Maximizing Storage Rate and Capacity and Insuring the Environmental Integrity of Carbon dioxide Sequestration in Geological Reservoirs

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Introduction

Carbon dioxide placement in deep saline aquifers offers an opportunity to sequester carbon dioxide near the point of production at many locations in the United States. The abundance of these aquifers has been documented recently. Utilizing these saline aquifers for carbon dioxide sequestration is reasonable, since the saline water contained in them has no economic value.

Objective

The major objective of this research activity is to develop a near optimal procedure for indefinitely sequestering carbon dioxide in deep saline aquifers. Another objective of this is research is to estimate the cost of this sequestration procedure so it can be quantitatively compared to alternative sequestration procedures.

Approach

A multidisciplinary approach is taken to this problem utilizing talent selected from universities, national laboratories and private industry. By this means all aspects of the task can be addressed starting with the details of geochemistry and fluid flow in porous media and then extending to management of the entire aquifer including the integrity of the seal over the aquifer. The identified tasks are being investigated in parallel to hasten the availability of directly useful results.

Project Technologies

The technologies being used in this project are described in the first quarterly progress for this research activity.ⁱⁱ That project report, in a slightly edited form, details the activities to date.

Integrity and Quality of Reservoir Seal (Texas Tech University)

The main objective during this first phase of the research has been to choose and obtain the shale samples. Texaco was contacted and two trips were made to their facilities in Houston. The first meeting at the end of January gained Texaco's support for the work. At the second meeting, on February 22, the core samples were picked from cores available in Houston.

Shale samples from at least two cores will be sent to the MRI-PAC laboratory in March. Samples from one well are black shales with varying amounts of glauconite and siderite iron-bearing minerals. The other sample set is a cleaner black shale from a well-characterized outcrop formation. Detailed petrophysical information as well as the

composition of the samples will be released to our laboratory. Discussion continues about adding other shales and rocks with microporosity to the sample set.

Interference by Iron Minerals on NMR Pore Size Analysis (Texas Tech University)

We have completed the NMR measurements on well-characterized synthetic core samples with known amounts of 30 nm Fe_2O_3 iron oxide added to the pore wall cement. SEM and x-ray analysis was provided by Dr. Necip Guven, a noted clay mineralogist and geologist located at Texas Tech. As expected, the iron lowered the T_2 distribution values due to the additional paramagnetic interaction. In addition, the T_2 distribution was stretched and skewed as the iron concentration was increased. Moreover, the apparent total porosity measurement was reduced by as much as 15% from the 'true' value. We believe that this indicates that the NMR relaxation in the presence of clusters of strong paramagnetic particles is no longer in the fast diffusion limit. A model is being developed.

Acidizing carbon dioxide injection wells with water (Texas Tech University)

Maximizing the long-term injectivity of carbon dioxide injection wells is necessary to minimize the cost of sequestration. In addition to hydraulic fracturing another unique opportunity exists for increased injectivity. That opportunity is acidizing the carbon dioxide injection wells with fresh water, as shown in the following simplified reaction:

$$CO_2 + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3$$

The above reaction is reversible, and so it is shifted to the right by high carbon dioxide pressures. The solubility of limestone in water saturated with carbon dioxide at elevated pressures has been estimated as shown in Table 1. If 150 cubic meters of water per day (943 bbl./day) were injected along with excess carbon dioxide at 15 MPa (2,176 psi) into limestone having 15% porosity the following amounts of limestone would possibly be dissolved:

Temperature C	Volume of limestone dissolved	Hypothetical length of 10 cm (4 in)
(F)	m ³ /day (ft ³ /day)	diameter wormhole
		meters/day (feet/day)
15 (59)	1.00 (35.4)	128 (419)
50 (86)	0.461 (16.3)	59 (193)

TABLE 1 Volume of limestone dissolved and dimensions of wormholes at different temperatures.

The amount of water injected in the above example, 150 cubic meters per day, is a quite small quantity, relative to the amount of carbon dioxide to be injected from an 800 MWe

coal fired power plant, 19,760 cubic meters per day (124,000 bbl/day). [This carbon dioxide volume was calculated at 14 MPa (2000 psi) and 27 C (80F).]

These estimated limestone solubilities need to be confirmed by using a more sophisticated computer program, such as the USGS PHREEQC-2 program. In addition, the presence of other dissolved ions such as chloride, sulfate, sodium, etc. should to be considered.

These initial calculations demonstrate the potential for acidizing carbon dioxide sequestration wells with water, in the presence of high pressure carbon dioxide. Maximizing the length and diameter of wormholes produced by water acidizing is an important research opportunity, which will be addressed experimentally and by computational fluid dynamics techniques.

Additional carbon dioxide – formation interactions (Texas Tech University)

More complex interactions occur when carbon dioxide contacts basic minerals such as feldspars, shales and clays. The neutralization reaction may free calcium and magnesium ions that are subsequently precipitated as carbonates. This reaction will sequester carbon dioxide as mineral carbonates. In addition, these precipitation reactions will decrease the porosity and permeability of the formation. By this mechanism opportunities for carbon dioxide to leak through the overburden will be self-healing. The downside is that injectivity may be decreased by such precipitation near the injection well. This injectivity problem can be managed by acidizing using injected water as discussed in the previous section and by hydraulic fracturing. It can be circumvented by selecting aquifers that contain few basic minerals that react with carbon dioxide.

Considerable literature exists detailing the above reactions. These publications are the result of investigations regarding enhanced oil recovery with carbon dioxide, disposal of carbon dioxide and other acid gases, and the mineralogy of natural carbon dioxide containing reservoirs. Review of this literature is continuing. In addition equilibrium mineral compositions can be calculated using existing computer codes. The actual reaction rates are dependent on fluid flow circumstances, mass transfer rates, as well as the kinetics of the reaction. Detailing these reaction rate concerns may not be a priority. If it becomes a priority both experimental investigations and computer simulations will be applied t o the task.

CARBON DIOXIDE Sequestration Economics (Texas Tech University)

The most significant economic parameters for carbon dioxide sequestration in deep saline aquifers are the amount of energy required for further compression of carbon dioxide prior to injection, and the per unit cost of this energy. This sensitivity is due to taking the difference of two very large numbers – payment received for carbon dioxide sequestered, and the compressor fuel cost — to result in a much smaller number, the annual cash flow. For this reason rather small changes in fuel quantities and/or cost can make very large changes in the net cash flow. This observation suggests that during design of carbon

dioxide injection processes, a considerable investment can be justified to reduce these compression costs. In addition, long-term sequestration plans must allow for escalation of compressor fuel costs. The above conclusions were based on a very speculative economic study. Although the preliminary results are favorable, the actual inputs are being refined and reconsidered in the future.

Injection Simulations and Analysis (Advantek)

The current report summarizes work that have been done or underway from the start of the project in October 2000 until March 13, 2001. Several areas of work have been covered. These include the following three work areas:

- 1. Identification of the parameter that impact sequestering carbon dioxide by injection in underground formations,
- 2. Definition of the tasks and processes that are required to provide design and operational assurance of the subsurface injection processes, and,
- 3. Compilation of the parameters involved in the processes of carbon dioxide injection in fractured wells and their impact on the economics of the sequestration.

The first area of work defined the gaps in the technology that are required to be addresses in order that an optimum simulation of the injection process can be carried out. The assurance process is highlighted in the second work area and the various steps needed to ensure both integrity and compliance of the injection design and operations are defined. The third work area generated a process for inclusion of the subsurface injection issues within the process of economic evaluation of carbon dioxide sequestration.

Work Area 1: Technical Gaps in Simulation

The following issues have been identified for further investigation to provide direction for current gaps in technology development needed for the simulation of subsurface carbon dioxide sequestering:

- Leakoff mechanisms
- Compressible fluid injection in formations
- Fracturing with compressible fluid
- Chemical interaction with proppant and geological formation

In addition, the stability of propped fracture under cyclic conditions generated during onoff operation of carbon dioxide sequestration needs evaluation.

Work Area 2: Environmental Integrity Assurance of Carbon Dioxide Sequestration

As in any waste disposal operations, containment and long-term environmental integrity of disposed carbon dioxide must be assured. In order to insure the environmental

integrity, specific procedures and guidelines must be established for operation design, operational quality assurance, and reporting, monitoring and analysis.

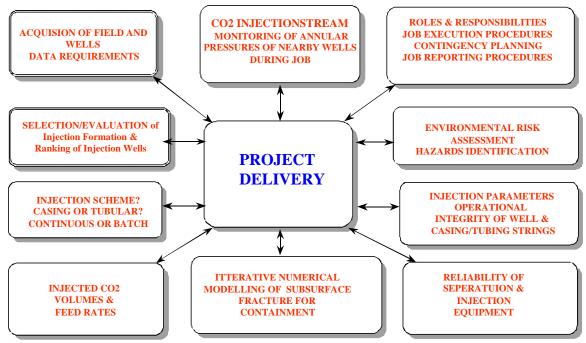


FIGURE 1 Relevant parameters for the injection design and their interaction to provide assurance of the process.

Each component is an integral part of the whole assurance processes. Each component may require specific best practice guidelines. For example, the design process requires estimates of carbon dioxide generation rate, formation characterization, disposal zone identification and selection, long-term containment of injected waste, number of wells required to dispose the generated carbon dioxide, injection operation parameters such as injection pressure, injection rate, injection pump requirement. Figure 1 shows the relevant parameters of the carbon dioxide injection design process and the necessary interaction to provide an assurance of the process.

Work Area 3: Economics of Injection

In this work area the parameters that must be considered the economic model of carbon dioxide injection are compiled. The collective experience with waste management and subsurface disposal indicates that there are several steps required for the design of these schemes. Various injection options must be evaluated, either separately at first then compared with each other. The following cost factors would also be delineated as part of the overall economics:

- No transportation costs (the injectors need to be close to the source).
- Geological formations characterization (logs, cores, surveys, seismic)
- Disposal zone selection and evaluation. (evaluation, options comparisons)
- Recovery, separation and injection of carbon dioxide.

- Engineering and design of the injection operation (Injection parameters such as injection rate, injection pressure, horsepower requirement, ...etc)
- Well evaluation and reservoir simulation.
- Monitoring, testing and verification.
- Risk assessment and hazards identification
- Operational procedures, hazards mitigation, and best practice guidelines.
- Reporting, compliance, and contingency response

Continuum Simulation of Multiphase Flow (Sandia)

We have focused on two areas: computational modeling using both finite and boundary element techniques and initializing model validation experiments. The boundary element code developed with UNM has been ported to Sandia's teraflop parallel computer and to Texas Tech University's High Performance Computing Center. Several benchmark cases using this code have been run in which two types of particles are modeled simultaneously at the particle-size level. Large particles are allowed to settle in a fluid to form a porous matrix and smaller, less dense particles are allowed to flow up through this matrix. As shown in Figure 2, continuum scale modeling has also progressed using the finite element technique and state-of-the-art interface tracking algorithms.

Validation experiments have also been initiated. Using an Ektapro 1000 high-speed video camera and image processing, we have tracked the position and shape of single bubbles rising through two different fluids. We plan next to study, both numerically and experimentally the rise of bubbles through idealized porous media. These efforts are directed to developing tools with which to study possible microseepage mechanisms.



FIGURE 2 The new model allows predictions of the velocity (left side) and pressure (right) when a single gas bubble floats through a fluid to a free surface and bursts.

Mesoscale And Macroscale Simulation of Multiphase Flow Through Porous Media (University of New Mexico)

The flow of a fluid in a porous formation can be modeled by combining Darcy's law with mass conservation, thereby obtaining a potential function. The velocity can be obtained from the potential solution, allowing the tracking of an interface between two fluids. This is of interest, because instabilities in the interface are the cause of large scale fingering, which typically results in poor sweep efficiency. In the case of carbon dioxide sequestration, the poor sweep efficiency leads to severe under utilization of the available

volume in the saline formation, because large pockets of brine are left interspersed with the carbon dioxide.

Most of the simulation work in the area of macroscale fingering has been in two dimensions. Very few articles on three-dimensional fingering are available. UNM is developing boundary element method potential codes that will allow the fully three-dimensional simulation of carbon dioxide flow from a fractured injection point into the formation. Advanced methods to describe the interface evolution will be used in order to observe fingering behavior.

The macroscopic flow in a porous medium is governed by the porosity of the formation. This can be anisotropic, and coupled with transport phenomena at the pore-size scale. For this reason, the program at UNM will emphasize the microscopic scale Stokes flow. There are two main difficulties here: the flow geometry is very complex, and the flowing fluid is composed of a multiphase fluid which may contain solid, liquid and gaseous phases. The major effort in the past reporting period has been to obtain a geometrical description of the flow geometry. This is shown in Figure 3.

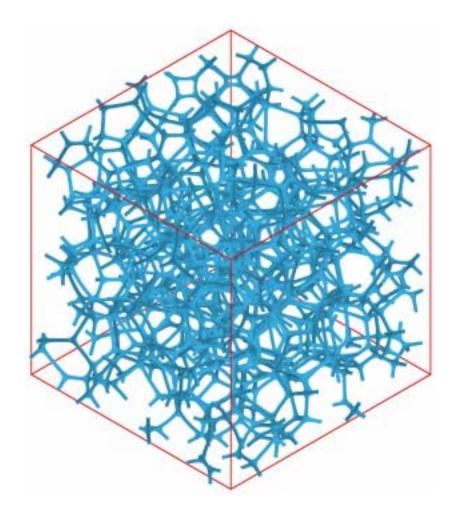


FIGURE 3 BEM mesh describing the flow geometry in a low porosity (2%) formation, consisting of the interstices between adjacent formation particles.

Multiphase flow will occur in such a geometry. With this topology, porosities of up to 10% can be obtained.

In parallel with the development of the microscale flow geometry, a PhD student at UNM has been developing a BEM code to model the flow of deformable bubbles in a flow geometry. This is currently being benchmarked. A typical configuration of bubbles flowing in a tube is shown in Figure 4. The tube geometry is for testing purposes only, and will be replaced by the porous formation geometry shown in the previous figure. Currently, bubbles are assumed rigid, with zero tangential stress boundary conditions. Particle deformation capabilities are currently being implemented. These simulations are extremely large, and massively parallel computers will be required to run the dynamic simulations of the pore-scale flow. Implementation of fast multipole techniques, that will allow these calculations to take place, is already at an advanced stage.

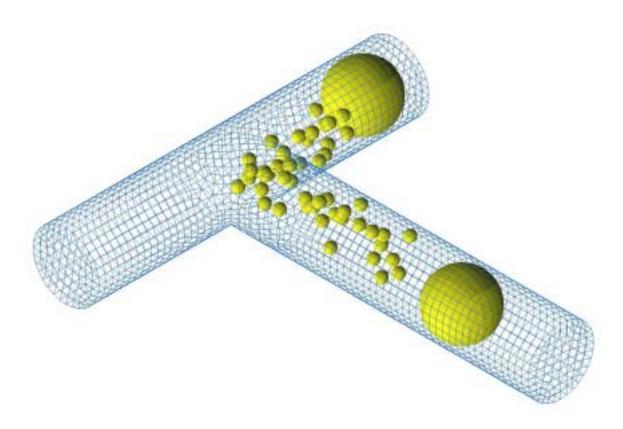


FIGURE 4 Bubbles flowing in a tube. Although the bubbles are initially spherical, deformation will occur due to flow.

Results

The initial results from this recently initiated research activity are incorporated with the description of the technologies involved.

Benefits

The primary benefit of this research will be comprehensive development and documentation of a means of carbon dioxide sequestration that can be utilized in many domestic locations.

Future activities

The planned future activities are itemized in the discussion of each technology. In addition, these various multidisciplinary activities will be integrated into a comprehensive plan and economic study for sequestration of carbon dioxide in saline aquifers.

References

- ⁱ Hovorka, S.D. M. L. Romero, A.G. Warne, W. A. Ambrose, T.A. Tremblay, R.H. Treviño, and D. Sasson, "Sequestration of Greenhouse Gases in Brine Formations." Bureau of Economic Geology, University of Texas At Austin, http://www.beg.utexas.edu/environqlty/carbon dioxideseq/dispslsaln.htm, (2000).
- ii Davis, L.A., A.L. Graham, H.W. Parker, M.S. Ingber, A. A. Mammoli, L.A. Mondy, Q. Guo and A. Abou-Sayed, "Maximizing Storage Rate and Capacity and Insuring the Environmental Integrity of Carbon dioxide Sequestration in Geological Reservoirs," Progress Report to the Federal Energy Technology Center, Morgantown, VA March, (2001).
- Parkhurst, D.L., and C.A.J.Appelo, "User's Guide to PHREEQC (Version 2) A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations," Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Dept. of Interior, Denver, CO, (1999).