Abstract

CO₂-sequestration in deep geological formations has been suggested as an option to reduce greenhouse gas emissions. Saline aquifers are one of the most promising options for carbon dioxide storage. It has been investigated that if the layer of aquifer is deep enough, at depths more than 800 meters, dissolution of CO₂ into brine causes density of the mixture to increase. If the corresponding Rayleigh number of the porous medium is enough to initiate convection currents, the rate of dissolution will increase. Early time dissolution of CO₂ in brine is mainly dominated by molecular diffusion while the late time dissolution is predominantly governed by convective mixing mechanism. In this paper, linear stability analysis of density-driven miscible flow for carbon dioxide sequestration in deep inclined saline aquifers is presented. The effect of inclination and its influence on the pattern of convection cells has been investigated and the results are compared with the horizontal layer. The current analysis provides approximations for initial wavelength of the convective instabilities and onset of convection that help in selecting suitable candidates for geological CO₂ sequestration sites.

Introduction

Carbon dioxide sequestration is the capture and safe storage of carbon dioxide that would otherwise emit to the atmosphere. Sequestration refers to any storage scheme that can keep CO₂ out of the atmosphere [1]. In general, storage sites of carbon dioxide can be divided into two categories, geological sites and marine sites. Carbon dioxide sequestration in deep geological formations has been suggested as a way of reducing greenhouse gas emissions. Geologic sequestration of CO₂ is the capture of CO₂ from major sources, transporting it usually by pipeline, and injecting it into underground formations such as oil and gas reservoirs, saline aquifers, and unmineable coal seams for geologically significant period of time [2, 3]. Unlike coal bed methane reserves and oil reservoirs, sequestration of CO₂ in deep saline aquifers does not produce value-added by-products, but it has other advantages. While there are uncertainties, the
world’s total capacity to store CO₂ deep underground is large
They are generally unused and are available in many parts of
the world. It has been estimated that deep saline formations
in the United States could potentially store up to 500 billion
tones of CO₂. Most existing large CO₂ point sources are within
easy access to a saline formation injection point, and therefore
sequestration in saline formations is compatible with a strategy
of transforming large portions of the existing energy and
industrial assets to near-zero carbon emissions via low-cost
carbon sequestration retrofits. However, it is important to
investigate the behavior of CO₂ injected into aquifers for
effective and safe use of storage. Geological storage of CO₂ as
a greenhouse gas mitigation option was proposed in the 1970s,
but little research was done until the early 1990s, when the idea
gained credibility through the work of individual research
groups.

When CO₂ is injected into the formation above its critical
temperature and pressure the density of supercritical carbon
dioxide is usually less than brine. This density difference causes
CO₂ to migrate upwards to the top of the formation and under
an impermeable cap rock. Carbon dioxide then spreads laterally
under the cap rock as a separate phase. During migration, a
fraction of the injected carbon dioxide will dissolve into
formation brine and some continue to migrate laterally.
Diffusion is a very slow process and because molecular
diffusion coefficient is very small, it will take a long time for
CO₂ to dissolve into brine.

As CO₂ free phase migrates through the formation, it can be
trapped by capillary pressure, which is referred to as residual
CO₂ trapping. Residual trapping may cause a significant amount
of CO₂ to be trapped in the formation. If capillary forces are
strong, CO₂ even cannot migrate to top of the formation. For
dipping formations, this can cause lateral spread of CO₂ to be
slow, since the effect of gravity segregation is less than
horizontal layers during upwards migration. When residual
trapping happens, most of the trapped CO₂ will dissolve
into the formation over time.

In the interface of free-gas phase and formation brine, CO₂ will
dissolve in water by molecular diffusion. The water in contact
with CO₂ will be saturated with CO₂ and a concentration
gradient of CO₂ in brine would establish. This process is very
slow and may take hundreds of years for CO₂ to be completely
dissolved in brine. Lindeberg illustrated that 143 kg of CO₂
will dissolve in an infinitely 1 m³ of water saturated reservoir
column under a CO₂ cap after 1000 years.

In the very long-term, mineralogical trapping would occur. In
this case, a sequence of geochemical interactions between
dissolved CO₂ and rock minerals, if appropriate minerals are
encountered, will form ionic species (ionic trapping). The
speed of the reaction depends on the formation mineralogy and
usually is in the order of hundreds of years. Decomposition of
these minerals over thousands of years or more will precipitate
new carbonate minerals, which will trap CO₂ in its most secure
storage state (mineral trapping). Carbonate minerals are stable
and this mechanism is the most permanent form of storage,
but it is very slow and will happen at the end of all the trapping
schemes.

Between the short-term (physical trapping) and long-term
(mineral trapping) processes, there is also a middle-term period,
solution trapping, which is a very important part of the storage.
The importance of the solution trapping is the reduction in
possibility of leakage of CO₂ from storage locations. As long as
CO₂ remains as a separate phase in the formation under the cap
rock, there is possibility of leakage of CO₂ to higher
permeability zones due to lateral movement. However, when
significant amount of CO₂ dissolves in brine, the risk of leakage
can be ignored. Therefore predicting the onset time of convection is very important in the fate of CO₂ sequestration.

The solution trapping occurs by diffusion and convective
mixing. In the early time, diffusion is the only mechanism of
dissolution. When CO₂ diffuses into brine, density of brine
increases slightly. This happen because the density of brine
saturated with carbon dioxide is approximately one percent
higher than original formation brine. At the early time
of CO₂ dissolution, diffusion causes a thin layer of brine to be
saturated with CO₂. The boundary layer of concentration in the
aquiifer column increases by time and at a specific time
convective currents start to happen (due to adverse density
gradient) which will enhance the dissolution rate of CO₂ into
brine.

In this work, a prediction of the beginning of convection along
with the pattern of fluid movement is made by using linear
stability analysis. The analysis is based on the growth of
perturbations in the system. Previous analyses were for a
horizontal layer whereas in this case, effect of inclination of the
formation on the instability time and pattern of convection cells
is investigated and results are compared with the horizontal
case.

Previous Work

Analytical study of the convective mixing in porous media was
first analyzed by Horton and Rogers and Lapwood. The
problem was for a horizontal fluid layer with constant boundary
temperatures under a linear and steady vertical temperature
gradient. They found the critical Rayleigh number to be 4π²,
above which perturbation grew and convection currents started.
In the case of CO₂ diffusing into brine, the condition is like the
heat transfer problem in which equation of heat is replaced by
mass transfer equation. In contrast to the Horton and Rogers and
Lapwood problem where the base state profile was steady and
linear, the base problem considered here is a nonlinear and
transient.

There are some approaches to the problem which all have some
drawbacks. In early attempts to account the nonlinear
temperature profile, quasi-steady state approximation (QSSA)
was used. This assumption is valid if the propagation rate of
the nonlinear profile is much smaller than the growth rate of
perturbations. This approximation is not valid at the early time
when the boundary layer and the diffusing profile change fast.
Another method is to use the amplification theory. This
method gives the critical time of instability and the wavelengths
of the start of instability. The wavelength that produces the
fastest growth is the wavelength of instability. In amplification
theory, one important factor is the choice of initial condition
to solve the equation. Another issue is the criteria for determining
onset of instability, which is somehow arbitrary due to the
imprecise definition of critical time. Foster and Homsy used this method for a thermal-diffusing boundary layer in an incompressible fluid. Caltagirone and Kaviany applied this method for a thermal boundary layer in a porous medium for a step change in temperature. Ennis-King and Paterson applied this method in the CO₂ sequestration problem for anisotropic porous media.

Another method is the global stability (energy) method
investigated by several authors. This method does not depend
on the initial condition and gives criteria of stability. In this
method, the onset time of instability is less than measured
laboratory data \cite{26}, and so it gives a lower bound for the onset of instability. It also does not give any information about the wave number of the disturbances. All the three methods have been applied to the convective mixing problem in porous media. The aim of this paper is to investigate the critical time of instability for the convective mixing occurred in the geological CO\textsubscript{2} storage process into aquifers due to increase of brine density upon dissolution of CO\textsubscript{2}. In this paper, linear stability analysis based on the amplification theory is used for an inclined homogeneous porous layer with the appropriate boundary and initial conditions. Results are compared with the horizontal porous layer and show correspondence with thermally induced density-driven flow in porous media.

**Governing Equations**

Consider a simplified-geometry saline aquifer, a cross section of which is shown in Figure 1 with the appropriate coordinate system. The aquifer is a homogeneous porous medium confined between two inclined, infinite parallel impermeable planes. The thickness of the layer is \( H \) and the fluid is initially quiescent. Diffusion of CO\textsubscript{2} from the top of the formation to the quiescent fluid increases density of the CO\textsubscript{2} saturated brine. The fluid is assumed to be incompressible:

\[
\nabla \cdot \mathbf{v} = 0 \quad \text{................................. (1)}
\]

We assume that fluid motion is governed by Darcy’s law and the transport of CO\textsubscript{2} into brine is governed by convection-diffusion equation. Due to the choice of the coordinate axis, gravity has two terms in the \( x \) and \( z \) directions leading to the following system of equations:

\[
\mathbf{v} = \frac{k}{\mu} \left( \frac{\partial \rho}{\partial x} - \rho g \cos \theta \nabla z - \rho g \sin \theta \nabla x \right) \quad \text{................................. (2)}
\]

\[
\phi \frac{\partial C}{\partial t} = D \phi \nabla^2 C - \mathbf{v} \cdot \nabla C \quad \text{................................. (3)}
\]

where \( \mathbf{v} \) is the Darcy velocity vector, \( D \) is the molecular diffusion coefficient of CO\textsubscript{2} into brine at the conditions in the porous medium, \( \phi \) is the effective porosity, \( \mu \) is the fluid viscosity, \( \rho \) is the fluid pressure, \( k \) is the permeability tensor, \( g \) is the gravity acceleration and \( C \) is the CO\textsubscript{2} concentration in brine. The model is assumed to be a homogeneous and isotropic porous medium, therefore the permeability tensor \( k \) can be replaced by a single-term permeability, \( k \). The coupling between equations occurs through the effect of CO\textsubscript{2} concentration on density in the form of:

\[
\rho = \rho_0 (1 + \beta C) \quad \text{................................. (4)}
\]

where \( \rho_0 \) is the density of unsaturated brine and \( \rho \) is the density of the solution being saturated with brine and \( \beta \) is the density increase coefficient. The relationship between density and concentration is linear since the concentration of CO\textsubscript{2} has very little effect on the partial molar volume \cite{27}. Boussinesq approximation is assumed valid where the dependence of density on concentration is only retained in the buoyancy term in equations 2 and 3. Effect of geothermal gradient is neglected for two reasons; first, it has little effect on the results and second it contributes to the destabilization.

**Stability Analysis**

The reference or base state of the concentration profile is given by the diffusive mass transfer equation. For pure diffusion with \( v = 0 \), concentration distribution satisfies:

\[
\frac{\partial C_{D}}{\partial t_{D}} = \frac{\partial^{2} C_{D}}{\partial z_{D}^{2}} \quad \text{................................. (5)}
\]

where \( t_{D} = D t / H^2 \) is the dimensionless time, \( z_{D} = z / H \), and \( C_{D} = C / C_{s} \) is the dimensionless concentration. The initial and boundary conditions are:

\[
C_{D} = 0 \quad \text{at} \quad t_{D} = 0, \quad 0 \leq z_{D} \leq 1 \quad \text{................................. (6)}
\]

\[
C_{D} = 1 \quad \text{at} \quad z_{D} = 0, \quad t_{D} \geq 0 \quad \text{................................. (7)}
\]

\[
C_{D} = 0 \quad \text{at} \quad z_{D} = 1, \quad t_{D} \geq 0 \quad \text{................................. (8)}
\]

The bottom boundary is supposed to be at zero concentration. However, no-flux \( \partial C_{D} / \partial z_{D} = 0 \) boundary condition can also be considered with the same analysis. Solution of Equation 5 is:

\[
C_{D} = 1 - z_{D} - 2 \sum_{n=1}^{\infty} \frac{1}{n \pi} \sin(n \pi z_{D}) \exp(-n^2 \pi^2 t_{D}) \quad \text{................................. (9)}
\]

For the stability analysis, velocities and concentration are subjected to small perturbations, \( u', v', w', \) and \( C' \), where \( u, v, \) and \( w \) are velocities in the \( x, y, \) and \( z \) directions, respectively. When perturbed velocities and concentration are substituted in equations 2 and 3, by neglecting second order non-linear terms, a system of linear equations will be formed as:

\[
\nabla^2 w'_{D} = \frac{k g H \rho \cos \theta}{\mu D} \left[ \nabla^2 C'_{D} - \frac{\partial^2 C'_{D}}{\partial x_{D} \partial z_{D}} \tan \theta \right] \quad \text{................................. (10)}
\]

\[
\frac{\partial C'_{D}}{\partial t_{D}} = \nabla \cdot C'_{D} - w'_{D} \frac{\partial C'_{D}}{\partial z_{D}} \quad \text{................................. (11)}
\]

where \( \nabla^2 \equiv \frac{\partial^2}{\partial x_{D}^2} + \frac{\partial^2}{\partial y_{D}^2} \), \( H \) is the thickness of the aquifer, \( \Delta \rho \) is the density difference between saturated and fresh brine, \( \theta \) is the dip of the aquifer, and \( w'_{D} = w' H / \phi D \) is the dimensionless perturbed velocity. Rayleigh number is defined as:

\[
Ra = \frac{k g H \Delta \rho \cos \theta}{\mu D} \quad \text{................................. (12)}
\]

By setting:

\[
\begin{bmatrix}
w'_{D} \\
C'_{D}
\end{bmatrix} = \begin{bmatrix}
w'_{D}(t_{D}, z_{D}) \\
C'_{D}(t_{D}, z_{D})
\end{bmatrix} \exp \left[ i (a_{x} x_{D} + a_{y} y_{D}) \right] \quad \text{................................. (13)}
\]
with \( a = (a_x + a_y)^2 \), and using Galerkin technique for the amplitude functions of velocity and concentration perturbations based on the boundary conditions as:

\[
\begin{align*}
\sum_{i=1}^{N} A_i(t_o) \exp \left[ i (\pi z, \theta) \right] &= 0 \quad (14) \\
\sum_{i=1}^{N} B_i(t_o) \exp \left[ i (\pi z, \theta) \right] &= 0 \quad (15)
\end{align*}
\]

the following equations for the time amplitude of the perturbed velocity and concentration are given:

\[
\left[ a^2 + (i \pi)^2 \right] A_i = \left[ a^2 - (i \pi a_x \tan \theta) \right] R a B_i \quad \text{for} \ i = 1, N 
\]

\[
\frac{d B_i}{d \theta} = -\left[ a^2 + (i \pi)^2 \right] B_i - 2 \sum_{m=1}^{N} A E_m 
\]

where \( E_m \) is an N by N matrix and for \( m = l \):

\[
E_m = -\left[ \frac{1}{2} \exp(-4i^2 \pi^2 t_o) \right] 
\]

and for \( m \neq l \):

\[
E_m = -\left[ \frac{1}{2} \exp(-(l-m)^2 \pi^2 t_o) - \exp(-(l+m)^2 \pi^2 t_o) \right] 
\]

Equations 16 and 17 can be solved numerically for \( A_i \) and \( B_i \) and the following definition, as in the work of Foster [22] and Caltagirone [24], is used for the amplitude of the velocity disturbance:

\[
\overline{w}(t_o) = \left( \int w^2(z, t_o) dz \right)^{\frac{1}{2}}
\]

All the coefficients in the Galerkin expansion of the concentration disturbance were set to unity for the initial condition, since white noise gives the fastest growth rate [28].

**Results and Discussion**

Results of the stability analysis are valid when the thickness of the diffusive boundary layer is much smaller than the thickness of the aquifer layer, which for typical parameters of storage sites is applicable [13].

In equations 16 and 17, wave numbers \( a \) and \( a_x \) are unknown. They are found by seeking which value gives the fastest growth of amplitudes in time. Based on the definition of \( a, 0 \leq a_x \leq a \).

Therefore, for each value of \( a, a_x \) is varied from zero to \( a \) and the effect of \( a_x \) is analyzed on the behavior of the velocity amplitude.

In the analysis, the onset of instability was chosen based on the magnitude of velocity amplitude to become one. It was found that if \( a_x = 0 \), velocity amplitude increases faster than any other values of \( a_x \). As \( a_x \) increases from 0 to \( a \), the onset of instability increases, but the interesting feature is that for a specific Rayleigh number greater than the critical value, no matter what is the value of \( a_x \), the onset of instability occurs at a specific wave number, \( a \). This means that the wave number, \( a \), is independent of \( a_x \). However, we know that \( a_x \) is related to \( a \) based on \( a = (a_x^2 + a_y^2)^{\frac{1}{2}} \). Again, we find that \( a_x \) should be zero.

These two reasons impose the wave number in the \( x \) direction to be zero and in this direction instead of convection cells, the instability manifest itself with convection coils. This is in accordance with experiments done for temperature instability in porous media [28, 30]. Pattern of convection rolls is shown in Figure 2 based on Bories’ experimental work.

Figure 3 relates onset of instability with Rayleigh number, which is similar to the horizontal case [28, 31]. Near the critical value of the Rayleigh number, \( 4\pi^2 \), the time of instability increases dramatically. It seems that based on our criterion of the onset of instability and linearization of equations, the estimated time of instability is an upper bound for it. Results in Figure 3 reveal that dimensionless instability time vary as the minus 2 power of the Rayleigh number at high \( Ra \). Since the dimensionless critical time is inversely proportional to the porous layer thickness \( H \), to the power of 2, this suggests that, the onset of convection is independent of the porous layer thickness. Another remark regarding Figure 3 is that the minimum Rayleigh number approaches \( 4\pi^2 \), corresponding to the critical Rayleigh number given by Horton and Rogers and Lapwood for a porous layer with a steady linear temperature gradient. In Figure 4 wave number, \( a \), is plotted versus Rayleigh number. The wave number is equal to the wave number in the \( y \) direction. This figure reveals that the wave number is proportional to the Rayleigh number for \( Ra \) larger than a few hundreds. This proportionality implies that the size of convection cells is independent of the porous layer thickness. The extrapolation of Figure 4 can be used to compare the wave number with the experimental values reported by Green and Foster [32]. The value of wave number in their experiment (0.18 cm) is greater than the relationship in Figure 4 (which gives a value of about 0.07 cm), for the Rayleigh number of about 10^4. They mentioned that this value is an overestimate due to the combination of streamers.

Figure 5 shows the onset of instability for the no-flux concentration boundary at \( z_o = 1.0 \). Figure 6 shows the growth of amplitude factor with time. At high Rayleigh numbers, amplitude factor increases sharply, at much shorter time.

The Rayleigh number in a sloping layer contains a \( \cos \theta \) term, which decreases the driving force required for convection compared to the horizontal layer. If \( \cos \theta = 0.1 \), the Rayleigh number can be less than the critical value and instability will not be induced. As the inclination increases, for fixed values of fluid and medium parameters, the onset of instability increases.

**Conclusion**

In this study, stability of a fluid in an inclined enclosed domain was studied. It was found that the effective driving force in an inclined layer is less than the horizontal case by \( \cos \theta \) factor, which retards the onset of instability. The pattern of convection currents was different from the horizontal case. While in the horizontal case, convection evolves with specific wave numbers in the horizontal plane, in the inclined layer the wave number in the direction of the slope is zero.

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NOMENCLATURE

A: Time component of the amplitude function for perturbed velocity
a: Dimensionless wave number
B: Time component of the amplitude function for perturbed concentration
C: Concentration
D: Diffusivity coefficient
d: Derivative
E: Square matrix
g: Gravitational acceleration
H: Aquifer thickness
i: Imaginary number, √−1
k: Permeability tensor
k: Permeability
N: Constant number in the summations
p: Pressure
Ra: Rayleigh number
t: Time
u: Velocity in the x direction
v: Velocity vector
v: Velocity in the y direction
w: Velocity in the z direction
w: Velocity amplitude factor
x: Coordinate direction parallel to the flow
y: Coordinate direction
z: Coordinate direction perpendicular to the flow
ϕ: Porosity
β: Density increase coefficient
μ: Viscosity
ρ: Density
θ: Dip angle of the aquifer
Δρ: Density difference
∇²: 2D Laplacian

Superscripts:
* Perturbed quantities
v: Amplitude of the perturbations

Subscripts:
0 Base state
D Dimensionless
l, m Summation index
s Equilibrium state
x, y x and y directions

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Figure 1. A schematic of the problem’s domain.

Figure 2. Convection coils in a sloped porous layer\textsuperscript{[30]}. 
\[ t_D = 130 \frac{1}{Ra^2} \]

Figure 3. Instability time versus Rayleigh number for \( C(z_D = 1) = 0 \).

\[ a = 0.052 \frac{1}{Ra} \]

Figure 4. Wave number versus Rayleigh number.
Figure 5. Instability time versus Rayleigh number for $\frac{\partial C}{\partial z_D}(z_D = 1) = 0$.

Figure 6. Amplitude factor versus dimensionless time.