

Pore-Level Modeling of Carbon Dioxide Infiltrating the Ocean Floor

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Ocean sequestration of carbon dioxide is considered to be a potentially important method of reducing greenhouse gas emissions (US DOE, 1999). Oceans are currently the largest atmospheric carbon dioxide sink; and certainly, enough storage capacity exists in the oceans to hold all of the CO₂ that we can emit for many years. Additionally, technologies exist that allow us to pump liquid CO₂ into the oceans at depths between one and two kilometers for extended periods of time and five times that deep for shorter durations.

The biggest unknown in the ocean sequestration process, however, is the fate and transport of the carbon dioxide once it is released. It could sink or float, depending on its density and the formation of hydrate, or it could react with sediments on the ocean floor. Over geologic time, any carbon dioxide anthropogenically introduced into the oceans will probably diffuse in the ocean water and cause a very small percent change in the total dissolved carbon concentration; however, the near-term local effects of releasing highly-concentrated CO₂ in the ocean are not well-understood.

Deep ocean storage is a widely-discussed potential method of carbon dioxide sequestration. In this scenario, one pumps liquid CO₂ at depths below which pure carbon dioxide is denser than water. Because the CO₂ is heavier, it would not return to the surface due to buoyancy forces. Unfortunately, such a system would require a very deep injection, on the order of 3km below sea level. It has been posited that such an injection will create the existence of a carbon dioxide “lake” on the ocean floor (US DOE, 1999). Although such a lake would not rise due to buoyancy forces, it could be translated horizontally by deep ocean currents over hundreds of years.

However, the carbon dioxide plume is not likely to stop at the ocean floor, but may continue downward through the porous sediment. It has long been known that when a connate fluid is vertically displaced by a denser, less-viscous fluid, significant fingering will occur in the invading front, and the CO₂ might penetrate the sea sediments to a much more significant distance than one would initially expect. A better understanding of the fluid displacement process in sea water-saturated porous media may aid in future modeling of the fate of liquid CO₂ beneath the ocean floor.

Introduction

Two-phase flow in porous media has long been a topic of interest in the scientific and engineering community, particularly in the environmental and petroleum fields. Generally, flow on a large scale is modeled by using a form of Darcy’s law to describe the movement of each phase through the medium. However, recent studies have shown

that in certain well-defined limits, the compact flow assumptions of Darcy's law are not accurate, at least on a small scale. A number of pore-level analytical and computer models, such as diffusion-limited aggregation and invasion percolation, have been developed to describe the fractal growth patterns known to occur in special flow situations (Feder, 1988; Ferer and Smith, 1994; Ewing and Berkowitz, 1998).

We have developed a rule-based, pore-level network model (similar to diffusion-limited aggregation and invasion percolation) to describe the processes of two-phase, immiscible, incompressible, non-wetting fluid invasion into porous media (Bromhal, 2000). This model generates random distributions of pore radii to simulate porous medium properties and incorporates fluid viscosities, fluid densities, and interfacial tension between the fluids into the flow calculations.

Objective

One objective of this work is to predict the proportion of CO₂ deposited in a "lake" on the ocean floor that will be trapped in the sediments beneath the ocean bottom. Additionally, we compare the rate of infiltration into the porous medium to that of dissolution into seawater. These relationships rely heavily on the type of soil and the height of the "lake" above the ocean floor. Of course, many others factors may affect the infiltration, including the formation of hydrates. A more complete discussion may be found in the next section.

Approach

Using the rule-based model, we simulate the infiltration of a liquid CO₂ plume into the sediments on the deep sea floor. Since carbon dioxide becomes denser than water only at depths approximating 3km and deeper, the depths being considered are from 3km to 6km below sea level. At these depths, the ambient pressure is greater than 300atm; additionally, a large percentage of the deep ocean floor falls within this range.

For this work, we consider a plume of pure liquid CO₂ sitting on the ocean floor, as shown in Figure 1. The carbon dioxide on the sea floor will be under a greater pressure than the surrounding ocean water because of the pressure head from the plume. If the pressure head is great enough, it will overcome the capillary pressure in the sediment and the CO₂ will infiltrate the ocean bottom. For all of the simulations in this work, an average throat radius of 50 μ m is assumed. This corresponds to a fine sand or a silty sand soil type. While some ocean sediments are smaller than this (fine silt or clay), a reduction in pore size would require a proportional increase in overburden pressure, and the size of a CO₂ plume required to penetrate the soil under such conditions is considered unrealistic. Experimental values of viscosity, density, and interfacial tension for carbon dioxide and the carbon dioxide-water mixture are presented in Table 1.

Other concerns are the formation of hydrates and chemical reactions between CO₂ and sediment. Depths below 3km are well within the hydrate formation region (Teng et al, 1997), so CO₂ hydrate will form relatively quickly in the bulk. However, it will not form as quickly in the sediment pores, and recent studies suggest that a thin fluid layer exists between the hydrate shell and solid surface (Tabe et al, 2000) so that the hydrate

will not block flow in the throats under such pressure differences. If ocean sediment reacts with the CO₂, it should aid in sequestration by binding the carbon dioxide in carbonates or other substances (Harrison et al., 1995). To be conservative, we do not include such reactions in our simulations.

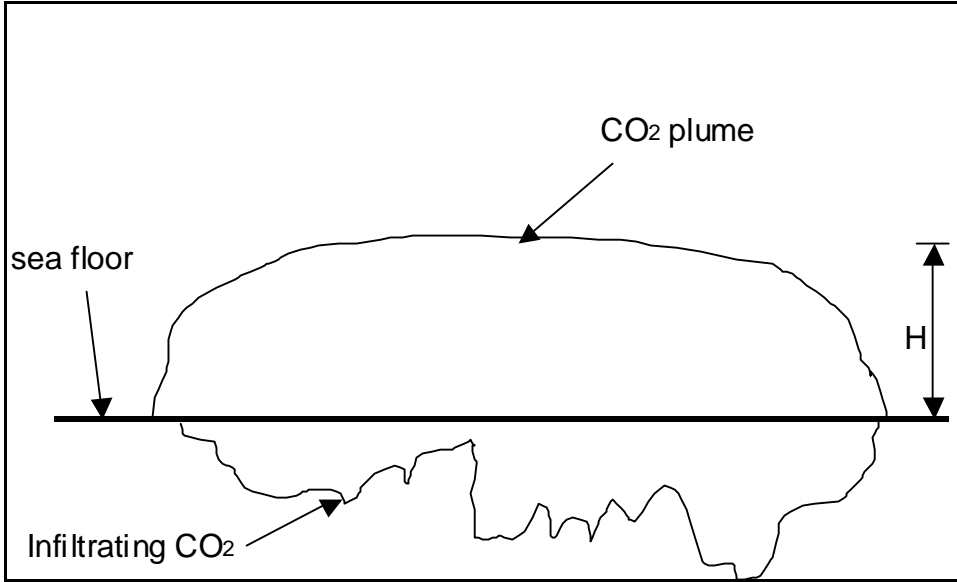


Figure 1. Diagram of a CO₂ plume on the ocean floor.

A 100x100 square network is simulated for the ranges of parameters shown in Table 1 at depths of 3km and 6km. An average surface tension of 22 mN/m is used, as the difference between 21 and 23 mN/m is small. For each depth, the head of the carbon dioxide plume, H, is varied up to 10m thick.

Table 1. Physical properties of CO₂ and CO₂-water interface at high pressure, low temp.

	Surface tension ¹ (mN/m)	Density ^{2,3} (g/cm ³)	Viscosity ³ (g/cm-s)
3km	21-23	1.05	0.0014
6km	21-23	1.11	0.0018

¹Chun and Wilkinson (1995) ²Angus et al. (1976) ³Michels et al. (1957)

Model Description

The model that we have developed is a pore-level network model, akin to cellular automata, that simulates non-wetting fluid invasion in porous media. A set of simple rules, based on the physics of the flow through each throat, defines how the invading fluid moves through the matrix. Modifications to the local rules have been made in an attempt to capture the global behavior of the system.

Because of its power and flexibility, such a model has great potential for describing the behavior of two-phase fluid flow across the entire range of important dimensionless parameters (Lenormand et al, 1988; Held and Illangasakare, 1995). It is fast enough that a typical 100x100 network simulation goes to breakthrough in minutes. However, this significant time savings comes at the cost of an imperfect representation of

the physics of the two-phase flow (in the form of an inexact pressure field). The velocity used in the model is only an estimation of the velocity than can be calculated in a mechanistic model. However, over a large number of simulations on multiple randomly-generated porous media realizations, the approximations used in the program should be adequate.

The porous pore structure is modeled as an $M \times N$ square matrix of pores (nodes) and a similar matrix of both vertical and horizontal throats (connections) as shown in Figure 1. A similar network has been used by many others (Lenormand et al., 1988; Blunt et al., 1992; Dullien, 1992; Ferer and Smith, 1994; Aker et al., 1998). Throats have radii but not volume, and pores have both. Variability in the soil structure is introduced through a random sampling of throat sizes. The radii of the horizontal and vertical throats (RH and RV in Figure 2) can be generated randomly from any closed-form probability distribution, though only uniform(0,1) distributions have been used in the simulations for this work.

To increase computational efficiency, the flow parameters (e.g., viscosity ratio and surface tension) have been transformed into variables that have been nondimensionalized. Also, because of this transformation, no system of units is assumed *a priori*. In the rule-based model, the throat length, defending fluid density, defending fluid viscosity, and the gravitational acceleration constant are set to unity. From these assumptions, values that correspond to other parameters are calculated. Equations 1a-d show how to transform the parameters into the model variables:

$$H' = \frac{H\rho_d}{\ell\rho_i}, \quad (1a)$$

$$\rho' = \frac{\rho_i}{\rho_d}, \quad (1b)$$

$$\mu'_i = \frac{\mu_i}{\mu_d}, \quad (1c)$$

$$\sigma' = \frac{\sigma}{g\rho_d\ell^2}, \quad (1d)$$

where H is the head, ρ is the density, μ is the viscosity, σ is the surface tension, g is the acceleration due to gravity, and ℓ is the unit length. Subscripts i and d correspond to invading and displaced fluids, respectively.

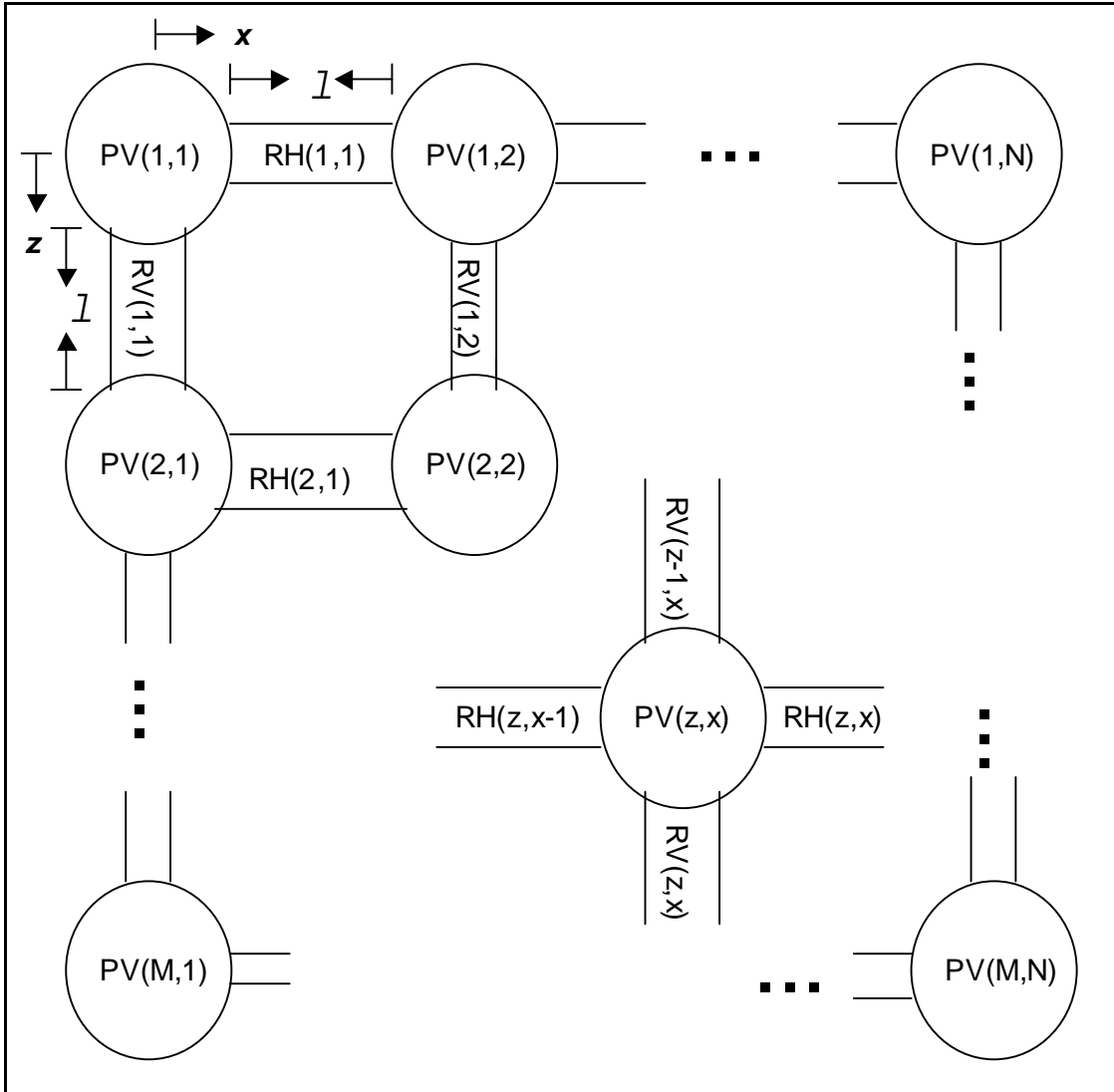


Figure 2. Schematic of $M \times N$ network of pores and throats. PV is pore volume; RH and RV are radii of horizontal and vertical throats, respectively; distance between nodes is l .

The model invokes an iterative process; during each time step, pores are scanned from the bottom of the flow domain to the top (the source):

- 1) Each pore is checked to determine if it is on the interface between the two fluids (i.e., if it is filled with defending fluid and a pore beside or above it is filled with invading fluid)
- 2) Each interfacial throat (a throat that connects an interfacial pore with a pore filled with invading fluid) is checked to see if the threshold pressure is reached.
- 3) If threshold is reached, then the pore is filled to a level that depends on the velocity of fluid in the throat; if threshold is not reached, then the pore does not fill.

- 4) If the pore is completely filled in that time step, then the surrounding pores are on the interface for the next step; if not, the value of the proportion filled is stored and added to in the next step, again at a rate depending on the velocity.
- 5) If the pore is overfilled, the surrounding pores are checked to determine if they can receive defending fluid; if so, the pores are filled according to step 3; if not, the time step is reduced and the pores are checked again, beginning at the bottom of the infiltration.

This procedure is similar to some modified invasion percolation procedures (Frette et al., 1992; Ewing and Berkowitz, 1998). The main differences between the models are that this procedure calls for filling (or partially filling) more than one pore in a time step, it uses different rules to decide if a pore should be filled, and the pore volumes and throat radii decide how quickly a pore is filled. The rule-based model process is also different from that of a mechanistic model because it does not link the pressures in all of the pores through a system of equations; instead, it estimates velocities in throats on the fluid-fluid interface to speed up the computational process. This simplifies the model so that it can run much faster than any mechanistic model; but of course, these simplifications are paid for by introducing some heuristic corrections.

In step 2 above, a threshold value is calculated using the modified Washburn equation (Dullien, 1992) expressed in terms of the variables used in the program code:

$$\rho'g'H' + (\rho' - 1)g'k - \frac{2\sigma'}{r'} > 0 \Rightarrow \begin{cases} \text{Yes : Fill the pore} \\ \text{No : Do not fill the pore} \end{cases}, \quad (2)$$

where $k = z / l$ (depth) and $r' = r / l$ (radius).

Once the threshold for a particular throat has been exceeded, the modified Washburn equation is used to estimate the velocity of the fluid through the throat:

$$\hat{u} = \frac{R^2}{8(\mu'L'_i + (N - k))} \left[\rho'H' + (\rho' - 1) - \frac{2\sigma'}{r'} \right], \quad (3)$$

where \hat{u} is the dimensionless velocity, R is average radius of the tube in units, N is the number of vertical pores in the network, and L'_i is stream length, found by assuming that the pores filled with invading fluid are equivalent to a single tube of pores connected in series (Bromhal, 2000).

As mentioned above, the velocity calculated using the modified Washburn equation is an approximation of the actual velocity through an interfacial throat. First, the stream paths in porous media are not as simple as the one described above; they may split and rejoin multiple times. Second, the idealized stream path is still just an approximation of a single stream path that does not include pores or the friction losses at locations where the radius changes. Finally, the flow through the entire tube is assumed to be steady state (similar to the assumptions made in mechanistic models for each throat).

In an attempt to correct for these approximations, a heuristic correction has been made to the calculation of velocity in each interfacial throat. Because one of the main objectives of this work is to study unstable fronts, the correction is based on the Saffman-Taylor (1958) stability analysis, derived from the Laplace equation and Darcy's law. The velocity at a point on the interface between two fluids in a Hele-Shaw cell can be connected to a parameter, γ , which relates the rate of growth of an (unstable) finger and the length of the finger.

For this correction, a total velocity for a throat is taken to be a linear combination of a velocity correction, \hat{u}_c , and the value of velocity, \hat{u} , from the modified Washburn equation. The method of redistributing the velocity is as follows. First, a value of γ' is determined for the throat on the interface:

$$\gamma' = \frac{(\mu' - 1)r'^2 \hat{v} + (\rho' - 1)g'}{(\mu' + 1)r'^2} n, \quad (4)$$

where \hat{v} is the averaged value of the velocities through throats on the frontal interface calculated from the modified Washburn equation for the previous time step and n is the wavelength of the infiltration front. A value of $\hat{u}_c = \gamma' x$ is then calculated (where x is the fingerlength). Since the component of velocity from the Saffman-Taylor analysis is added to the average velocity at all points on the interface so that these corrections sum to zero, the velocity corrections (\hat{u}_c) are therefore normalized. The total velocity for a throat is calculated by:

$$\hat{u}_t = \hat{u} + \beta \hat{u}_c, \quad (5)$$

where β is a weighing factor for the velocity correction.

Thus, the total velocity through a throat for a time step used in the program is taken from Equation 5. Since the throats are assumed to have no volume, the amount of invading fluid that reaches the pore in each time step is calculated using the total velocity times the area of the throat (to reach a flow rate). This flow rate is then multiplied by a dimensionless time parameter, giving a value that is compared to the volume of the pore. If this value exceeds the value of the pore volume, the pore is filled, and the remaining fluid begins to fill a connecting pore through the largest throat using the same procedure as above. If the volume of fluid does not exceed the volume of the pore, it is stored for the next iteration; then, the volume of invading fluid in the pore adds up over successive iterations until the pore is completely invaded, and the pore is designated as filled. Then, its connecting throats are assumed to be on the interface. If there are no surrounding pores that can accept invading fluid (i.e., they are already filled with invading fluid or the threshold is too high) or if the amount of "excess" fluid would fill more than half of a pore, then the time step is reduced, all of the values for all of the pores are reset, and the iteration is begun again.

Once all of these steps are completed, the program moves on to the next pore to decide if it should be filled. This process is repeated until the invading fluid reaches the lowest layer of pores in the model, at a chosen depth from the ocean floor. A more complete description of this model and its simulation process can be found in Bromhal (2000).

Results

In this section, we present results from simulations for different heads of the CO₂ plume at two different depths, as discussed above. Tables 2a-b show the velocity (flow rate per unit area), saturation, and fractal dimensions of the infiltration patterns at breakthrough. For each combination of input parameters, the random network (of throat sizes) was generated thirty times. The results from these realizations were averaged to get the numbers seen in Tables 2a-b. Standard deviations are within about 10% of the mean for all results but the fractal dimension, which was typically within ± 0.02 of the mean.

Because of the capillary pressure between the fluids in the pores, a significant pressure head was required to propagate the fluid into the sediment. At a depth of 3km, the density difference between the fluids was so small that a head of 9.7m was required to cause movement. For the 6km depth, the density difference was much more significant, and a head of only 1.4m was required. No one to our knowledge has predicted a realistic height of a CO₂ “lake” on the sea floor, but our model could help predict the plume height if a steady state occurs.

We can estimate fluxes of carbon dioxide into the sediments by simply multiplying the velocity by the saturation. These values are also shown in Tables 2a-2b. Diffusive flux can be estimated in the bulk using simple Fickian diffusion. Assuming no hydrate formation (a very conservative assumption) and a diffusivity coefficient of 1.39m²/s (Inoue et al., 1996), we have estimated the vertical (upward) flux of carbon dioxide into the ocean water. The vertical volume flux is on the order of 4mm/s, in contrast to the fluxes in the ocean sediment.

Table 2a. Velocity, saturation, and fractal dimension for 3 different heads at a depth of 3km

Head	1m	5m	10m
Vel ($\mu\text{m/s}$)	0	0	34.73
Saturation	0	0	36.42
Fractal dim.	0	0	1.843
Flux (mm/s)	0	0	0.0126

Table 2b. Velocity, saturation, and fractal dimension for 3 different heads at a depth of 6km.

Head	1m	2m	5m	10m
Vel ($\mu\text{m/s}$)	0	31.76	113.9	245.9
Saturation	0	38.34	37.09	34.84
Fractal dim.	0	1.783	1.772	1.764
Flux (mm/s)	0	0.0122	0.0422	0.0857

Conclusion & Future Work

The most notable conclusion is the high heads required to facilitate penetration of the ocean floor, ~10m at 3km deep and ~1.5m at 6km deep. Since the average pore size was 50 μ m, which is at the upper end of what we would find on the ocean floor, it is likely that heads of 20-100m would be required to move the plume for clays and other common sediment types with an average pore size of 5 μ m or less. Such high plumes seem unlikely, so we conclude that infiltration is improbable for fine soils.

In contrast, flow most likely will occur in the sandy and silty soils. In the cases presented here, the flux into the soil appears to be between 5 and 15 times smaller than the diffusive flux, with the most favorable being the 6km deep, 10m high plume and the least favorable being the 3km deep, 10m high plume. In these cases, flow into the sediment is not insignificant, but it much less a factor than diffusion.

However, hydrate formation was not taken into consideration in the bulk phase. Inoue et al (1996) have shown that the presence of hydrate in such a CO₂ lake will significantly slow the diffusion, by at least an order of magnitude. In this case, the fluxes are about equal (or the downward flux is greater), and so flow into the sediment appears to be as much or more important than diffusion.

Thus, infiltration into sediment on the ocean floor should not be overlooked when one considers deep ocean sequestration options near high permeability sediments. Such trapped CO₂ would be more stable than that in liquid or hydrate form. Future work should consider the nature of hydrates that form in the ocean sediment. This is a significant unknown in the process, and it is possible that the presence of hydrate in the pores will slow the downward flux as much or more than hydrate in the bulk. Modeling of hydrate formation in porous media and its effects on flow would be very useful to this analysis.

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