Streamline-based simulation of carbon dioxide storage in a North Sea aquifer

Eguono-Oghene I. Obi1,2 and Martin J. Blunt1

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1 We model carbon dioxide (CO2) storage into a deep North Sea aquifer using streamline-based simulation. We assume incompressible flow of liquid-like CO2 and aqueous phases. We simulate dissolution of CO2 and a rate-limited precipitation reaction. Advective transport and reactions are solved along streamlines, while dispersion and flow due to gravity segregation of the phases are solved on the underlying grid. Geological storage is modeled on a one million cell model. The distribution of CO2 after injection is dominated by advective transport due to multiphase flow, and CO2 moves preferentially through high-permeability channels. Without reaction the regional groundwater flow causes the CO2 to continue to migrate until it reaches residual saturation, where it continues, slowly, to dissolve. Precipitation leads to a decrease in porosity and permeability, while CO2 is stored in the solid phase. The storage efficiency is low, around 2%, because of aquifer heterogeneity.


1. Introduction

[2] Underground injection and long-term storage of CO2 is one possible method to reduce CO2 emissions to the atmosphere. Candidate sites for injection include abandoned coal seams, depleted oil and gas fields and deep saline aquifers. While injection into coal seams and hydrocarbon reservoirs have benefits associated with enhanced oil and gas production, aquifers have the greatest storage potential. It is estimated that up to 10,000 Gt of CO2 could be stored worldwide in aquifers, which is equivalent to many centuries of CO2 emissions at the current rate of 25 Gt/year (6 Gt carbon/year) [International Energy Agency, 1994]. One attractive possible site for sequestration is the North Sea. This is a major oil and gas producing province containing relatively well-characterized geological formations with an existing pipeline infrastructure close to fossil-fuel-burning power stations in the UK. The offshore location reduces possible hazards due to accidental leaks of CO2. It has been estimated that aquifers in the North Sea have a storage potential of 736 Gt CO2, in contrast to 5.8 Gt in oil fields and 13.3 Gt in gas fields [Holloway and Savage, 1993; British Geological Survey, 1996]. At present the Sleipner project in the Norwegian North Sea that injects CO2 produced from an offshore gas field is the world’s only aquifer disposal scheme [Korbøl and Kaddour, 1995]. However, the potential for further projects is enormous.

[3] This paper will study issues associated with the flow and transport of CO2 underground. There are three principal physical processes that influence CO2 migration. First, the injected CO2 will form its own phase. At conditions typical of disposal into the North Sea (pressures around 30 MPa and temperatures around 250 K) CO2 is supercritical with liquid-like properties. The extent of CO2 migration in its own phase will depend on the relative permeabilities and densities of the CO2 and aqueous phases as well as the distribution of permeability. Typically the aquifer will contain structures with large correlation lengths that will significantly impact the flow pathways. Second, CO2 will dissolve in water: at high pressure the amount of dissolved material can be comparable to CO2 in its own phase. Dissolved material will flow with the groundwater creating a plume that over long timescales may migrate far from the injection point. Third, the injected CO2 can react with the rock. The CO2 may precipitate, forming mineral carbonates or dissolve carbonate rock. While dissolution is an effectively instantaneous process, geochemical reactions between CO2 and the rock occur over hundred to hundred thousand year timescales [Xu et al., 2003]. If there is significant precipitation, CO2 may be stored as an immobile solid phase, which is ideal for sequestration. We will show that for typical sequestration scenarios the amounts of CO2 in its own phase, dissolved or converted into solid can be of comparable magnitude.

[4] Simulation models of carbon sequestration need to account for multiphase flow, equilibrium and nonequilibrium reactions and phase partitioning in a highly heterogeneous system. Many authors have presented simulations of CO2 injection and migration [Van der Meer, 1993, 1995, 1996; Holt et al., 1995; Weir et al., 1995; Law and Bachu, 1996; Lindeberg, 1997; Johnson et al., 2000; Ennis-King and Paterson, 2002; Wellman et al., 2003; Pruess et al., 2003; Xu et al., 2003; Kumar et al., 2005]. Holt et al. [1995] and Law and Bachu [1996] used petroleum reservoir simulators that accounted for multiphase flow, but ignored rate-limited reactions with the rock. Malik and Islam [2000] performed a reservoir simulation study for the Weyburn...
field where CO₂ collected from a power station was injected into an oilfield. The objective was to determine the optimal well placement to maximize CO₂ storage and hydrocarbon recovery. Brinks and Fanchi [2001] performed a study that coupled CO₂ movement to seismic response using a homogeneous coarsely gridded model (231 blocks) of an aquifer. Xu et al. [2003] and Pruess et al. [2003] used a detailed geochemical model to study rock/fluid interactions during radial flow. Pruess [2004] studied CO₂ leakage, accounting for thermal and multiphase flow effects when the CO₂ becomes subcritical and forms two nonaqueous phases. Again the simulations were performed in a radial geometry. Ennis-King and Paterson [2002] performed a detailed study of the factors affecting sequestration, including gravitational effects and also considered radial flow. Kumar et al. [2005] performed a detailed sensitivity analysis of CO₂ storage using a commercial geochemical simulator and a heterogeneous grid with 64,000 blocks representing properties typical of a Gulf Coast aquifer. They concluded that trapping of the CO₂ was a significant permanent storage mechanism. Other authors have considered the roles of relative permeability hysteresis [Spiteri et al., 2005], dispersion [Calabrese et al., 2005], and convective mixing [Ennis-King and Paterson, 2005] on storage.

[5] In contrast to previous studies of CO₂ storage that have captured the geochemistry in detail, while using rather simple geological models, we will focus our attention on how aquifer heterogeneity affects the flow and transport of CO₂. We will simulate transport in a fine-grid model that realistically represents the geology of a deep sandstone aquifer.

[6] To model the advective movement of injected fluids we will use streamline-based simulation, which is an appealing complement to traditional grid-based simulation for cases where the flow field dominates the fluid movement [Batycky et al., 1997; Crane and Blunt, 1999; Di Donato et al., 2003]. Bommer and Schechter [1979] showed that streamline-based methods elegantly decouple the effects of the flow field from the geochemistry, allowing reactions to be treated as a series of one-dimensional transport equations along streamlines. This makes the method ideal for the study of well placement and aquifer heterogeneity on transport, in contrast to grid-based methods that tend to be more computationally demanding since they have to solve a series of three-dimensional transport equations. For advectively dominated transport in heterogeneous systems, streamline-based simulation is typically 10–100 times faster than grid-based approaches, while giving essentially identical results when numerical dispersion in the grid-based codes is controlled [Batycky et al., 1997; Huang et al., 2004]. Crane and Blunt [1999] used this approach to model the transport of sorbing and decaying tracers. Obi and Blunt [2004] incorporated dispersion and diffusion in a streamline code using an operator splitting technique, while Di Donato and Blunt [2004] studied rate-limited reaction and flow in fractured reservoirs. Jessen et al. [2005] presented a streamline-based simulator to model CO₂ injection into oil fields. The phase exchange between multiple components in the oil and gas was computed along streamlines [Thiele et al., 1997]. Turan et al. [2002] used streamline simulation to evaluate CO₂ injection into the Forties oilfield. A tracer model was tuned to reproduce the results of grid-based compositional modeling of a sector of the field.

[7] We will study aquifer disposal of CO₂ extending current streamline methods to incorporate dissolution and will allow the porosity, permeability and hence the flow field to evolve over time as a consequence of mineral precipitation or dissolution. By accounting for all the pertinent physical and chemical processes, while also capturing the impact of heterogeneity, we hope to predict the migration of CO₂ in the subsurface accurately.

[8] We will first describe the model used to handle transport and reaction and discuss the approximations used. We will run a series of one-dimensional simulations to illustrate the different physical processes. Then threedimensional simulations of sequestration in a million-cell reservoir model representing a North Sea sandstone will be performed. It will be shown that permeability heterogeneity causes CO₂ to migrate much further than predicted from a homogeneous one-dimensional model, leading to much lower storage efficiencies. However, dissolution, trapping and reaction can significantly impede the movement of CO₂ in its own phase and offers a very attractive scenario for sequestration in deep aquifers.

2. Transport and Geochemical Models

2.1. Flow and Transport

[8] We assume incompressible two-phase flow and ignore capillary pressure. We consider flow of aqueous (water) and CO₂ phases. In the aqueous phase we only model the transport of a single dissolved species, CO₂. The governing equation for CO₂ in its own phase (denoted by the subscript c) is

\[ \frac{\partial s_c}{\partial t} + \bar{u} \cdot \nabla f_c + \nabla \cdot \bar{G}_c = -T_d, \]

where \( S_c \) represents saturation, \( u_c \) is the total Darcy velocity and \( \phi_c \) is the porosity, which is time dependent. \( T_d \) represents the transfer of material to the aqueous phase due to dissolution and has units of inverse time. The fractional flow of the CO₂ phase \( f_c \) ignoring gravity is given by

\[ f_c = \frac{k_w/\mu_c}{k_w/\mu_c + k_w/\mu_w}, \]

where the subscript \( w \) labels the aqueous (water) phase, \( k_c \) is the relative permeability and \( \mu \) is the viscosity. \( G_c \) is the velocity due to gravity segregation of the phases

\[ G_c = -K \cdot \frac{k_w}{\mu_w}(\rho_w - \rho)g \nabla h. \]

\( K \) is the absolute permeability of the porous medium and \( \rho \) is the density.

[10] The transport equation for a conservative species (CO₂) dissolved in the aqueous phase is

\[ \frac{\partial (1 - S_c)C_c}{\partial t} + \bar{u} \cdot \nabla (1 - S_c)C_c = \nabla \cdot \phi D C + m_cT_d - m_cT_r, \]
where $D$ is the dispersion tensor and $T_r$ is the transfer of material to the solid phase due to reaction. $C$ is the concentration of CO$_2$ in the aqueous phase measured in moles per unit volume. $m_r$ is the density of CO$_2$ in its own phase with units moles per unit volume, while $m_s$ is the density of the precipitated solid phase with the same units.

[11] The governing transport equations are first transformed into equations along streamlines by defining the time of flight, $\tau$, that is the time taken for a neutral tracer particle to travel a distance along a streamline in single-phase flow [Gelhar and Collins, 1971]

$$\tau(s) = \int_0^s \frac{\phi}{|\mathbf{u}|} ds.$$  (5)

Then equations (1) and (4) become

$$\frac{\partial \phi}{\partial t} + \phi \frac{\partial F_c}{\partial \tau} + \nabla \cdot \mathbf{G}_c = -T_d,$$  (6)

$$\frac{\partial \phi(1-S_c) C}{\partial \tau} + \phi \frac{\partial (1-F_c) C}{\partial \tau} = \nabla \cdot \mathbf{D}_c \nabla C + m_s T_d - m_s T_r.$$  (7)

These are not strictly one-dimensional equations since gravity segregation (equation (6)) and transverse dispersion and diffusion (equation (7)) are not aligned along streamlines. They will be solved using an operator splitting technique, described in section 3.

2.2. Geochemistry

[12] A simple geochemical model will be used. It will be assumed that dissolution occurs instantaneously.

$$C = K_D \quad S_c > 0$$  (8a)

$$T_d = 0 \quad S_c = 0$$  (8b)

where $K_D$ is the dissolution constant that is a function of temperature and pressure.

[13] For rate-limited mineral precipitation we assume an effective reaction that represents the dissolution of primary minerals followed by the precipitation of secondary material

$$CO_2 + XO \rightarrow XCO_3,$$  (9)

where CO$_2$ is dissolved in the aqueous phase, XO is the primary mineral and XCO$_3$ is the secondary mineral that is precipitated. The simplest possible model is to assume that only the forward reaction occurs at a constant rate independent of the concentration of any of the species, as long as dissolved CO$_2$ is present, and independent of the saturations. The reaction rate is assumed to be proportional to porosity. If $m_o$ is the molar density of the primary material, then the porosity change is governed by the following equation

$$\frac{\partial \phi}{\partial \tau} = -\left(1 - \frac{m_o}{m_s}\right) T_r = -k \phi \quad C > 0,$$

$$= 0 \quad C = 0,$$  (10)

where $k$ is a rate constant.

[14] Permeability is updated using the expression [Wellman et al., 2000]

$$K_{new} = K_{old} \left( \frac{\phi_{new}}{\phi_{old}} \right)^{3.4}.$$  (11)

3. Streamline-Based Model

3.1. Model Description

[15] The procedure for the simulation is as follows.

[16] 1. CO$_2$ saturation and concentration, permeability and porosity are defined on the underlying grid.

[17] 2. Invoking volume balance over all phases, a pressure equation is developed that is solved using an algebraic multigrid method on the grid [Stüben, 2001]. The effect of porosity change is ignored in the pressure solution.

[18] 3. Using Darcy’s law and the known pressures, streamlines are traced across the grid using the method due to Pollock [1988]. All grid blocks have at least one streamline going through them [Batycky et al., 1997].

[19] 4. Saturation, concentration and porosity defined on the grid are mapped onto streamlines and discretized in equal increments of the time of flight $\Delta \tau$ [Batycky et al., 1997].

[20] 5. Equations (6) and (7) are solved along streamlines, assuming that the porosity is constant and ignoring reaction, dissolution, gravity segregation and dispersion. Hence the following equations along streamlines are considered:

$$\frac{\partial \phi}{\partial t} + \frac{\partial F_c}{\partial \tau} = 0;$$  (12)

$$\left(1 - S_c\right) \frac{\partial C}{\partial t} + (1 - F_c) \frac{\partial C}{\partial \tau} = 0$$  (13)

Equations (12) and (13) are solved using single-point upstream weighting:

$$S_{i,j}^{int} = S_{i,j}^{n} - \frac{\Delta \tau}{\Delta \tau} \left(F_c \left(S_{i,j}^{n} - F_c \left(S_{i,j}^{n-1}\right)\right)\right),$$  (14)

$$C_i^{int} = C_i^{n} - \frac{\Delta \tau}{\Delta \tau} \left(1 - F_c \left(C_{i,j}^{n}\right)\right) \left(1 - S_{i,j}^{int}\right),$$  (15)

where the subscript $i$ labels the cell in the discretization along a streamline, $n$ is the time level, $\Delta \tau$ is the time step and the superscript int indicates the updated saturation and concentration due to advection only.

[21] 6. Reaction is then considered. The total number of moles of CO$_2$ in both fluid phases per unit volume is computed,

$$m_{ii}^{\text{int}} = \phi_{ii}^{n} \left(1 - S_{i,j}^{\text{int}}\right) \left(m_{ii}^{\text{n}} + m_{ii}^{\text{int}}\right).$$  (16)

Then to account for the porosity change, using equations (10) and (16):

$$\phi_{ii}^{n+1} = \phi_{ii}^{n} e^{-k \Delta \tau} \phi_{ii}^{\text{int}} \geq m_{\text{eff}} \phi_{ii}^{n} \left(1 - e^{-k \Delta \tau}\right),$$  (17a)

$$\phi_{ii}^{n+1} = \phi_{ii}^{n} - \frac{m_{\text{eff}}^{\text{int}}}{m_{\text{eff}}^{\text{n}}} m_{ii}^{\text{int}} < m_{\text{eff}} \phi_{ii}^{n} \left(1 - e^{-k \Delta \tau}\right),$$  (17b)
where

$$m_{\text{eff}} = \frac{m_i}{1 - \frac{m_o}{m_i}}.$$  \hspace{1cm} (18)

If the second condition in equation (17) is met, all the CO$_2$ in the fluid phases is consumed by reaction and $S_t^{n+1} = C_t^{n+1} = 0$.

[22] 7. Dissolution is accounted for. The total moles of CO$_2$ in the liquid phases is updated from step (6)

$$m_n^{n+1} = \phi_j^{n+1} \left( (1 - S_t^{n+1}) C_t^{n+1} + m_{\text{eff}}^{n+1} \right)$$

$$= m_{\text{init}}^{n+1} - m_{\text{eff}}^{n+1} (\phi_j^{n+1} - \phi_j^{n+1}).$$  \hspace{1cm} (19)

Then

$$C_i^{n+1} = K_D; \quad S_t^{n+1} = \frac{m_n^{n+1} - \phi_j^{n+1} - K_D}{m_i - K_D} \quad m_n^{n+1} \geq \phi_j^{n+1} K_D$$  \hspace{1cm} (20a)

$$C_i^{n+1} = \frac{m_{\text{init}}^{n+1}}{\phi_j^{n+1}}; \quad S_t^{n+1} = 0 \quad m_n^{n+1} < \phi_j^{n+1} K_D$$  \hspace{1cm} (20b)

[23] 8. The saturation, concentration and porosity are mapped onto the grid

$$\phi_{\text{block}} = \frac{1}{\sum_j \phi_j^{n+1} \Delta \tau_j} \sum_j \phi_j^{n+1} \frac{\Delta \tau_j}{\sum_j \Delta \tau_j},$$  \hspace{1cm} (21)

where the subscript block labels the grid block, and $j$ labels the streamlines that pass through the block. A total of $l$ streamlines cross the block. $\Delta \phi_j$ is the average porosity over the time of flight increment $\Delta \tau_j$ to traverse the block. This is equivalent to a volume-weighted average. Similar expressions are used to map concentration and saturation to the grid [Batycky et al., 1997; Crane and Blunt, 1999].

[24] 9. Fluid segregation due to gravity is simulated on the grid using an operator splitting technique [Bhatvedt et al., 1996]; the conservation equation for CO$_2$ saturation, equation (6), is solved considering only movement due to gravity segregation.

[25] 10. Dispersion and diffusion are accounted for by solving the dispersive part of the conservation equation for aqueous CO$_2$ on the grid [Bensabat et al., 2000; Zheng and Bennett, 1995]. Details of the implementation are given by Obi and Blunt [2004], who also provide a detailed error analysis of the effects of mapping properties from streamlines to the grid; these are small for the cases we consider since advective movement dominates the transport.

[26] 11. The permeability values in each grid block are updated due to the porosity change using equation (11). Whenever the flow field changes significantly due to permeability changes, changing boundary conditions or because of the mobility contrast between the phases, streamlines are recomputed and the simulation returns to step (1). This decoupling of permeability changes from the transport step is only a valid approximation if the permeability alteration occurs over a timescale that is much longer than the timescale for transport. In these simulations this is a valid approximation; as we show later, the fastest reaction rate we consider has a time constant of 2,000 years. In contrast, significant changes in saturation occur over times of less than a year at the grid block level.

### 3.2. Approximations Made

[27] The simulation makes a number of significant approximations. However, we believe that the results we present later are valid since we accurately capture the process that principally affects the location of CO$_2$, namely advective transport in a complex flow field. The main approximations that have not been discussed already are as follows.

[28] 1. We use a simple geochemical model. Other authors [see, e.g., Xu et al., 2003] have developed sophisticated codes to account for equilibrium and rate-limited reaction during CO$_2$ sequestration involving many components. Our model is the simplest possible formulation that can account for rate-limited dissolution and precipitation. The emphasis of this paper is on the effect of heterogeneity on the advective movement of the injected material. However, since all the reactions are computed along streamlines, this method could be extended to incorporate a more elaborate geochemical model, resulting in a simulation technique that accounts for chemistry accurately in the one-dimensional transport equations along streamlines while also elegantly capturing the three-dimensional flow field. Furthermore, as discussed later, the values of the rate constants are very uncertain and in many cases cannot be reliably determined in the field to within an order of magnitude. Our approach is simply to assume some fixed rate over the timescale of interest. This effective rate could be estimated from a more detailed one-dimensional numerical study in combination with laboratory and field measurements [Wetland et al., 2003]. This allows us to capture the key physical processes that occur, dissolution and porosity change due to mineral precipitation, without having to account for multiple reacting species in a finely resolved three-dimensional transport simulation. Hence we believe that the results presented here do give a realistic representation of the effects of precipitation reactions for different effective rate constants.

[29] 2. We assume incompressible flow. The CO$_2$ is relatively incompressible in the examples studied since we consider pressures well above the critical pressure. Water and most deep consolidated rocks also have a low compressibility. Hence this approximation is not significant in determining the correct flow paths for the fluids. In a completely confined aquifer, injection results in a large increase in pressure that cannot be predicted using an incompressible formulation. In this work we apply constant pressure boundary conditions at the edge of the domain to represent an effectively infinite-acting aquifer, similar to the approach used to simulate sequestration in the Sleipner field [Johnson et al., 2000] and so our predicted pressures are accurate. Compressibility effects have little impact on the flow paths for $c \Delta P < 1$ and do not significantly affect the predicted pressures when $\Delta P/c < 1$, where $c$ is the total compressibility of the rock and fluids, $\Delta P$ is the maximum pressure change in the simulation and $P$ is the average initial reservoir pressure [Aziz and Settari, 1979]. In our simulations $c \Delta P < 0.01$ and $\Delta P/P < 0.03$. Hence ignoring
compressibility is a valid assumption for the cases presented in this paper.

We ignore geomechanical effects. Injection of CO\(_2\) leads to an increase in pressure in the field. This in turn can lead to fracturing and changes in porosity and permeability. We ignore these effects in this work and assume that the injection pressure is below the pressure necessary to induce fracturing.

4. Fluid Properties

Table 1 lists all the fluid properties used in the simulations.

### 4.1. Density and Viscosity of CO\(_2\)

We assume a fixed viscosity and density of the CO\(_2\) at a reference temperature of 353 K (80°C) and a reference pressure of 27 MPa - 6 \times 10^{-5} Pa s and 710 kg m\(^{-3}\) respectively [Pruess et al., 2003]. We assume isothermal conditions and the reservoir pressure in our simulations varies between 28 MPa and 27 MPa and so this approximation is not significant.

4.2. Aqueous Properties

We use the following expression to compute the dissolution constant [Pruess et al., 2003]

\[
X_D = \frac{P}{K_h} e^{-\frac{w}{T}}.
\]

\(X_D\) is the mole fraction of CO\(_2\) that can dissolve in water, \(T\) is the absolute temperature and \(R\) is the universal gas constant. We have assumed a fugacity coefficient of 1. \(w\) is the apparent molar volume of CO\(_2\) at infinite dissolution which we take to be 3.21 \times 10^{-5} m\(^3\) mole\(^{-1}\).

\(K_h\) is the Henry’s law coefficient (with units of pressure) that is 497 MPa at \(T = 353\) K [O’Sullivan et al., 1985].

To find the dissolution constant, \(K_D\), with units moles per unit volume of aqueous phase we assume ideal mixing

\[
K_D = \frac{X_D m_w}{1 - X_D \left(1 - \frac{m_w}{m_o}\right)}.
\]

where \(m_w\) is the molar density of water containing no dissolved CO\(_2\).

5. Results

We will consider injection from a single well at a rate of 1,800 m\(^3\) d\(^{-1}\) (at reservoir conditions) for 20 years. This rate represents the injection of 0.47 Mt of CO\(_2\) (0.13 Mt
carbon) per year. This is approximately equivalent to 50 MW of electricity production from a coal-fired power station. A larger project that collects all the CO₂ from a large power station (500 to 1,000 MW) is likely to use several injection wells. We then simulate transport and reaction for a further 180 years with a regional groundwater flow.

5.1. One-Dimensional Simulations

We will study the different physical phenomena involved in CO₂ sequestration through a series of one-dimensional simulations. In one dimension our streamline model becomes equivalent to a standard grid-based simulation method [Zheng and Bennett, 1995]. CO₂ is injected near the center of the domain for 20 years. Constant pressure boundary conditions (27 MPa) are maintained at the two edges of the system. During injection the pressure at the injection well is approximately 28 MPa. After injection the pressure is approximately 27 MPa throughout the domain, with a small gradient that results in a regional groundwater Darcy velocity of approximately 0.18 m/year⁻¹. The simulation continues until there is no further movement of the CO₂ phase or dissolution or reaction. The system has dimensions 2000 m × 1500 m × 200 m in the x, y and z directions respectively and is discretized into 400 × 1 × 1 grid blocks. The initial porosity and permeability are 0.15 and 100 md respectively. The dispersivity = Δv/10 = 0.25 m. Molecular diffusion is ignored.

We first consider a case where there is no reaction and no dissolution. In this case transport is by advection and dispersion only. This represents an unreactive rock, such as quartz, in an aquifer that already holds the maximum aqueous concentration of CO₂. Figure 1 shows the CO₂ saturation at 20 years (after injection) and at 200 years. During the injection phase, CO₂ saturation follows a Buckley-Leverett profile [Bear, 1972] with a leading shock displacing water. The numerical results very closely match the analytical solution [Bear, 1972]. The slight asymmetry of the profile after 20 years is due to different pressure gradients to the left and right of the injection point caused by constant pressure boundaries at the edges of the domain.

During the injection phase, CO₂ is injected, then the CO₂ will be close to residual saturation after approximately 300 years. After the injection phase, groundwater flow causes the trailing edge of the saturation profile to dissolve. After approximately 1800 years, all the CO₂ will have dissolved.

Figure 2. CO₂ saturation for a one-dimensional simulation including dissolution and dispersion but ignoring reaction. Compared to Figure 1 the saturations have migrated less far due to dissolution. After the injection phase, groundwater flow causes the trailing edge of the saturation profile to dissolve. After approximately 1800 years, all the CO₂ will have dissolved.
In our simulations \( Q = 150 \text{ m}^3 \text{ d}^{-1} \) giving a dissolution time of 1,800 years.

[42] Figure 3 shows the dissolved concentration of CO\(_2\). Wherever there is CO\(_2\) in its own phase, the dissolved concentration is at its saturated value. The saturated value is slightly higher during the injection phase since the pressure is higher. Dispersion causes a negligible smearing of the plume in this case.

[43] The third case is when dissolution and reaction are both considered. Using linear relative permeabilities it is possible to construct analytical solutions for this case that compare well with the numerical results [Di Donato and Blunt, 2004]. The saturation profile is shown in Figure 4. During the injection phase the profile is very slightly slowed down due to reaction compared to Figure 2. However, after 200 years, the impact on the saturation profile is dramatic since there has been sufficient time for a significant amount of precipitation. Reaction causes the CO\(_2\) saturation to fall below its residual value and contains the profile within a smaller volume than before. CO\(_2\) is now barely mobile in its own phase with a maximum saturation of only 0.225 after 200 years. As before, the dissolved concentration is at its saturated value wherever CO\(_2\) in its own phase is present.

[44] When the CO\(_2\) in its own phase is immobile we can estimate the rate of decrease of saturation due to precipitation if we assume that aqueous phase concentration and porosity stay constant. Then from equation (7) \( m_cT_d = m_sT_s \) and from equations (6) and (10) we find:

\[
\frac{\partial S_c}{\partial t} = \frac{km_{\text{eff}}}{m_c}, \tag{28}
\]

which implies that the time for all the CO\(_2\) in its own phase to disappear, starting from the residual saturation, \( S_{cr} \) is:

\[
t_R = \frac{S_{cr}m_c}{km_{\text{eff}}}. \tag{29}
\]

This is only an approximate solution to the transport equations (6), (7) and (10) since concentration and porosity also change with time. However, it does provide a quick estimate of the time necessary to sequester CO\(_2\) in a solid phase. For our simulation we have \( t_R = 243 \) years. In this case, the CO\(_2\) saturation is above residual for just over 200 years, meaning that we predict that all the CO\(_2\) would reside in the solid phase after 200 + 243 or around 440 years. From the simulations we find that it takes approximately 470 years for all the CO\(_2\) to be sequestered in the solid phase.

[45] If the dissolution time is less than the reaction time computed by equation (29), then material will precipitate principally from the aqueous phase with no free phase CO\(_2\) present. In this case, a similar argument used to derive equation (29) gives a reaction time

\[
t_R = \frac{K_D}{km_{\text{eff}}}. \tag{30}
\]

[46] Figure 5 shows the porosity distribution. At 200 years \( kt = 0.1 \) and so, as expected, the porosity has decreased by up to 10\%. A large decrease in CO\(_2\) saturation causes only a small decrease in porosity. This is because the solid precipitated phase has a higher molar density than liquid CO\(_2\) and so stores the same amount on carbon in less volume. Figure 6 shows the corresponding permeability. The permeability does decrease, although in this case the decrease is not sufficient to alter the flow field significantly.

[47] Another way to analyze the results is to consider the fractions of the total mass of CO\(_2\) contained in each phase, shown in Figure 7. It can be seen that after 200 years, approximately equal amounts of material are contained as free phase, dissolved, and in the solid.

[48] The sequestration or storage efficiency \( E \) is defined by Van der Meer [1995] as “the ratio between the maximum storage volume and the actual injected volume.” We define the maximum storage volume as the volume of CO\(_2\) in its own phase that could be stored in the reservoir with a saturation of 1 and the original porosity. We define the volume of the reservoir to be that volume where any CO\(_2\) resides in its own phase, or where the porosity is altered, or where dissolved material is present. In other words, take any part of the aquifer where any CO\(_2\) in any phase is present. Now assume that the same aquifer volume were completely filled with CO\(_2\) in its own phase with a saturation of 1 (this is the most CO\(_2\) that could be stored in this volume). \( E \) is the

\[
E = \frac{\text{Maximum storage volume}}{\text{Actual injected volume}}.
\]

Figure 3. Dissolved CO\(_2\) concentration for a one-dimensional simulation including dissolution and dispersion but ignoring reaction. Wherever there is CO\(_2\) in its own phase, the concentration is at its saturated value. The saturated value is slightly higher during the injection phase since the pressure is higher. Dispersion causes a negligible smearing of the plume in this case.

Figure 4. CO\(_2\) saturation for a one-dimensional simulation including dissolution, dispersion, and reaction. Precipitation causes the CO\(_2\) saturation to fall below its residual value and contains the extent of the plume. After 470 years, all the CO\(_2\) resides in the solid phase and the saturation is zero.
ratio of the actual volume to the maximum volume. \( E = 0.29 \) for advection only after 200 years, falling to 0.2 once the CO\(_2\) saturation is residual everywhere (after 300 years). Including dissolution, the efficiency is 0.34 at 200 years but decreases to 0.27 at late time (after 470 years) because precipitation limits the spread of the plume. We will show later, however, that preferential flow in a heterogeneous three-dimensional system leads to much lower efficiencies.

We have studied a case with a relatively rapid reaction rate and groundwater flow. Apart from the initial injection period, the results would be similar if we decreased the reaction rate and groundwater flow by some factor and increased time by the same factor.

5.2. Three-Dimensional Simulations

We now simulate flow in a highly heterogeneous three-dimensional aquifer. The model is described on a regular Cartesian grid of dimensions 4800 \( \times \) 8800 \( \times \) 200 m; the number of grid cells are 1,122,000, given by 60 \( \times \) 220 \( \times \) 85 in the \( x \), \( y \), and \( z \) directions respectively. We use a model based on a North Sea oilfield with two major layers: the lower portion of the field (bottom 50 layers) represents the Upper Ness that is fluvial with high-permeability meandering sand channels surrounded by low-permeability shale, while the upper zone (top 35 layers) represents the Tarbet formation that has a prograding nearshore depositional environment \cite{Christie2001}. The permeability tensor has \( K_x = K_y = 10 K_z \) in each grid block. The logarithm of the permeability distribution has a normalized standard deviation of 3.5 with a variation in permeability of over 5 orders of magnitude. Horizontal and vertical slices through the permeability field are shown in Figure 8. All the horizontal slices are taken for the 31st layer from the bottom, in the lower, fluvial, portion of the field. The porosity initially has a constant value of 0.15. As in the one-dimensional simulations we have a single well injecting CO\(_2\) at a rate of 1,800 m\(^3\) d\(^{-1}\) for 20 years followed by a further 180 years of transport in a regional groundwater flow with an average Darcy velocity of approximately 0.16 m/year, similar to the one-dimensional examples. The same injection pressure was used as before.

We ran three cases: one with no dissolution or reaction; one with dissolution but no reaction; and one with dissolution and reaction. The run time for the example with dissolution and reaction was 11 hours on a 1.5 GHz PC with 1 GB of memory. Ignoring reaction and/or dissolution did not significantly reduce the run time since solving for the pressure field is the most computationally demanding part of the simulation. The one-dimensional simulations were much faster, taking less than a minute to run in all cases. We were unable to compare run times and results using grid-based simulation for this case. However, comparisons of streamline-based and grid-based simulations ignoring reaction, but using the same three-dimensional reservoir model, have been performed previously: the streamline model is approximately 50 times faster, but gives almost identical results in terms of pressure response and saturation profiles \cite{Huang2004, Christie2001}.

Figure 9 shows a horizontal slice of the CO\(_2\) saturation at 20 and 200 years for the case with no dissolution and reaction, while Figure 10 shows a vertical slice. The CO\(_2\) channels through the high-permeability layers and rises upward since it is less dense than water. The amount of vertical movement is significant in this example. A continuous barrier of low permeability approximately 80 m from the bottom of the field prevents CO\(_2\) moving between the
Upper Ness and Tarbet formations. After 200 years almost all the CO$_2$ is at residual saturation and effectively immobile. The permeability contrast dominates the transport and the CO$_2$ is much more spread out at lower saturation than in the one-dimensional example (Figure 1).

Figure 11 shows a vertical cross section of the CO$_2$ saturation for the case without reaction but where there is dissolution. The saturations are lower and less dispersed than the corresponding case without dissolution (Figure 10), as expected. The decrease in CO$_2$ saturation is more dramatic in the lower zone of the field. This is because the permeability is lower in this region and as a consequence less CO$_2$ is injected than in the upper zone. In addition gravitational effects favor injection into the upper portions of the domain. Dissolution is thus able to remove substantial fraction of the free phase in the lower region. Figure 12 shows the aqueous CO$_2$ concentration in vertical cross section; the CO$_2$ in its own phase, rising to the top of the system, acts as a source for aqueous CO$_2$. However where the concentration is high, the aqueous phase density is also high and the dissolved CO$_2$ plume moves slowly downward over time. In horizontal cross section (Figure 13) the plume is considerably more dispersed than the CO$_2$ saturation (not shown, but even more contained than with no reaction, Figure 9). This is different from the one-dimensional simulation results (Figures 2 and 3), where the CO$_2$ saturation moved faster than CO$_2$ in the aqueous phase. In three dimensions, the CO$_2$ reaches residual saturation quicker because of channeling and gravity segregation that disperses the CO$_2$ rapidly, allowing the aqueous phase to move ahead through high-permeability channels and to occupy a much larger volume than would be predicted from a one-dimensional analysis (Figure 3).

Figure 14 shows the CO$_2$ saturation in vertical cross section when dissolution and reaction are accounted for. Notice that the saturations are considerably lower than if reaction is ignored (Figure 11) and that after 200 years the saturation is zero everywhere except for a thin zone near the top of the domain. This contrasts with the one-dimensional simulations (Figure 4) where appreciable quantities of CO$_2$ in its own phase were still present after 200 years. The variation of permeability allows the CO$_2$ to be rapidly dispersed giving a greater volume over which reaction occurs, allowing more material to be sequestered into the
Figure 10. CO₂ saturation for a three-dimensional simulation ignoring dissolution and reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. (a) Saturation after 20 years of injection. (b) Saturation after 200 years.

Figure 11. CO₂ saturation for a three-dimensional simulation with dissolution but no reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. (a) Saturation after 20 years of injection. (b) Saturation after 200 years.

solid phase. Figure 15 shows the corresponding aqueous phase concentrations: after 200 years, reaction has limited the extent of the plume in comparison to the case with no reaction (Figure 12). Again the effect is more dramatic in the lower zone, where less CO₂ was injected initially. Figure 16 shows the porosity distribution: the magnitude of the decrease in porosity is similar to that predicted using one-dimensional simulation since the reaction rates are the same (Figure 5), but the extent of the region affected by reaction is much larger. Figure 17 shows the corresponding

Figure 12. CO₂ aqueous phase concentration for a three-dimensional simulation with dissolution but no reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. Wherever CO₂ in its own phase is present (Figure 11), the concentration is high. The plume moves with the groundwater flow and falls slowly under gravity. (a) Concentration after 20 years of injection. (b) Concentration after 200 years.

Figure 13. CO₂ concentration after 200 years for a three-dimensional simulation with dissolution but no reaction. A horizontal slice is shown, corresponding to the permeability field in Figure 8. Notice that the plume is considerably more dispersed than in one dimension (Figure 3) because of the extreme permeability contrast.
change in permeability. In this example the change in permeability is modest in comparison with the enormous permeability contrast in the aquifer and so has little impact on the flow field.

Figure 14. CO₂ saturation for a three-dimensional simulation with dissolution and reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. (a) Saturation after 20 years of injection. (b) Saturation after 200 years. Notice that with reaction the saturation is zero almost everywhere, in contrast to the case without reaction (Figure 11).

Figure 15. CO₂ aqueous phase concentration for a three-dimensional simulation with dissolution and reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. (a) Concentration after 20 years of injection. (b) Concentration after 200 years. Notice that the plume is less extensive than the corresponding case without reaction (Figure 12).

Figure 16. Porosity distribution for a three-dimensional simulation with dissolution and reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. (a) Porosity after 20 years of injection. (b) Porosity after 200 years.

[55] Figure 18 shows the fraction of the total mass initially injected that resides in solid, aqueous and free phases as a function of time. In comparison to the corresponding graph for the one-dimensional simulations (Figure 7) more mass is sequestered in the solid phase since the permeability variation allows the CO₂ to be more dispersed giving a greater volume over which reaction can occur, as mentioned earlier. After 200 years most of the

Figure 17. Permeability alteration for a three-dimensional simulation with dissolution and reaction. A vertical slice through the center of the field is shown, corresponding to the permeability field in Figure 8. The ratio of the permeability to the original value is shown. (a) Alteration after 20 years of injection. (b) Alteration after 200 years.
mass is in the solid phase and the amount of material that is dissolved is decreasing.

[56] The sequestration efficiencies, \( E \), are more than an order of magnitude lower in the three-dimensional case since the \( CO_2 \) occupies a much larger volume than predicted from a one-dimensional model. We define the reservoir volume as the volume of the smallest box-shaped region that contains all the injected \( CO_2 \) regardless of the phase it is in. Using this definition, after 200 years \( E = 0.021 \) with no reaction and dissolution, \( E = 0.019 \) with dissolution and no reaction and \( E = 0.022 \) with reaction and dissolution. These numbers are similar to those quoted by other authors [Van der Meer, 1995], although at the lower end of previous estimates since we have studied a realistically heterogeneous aquifer.

6. Conclusions

[57] We have developed a streamline-based model incorporating equilibrium mass transfer between phases (dissolution) and rate-limited reaction (precipitation) and applied it to the study of \( CO_2 \) sequestration in a deep saline aquifer. We modeled advection due to the movement of \( CO_2 \) in its own phase, dissolution and transport of aqueous \( CO_2 \), and porosity and permeability changes due to reaction. We illustrated the method by simulating sequestration in a highly heterogeneous million grid block model of a North Sea reservoir. The advective transport of \( CO_2 \) was dominated by high-permeability channels in the system that lead to a much more extensive movement than predicted using one-dimensional simulation. This allowed precipitation reactions to occur over a large reservoir volume, but led to low sequestration efficiencies of around 2\%. Trapping of residual \( CO_2 \) was shown to be the most rapid and effective mechanism for rendering the injected gas immobile. The study demonstrates the need to model accurately flow in a heterogeneous aquifer, as well as the relevant geochemical processes.

[58] The model assumed a constant reaction rate independent of brine composition. This is an effective reaction rate whose value could be determined from a thorough geochemical analysis. Furthermore, this model could be extended to consider more complex geochemistry.

[59] Mathematically the streamline method elegantly decouples a three-dimensional system into a series of one-dimensional equations, making solving for reaction no more difficult than in present one-dimensional models, while also accurately accounting for a complex flow field.

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M. J. Blunt, Department of Earth Science and Engineering, Imperial College, London, SW7 2AZ, UK. (m.blunt@imperial.ac.uk)

E.-O. I. Obi, Geoscience Research Centre, Total E&P UK plc, Crawpeel Road, Altens Industrial Estate, Aberdeen AB12 3PG, UK.