initially, the lower half of the reservoir is occupied by CO_2 whereas CH_4 is in the upper one. The diffusion time scale of 800 years has been obtained for a 100 m thick reservoir at the pressure of 30 atm and the temperature of 340 K. The time when a detectable concentration of CO_2 builds up at the top of the reservoir is estimated as 100 years. Presence of connate water retards CO_2 diffusion even further.

Several approaches to solving the initial and boundary-value problems for the diffusion model have been explored. In all cases, the solution is obtained either in analytical or semi-analytical form. Fourier method produces the exact solution to a linear model. However, the structure of this solution is quite complicated. Therefore an integral, polynomial solution is proposed. Although the polynomial solution is approximate, it produces very simple estimates of high accuracy. Self-similar solutions are obtained in two non-linear diffusion cases, one involving the CO_2 retardation by connate water, and the second involving a nonlinear effective diffusion coefficient of CO_2. Further work is needed to obtain a simple approximation of the exact solution to a nonlinear problem at larger times.

9. Acknowledgement

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