II.3  Introduction to Geologic CO\textsubscript{2} Sequestration

Fossil fuels currently dominate commercially supplied energy worldwide, and most estimates of energy use over the next 30 years suggest that use of fossil fuels will grow as the developing economies make greater use of energy. If that prediction is correct, then reduction of the amount of CO\textsubscript{2} emitted to the atmosphere will require that the CO\textsubscript{2} that results from combustion reactions be captured and stored. While many techniques are available for CO\textsubscript{2} separation, the cost of separation is still unacceptably high, and hence there is an opportunity for research in this area to lay the fundamental basis for more efficient separation methods. If the costs of separation can be reduced, then there is still the issue of where the CO\textsubscript{2} will be stored. This report deals with the possibility of storage in three geologic settings: oil and gas reservoirs, deep saline aquifers, and coalbeds. In each of these settings, sites will have to be selected that have appropriate geologic seals, efficient methods for flow predictions will be needed for process design and for permitting, and monitoring systems appropriate to various stages of a project will have to be designed. This report describes research to develop a suite of prediction tools appropriate to the flow settings and physical mechanisms that act and interact in the three geologic settings.

Oil reservoirs have considerable appeal as storage locations because they are known to have a geologic seal that trapped the hydrocarbons. Thus, as long as operations during oil production have not damaged that seal, the reservoir should be able to hold injected CO\textsubscript{2} indefinitely. Because oil (and also gas) reservoirs have known seals and because there is a regulatory structure that has experience in permitting gas-injection operations, existing oil fields are likely to be the first places that CO\textsubscript{2} sequestration is undertaken if it is to be done at large scale.

Storage of CO\textsubscript{2} can take place in zones in which CO\textsubscript{2} replaces reservoir oil or water. CO\textsubscript{2} is soluble in water, and it is about ten times more soluble in undisplaced oil. A separate CO\textsubscript{2}-rich phase can also occupy significant pore volume. Movement of oil and gas in a reservoir is dominated by the pressure gradient created between injection and production wells and by the heterogeneity of the rocks. The viscosity of CO\textsubscript{2}, a few hundredths of a centipoise over a wide range of pressures and typical reservoir temperatures, is low compared to most oils and any water present in the reservoir. The injected CO\textsubscript{2} invades high permeability flow paths as it makes its way to production wells. Accurate prediction of the timing of breakthrough of injected CO\textsubscript{2} at production wells and the amount of CO\textsubscript{2} produced with the oil requires detailed description of the permeability distribution in the reservoir. Those predictions are important because they forecast the amount of subsequent production, recompression, and recycling of CO\textsubscript{2} that is produced with oil.
CO₂ injection into gas reservoirs has been proposed but not yet been attempted. CO₂ could be used for pressure maintenance or for condensate vaporization, but the cost of purchasing CO₂ has so far prevented these applications in the absence of incentives for CO₂ storage. In fields that contain some condensate saturation, CO₂ can vaporize the light hydrocarbons that make up the condensate quite efficiently (see below), and it is even possible for CO₂ to develop multicontact miscibility with two-phase gas and condensate mixtures. If CO₂ sequestration were undertaken in a substantial way, gas reservoirs would be candidate storage locations, again with a known geologic seal capable of holding gas indefinitely.

Storage of CO₂ in a gas reservoir would have the advantage that all CO₂ that results from oxidation of CH₄ produced from the reservoir could be stored in the same reservoir, at the same temperature and pressure, with volume left over. One mole of CO₂ is produced for each mole of CH₄ oxidized, and the molar density of CO₂ is always larger than that of CH₄ at a given temperature and pressure. Figure 1 shows molar densities of CH₄ and CO₂ calculated with the Peng-Robinson equation of state² with volume translation³. The higher molar density of CO₂ means that the volume of CH₄ produced from a gas reservoir could be replaced by a mixture of N₂ and CO₂. In other words separation of all of the N₂ from a flue gas, for example, would not be required to match injection and withdrawal volumes, although there would be additional cost associated with compression of the N₂/CO₂ mixture over that for CO₂ alone. Figure 2 shows that a mixture of 60% N₂ and 40% CO₂ has approximately the same density as pure CH₄ at 50, 75, and 100°C.

![Figure 1: Molar density of CH₄ and CO₂.](image-url)
II.3 Project Results: Geologic CO₂ Sequestration

Oil and gas reservoirs are not uniformly distributed geographically, and there are many locations where anthropogenic CO₂ is generated that are not close to potential storage sites in oil or gas reservoirs. Deep formations that contain salt water are more widely distributed, however.

In this setting, injected CO₂ will also flow more easily through high permeability paths, but the flow will not be dominated by the pressure gradients imposed by injection and production wells. Gravity segregation caused by the difference in density of the injected CO₂ and brine will cause preferential flow at the top of the aquifer, though injection of the CO₂ well below the top of the aquifer can mitigate this gravity segregation to some extent. Aquifers with large volume, reasonable permeability and thickness, and good pressure communication over long distances will be most attractive, so that large volumes could be injected without raising aquifer pressure significantly. The injected CO₂ will dissolve, eventually, in the brine, and the resulting brine/CO₂ mixture will be slightly denser than the brine alone⁴,⁵. Slow vertical flow of the denser brine will cause further dissolution, as fresh brine is brought in contact with the CO₂ phase. Trapping of a separate CO₂ phase by brine can also act to immobilize CO₂ as a residual phase⁵. Estimates of the time scales for dissolution and the resulting vertical convection suggest that hundreds to thousands of years will be required to dissolve all the CO₂⁴,⁵, but by that time, much of the CO₂ will exist in a trapped residual phase⁵. Relatively slow chemical reactions, depending on the chemical composition of the brine and the minerals present in the aquifer may then sequester some of the CO₂ as minerals⁶.

In oil and gas reservoirs and aquifers, injected CO₂ occupies the pore space as a separate phase or is dissolved in water or oil. Deep, unmineable coal beds offer a different storage mechanism—the same mechanism that is the source of coal bed methane. Gases like CH₄ or CO₂ adsorb at high pressure on the surfaces of coal particles. They show what is typically observed: significantly more CO₂ adsorbs at a given

Figure 2: Molar density of CH₄ and a mixture containing 60% N₂ and 40% CO₂.
II.3 Project Results: Geologic CO2 Sequestration

pressure and temperature on coal than does CH4 or N2. In addition, the hysteresis of the adsorption curves suggests that once the CO2 is adsorbed, much of it will stay adsorbed even if the pressure is decreased at a later time.

Flow in coal beds will occur primarily in the fracture network (fractures in coal are known as cleats). Injected CO2 will flow through the cleats, diffusing into matrix blocks, where replacements of adsorbed CH4 by CO2 will occur. If that replacement occurs at reasonable rates, CO2 can be used to enhance CH4 recovery. This displacement process is similar to adsorption chromatography. Because CO2 adsorbs more strongly than either CH4 or N2, it should be possible to use the coal bed to separate a mixture of N2 and CO2, though at the cost of compression of the N2 in addition to the CO2 and the separation of N2 from produced CH4. There is evidence that coal permeability changes with the amount of adsorbed gas. As CH4 is removed from coal, permeability typically increases, and as CO2 adsorbs, permeability decreases. Thus, displacement processes in coal beds will involve a complex interplay of flow in the cleat system, changes in permeability, diffusion, and adsorption.

An important question, of course, is whether there is sufficient capacity available for storage of large quantities of CO2 in the subsurface. Table I summarizes two sets of estimates of storage capacity in the subsurface. The ranges of the numbers are very large, an indication of the uncertainty in the estimates. Even so, the estimates are large enough to suggest that there is sufficient capacity to store a significant fraction of expected CO2 emissions through 2030 and beyond. Current emissions are about 24 GtCO2/yr (1 GtCO2 = 1 billion metric tons of CO2), and according to the estimates of the International Energy Agency, are expected to rise to 38 GtCO2/yr. If the rise in emission were roughly linear, then the total emissions would be about 1300 GtCO2 for the period from 2000 to 2030. Thus, even given the uncertainty in the estimates, the capacity of geologic formations to store CO2 appears to be sufficient to permit storage at significant scale.

<table>
<thead>
<tr>
<th>Storage Option</th>
<th>Parson &amp; Keith</th>
<th>Gale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil and gas reservoirs</td>
<td>740-1850</td>
<td>920</td>
</tr>
<tr>
<td>Deep saline aquifers</td>
<td>370-3700</td>
<td>400-10,000</td>
</tr>
<tr>
<td>Coal beds</td>
<td>370-1100</td>
<td>40</td>
</tr>
</tbody>
</table>

The existence of volumetric storage capacity is not sufficient, of course, to guarantee that CO2 injection into the subsurface can be undertaken at scale. Many individual projects would be needed to accommodate the volumes of CO2 that would have to be injected. For example, the Sleipner Project is currently injecting about 10^6 tCO2/yr into a high permeability sandstone formation in the North Sea. One thousand similar projects would be required to store 1 GtCO2/yr, and if the injected CO2 had a density of 500 kg/m^3 at reservoir conditions, the total injected volume would be about 34 million barrels per day. Thus, handling even 1 GtCO2/yr, about 4% of current emissions, would require
substantial investment in separation capacity, infrastructure for transportation of the CO\textsubscript{2}, and wells and facilities for injection.

Identification of appropriate sites for geologic storage of CO\textsubscript{2} will require work to establish that the injected CO\textsubscript{2} will be retained in the subsurface. Research on the filling of oil and gas reservoirs indicates that stress changes associated with injection or depletion can affect the integrity of the geologic seals that contain the fluids\textsuperscript{13,14}. Accumulation of oil, gas, or CO\textsubscript{2} can activate faults and cause leakage or can change the state of stress in such a way that leakage is less likely, so careful analysis will be required. More is likely to be known about the state of stress in oil and gas reservoirs than for aquifers or coal beds, so there will be a need for additional research in this area. Wellbores, which always penetrate the geologic seal, offer one potential pathway for leakage. Care will have to be taken to avoid sites and formations where there are abandoned wells that offer leak paths, and active wells will need to be well maintained. While operations at significant scale in enhanced oil recovery projects indicate that it is possible to conduct CO\textsubscript{2} injection safely, careful attention will be needed to maintain safe operations in the many injection projects that will be required if geologic storage of CO\textsubscript{2} is to take place at large scale.

Appropriate levels of monitoring of storage projects will also be needed. It is likely that more monitoring will be needed early in the life of a project than will be required later, but appropriate methods will need to be established for the various stages of a project. A variety of monitoring techniques have potential for use in CO\textsubscript{2} storage projects. Seismic methods, which include time-lapse reflection\textsuperscript{15} or tomographic imaging\textsuperscript{16} and possibly passive seismic approaches can be used to detect subsurface migration and leaks. Gravity measurements and deformation methods such as synthetic aperture radar or tiltmeter measurements also have potential, though they will provide lower resolution indications of fluid movement.

Finally, use of geologic storage of CO\textsubscript{2} at large scale will require establishing appropriate permitting processes\textsuperscript{17} for projects in deep saline aquifers, and perhaps for coal beds in some locations. It will be important in the design and permitting of projects to choose sites where the geologic seals provide long-term containment, to predict where the injected CO\textsubscript{2} will migrate during injection, to monitor at appropriate levels where the injected CO\textsubscript{2} has gone, and to understand the ultimate fate of the injected CO\textsubscript{2}. While a solid base of experience exists, there is much more to be done to design and optimize large-scale CO\textsubscript{2} storage projects in geologic formations. In the remainder of this report, we consider three areas of research related to geologic storage of CO\textsubscript{2}: seal capacity, prediction of fluid movement, and monitoring.