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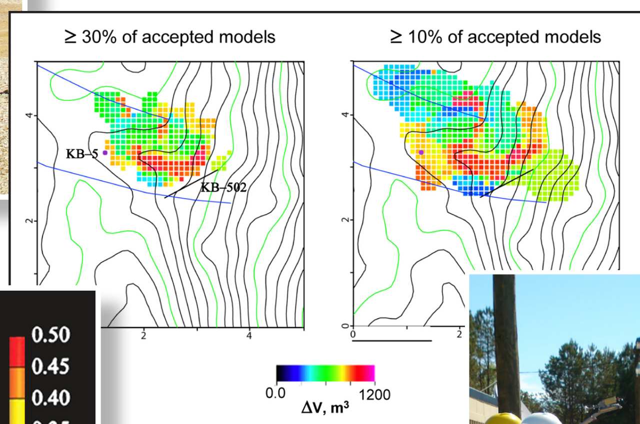
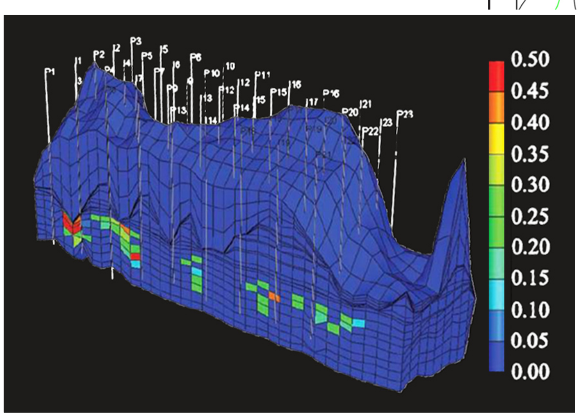
BEST PRACTICES for:

Risk Analysis and Simulation for Geologic Storage of CO_2





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NATIONAL ENERGY TECHNOLOGY LABORATORY

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Risk Analysis and Simulation for Geologic Storage of CO_2

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List of Acronyms and Abbreviations

Acronym/Abbreviation	Definition
2-D	Two-Dimensional
3-D	Three-Dimensional
ALARP	"as low as reasonably practical"
ANSI	American National Standards Institute
AoR	Area of Review
BLR	Brine Leakage Risk
BSCSP	Big Sky Carbon Sequestration Partnership
CASSIF	Carbon Storage Scenario Identification Framework
CBM	Coalbed Methane
CCS	Carbon Capture and Storage
CF	Certification Framework
CH_4	Methane
CLR	CO_2 Leakage Risk
CO_2	Carbon Dioxide
CO_2-EOR	Carbon Dioxide-Enhanced Oil Recovery
CRBG	Columbia River Basalt Group
$CaCO_3$	Calcite
$CaMg(CO_3)_2$	Dolomite
DAS	Detailed Area Study
DFN	Discrete Fracture Network
DNV	Det Norske Veritas
DOE	U.S. Department of Energy
DST	Drillstem Test
ECA	Emission Credits and Atmosphere
ECBM	Enhanced Coalbed Methane
EERC	Energy & Environmental Research Center
EOS	Equation of State
ESL	Evidence-Support (three-valued) Logic
FEPs	Features, Events, and Processes
GIS	Geographic Information System
GWB™	Geochemist's Workbench
H_2O	Water
HMR	Hydrocarbon and Mineral Resources
HNP	Huff 'n' Puff
HS	Health and Safety

Acronym/Abbreviation	Definition
HSE	Health, Safety, and the Environment
IEAGHG	International Energy Agency Greenhouse Gas Programme
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LpNORM	Linear Program Normative Analysis
MGSC	Midwest Geological Sequestration Consortium
MINC	Multiple-Interacting Continua
MMPA	Multimineral Petrophysical Analysis
MRCSP	Midwest Regional Carbon Sequestration Partnership
MVA	Monitoring, Verification, and Accounting
N_2	Nitrogen
NETL	National Energy Technology Laboratory
NSE	Near-Surface Environment
NaCl	Sodium Chloride
OFT	Ortley Flow Top
OOIP	Original Oil in Place
P	Pressure
P&R™	Oxand Performance & Risk Methodology
PA	Performance Assessment
PCOR	Plains CO_2 Reduction (Partnership)
PDFs	Probability Distribution Functions
PIDs	Process Influence Diagrams
PSI	Pounds per Square Inch
RA	Risk Assessment
RCSP	Regional Carbon Sequestration Partnership
REV	Representative Elemental Volume
RISQUE	Risk Identification and Strategy using Quantitative Evaluation
RRAG	Risk Response Action Group
RRA	Risk Response Action
RST	Reservoir Saturation Tool
RTC	Reactive Transport Code
SACROC	Scurry Area Canyon Reef Operators Committee
SCFT1	Slack Canyon #1 Flow Top
SCFT2	Slack Canyon #2 Flow Top
SECARB	Southeast Regional Carbon Sequestration Partnership

Acronym/Abbreviation	Definition
SI	Saturation Indexes
SRF	Screening and Ranking Framework
SSIC	Site Screening, Selection, and Initial Characterization
STB	Stock Tank Barrels
SWP	Southwest Regional Partnership on Carbon Sequestration
T	Temperature
TDS	Total Dissolved Solids
THMCB	Thermal, Hydrologic, Mechanical, Chemical, and Biological (Processes)
USDW	Underground Sources of Drinking Water
VEF	Vulnerability Evaluation Framework
VSP	Vertical Seismic Profile
WAG	Water-Alternating-Gas
WESTCARB	West Coast Regional Carbon Sequestration Partnership
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Executive Summary

The ultimate goal of geologic carbon dioxide (CO_2) storage is to help reduce the amount of greenhouse gas (GHG) emissions in the atmosphere by ensuring safe, secure, and verified permanent storage in geologic formations. Risk analysis and numerical simulation are critical tools used iteratively in conjunction with site characterization, monitoring, public outreach throughout all of the stages of a geologic CO_2 storage project (site screening, site selection, project design, project operation, and long-term stewardship of carbon dioxide capture and storage [CCS] projects) to help meet the goals of safe, secure, and verifiable permanent storage.

Risk is defined as the product of the probability of an event or outcome and the likely cost or consequence of it. Risk analysis is used in many disciplines and can be applied broadly in geologic CO_2 storage projects to understand and mitigate an array of potential impacts on and from a project. Three steps in risk analysis include risk source assessment, risk characterization and risk management. This Best Practices Manual focuses mainly on the risks arising from unplanned migration of injected CO_2 from the confining zone and provides an overview of these concepts as applied to geologic CO_2 storage.

Numerical simulations or models are used to predict the movement and behavior of CO_2 once it is injected into the subsurface. Models serve as critical tools in a framework to identify, estimate, and mitigate risks arising from CO_2 injection into the subsurface. They are also used to optimize monitoring design and facilitate more effective site characterization. This BPM discusses the ways in which the partnerships have used codes to model the specific processes (thermal and hydrologic, chemical, mechanical, and biologic) in the subsurface that need to be considered in modeling the behavior of injected CO_2.

The manual illustrates the concepts of risk analysis (risk assessment) and numerical simulation by describing the experience gained by the DOE Regional Carbon Sequestration Partnerships as they implemented multiple field projects.

This manual is organized into 6 major sections:

1. Introduction
2. Fundamental Aspects of Risk Analysis
3. Fundamental Aspects of Numerical Simulation
4. Application of Risk Analysis and Numerical Simulations
5. Conclusion
6. Appendices

Successful implementation of geologic CO_2 storage projects will require developers to compare critical criteria among candidate sites including storage capacity, health and environmental safety, economics, local regulatory constraints, monitoring efficacy, and potential ancillary benefits, such as enhanced hydrocarbon production. Risk analysis and numerical simulations will guide CCS implementation by providing stakeholders (operators, project developers, general public, and regulators) with information to predict the long-term fate of CO_2 including, but not limited to the projected amount of long-term CO_2 storage, potential risks and consequences of CO_2 leakage in that area, and probabilistic leakage rates from specific geologic formations where CO_2 is injected. Over time, by comparing measured data to the predicted risk assessment and model results, the operator should be able to "history match" the predicted location of the CO_2 and its measured location. This history match becomes an important part of the process of ensuring that a project is safely storing CO_2 and can be safely closed once the site has reached a point of verified negligible risk.

Risk Analysis and Simulation for Geologic Storage of CO_2

1. Introduction

1.1 Background

The U.S. Department of Energy (DOE) is actively developing and demonstrating practical, safe, and effective carbon emissions reduction technologies. One of the promising technologies under development is carbon capture and storage (CCS), whereby carbon dioxide (CO_2) is captured at a source, transported to a suitable location, and injected into deep geologic formations for long-term storage. The goal of DOE's Carbon Sequestration Program is to demonstrate that CO_2 can be successfully and securely stored over extended periods of time in a manner that is compliant with the best engineering and geological practices; Federal, State, and local regulations; and the best interests of local and regional stakeholders. This will directly link the national interest in reducing greenhouse gases with regional and local economic, environmental, and social interests.

As part of the DOE Sequestration Program, the Regional Carbon Sequestration Partnership (RCSP) Initiative established seven partnerships tasked with determining the most suitable technologies for carbon storage. An objective of the RCSP Initiative is to develop the foundation for demonstration and commercialization of CCS technologies. The RCSP Initiative is being conducted in three phases. During the first phase, called the Characterization Phase, the Partnerships characterized the potential geologic storage opportunities within each of their respective regions. In the Validation Phase, each Partnership implemented a series of small-scale CO_2 storage projects in a variety of geologic and geographic settings. Building on the knowledge developed during the Validation Phase, the Partnerships are implementing large scale (e.g., 1 million metric tonnes or greater) CO_2 storage projects during the third phase of the RCSP Initiative, termed as the Development Phase. By conducting the pilot and larger scale projects, the RCSPs are addressing regulatory and policy issues while developing technical expertise within their respective regions of the United States and portions of Canada.

CCS is an approach that draws on more than a century of experience in the oil and gas industry and, more recently, several decades of other analogous subsurface injection techniques.[1] However, like any technology, this practice has risks which need to be analyzed and properly managed. This Best Practices Manual (BPM) builds on the experience of the RCSP Initiative and efforts within the research community, notably the IEAGHG R&D Program review of risk assessment guidelines,[2] to develop an approach for utilizing risk analysis and numerical simulation throughout the process of CO_2 storage project site selection, design, operation and closure. Together, risk analysis and numerical simulation are integral to decision-making for CCS project developers, operators, regulators, and public stakeholders. The results from risk analysis and simulation are relevant to decisions made at all stages in a CCS project, from site screening and selection to closure. These analyses need to be routinely undertaken throughout the life of a project and updated as experience and operational data are obtained.

1.2 The Integration and Iterative Applications of Risk Analysis, Numerical Simulation, Site Characterization, Monitoring, and Public Outreach in CCS Project Implementation and Accounting

Risk analysis and numerical simulation serve as critical tools in a framework to identify, estimate and mitigate risks arising from CO_2 injection into the subsurface. They are used not only to evaluate and quantify risks, but also to optimize monitoring design and facilitate

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1 For additional information on CCS see the following resources: DOE Carbon Sequestration website: http://www.netl.doe.gov/technologies/carbon_seq/index.html; the IEA CCS roadmap: http://www.iea.org/papers/2009/CCS_Roadmap.pdf; the IPCC special report on CCS, Summary for Policy Makers: http://www.ipcc.ch/pdf/special-reports/srccs/srccs_summaryforpolicymakers.pdf; or the World Resources Institute CCS Guidelines: http://www.wri.org/publication/ccs-guidelines.

2 IEA GHG Risk Assessment Network, "A Review of the International State of the Art in Risk Assessment Guidelines and Proposed Terminology for Use in CO2 Geological Storage," Technical Review 2009/TR7, December, 2009.

more effective site characterization. Monitoring and site characterization are critical for developing improved models, associated risk analysis and also play a role in accounting and verification. Effective risk communication is a key component of educating the general public and serves as the basis for obtaining useful feedback from communities. Public outreach and communication is both informed by these activities and also generates input for the analysis, in the form of public views, concerns, and suggestions. All five activities, risk analysis, numerical simulation, site characterization, monitoring, and public outreach, are interdependent. Lessons learned from the RCSP Initiative indicate that all of these activities need to be carried out in an integrated manner.

The practical application of these tools is not only integrated, it is iterative. Figure 1 illustrates this relationship. These tools are used in tandem for initial candidate site comparison, leading to site selection and development. Site characterization, monitoring, and public outreach have been described in separate Best Practice Manuals developed by the DOE through the RCSP Initiative.[3]

At the start of site selection process there will be a number of uncertainties associated with any specific site. The initial risk analysis and numerical simulation conducted at this time will help bound these uncertainties. Further site characterization activities will reduce some of the uncertainties, but some will remain that will guide development of the site monitoring plan. Data collected during monitoring can then be used to refine the initial risk analysis and numerical simulation. For example, the non-uniform nature of the injection zone could affect the size of the CO_2 plume. Site characterization can supply additional information on the non-uniform geologic nature of the injection zone. However, if the plume size has significant consequences, project developers may choose to collect additional subsurface data or implement more advanced monitoring activities. As project implementation progresses, the iterative cycle would be used to lower uncertainties and improve risk profile of CCS projects.

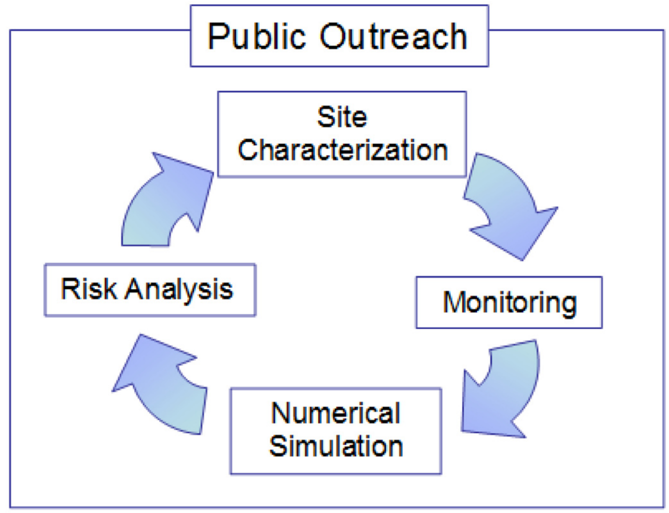


Figure 1. Iterative Nature of Site Characterization, Risk Analysis, Numerical Simulation, Monitoring, and Public Outreach in CCS Project Implementation.

If refined models match observed reservoir response, uncertainties decrease and risk is diminished. Under these favorable conditions, frequency and number of monitoring measurements could be decreased. In contrast, if monitoring shows that the fates of CO_2 and brine migration are poorly understood in ways that have potentially significant consequences, the risk profile may increase. Such increased risk may trigger a need for increased monitoring to reassess project viability. For example, if the non-uniformity of the injection zone causes large parts of the injection zone to be bypassed by CO_2, and a thin, widespread plume to develop, there may an increased risk of unplanned CO_2 migration from the confining zone. Increased monitoring could be needed to ensure that protected resources are not impacted (Figure 2). In effect, much like the natural processes in the subsurface, site characterization, risk analysis, numerical simulation, and monitoring are "fully coupled."

[3] See the NETL Carbon Sequestration Program Reference Shelf for a link to these Best Practice Manuals: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.

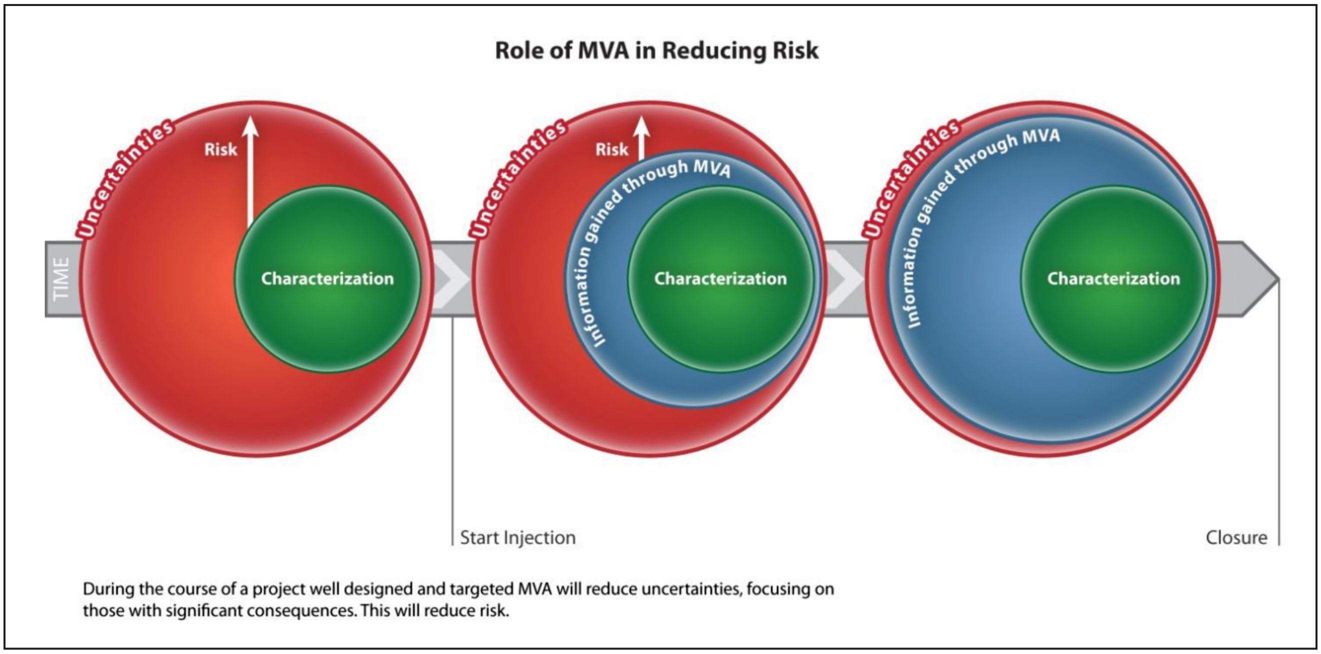


Figure 2. Role of Targeted Monitoring Activities in Reducing Risk.

1.3 Overview of the Manual

This manual focuses on the risks arising from the risk of unplanned migration of CO_2 from the confining zone. It provides an overview of the basic concepts of risk analysis and numerical simulation as applied to the analysis of geologic storage and it summarizes work by the U.S. Department of Energy (DOE) Regional Carbon Sequestration Partnerships (RCSPs) to use formal and quantitative methods to select and implement geologic storage projects safely and effectively. This manual complements a series of Best Practice Manuals (BPM) that have already been published by DOE.

Section 2 reviews the fundamentals of risk analysis. The term "risk analysis" used in this BPM draws on the larger discipline of risk analysis used for evaluating the risk associated with different industries and technologies. The risk analysis process involves identifying pertinent risks, estimating their impacts, and developing methodologies to mitigate the impacts from such risks. The risks to many stakeholder groups are those associated with unintended CO_2 migration out of the confining zone from storage project. This section of the manual presents the concepts and steps involved in a developing a qualitative and/or quantitative evaluation of the risk such migration could pose to human health, safety, the environment, and operational aspects of a storage project. It summarizes the tools which have recently become available for carrying out risk analysis. And, this section discusses the potential major pathways for migration of CO_2 out of the confining zone and approaches to mitigate, remediate, and control such migration. The intended audience for Section 2 includes engineers, regulators, project developers and professionals who are interested in the applications of risk analysis principles to geologic CO_2 storage.

While the primary focus of this BPM is on risks associated with events and processes in the subsurface, it also recognizes that surface activities associated with CCS also entail risk. Therefore, Section 2 also provides a summary of some recent work on the development of an approach for risk analysis and simulation of the surface infrastructure required for geologic CO_2 storage.

Section 3 focuses on numerical simulation, the use of computer codes to model the hydrologic, mechanical, and chemical processes associated with CO_2 injection and movement in the deep subsurface. Numerical simulators are used to predict how far the CO_2 will move, how fast, what pressures will be created, what kind of chemical reactions will occur, and what happens to the products of those reactions. Numerical simulation is a very highly developed discipline, built upon decades of development driven by applications such as oil and gas production, geothermal energy development, and groundwater use. However, technical issues remain with application to geologic CO_2 storage. Much of the discussion of simulation in this document is geared toward the reservoir engineering specialist, beginning with the governing equations for the processes being simulated. Coupling between processes, and the numerical approaches taken to represent the processes is discussed in Section 3.

Section 4 discusses the application of both risk analysis and simulation to actual field sites being investigated by the RCSPs. Although the disciplines of risk analysis and numerical simulation are not new, their application to CCS is relatively new: guidelines and proposed terminology for use in geologic CO_2 storage were first published in 2009. The formative nature of this application is evident in the diverse approaches taken by the various RCSPs. Section 4 discusses technical issues such as model grid development, parameterization, scaling, and fluid and rock property description in the context of the field pilot studies being carried out by the RCSPs. Detailed accounts of individual RCSPs simulations are described in separate document, available from the NETL website.[4]

And finally, the Appendices contain additional detailed information on specific aspects of risk analysis and simulation.

This manual is not intended to be prescriptive but rather shares the experiences and lessons drawn from the risk analysis and numerical simulation activities of the RCSPs. Collectively this experience may serve as a foundation for developing a best practice approach to risk analysis and numerical simulation.

2. Risk Analysis

For purposes of this manual, risk is defined by the probability of an event resulting in adverse impacts and the magnitude of those adverse impacts or consequences. In its most general form, overall risk is the sum of the products of individual risk impacts and probabilities. As applied to geologic storage, the primary focus is on the adverse impacts from a potential loss of CO_2 storage integrity resulting in unplanned CO_2 migration out of the confining zone. A more comprehensive risk analysis would also explore the potential for adverse impacts from other project-related operational and financial events such as events that take place on the surface or in the policy arena. Some of the potential consequences associated with loss of CO_2 storage integrity are related to public safety and health, environmental (ecosystem) safety, greenhouse gas (GHG) emissions to the atmosphere, damage to natural resources (e.g., water and hydrocarbons), and financial loss for investors or insurers.

2.1 Fundamentals of Risk Analysis

Risk analysis is the iterative process of identifying, evaluating, and mitigating risks. It consists of several steps including risk assessment, risk management and risk communication, as shown in Figure 3 (IEAGHG, 2009; Rechard, 1999). Risk assessment for geologic CO_2 storage involves identifying the risks (*risk source assessment*), determining the probability of the occurrence of (*exposure assessment*), and the magnitude of loss from individual risk events (*effects assessment*), and integrating the exposure-effect data to produce qualitative, semi-quantitative, or quantitative measures of risk (*risk characterization*). In the risk management step, inputs from the risk assessment process, and a variety of social, political, and techno-economic parameters are used to prioritize, monitor, control and mitigate risks. Risk analysis also involves the interactive exchange of risk information among risk assessors, risk managers, regulators, local community, news media and interest groups, which is addressed by the "Public Outreach and Education for Carbon Storage Projects" BPM.

[4] http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.

Commercial-scale geologic storage will require the development and implementation of an effective risk assessment protocol tailored specifically to each storage site. The site-specific risks are identified and vulnerabilities (risk scenarios) are assessed in the risk source assessment stage. Project-specific features, events and processes (FEP) analysis is performed at this stage. Next, detailed site characterization and simulation provide data to assess exposure due to the vulnerabilities in a qualitative or quantitative manner. The estimated exposure indicates the probability that a particular negative event would occur. In the subsequent step, the effects of the vulnerabilities (impacts) are assessed using qualitative or quantitative tools. The impacts and exposure data from the previous two stages are used to assess the risk in the final step of the risk assessment process, namely, risk characterization. Ultimately, the set of quantitative and qualitative risk factors and their potential impacts become the basis for developing practical risk management and mitigation plans. The application of these steps in risk analysis to CO_2 storage projects are discussed in greater detail in the subsequent sections.

Risk analysis has different functions depending on the stage in the process it is implemented. A qualitative type of risk analysis is often performed at the early stages of a project to help in site screening, selection, communicating project aspects to the public, and aiding regulators in permitting projects (see "NETL Best Practices for: Site Screening, Site Selection, and Initial Characterization for Storage of CO_2 in Deep Geologic Formations"). Subsequent to more detailed site characterization and modeling efforts, quantitative risk analysis may be performed to estimate the likelihood of human health and environmental risks. Furthermore, stakeholders such as regulators and insurers may require risk analysis to support incentives, such as loan guarantees to large projects. A successful risk analysis will always be linked to monitoring and modeling plans for a given storage site. As more site-specific data is obtained,

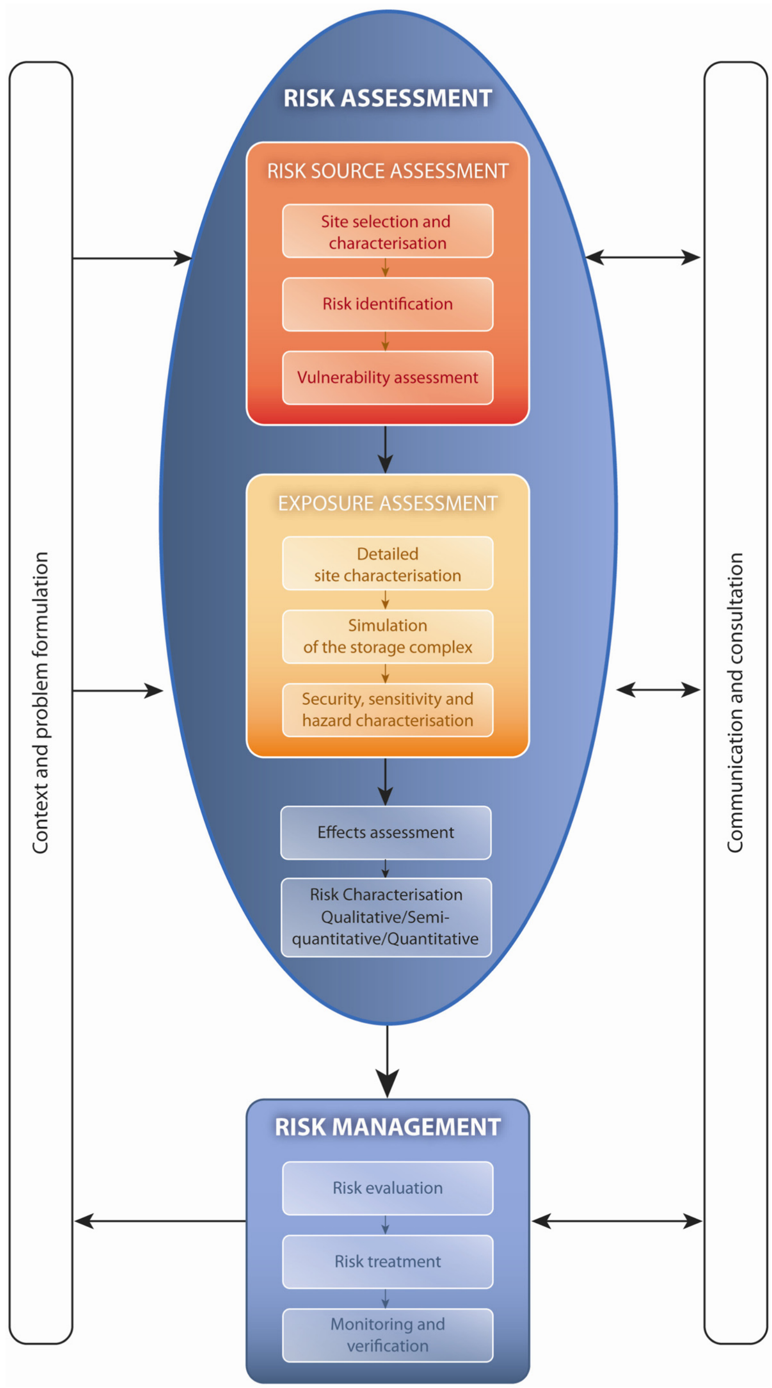


Figure 3. Risk Management Workflow Diagram for a Commercial-Scale Storage Deployment Program. Adapted from IEAGHG (2009).

information is passed iteratively between monitoring (see "NETL Best Practices for MVA of CO_2 Stored in Deep Geologic Formations"), numerical simulation, risk analysis, and site characterization functions, as illustrated in Figure 1.

Ultimately these risk analysis results can also be used by industry, investors, and insurers to understand the potential liability associated with projects and build that into the cost of developing a CCS project.

2.2 Application of Risk Analysis to Geologic Storage of CO_2

As noted above, commercial-scale geologic CO_2 storage will require the development and implementation of an effective risk analysis protocol tailored specifically to each storage site. This section focuses on the primary steps in risk analysis as they apply to CO_2 storage projects:

1. *Risk source assessment* through which potential project risks are identified
2. *Risk characterization* through which one determines the probability of the occurrence of events (exposure assessment) and the magnitude of loss from them (effects assessment). In risk characterization exposure and effects data are integrated to produce qualitative, semi-quantitative, or quantitative measures of risk.
3. *Risk management* through inputs from the risk source assessment and characterization are considered along with a variety of social, political, and techno-economic parameters in order to prioritize, monitor, control and mitigate risks.

2.2.1 Risk Source Assessment: Identification and Description of Potential Risks to Long-Term Storage

Risk source assessment involves the identification of specific risk features, events, and processes (FEPs) that could contribute to, or prevent, unplanned CO_2 migration from the confining zone. These FEPs, along with any programmatic and safety risks, constitute the risk registry. Some examples of FEPs are:

- leaky wellbores or faults (features)
- injection pressure increases or earthquakes (events)
- gravity-driven CO_2 movement or residual saturation trapping (processes)

An extensive database of nearly 200 potential FEPs for storage was assembled and published by Quintessa. This database is publicly accessible at http://www.quintessa.org.

Because the future evolution of a geologic system cannot be precisely determined, various possible scenarios for possible evolutions of the system and situations of particular interest are developed. Typically, FEP analysis and scenario development are performed using expert inputs.

During the risk source assessment, the project team identifies potential "pathways" for leakage, potential receptors, and specific consequences if they can be identified. A typical FEPs analysis may lead directly to the identification of consequences. For geologic CO_2 storage, some consequences of critical concern include brine-contamination of underground sources of drinking water (USDW), unintended migration of CO_2 into hydrocarbon resources or other infringement on mineral rights, and long-term CO_2 seepage into the atmosphere. Following identification of specific FEPs and development of a risk registry for a specific site, a list of potential consequences must also be identified and associated with the FEPs.

2.2.1.1 Approaches for Using Numerical Simulation to Enhance Risk Assessment

Numerical simulation tools are discussed in detail in Section 3, but since they are a key tool in risk source assessment, they will also be briefly presented here. Numerical simulations which reliably predict, assess, and optimize the geologic storage of CO_2 in the subsurface are required for widespread adoption of CCS and to improve public confidence in this technology. These numerical simulations also provide quantitative information on the exposure due to a potential scenario and possibly on the resulting impacts to various receptors such as human health, safety, environment, and project viability. The numerical simulation tools used for risk assessment include process models of individual 'compartments' of the geologic system or simplified system-level models representing all safety-relevant aspects of the system. Various research studies are developing (or adapting) formal systems-modeling approaches for full quantitative risk assessment. This type of approach is not new, but rather is adapted from specific risk assessment needs in other industries.

Site-specific numerical simulation involves predicting the behavior of the total system at the site based on the key FEPs. A systems-modeling framework provides a means for integrating the different FEPs, their associated potential or uncertainty, and associated impacts. Figure 4 illustrates the relationship among features, events and processes and potential risk impacts. For example, the storage reservoir may have insufficient capacity or injectivity, leading to the risk that CO_2 injection cannot be sustained over the life of the project. The impact assessment would estimate the techno-economic and societal impacts of such a scenario.

2.2.2 Risk Characterization: Exposure and Effects Assessment, Determination of Risk Probabilities, and Impacts

The next step in a detailed risk assessment is the assignment of probabilities to potential consequences and an evaluation of the impacts of potential consequences. The first stage in that process is often a qualitative or semi-quantitative prioritization of the risks, where risks are categorized and ranked in terms of likelihood and magnitude of consequence. From this analysis, risks that require immediate responses can be identified and addressed. The ranking allows high-priority risks to be identified and plans for mitigating or controlling them to be developed, while lower-priority risks can be placed on a watch list. Other risks, with mid- or unknown-priorities, may undergo further analysis or investigation. As more information is obtained from site characterization, modeling, and monitoring, the risk priorities can be updated. Later stages may also include model simulations to assess the probabilities and impacts of selected scenarios. These simulations may rely on different model types include:

- Conceptual models of individual aspects of the storage system,
- Process-level models to simulate the behavior of various system compartments, or
- System-level models to review impacts across the entire system in which the storage site is located.

Quantitative, semi-quantitative, or qualitative inputs generated in this process are used to rank and prioritize risks in the risk management step.

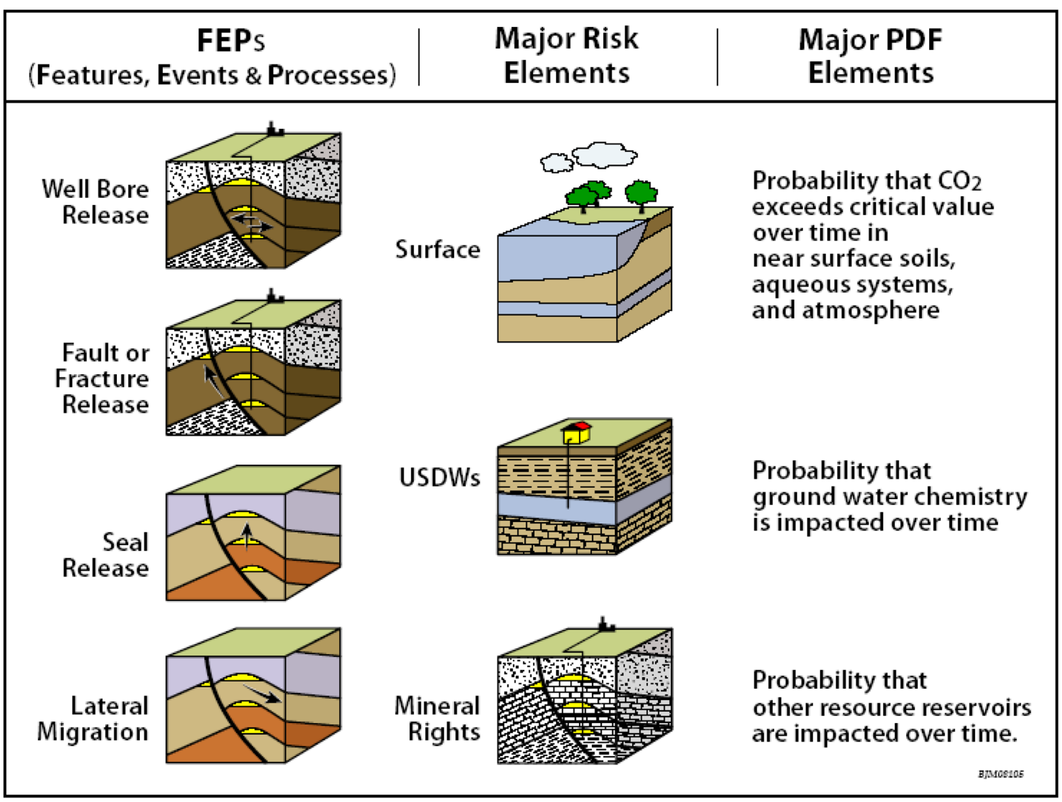


Figure 4. Examples of relationships among Features, Events, Processes, and Potential Impacts.

2.2.2.1 Quantitative Uncertainty Analysis

Uncertainty is a critical factor to assess in the context of risk/performance assessment. With the advent of new carbon storage simulation tools, interest in the quantitative assessment of geologic uncertainty associated with subsurface injection and storage has grown over the last few years. In the hydrocarbon industry, several different approaches have been used to obtain probability distribution functions (PDFs) of desired parameters to help understand the uncertainty around aspects of subsurface injection and storage, such as the amount of hydrocarbons-in-place, recovery factors, etc. Applying this knowledge to geologic CO_2 storage, might identify critical fault properties that could cause a breach in the confining zone or failure of hydrodynamic trapping (trapping mechanisms are discussed in Appendix 1). Two standard methods for developing effective PDFs are experimental design-based methods and Bayesian probabilistic formalisms; both methods may be employed for defining PDFs of critical parameters for each relevant risk element. In general, experimental design methods are based on generating simpler response surfaces using selected rigorous simulations (e.g., of reservoir models with appropriate fully-coupled phenomenological process models) followed by Monte Carlo simulations to identify the parameters that are most critical in affecting the targeted outcome (Rohmer and Bouc, 2010). Initial models must honor observed data, and need to examine a wide variety of possible combinations of parameters relevant to CO_2 fate and transport. History matching exercise is critical to the success of the experimental design-based method to define PDFs.

The structure and properties of the subsurface are inherently heterogeneous and variable at many scales. Because of practical economic and scheduling constraints, it is therefore likely that sufficient data to "validate" or test models of trapping mechanisms and associated failure modes with complete certainty are unlikely. For example, the number of wells that could provide calibration data, including log and rock data, is generally limited at saline formation sites. While core data are ideal input for characterization of FEPs for a site, it is possible that data available from wells may be limited. Therefore, numerical simulations could be used to develop a better understanding of this heterogeneity when data is not available.

Bayesian frameworks are often used to obtain probability distributions of critical parameters when data are limited, as in the example of well data above. In this approach, several conceptual models (geologic or operational, for example) are constructed based on all available data. Each scenario is then represented using a spatial variability model – several choices of spatial variability models (such as variograms) are available. A global estimate of a given target variable is constructed using the interpretation of the quantitative data under a given geologic scenario; it is often assumed that sampled data will be representative of all samples. Once the uncertainty of a given parameter is quantified, experimental design tools will be used to plan monitoring programs with a goal of reducing uncertainty associated with that particular parameter. At this stage, additional data (such as wellbore seismic, logs, etc.) may be acquired to reduce uncertainty and redefine associated PDFs.

In summary, a general approach for developing appropriate PDFs for each critical parameter could employ both experimental design-based methods and Bayesian probabilistic formalisms. A Bayesian probabilistic approach may be among the best approaches to develop initial PDFs for sites with sparse high-resolution data. As discussed previously, an experimental design-based method may facilitate definition of relevant PDFs, based on data gained from new laboratory and field tests. Data derived from experiments can be used to develop explicit phenomenological (empirical) process models associated with critical parameters, improve the speed and reduce the size of computer simulation models, and serve as a basis for defining PDFs. As new experimental data are acquired, phenomenological model relationships can then be refined and the suite of PDFs updated. Such an iterative approach is dependent on the quality and resolution of the characterization data gathered, but at least uncertainty can be estimated. Finally, cost and schedule management aspects must also be considered to further refine PDFs that characterize risk potential. This last step is extremely important and involves quantifying the costs associated with various risks. This information can provide investors, insurers, and regulators the information needed to understand the true cost of the CCS project. As new data become available from field tests, this general process will become more definitive.

2.2.2.2 Examples of Risk Assessment Tools and Ongoing Systems-Modeling Efforts

A survey of various risk assessment tools that incorporate geologic CCS risk assessment methodologies was conducted and updated with feedback from individuals involved in the development of specific risk assessment methodologies. A high-level summary of the results from the survey is presented in Table 1. Appendix 2 provides further details on the specific application of these tools to projects including assessed risk, inputs, workflow, outputs from the risk assessment, and the types of risks that can be addressed with a specific tool.

2.2.3 Risk Management: Mitigation/Remediation Plans

Many potential consequences of geological CO_2 storage may be identified through risk assessment. A necessary step in a complete risk analysis is the development of a mitigation and control plan to address potential consequences. Such plans will heavily rely on monitoring data and will generally function in an "if-then" manner – that is, if the monitoring system detects

Table 1. A Summary of Geologic Carbon Storage Risk Assessment Tools

Tool	Methodology Family
Quintessa FEP database	Qualitative, FEPs screened by experts
TNO Risk Assessment Methodology	Expert-elicited probability and consequence matrices
CO2QUALSTORE guideline, DNV	Qualitative/Semi-quantitative with "panel" inputs
Carbon Storage Scenario Identification Framework (CASSIF), TNO	Qualitative, scenario-based
Risk Identification and Strategy using Quantitative Evaluation (RISQUE), URS	Semi-quantitative, expert-elicited probability and consequence matrices
Screening and Ranking Framework (SRF), LBNL	Qualitative, expert-elicited probabilities
Certification Framework (CF), LBNL	Quantitative, system-level model, probabilities partly calculated using fuzzy logic
Vulnerability Evaluation Framework (VEF), U.S. EPA	Qualitative
Performance Assessment (PA), Quintessa	Evidence-support (three-valued) logic (ESL) Distinguishes cases of poor-quality data from uncertain data
CarbonWorkFlow* Process for Long-term CO_2 Storage	Semi-quantitative; FEPs ranked through expert elicitation using a risk matrix approach
CarbonSCORE* software to preassess potential CO_2 storage sites	All evaluated criteria are quantitatively weighted, jointly evaluated, and summarized
Oxand Performance & Risk (P&R™) Methodology	Quantitative Risk matrix evaluation: semi-quantitative
CO_2-PENS, LANL	Quantitative, hybrid system-process model

** mark of Schlumberger*

a problem, then certain actions will be performed to address that problem. Some findings will require immediate action and others will signal the need for an additional, focused monitoring. A good monitoring and mitigation plan will decrease the risk and uncertainty associated with many potential consequences.

Risk mitigation plans generally address two primary aspects: (1) programmatic risks, including resource and management risks, which may affect project progress or costs, and (2) storage (technical) risks, which may affect the achievement of the scientific and engineering objectives of a storage project. There is a great deal of experience in managing programmatic risk that has been built over time by oil and gas industry and more recently (during the last three decades) by other companies involved in subsurface operations.

Storage in Oil and Gas Reservoirs

Oil and gas reservoirs have some notable differences than saline formations that can have an impact on the risks of storage in these formations.

A major risk reduction factor for CO_2 storage in oil and gas reservoirs is the existence of a proven hydrocarbon confining zone and trap. While it can not be said that every hydrocarbon trap will necessarily function as an effective trap for CO_2, the existence of the reservoir, itself, means that a confining zone of low permeability and high structural integrity was sufficient to keep buoyant hydrocarbons in place for geologic time. In saline formations, the existence and effectiveness of the confining zone must be demonstrated through careful characterization before injection and monitoring after injection begins. A variety of techniques are available to assess and monitor confining zone effectiveness in saline formations, but lack of access to the subsurface, and its inherent variability and heterogeneity, may result in considerable uncertainty when quantifying the probability and impacts.

A potential factor in increasing the risk of unplanned CO_2 migration through the confining zone of an oil and gas formation is the presence of pre-existing wells that penetrate the primary confining interval. While the data from these wells can considerably reduce uncertainties about the subsurface they are also a potential migration pathway for injected CO_2. This is particularly the case for oil and gas fields developed many decades ago. In addition, reservoir pressure reduction due to extraction and reservoir stimulation procedures in oil and gas fields can affect the integrity of the confining zone.

Many of these lessons are embodied in industry best practice standards such as those published by the American Petroleum Institute (API) and Society of Petroleum Engineers (SPE). For geologic CO_2 storage, programmatic risks rely in part on the technical risks and vice-versa, and therefore the two are inextricably linked. The primary focus of this chapter is risk management of technical risks related to storage.

2.3 Accounting for Surface Infrastructure in Numerical Simulation

The surface infrastructure for geologic CO_2 storage projects has been modeled to achieve various objectives. For example, the Congressional Research Service (2007) analyzed the regulatory and legal risks of CO_2 pipelines. The current discussion is focused on the use of process-level (techno-economic) or dynamic models to aid in surface risk analysis. In a techno-economic model, the transport system is broken down into engineering modules, such as pipelines, compressors, separation plant, and injection facilities. Operating and capital costs are incorporated within each module. Subsequently, the individual modules are integrated to develop a levelized cost (e.g. incorporating both operating costs and overnight capital costs for a given transport rate). Examples of these models are Kobos et al. (2007) and McCollum and Ogden (2006).

CO_2 pipeline simulation may also be performed on a system-wide, dynamic basis to conceptualize the required CO_2 pipeline system. Examples of these efforts include the "String-of-Pearls Model" (Kobos et al., 2007) and MIT geographic information system (GIS)-based project, which lays out future pipelines on actual maps that include current infrastructure and rights-of-way.

Simulation of the surface CO_2 infrastructure is a critical component of surface risk analysis. Koornneff et al. (2009) studied uncertainties in risk analysis aimed at analyzing the impact of a point source plume release from a pipeline. The conclusions indicated that the international exposure thresholds for CO_2, which are necessary for risk analysis, are lacking. Koornneff et al. also found that knowledge gap and uncertainties have a large effect on the assessed risks of CO_2 pipelines. This report is only an example of a specific scenario and needs to be integrated with a system engineering framework.

CO_2 Storage in Coal Seams

Coal seams have some notable differences than saline formations that can have an impact on the risks of storage in these formations.

There are three behaviors in coal worth noting:

- Gases in coal seams are stored through sorption within the coal matrix, rather than as a free gas in the pore spaces (Bromhal et al., 2005).
- Transport in coal is both by diffusion and advection – diffusion through the bulk coal, and advection through natural fractures (cleats) rather than through pore spaces between grains (Remner et al., 1986).
- Unlike most reservoir rock, coal shrinks and swells as gases are produced or injected based on the amount of gases sorbed and the effective stresses on the coal (Palmer and Mansoori, 1998).

These behaviors result in risks associated with storage of CO_2 in coal seams that are atypical for traditional geologic storage formations, both in positive and negative ways. Coal seam storage of CO_2 in the sorbed phase is generally considered a more secure form of storage than as the free gas phase. Coal seams have been proven to hold significant amounts of methane, CO_2, and other gases over geologic time periods. However, no long-term studies to address the security of CO_2 storage in coal have been performed to date. Thus, an adequate confining zone is still required above any coal seam used for carbon storage.

In any geologic formation in which flow is dominated by fractures, models which do not explicitly include fractures are likely to under-predict flow distance. This is also true of coal seams. Another risk to the successful operation of coal seam storage may be the reduction in injectivity due to the swelling of the coal matrix during the injection of CO_2. In some coal seams, CO_2 sorption may cause such a large amount of both horizontal and vertical swelling that project failure risk is higher due to significant reduction in injectivity over time (van Wageningen and Maas, 2007).). Though the phenomenon of coal swelling is well defined, further study is needed in order to reliably predict the amount of reduction in injectivity that will likely occur under site-specific conditions. An additional effect of coal seam swelling is ground surface deformation. Since coal seams swell horizontally and vertically, this swelling can cause uplift that could lead to ground deformations at the surface. Depending on the swell potential of the coal, these deformations might even exceed those encountered in a conventional geologic formation. Further discussion of geomechanical risks associated with the injection of CO_2 in coal beds can be found in Myer (2003).

Another issue unique to coal seams is that sorption would allow coal seam storage sites to be much shallower than 800 m deep (a depth typically considered for CO_2 to be in the supercritical phase), because sorption allows for significant storage at those depths. If the confining zone for these formations has imperfections, then the gas phase CO_2, which is much more buoyant than the brine or water in surrounding rocks, could escape to overlying formations. Due to the adsorptive qualities, the coal seams also act as sponges for CO_2 which might leak from formations in deeper strata and could reduce the risk of leakage. Also, as the CO_2 is injected into a seam, it may displace and mobilize naturally occurring methane within the seam which could either be produced during recovery

Produced waters associated with traditional coalbed methane (CBM) recovery can have an impact on river and groundwater quality, if not treated and disposed of properly (Rice et al., 2000). Because coal seam storage scenarios involve the enhanced production of methane from coal seams as an economic incentive, these produced waters will also need to be dealt with at storage sites. Because ECBM is an emerging technology, the role of CO_2 injection in reducing the production of water from coal bed methane formations is unknown. If ECBM operations result in lower amounts of produced water, CO_2 injection is unlikely to make the problem significantly worse than commercial CBM recovery efforts.

Finally, because coal is also a resource that can be exploited for energy consumption, proposed injection into coals for storage purposes is only for "unmineable" coals (Winschel and Douglas, 2006). However, as technologies and demand for coal evolve, the definition of unmineable may also evolve. Thus, seams that are considered for storage today could be targets for mining in the future. While CO_2 does not directly damage coal seams and the future use of it as a fuel, the gas will be released if depressurized.

Det Norske Veritas (DNV) (2003) embarked on a system-analysis of risk associated with the entire CO_2 separation and storage system (plant-to-well). As part of this work, an approach for risk analysis and simulation of the surface infrastructure required for storage was developed. The approach reflects how a large insurance and safety analysis company addresses the industrial risks associated with an activity.

Multiple studies have noted that the lack of standardized-performance or risk criteria for storage systems and CO_2 is a significant issue for risk assessment. DNV (2003) defined a set of criteria by which risk can be assessed for surface infrastructure:

The criteria used are:

- CO_2 at 15,000 ppm (over 15 minutes) for damage to individuals.
- CO_2 at 2,000 ppm (over 15 minutes) for damage to the environment.
- The risk analysis was presented in terms of risk to individual and to the environment. A societal risk was also calculated based on population densities.

DNV utilized a modular approach to the risk analysis in which they broke the surface infrastructure into the following five components:

1. CO_2 Recovery at the Source
2. Converging Pipelines (gathering system)
3. Booster Station
4. Pipeline
5. Injection System

Each of these systems was analyzed as generic plant or component models. The failure data was derived from surface and offshore incident frequencies for existing hydro-carbon infrastructure. Such data have been accumulated by DNV as part of its commercial safety business. DNV failure data was generally "derived from recorded losses on site and will incorporate operational losses (e.g. operator error), as well as leaks and ruptures". System components such as flanges, valves in line, instrument connections of specific size and take-offs constitute each module. Each component is reported as a failure rate per unit specific unit of measure (e.g. per item or unit length). These modules were analyzed for full-bore (hole size greater than 150 mm), large-hole size (50 to 150 mm), medium-hole size (10 to 50 mm), and small-hole size (3 to 10 mm) release pathways.

The DNV (2003) integrated CO_2 analysis concluded that the highest frequencies of impact on people would be associated with the CO_2 recovery operation at the source (e.g. coal-fired generating plant and at the injection facility above the geological storage site. These represent complex process facilities with multiple potential points of leakage. Pipelines are less complex and have lower frequencies of impact, even though the potential inventories of CO_2 are high. The results from the DNV analysis indicate that significant mitigation of risk can be accomplished by establishing a 450-m radius buffer for non-workers around CO_2 compression booster plants. Similarly, mitigation of risks for CO_2 pipelines can be accomplished by a 25-m buffer. Additionally, results from the DNV study also indicate that CO_2 injection plants may mitigate impacts on non-workers with a 50 m buffer.

DNV (2003) also set up a process to analyze the yearly releases on CO_2 to atmosphere during operations of the different components of the surface infrastructure for CO_2 storage. The analysis was based on a simple-event tree. This event tree includes the size of the leak path, whether the leak would be auto-detected or manually detected, the fraction of the leak that can be isolated if detected, and frequency of CO_2 releases. From this event tree analysis, DNV calculated the fraction of a module's flow that was lost. With the fraction calculated and the known flow rate for the module, DNV calculated the yearly production losses.

The DNV (2003) report lays out a framework to analyze infrastructure risk for storage framework. The initial analysis was based on a large database of hydrocarbon infrastructure release and reportable events. Hydrocarbon infrastructure data is extensive, simplifies the probability distributions, and also includes corrosive streams, such as H_2S, sour gas, and H_2.

CO_2 streams with varying degrees of impurity may behave differently compared to hydrocarbons. Because CO_2 is heavier than ambient air, the dispersal of CO_2 from leaks may require computational fluid dynamic analyses significantly distinct from the hydrocarbon dispersion case studies. The further development of larger-scale CO_2 infrastructure systems will provide better information regarding performance of the surface infrastructure.

The process of surface infrastructure risk assessment and simulation may be streamlined in the future. New modular software such as SimuLink or frameworks such as GoldSim can speed the analysis. The DNV infrastructure generic models can be programmed as reusable modules using such modular frameworks.

In the past, the tradeoff between the need for deterministic models and financial and time constraints has led to probabilistic risk assessment. Gaps in our knowledge of surface CO_2 infrastructure must be addressed to decrease the uncertainty in such probabilistic analyses.

3. Numerical Simulation

Numerical simulations are used to predict the movement or behavior of CO_2 once it is injected into the subsurface. These simulations serve as critical tools in risk analysis and are used to optimize monitoring design and facilitate more effective site characterization. Numerical simulations are also used to inform geologic CO_2 storage project design, operations and closure. This BPM summarizes the state-of-the-art of numerical simulation as applied to geologic CO_2 storage. The extensive work of the DOE RCSPs on field pilot projects provides lessons learned on the application of multiple simulation techniques and tools at the various stages of CCS projects.

3.1 Modeling Subsurface Processes

The fundamental aspects of models of geologic CO_2 storage can be explained by using four basic physical subsurface processes:

i. thermal and hydrologic
ii. geomechanical
iii. chemical
iv. biological

Collectively, these processes are referred to as THMCB. However, it is important to note that the role played by biological processes in affecting geologic CO_2 storage and transport is currently unclear; it is included for sake of completeness in this discussion. THMCB numerical models are based on first principles relations for conservation of mass, momentum, and energy. Added to these are phenomenological or empirical equations of state, kinematic conditions, transport laws, rate expressions, and other constitutive relations that express the interdependencies or couplings between processes.

Examples described in the individual RCSP case studies[5] and the sidebars of Section 4 illustrate that reliable numerical simulation of CO_2 behavior in the subsurface (either during injection or long thereafter) will benefit strongly from the use of coupled, three-dimensional THMCB models. Note that the term “coupling” may refer to the physical processes described by a model, or to a numerical scheme in which all partial differential equations describing physics of a set of processes are solved simultaneously, or a partial or “loosely-coupled” scheme in which equations, or portions of the equations, are solved separately. An example of the loosely-coupled models would be the sequential execution of a hydrologic model and a geomechanical or geochemical model. As suggested in Figure 5, many factors and processes operating within a

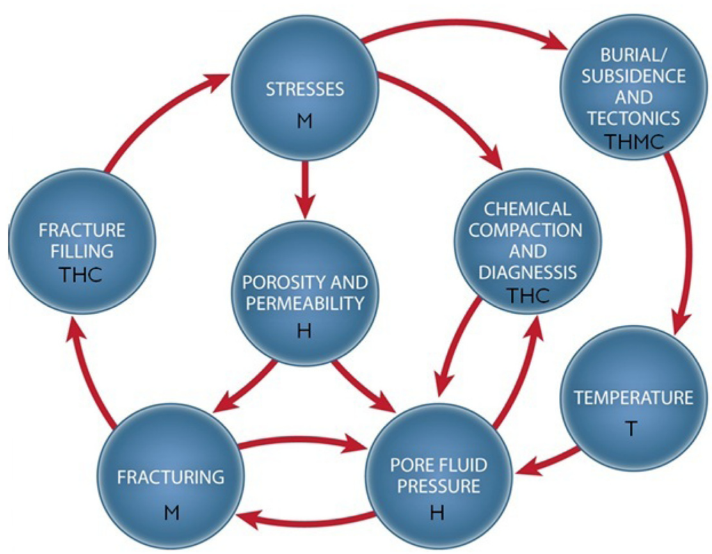


Figure 5. Potential Coupling of Physical Processes During Subsurface Carbon Storage.

5 http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.

reservoir are strongly interdependent, or ‘coupled’. The coupling can be one-way or both ways amongst a set of THMCB processes. An example would be coupling between hydrological and chemical processes: once injected, CO_2 has the potential to react with minerals present in the rock resulting in new compounds in solid (e.g., precipitates) or fluid form. Numerical simulations may factor into account the secondary reactions, known as multiphase flow effects, (for two-way coupling) or may not (for one-way coupling) by considering in their ability of these new compounds to affect porosity or permeability in the injection zone.

The most sophisticated numerical simulations will review the value of coupling a number of processes including multiphase flow, heat transfer, reactive transport and geomechanical processes. Further, robust model development also requires accurate characterization of the component transport properties (e.g., CO_2, water, sodium chloride (for the case of saline formation injections)) across a large range of temperatures and pressures. Such thermophysical properties, including mutual solubility effects, control the amount of CO_2 that may dissolve into brine and therefore affect the ultimate behavior of the injected CO_2.

Many decades of research and development have resulted in highly sophisticated modeling codes for applications to hydrocarbon production (including CO_2-EOR), geothermal energy production, and groundwater resource management. Methods for representation of the physical domain (the subsurface) in a numerical simulation, techniques for solving equations, and methods for processing and displaying results are directly applicable to modeling of CO_2 storage. The relevant fundamental equations for heat and fluid flow, mechanical deformation, and chemical interactions, are also common among all these applications. Much of the effort in adapting tools for simulation of CO_2 storage has been focused on modifications to enable solution of these equations for the specific properties, conditions, and processes relevant to geologic CO_2 storage. Table 2 provides a list of numerical geologic CCS simulation codes and a brief description of the specific processes modeled by each code.

Practicality dictates that the degree of coupling in numerical simulation should be “fit for purpose” in that every simulation of CO_2 injection and storage need not include all phenomena. For example there may be post-injection or closure scenarios when geomechanical considerations are not important. The key to successful modeling endeavors is knowing how and when to include a subset of relevant phenomena, which may be on the basis of relevant time and length scales.

Appendix 3 provides brief overviews of individual aspects of coupled processes relevant to geologic CCS and associated simulation analyses are provided, including thermal and hydrological, mechanical, chemical and biological processes. Each of these areas is briefly discussed.

3.1.1 Thermal and Hydrologic and Processes

Modeling of the heat transfer and flow aspects of CO_2 behavior in the subsurface is a primary component of numerical simulation, and is used to address issues such as wellbore leakage, area-of-review delineation, and monitoring well location. The reservoir-scale or basin-scale groundwater/brine, and CO_2 transport processes are represented using mass, momentum and energy balances. One of the objectives driving numerical simulations of heat transport and flow is to obtain information on the extent of the CO_2 plume in the subsurface at a given point in time. Moreover, because fluid transport properties (such as viscosity, density) and the Darcy velocity depend on all three transport processes, they are numerically represented using ‘coupled’ partial differential equations for multiple phases, such as supercritical CO_2, water, salt, and oil. One input to the solution of the coupled partial differential equations is capillary pressure, which represents the force required to pass an immiscible phase (CO_2) through the pore space. Because this depends upon the presence of other phases, such as oil and brine, capillary pressure depends on the saturation of the dominant, or ‘wetting phase.’ Capillary pressure and relative permeability data represent one of the inputs critical to modeling hydrologic processes. Because plume migration also depends upon calculation of the amount of CO_2 trapped in the residual phase, and this requires that the codes incorporate complex hysteretic flow processes.

Table 2. A Summary of Numerical Codes for Geologic CCS Simulation

Name of Code	Developer/ Supplier	Coupling	Processes Modeled
NFFlow-FRACGEN	NETL	H	Two-phase, multi-component flow in fractured media
Eclipse	Schlumberger	T,H	Non-isothermal multiphase flow in porous media
MASTER	NETL	T,H	Black oil simulator, compositional multiphase flow
TOUGH2 (TOUGH+)	LBNL	T,H	Non-isothermal multiphase flow in unfractured and fractured media
GMI – SFIB	Geomechanics International	M	Three-dimensional stress modeling for compressional (wellbore breakout) and tensional (tensile wall fractures) stress failure, fracture modeling
ABACUS	SIMULIA	T,M	Geomechanical, single and two-phase flow
COMET3	ARI	T,H,M, sorption	Black oil production, hydrocarbon recovery from desorption-controlled reservoirs
TOUGH-FLAC	LBNL	T,H,M	Non-isothermal multiphase flow in unfractured and fractured media with geomechanical coupling
The Geochemist's Workbench	University of Illinois	C	Chemical reactions, pathways, kinetics
PSU-COALCOMP	Penn State University /NETL	T,H, sorption	Compositional simulator with dual porosity, sorption
CrunchFlow	LLNL	T,H,C	3-D, multiphase transport with equilibrium and kinetic mineral-gas-water reactions
GEM-GHG	Computer Modelling Group Ltd.	T,H,C	Non-isothermal multiphase flow in porous media
NUFT-C	LLNL	T,H,C	Non-isothermal multiphase flow and chemical reactions in porous media
PFLOTRAN	LANL	T,H,C	Non-isothermal multiphase, multicomponent, chemically reactive flows in porous media. Can be run coupled or uncoupled
PHAST	USGS	T,H,C	Multicomponent, 3-D transport with equilibrium and kinetic mineral-gas-water reactions
STOMP-family of codes	PNNL	T,H,C	Non-isothermal multiphase flow in porous media, coupled with reactive transport.
TOUGHREACT	LBNL	T,H,C	Non-isothermal multiphase flow in unfractured and fractured media with reactive geochemistry
OpenGeoSys: [Couples GEM, BRNS, PHREEQC, ChemApp, Rockflow]	UFZ-BGR-CAU-GFZ-PSI-TUD-UE	T,H,M,C	Porous and fractured media THMC simulation
FEHM	LANL	T,H,M,C	Non-isothermal, multiphase flow (including phase-change) in unfractured and fractured media with reactive geochemistry & geomechanical coupling
CO_2-PENS	LANL	–	Systems-level modeling of long-term fate of CO_2 in sequestration sites
COMSOL	COMSOL	–	General partial differential equation solver with finite element solver

In its simplest forms, modeling of geologic CCS may be represented by analytic, semi-analytic or simplified numerical solutions to fluid flow. Such approaches (see for example, Celia and Nordbotten, 2010, and references cited therein) are useful to study basin-wide flows, wellbore leakage, obtain quick estimates of the rates of CO_2 transport, and may be used as components for probabilistic risk assessment. Many other numerical coupled groundwater and heat flow models. Many other numerical coupled groundwater and heat flow models have been developed and applied by different researchers for modeling research specific to thermal processes. Although these other groundwater and heat flow models are not CCS-focused, they provide good examples of research problems faced by the geologic CO_2 storage community and are discussed further in Appendix 3. Various sophisticated models of coupled single-phase groundwater and heat flow are found in the literature and serve as good examples of modeling practice. A number of two- and three-dimensional numerical codes have been recently adapted or independently developed for addressing problems specific to geologic CO_2 storage. They can be classified into two categories, although, this is not exclusive:

- General purpose subsurface flow and heat transfer simulation codes:
  - TOUGH2 is a general purpose simulator for multiphase fluid flow and heat transport in porous and fractured media. The TOUGH-family of codes has been applied to geothermal engineering, nuclear waste disposal and geologic CO_2 storage, with the use of relevant fluid property modules, capillary pressure hysteresis curves, and other modifications.
  - STOMP-WCSE, ‘Subsurface transport over multiple phases – Water, CO_2, salt and energy’ simulates thermal and hydrogeologic flow and other transport phenomena in the subsurface through mass, momentum and energy balances for the fluid phases and salt (for saline aquifer injections).
- Hydrocarbon reservoir simulation codes:

  ECLIPSE, GEM, VIP, and COMET3 are examples of reservoir simulators used to model hydrocarbon recovery. The VIP simulation suite, and ECLIPSE and GEM families of codes have been applied to study CO_2, oil and water flow and heat transfer subsurface processes by modeling appropriate physical (CO_2 solubility) and chemical phenomena relevant to CO_2 injection in hydrocarbon reservoirs.

Many of these codes have been tested, compared, and benchmarked against other codes for geologic CCS simulation in code comparison studies (Pruess et al., 2002).

3.1.2 Geomechanical Processes

The process of CO_2 injection will result in an increase in stress in the injection zone and the confining zones. If the stresses become too large the rock formation could fracture or pre-existing fractures or faults could move, affecting storage integrity. Therefore, numerical models of coupled hydrologic-geomechanical processes are vital for evaluating the potential for FEPs such as overpressures, migration through *in situ* fracture networks, fracture generation, and induced seismicity. In broadest terms, geomechanical processes include effects of fluid pressure, elastic and non-recoverable deformation, fracture opening and closing, and larger-scale faulting. Coupling geomechanics and other processes in numerical simulations of geologic CO_2 storage is done mainly through fluid pressure and the effects of deformation on absolute and relative permeability. This coupling between hydrologic and geomechanical processes may be examined in two ways:

- The sole effect of fluid pressure on mechanical response (effective stress): For example, the millimeter-scale surface deformation observed at In Salah, Algeria upon CO_2 injection (Rutqvist et al, 2009).
- The effects of mechanics (strain and stress) on the hydrologic response, especially via permeability modification: For example, the changes in the permeability of coal seams caused due to shrinkage and swelling, associated with methane production and CO_2 injection.

Both of these coupling pathways can be equally important. However, one or both are often ignored in analyses of geologic CO_2 storage and other applications. Many conditions or situations call for simplification in the form of neglecting one direction of this coupling.

Deformations may be elastic (linear response to subsurface pressure), or inelastic (irreversible). Small, reversible deformations in porous media are represented by using the linear theory of poroelasticity, which relates the mean stress to the excess pore pressure, which in turn is controlled by hydrogeologic and thermal processes. Applications of such poroelastic formulations, rock deformation and numerical solutions are discussed by Ge and Garven (1992), McPherson and Garven (1999) and Person et al. (1996). In contrast inelastic deformations (which include plasticity and creep) induce irreversible changes in the subsurface. Pore collapse due to fluid drainage, or opening of local fractures caused by excess stress are some examples of inelastic deformation. Such inelastic deformations are addressed by 'cap plasticity models,'[6] implemented in commercial software such as ABAQUS™ and FLAC3D™. In clay-bearing confining zones, the coupling between flow, mechanical, and chemical processes is exemplified by physical phenomena with potential implications for geomechanical integrity, such as dry-out, clay swelling or shrinkage via interactions with the injected fluids, and displaced brines. In such cases, the shale confining zone deformation can be strongly coupled to multiphase flow, thermal effects, and chemical reactive transport (Borja, 2004).

3.1.3 Chemical Processes

A study of rock-CO_2-formation fluid chemical interactions is relevant to assess storage integrity, to evaluate injected CO_2 behavior, and to guide monitoring efforts during and after injection. Some of the storage integrity issues which can be addressed by reactive transport modeling of CO_2 and other fluid flows in the subsurface include confinement in the injection zone, CO_2 partitioning into the rock and fluid phases via mineralization and dissolution, and the potential impacts to groundwater from CO_2 leakage, and storage integrity. Various codes are available to model chemical processes in the subsurface, ranging from equilibrium models, path-of-reaction models, and kinetic models to coupled reactive transport models. Equilibrium models calculate the chemical species in the solid phase (minerals), gases, and solutions (supercritical CO_2, water) at equilibrium; they use a set of thermodynamic and physical property data. Path-of-reaction models also determine the equilibrium speciation, but additionally indicate the intermediate species that are formed in the series of chemical reactions leading up to equilibrium. Kinetic models incorporate the rates of heterogeneous chemical reactions (e.g., solid-gas, solid-liquid and gas-liquid), which occur more slowly than reactions involving chemical species in solution/same phase (homogeneous reactions). Equilibrium, path-of-reaction, and kinetic modeling codes such as Geochemist's Workbench, PATHARC, and SOLMINEQ do not account for the migration of CO_2 in the injection formation, and are essentially closed system, or 'batch' models. In contrast, reactive transport models incorporate the coupling between CO_2 transport and chemical reaction. They are more computationally intensive because the addition of even a single reaction to the set of equations adds multiple variables and associated degrees of freedom. To some extent, the number of variables may be reduced by expressing a subset of chemical species (secondary species) in terms of the *primary* chemical components. However, the relatively-coarser grids used in reservoir hydrogeologic and geothermal simulators may not capture the fine-scale reaction fronts and chemical gradients that arise in subsurface engineering scenarios. Given the disparate size and time scales among the THMCB processes, methods for using different grids, or using nesting or adaptive grids, have been explored and may be necessary for coupled reactive transport codes such as PFLOTRAN, NUFT, CRUNCH, PHAST and TOUGHREACT.

Chemical processes relevant to subsurface CO_2 storage include aqueous speciation, dissolution/precipitation, microbial-mediated redox reactions, ion-exchange between solutions and minerals, surface chemical reactions occurring at phase interfaces (i.e. surface complexation, sorption), the effects of these processes on porosity and permeability, coupling with mechanical effects (e.g. water-assisted creep and crack growth; fracture healing, clay mineral swelling). Further, transport processes involved in multiphase reactive flow include advection, dispersion, and multicomponent diffusion. Because of these inherent complexities, time and length scales under consideration, reactive buffering capacity (e.g. of gases and minerals), limitations on thermodynamic and kinetic data for the system in question, options for model validation, geochemical and biological processes to include, and what can be excluded from consideration, should all be considered when choosing a model.

[6] Note that 'cap plasticity model' need not be confined, or related to 'caprock'.

3.1.4 Biological Processes

Research into the specific conditions in which microbial processes play a role affecting geologic CCS is needed to better understand the THMCB couplings governing the ultimate behavior of injected CO_2. The activities of microorganisms can have a considerable chemical and physical impact on subsurface environments. In the context of geologic CCS, cellular and extracellular biomass production can clog pores in the subsurface, leading to decreased permeability (Taylor et al., 1990). Microorganisms can also affect permeability by driving mineral dissolution and precipitation. This is an area for further investigation.

4. Application of Risk Analysis and Numerical Simulations in the RCSP Initiative

4.1 Introduction

Because the numerical simulation of geologic CO_2 storage is interlinked to risk analysis, monitoring, and site characterization efforts, robust simulations are required to accurately model the transport and fate of CO_2. Simulation development involves the collection and use of site-specific information and scientific data as well as model validation, calibration, analysis and testing before, during and after CO_2 injection. Similarly, the process of risk analysis also involves steps such as risk source assessment, risk characterization and risk management. The current discussion is a summary of the actual risk analysis and numerical simulation methodologies used by RCSPs in their various Phase II and Phase III CO_2 injection pilots. Summary information about these pilot tests and model simulations, presented in Table 3 and Table 4, illustrates the vast differences in sizes, types of geologic formations, type of injection (e.g., EOR, saline bearing formations, coal-bed) and other aspects among various RCSP efforts.

4.2 Synthesis of Site-Specific Information and Scientific Data into Numerical Simulations

4.2.1 Geologic Model Development

A geologic model forms the basis for risk analysis and numerical simulation. The geologic model depicts the reservoir formation, the confining zone and the lithologies of the rocks overlying the confining zones up to the surface of the earth. The model shows the thickness of the various lithologies, and their structure (dip, folding, etc), and contains information on the relevant THMCB properties of the rocks and contained fluids. The geologic model is not static, but evolves throughout the life of the storage project. Development of the geologic model begins during the process of site screening and site selection and is the focus of detailed studies carried out during site characterization. During the operational phase of a project the model is updated based on monitoring measurements. The DOE best practice manuals for "Site Screening, Selection, and Initial Characterization for Storage of CO_2 in Deep Geologic Formations" and "Monitoring, Verification, and Accounting of CO_2 Stored in Deep Geologic Formations" describe the use of various characterization techniques to select a site for CO_2 injection and develop the geologic model for that site. The best practice manual, "Monitoring, Verification, and Accounting of CO_2 Stored in Deep Geologic Formations", also describes techniques and approaches for measurement of data used to update the geologic mode.

Any numerical simulations of CO_2 flow in porous media should accurately account for the hydraulic, thermal, mechanical and chemical properties of the fluids (brine, CO_2, hydrocarbons), the target injection and confining zones. Further, the RCSPs have subjectively rated the *quality* of each rock and fluid property.

Table 3. A Summary of the Type of CO2 Storage and Target Formations in Various RCSP Models

		BSCSP- Wallula	MGSC -Tanquary	MGSC - Sugar Creek, Mumford Hills: EOR	MRCSP: Cincinnati Arch	PCOR: NW McGregor	SECARB - Plant Daniel	SECARB - Cranfield	SECARB-Russell County	SWP: EOR [Aneth, SACROC]	SWP- Pump Canyon	WESTCARB: Kimberlina
Type of CO_2 injection	Storage Type	Basalt injection	Coal seam	Depleted oil reservoir	Deep saline formation	Depleted oil field - CO_2 Huff 'n' Puff	Deep saline formation (sandstone)	EOR, Saline formation next to EOR field	Coal seam	CO_2-EOR field	Coal seam	Deep saline formation
	Target, Formation	Basalt	Undersaturated coal seam with no previous coalbed methane production or pressure depletion	Thick, channel sandstones/ Thin lenses of sandstone interbedded with shales	Mt. Simon Sandstone	Fractured-carbonate oil reservoir	Sandstone/marine shale	Mostly sandstones with some silt/clay intercalations and conglomerates at the base	Coal seam, Pocahontas and Lee Formations coals that have been produced for coalbed methane	SACROC: Limestone (Cisco and Canyon) formation, Aneth: Desert Creek	Fruitland coal seams	High-permeability sandstone overlain by thick shale
	Geologic Classification	Basalt	Coal	Clastic, Fluvial channels	Strandplain	Shallow shelf open	Delta	Fluvial	Coal	SACROC: Reef	Coal	Shallow shelf
	Unique Features		Organic shale confining layers	Liquid-CO_2 flood (Mumford Hills) Immiscible-CO_2 gas flood - Sugar Creek	First injection test in the Mt. Simon, a major CO_2 storage target in the Midwest United States	Several perched-oil lenses, highly fractured carbonate reservoir, low matrix permeability	Sands extremely permeable (> 2D), net sand thickness: 210', confining zone: >300' of low-permeability grey shale	Deep (>10,000') and hot (> 250 °F), but normallypressured. Extremely heterogeneous confining zone and injection formation	Targeted coal seams are interbedded with carbonaceous shale that are known confining zones	Stacked system: high porosity carbonate rock and low-porosity carbonate muds. Miscible CO_2-EOR, 120 m average reservoir thickness	Low water-content, high methane content, high permeability coals compared to other regional coal formations.	Multiple sandstones separated by shales

Table 4. A Summary of Pertinent Features of Various RCSP Models

	Big Sky-Wallula	MGSC –Tanquary / CBM	MGSC - Sugar Creek	MGSC - Mumford Hills	MRCSP - (Michigan Basin):	MRCSP Cincinnati Arch	PCOR	SECARB Plant Daniel Site	SECARB - Cranfield	SECARB-Central App CBM	SWP: EOR - Aneth/ SACROC	SWP- Pump Canyon	WESTCARB: Kimberlina
Storage Type	Basalt	Coal bed	Hydrocarbon reservoir	Hydrocarbon reservoir	Deep Saline Formation	Deep Saline Formation	Hydrocarbon reservoir	Saline formation	Hydrocarbon reservoir/Saline	Coal bed	Hydrocarbon reservoir	Coal bed	Saline formation
Initial conditions, (T: °C, P: MPa)	NA	20 ˚C, 2.59 MPa	27 ˚C, 2.75 MPa	27 ˚C, 7.4 MPa	NA	NA	NA	NA	NA	23 ^{O}C, 4.8MPa	120 °C, 40 MPa	52.2 °C, 10.2 MPa	81 ˚C, 22 MPa
Model lateral extent, million square km	0.29	1.09	1.83	190.5 m x 109.5 m	2	~1500 x 1500 m	0.03	2.83	~6	1.7	Aneth: 119, SACROC: 40	2.6	121
Injection rate (short tons/d)	71	0.5-0.75	33	33	300-600	500	346	135	2740	41	2740 – 10,000	50	685
Qty injected (short t)	1,000	100	6,000-8,000 (active project)	6,000-8,000	60,000 metric tons	1000 metric tons	440	2,970	1,000,000	1,000	88,000 – 150,000 per year	18,400	1,000,000
Software Used	STOMP-WCS	COMET3	VIP	VIP	STOMP-WCSE	STOMP-WCSE	GEM-GHG	CMG-GEM	CMG-GEM	COMET3	TOUGHREACT, pFLOTRAN, CMG-GEM	COMET3	iTOUGH2

NA: Not available

FLIP PAGE TO TABLE

4.2.2 Rock Properties

Rock properties are estimated by reviewing data that provides information on porosity, permeability, relative permeability, capillary pressures, fluid saturation, mechanical properties, and mineralogy. In order to develop the input parameters for their numerical simulations, modelers must average data over spatial areas or rely on factors developed in the literature. As more data are collected those parameters can be calibrated and improved to improve the confidence in the predictions resulting from the models. This section reviews the approaches taken by the RCSPs to develop this data.

Porosity is a measure of the void space within the rock which fluids or gases may occupy. A variety of techniques including well/wireline logs (ex: neutron, density and sonic), core analyses, and thin-section analysis may be employed to measure porosity. Information on porosity is also obtained from in situ hydrologic measurements and seismic survey results. It is important to calibrate results obtained through downhole logs and core measurements over time. The resulting data produces estimates that vary from pore to near-borehole to reservoir-scale resolution. Some methods of examination may estimate the distribution of pore sizes at high resolution, or identify porosity-mineralogy relationships.

Permeability refers to the flow rate of a single fluid under a specific pressure regime known as hydraulic head. Permeability may be measured using core plugs, and hydrologic tests (long-term pumping tests, drillstem tests), or estimated from wireline logs. By calibrating the results obtained from wireline logs and core analysis, modelers can increase their confidence in estimate of permeability for the formation. Additional measurements of permeability may examine heterogeneity in the vertical and horizontal directions, through fractures, or with different viscosity fluids.

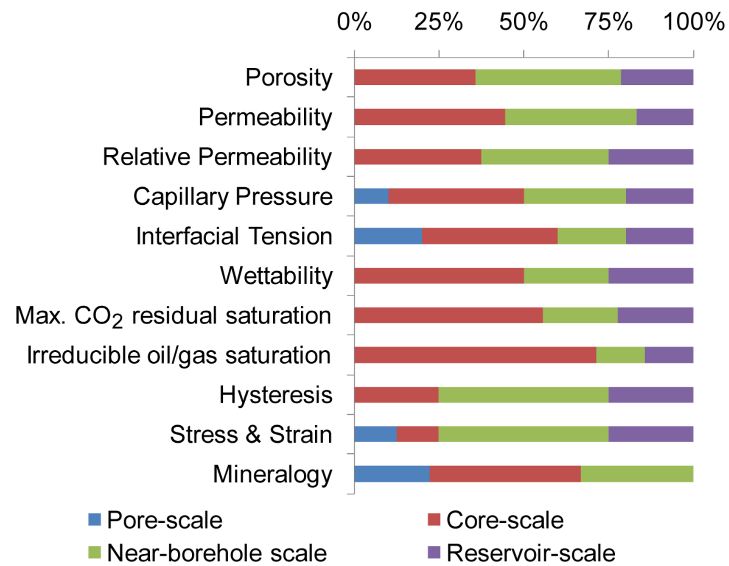
Relative permeability is a concept in which two immiscible fluids (e.g., oil and brine, CO_2 and brine) must share the same pore space available for flow. The flow rate of each phase is therefore reduced relative to what it would be in the absence of the other phase. This phenomenon is strongly related to the saturation of each fluid, but also involves pore size and capillary pressure/interfacial tension. Relative permeability curves are estimated using lab measurements on cores, estimated from core analysis data, or from literature.

Capillary pressures and the related measurements of interfacial tension are properties that describe the surface tension of a fluid spanning a pore throat, and the pressure required to penetrate a second phase through that pore throat. Measurements are made on cores and values inferred from wireline log analyses, but capillary pressure curves are commonly estimated from literature. Wettability (core-scale) was also determined from the literature, however, the evolution of wettability upon prolonged CO_2 exposure is still not well understood.

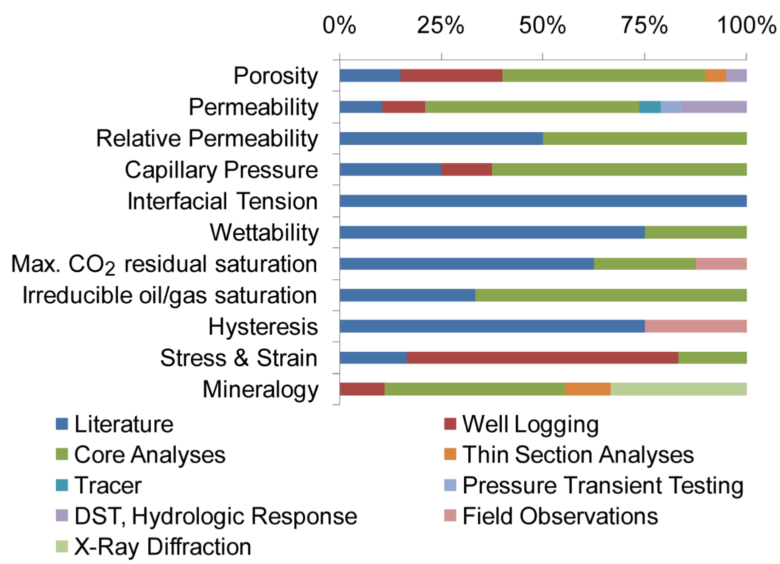
Fluid saturation refers to the percentage of the pore space occupied by each fluid that may be present within the reservoir. Subsurface rocks naturally contain some amount of water, brine, oil and gas that must be compressed or displaced in order to accept injected CO_2. The CO_2 will not displace 100% of the other fluid, and the amount that remains is referred to as the irreducible saturation of that phase. The maximum CO_2 saturation that may be attained (the difference between porosity and irreducible saturation of other phase) strongly reflects the physical trap volume in a reservoir, and is often inferred from waterflood literature, field observations, literature, historic reservoir data, or lab measurements. Oil, gas and water/brine irreducible saturation can be estimated from operator core analysis, measured in the lab, or estimated from the literature at the core scale. Hysteresis (a measurement of residual trapping) is a less common calculation, but may be determined from field observations and/or literature. Mechanical properties such as stress-strain relationships are commonly calculated from laboratory measurements, inferred from wireline logs, or estimated from the literature, and vary in resolution from the pore to near-wellbore and reservoir scale.

Mineralogy is the chemical composition of rock formations and is critical to the long-term storage of CO_2, especially for basalt injections. Mineralogy is typically determined by wireline logs, thin-section/petrographic analysis, and x-ray diffraction (XRD), x-ray fluorescence (XRF) studies on drill cuttings, and core samples. Other tests such as ion chromatography may be performed on fluid samples. Mineralogy is very important to consider when both modeling and simulating a reservoir as each of the above properties can be affected by chemical reactions between the fluids and the minerals.

A summary of the approaches taken by partnerships to estimate rock properties is presented in Figure 6. The length of each colored bar Figure 6(a) indicates the number of times a particular property was measured at a given scale (e.g.,) 43% of porosity measurements were at near- borehole scale. Likewise, the actual technique used to estimate a particular rock property is compared against all techniques used to measure the property in Figure 6(b). The length of each colored bar in Figure 6(b) indicates the number of times a particular property was derived using a particular method, (e.g.,) 50% of porosity values were derived from core analyses. Note that relative comparisons among the percentage values are more relevant than the absolute percentage values.



(a)



(b)

Figure 6. (a) A Bar Chart Summary of the Resolution for Each Rock Property. The length of each colored bar indicates the number of times a particular property was measured at a given scale (e.g.,) 43% of porosity measurements were at near borehole scale. (b) Summary of the Methods Used by RCSPs To Estimate Rock Properties. The length of each colored bar indicates the number of times a particular property was derived using a particular method, (e.g.,) 50% of porosity values were derived from core analyses. Note that relative comparisons among the percentage values are more relevant than the absolute percentage values.

West Coast Regional Carbon Sequestration Partnership

Investigation of CO_2 Plume Behavior in a Deep Saline Formation

The hydrodynamic behavior of CO_2 injected into a deep saline formation is investigated, focusing on trapping mechanisms that lead to CO_2 plume stabilization. A numerical simulation of a candidate storage formation, a dipping formation made up of interleaved high-permeability sand layers and low-permeability shale layers, is developed to simulate the injection of 1,000,000 metric tons of CO_2 is injected over a 4-year period, and the subsequent evolution of the CO_2 plume for hundreds of years. A key measure is the time evolution of the partitioning of CO_2 between dissolved, immobile free-phase, and mobile free-phase forms (Figure 7). Model results indicate that the free-phase CO_2 plume is effectively immobilized at 25 years. At that time, 38% of the CO_2 is in dissolved form, 59% is immobile free phase, and 3% is mobile free phase. Sensitivity studies that were carried out to investigate the effect of poorly constrained model parameters permeability, permeability anisotropy, and residual CO_2 saturation indicate that small changes in properties can have a large impact on plume evolution, causing significant trade-offs between different trapping mechanisms. For example, an all-sand model shows less CO_2 is dissolved at plume stabilization than does the layered sand/shale model, due to less contact area between free-phase CO_2 and brine for the one large plume that develops in the former model instead of the five smaller plumes that form in individual sand layers in the latter. However, over long time periods, much stronger natural convection develops in the all-sand model, greatly enhancing CO_2 dissolution, so that the free-phase plume disappears almost ten times sooner.

Numerically simulated spatial distributions of CO_2 at plume stabilization and pressure increase at the end of the injection period for the base case and the suite of sensitivity studies provide the primary input to the Certification Framework process for Risk Assessment. The locations of potential conduits (wells or faults) for leakage are collected from regional geological and well-record information, and the likelihood of intersection between the CO_2 plume or pressure-increase region and these conduits is assessed. For CO_2, the plume is so small that the likelihood of intersection is near zero. The area of pressure increase is much larger, and intersection is near certain, but the likelihood of actual leakage through the conduits and subsequent impact on compartments (e.g., USDW or health, safety, and the environment) is deemed to be small, due to the small magnitude of the pressure increase and expected limited ability of the conduits to sustain the upward flow of brine.

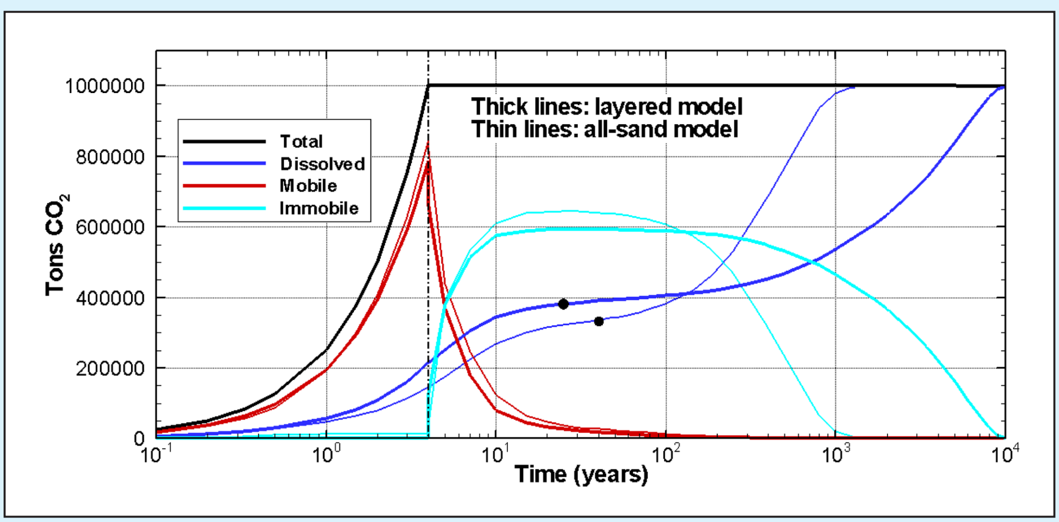


Figure 7. Time evolution of the CO_2 mass distribution, for a sand/shale layered model and for an all-sand model. The black dots show the times at which the plumes are effectively immobilized.

4.2.3 Fluid Properties

Thermophysical fluid properties such as density, viscosity, and CO_2/oil CO_2/brine solubilities are typically calculated by equations of state from the literature/correlations. These values can be checked by measurements on samples obtained from wells using techniques such as U-tube measurements. These properties were collected by the RCSPs at various scales in different models, ranging from lab scale to the core/near-wellbore/reservoir scales. In addition to thermophysical properties, geochemical analyses of water/brine, oil and gas samples were also conducted to better characterize the chemical constituents in the reservoir.

Fluid chemical properties such as the concentration of major cations, major anions, trace metals, total dissolved solids, ammonia-nitrogen, total dissolved inorganic carbon, and pH, dissolved oxygen, redox potential, specific conductance and alkalinity may be measured on brine and groundwater samples which are collected with downhole U-tube sampling or drill stem tests (DSTs) on monitoring, observation and/or production wells. Additional geochemical properties were estimated from literature by the RCSPs. In deep saline and basalt injections, dissolved gas compositions were obtained from well fluid samples at the end of long-term pumping tests, as well as surface and bottom water samples.

Fluid (oil/brine/groundwater) samples from the subsurface or shallow groundwater, and headspaces and annuli of wells were used to measure isotope (^4He, ^{13}C, ^{18}O, ^{34}S, ^3H, ^{36}Cl) concentrations and isotopic ratios. Detailed information on the application of isotope analyses to aid in situ subsurface characterization, model calibration and leak detection is provided in the "Monitoring, Verification, and Accounting of CO_2 Stored in Deep Geologic Formations" best practices manual.

4.2.4 Well Information

It is critical to account for all known wells, operational, planned and abandoned within the modeled area. Well information may be collected by compiling inventories of existing wells around the injection site, or via available well databases. Well integrity testing can be performed, or operator logs analyzed to characterize wells relative to their potential impact on model results. The individual RCSP case studies[7] indicate that numerical simulations can provide guidance for selection of locations for CO_2 injection wells or monitoring wells.

4.3 Simulation Model Development

4.3.1 Grid Building

Grid building is the process of dividing up the modeled domain into elements. The choices involved with grid building are very project specific, whereas high resolution models can provide great detail, they become increasingly difficult to manage and compute. It is generally accepted that vertical cell resolution should not be finer than the data that will be used to populate it, and horizontal cells should be kept to a reasonable size, balancing detail and time. Complex grids may be developed that contain higher resolution, finer gridding near the wellbore, and larger cells as the distance from the well increases.

The first step in grid building involves the delineation of the domain. Construction of a model grid involves the selection of appropriate model domain sizes and grid resolution, accounting for specific features such as faults and fractures, and any necessary upscaling. An optimally-sized model domain should:

- Encompass all the major flow units and confining zones of interest (injection zone, overlying and underlying formations).
- Include the injection, monitoring and any production wells as well as known existing wells in the study area.
- Adequately encompass the extent of pressure response area.
- Be computationally tractable.

The size of the model domains chosen by various partnerships vary due to the size (rate and duration) of CO_2 injection, the type of project (EOR, coal, saline) and the time frame allowed for monitoring. Because of the differences among various injection pilots, the sizes of model domains varied widely from the sub-square kilometer range to hundreds of square kilometers in lateral extent.

[7] http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.

Approaches to grid coarsening varied according to specific site characteristics. For example, in some cases where the x- and y-grid dimensions were increased by an order of magnitude, the vertical (z-) dimensions were unchanged whereas in other cases, the grid size in the vertical direction was coarsened. Grid coarsening can create numerical dispersion in the model, which causes a smearing-out effect for the CO_2 plume. Grid coarsening should be evaluated carefully with sensitivity studies using multiple grid resolutions to choose a resolution that would allow for a reasonable computational time while maintaining heterogeneity, and have sufficient accuracy to calculate pressure and saturation changes. Grid sizes in the x- and y-directions varied from 2.4 m (~8 feet) for the smaller model domains to approximately 330 m (~1082 feet) for the largest model domain. Vertical grid sizes varied from 0.6 m (~2 feet) to 25 m (~75 feet).

Flow at the rock matrix-fracture interface can be modeled by the dual-continuum approach such as the double porosity model, dual-permeability approach, or the more general multiple-interacting continua [MINC] method (Pruess and Narasimhan, 1982, 1985)). In reservoirs with extensive, well-connected fractures, the MINC-method was used to model the transport processes. Some of the other RCSP models implemented a dual-porosity/permeability approach to model the flow at the fracture - rock matrix interface. Modeling efforts by the RCSPs also used discrete fracture network modeling simulations to evaluate potential impacts of the discrete fractures that may account for a major part of the flow and to construct a dual porosity, permeability model.

Faults, when present, were incorporated either by specifying no-flow boundaries (normal to the fault direction), dual porosity and manually-delineated high-permeability or by including lateral permeability-anisotropy in the direction parallel to the fault orientation.

Both structured and unstructured grids were used in various partnership model simulations. The RCSP models were developed with both node-centered and corner-point grids. One pilot modeling study used a hybrid grid to improve the treatment of wells in simulations. Finite-difference as well as finite-volume discretization schemes were applied in various model simulations. In cases where limited actual data were available for the reservoir, or where the model domain was small, grid upscaling was not performed. In other cases, grid upscaling was done either with the auxiliary simulation software, or by orthogonal grid mapping.

4.3.2 Property Assignment

The next phase in developing a numerical simulation is the assignment of rock and fluid properties to the defined grid blocks. This involved upscaling the properties (derived from the geological model) obtained at a high resolution to the more coarsely resolved grid blocks. Initial and boundary conditions were also assigned at this stage. Property assignment should consider the reservoir at stake, for example, cleat permeability within a coal seam may incorporate data from pressure transient and interference tests.

Properties need to be assigned to reflect their spatial variability as well as any anisotropic, or directional-dependent trends. Geostatistics, prior knowledge of the particular field, extensive core data, and extensive well log data were routinely used by the RCSPs to estimate the heterogeneity and anisotropy. Sand-shale facies, as reflected in horizontal/vertical permeability-anisotropy, and Leverett-scaling of capillary pressures were used to initialize corresponding model grid properties in one of the RCSP model simulations. For basalts, hydraulic properties of each model layer may be determined from pumping test results, which differentiate the tight crystalline layers from the gravel-like beds.

Geologic characterizations typically represent variations of porosity and permeability on a much finer resolution than can be handled using the state-of-the-art computing. Upscaling is the process of converting the fine-scale properties and features in the geologic model to a coarser grid while preserving the geologic features and properties. This involves two steps. First, the fine layers in the geologic model are combined into fewer layers in the coarse simulation model. Second, the coarse grid is subsequently populated with properties such as permeability and porosity using mathematical methods with fine grid properties as inputs. Therefore, both property-upscaling and grid-upscaling are typically performed. Various methodologies were adopted to account for this in the RCSPs' models. Upscaling may be performed in simulation software itself. Or, the geologic model may be developed at a resolution where no upscaling is necessary while still capturing the vital geologic features. In other cases,

Southwest Regional Partnership on Carbon Sequestration: Trapping Mechanisms Involved in the Injection of CO_2 in an Oil Reservoir

"CO_2 trapping mechanisms" in geologic sequestration are the specific physical and chemical processes that hold CO_2 underground in porous formations after injection. Main trapping mechanisms of interest include: (1) fundamental confinement of mobile CO_2 phase under low-permeability caprocks, or stratigraphic trapping, (2) conversion of CO_2 to mineral precipitates, or mineral trapping, (3) dissolution in in situ fluid, or solubility trapping, and (4) trapping by surface tension (capillary force) and, correspondingly, remaining in porous media as an immobile CO_2 phase, or residual CO_2 trapping. The RCSPs strive to evaluate and quantify the competing roles of these different trapping mechanisms, including the relative amounts of storage by each. For the sake of providing a realistic appraisal, SWP conducted trapping mechanism analyses on a case study site, the SACROC Unit in the Permian basin of western Texas. CO_2 has been injected in the subsurface at the SACROC Unit for more than 35 years for the purpose of enhanced oil recovery. Analysis of the SACROC production and injection history data suggests that about 93 million metric tons of CO_2 were injected and about 38 million metric tons were produced from 1972 to 2005. As a result, a simple mass-balance suggests that the SACROC Unit has accumulated approximately 55 million metric tons of CO_2.

The SWP study specifically focuses on the northern platform area of the SACROC Unit where about 7 million metric tons of CO_2 is stored. In a computer simulation model describing the SACROC northern platform, porosity distributions were defined from extensive analyses of both 3-D seismic surveys and calibrated well logging data from 368 locations. Permeability distributions were estimated from determined porosity fields using a rock-fabric classification approach. The resulting 3-D geocellular model representing the SACROC northern platform consists of over 9.4 million elements that characterize detailed 3-D heterogeneous reservoir geology. To facilitate simulation using conventional personal computers, the SWP upscaled the 9.4 million elements model using a "renormalization" technique to reduce it to 15,470 elements. Analysis of groundwater chemistry from both the oil production formations (Cisco and Canyon Groups) and the formation above the confining zone suggests that the Wolfcamp Shale Formation performs well as a confining zone at the SACROC Unit. However, results of geochemical mixing models also suggest that a small amount of shallow groundwater may be contaminated by reservoir brine possibly due to: (1) downward recharge of recycled reservoir brine from brine pits at the surface, or (2) upward leakage of CO_2-saturated reservoir brine through the Wolfcamp Shale Formation.

Using the upscaled 3-D geocellular model with detailed fluid injection/production history data and a vast amount of field data, the SWP developed two separate models to evaluate competing CO_2 trapping mechanisms at the SACROC northern platform. The first model simulated CO_2 trapping mechanisms in a reservoir saturated with brine only. The second model simulated CO_2 trapping mechanisms in a reservoir saturated with both brine and oil. CO_2 trapping mechanisms in the brine-only model show distinctive stages accompanying injection and post-injection periods. In the 30-year injection period from 1972 to 2002, the amount of mobile CO_2 increased to 5.0 million metric tons without increasing immobile CO_2, and the mass of solubility-trapped CO_2 sharply rose to 1.7 million metric tons. After CO_2 injection ceased, the amount of mobile CO_2 dramatically decreased and the amount of immobile CO_2 increased. Relatively small amounts of mineral precipitation (less than 0.2 million metric tons of CO_2 equivalent) occurred after 200 years. In the brine-plus-oil model, dissolution of CO_2 in oil (oil-solubility trapping) and mobile CO_2 dominated during the entire simulation period. While supercritical-phase CO_2 is mobile near the injection wells due to the high CO_2 saturation, it behaves like residually trapped CO_2 because of the small density contrast between oil and CO_2. In summary, the brine-only model reflected dominance by residual CO_2 trapping over the long term, while CO_2 in the brine-plus-oil model was dominated by oil-solubility trapping.

Southwest Regional Partnership on Carbon Sequestration: Trapping Mechanisms Involved in the Injection of CO_2 in an Oil Reservoir (cont'd)

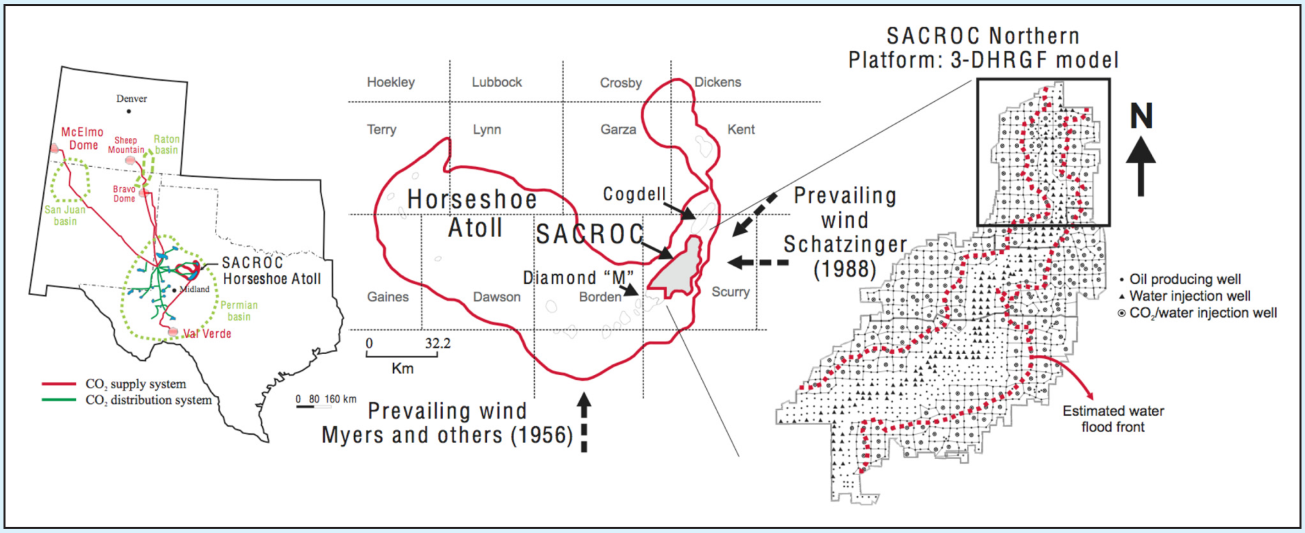


Figure 8. (a) SACROC Unit at the Horseshoe Atoll in western Texas and CO_2 supply system from natural CO_2 reservoirs, (b) Magnified map of the SACROC Unit within the Horseshoe Atoll with indication of paleo-wind direction, (c) Well locations of SACROC Unit with the estimated water-flooding fronts at the end of water-flooding period in 1973 (Kane, 1979).

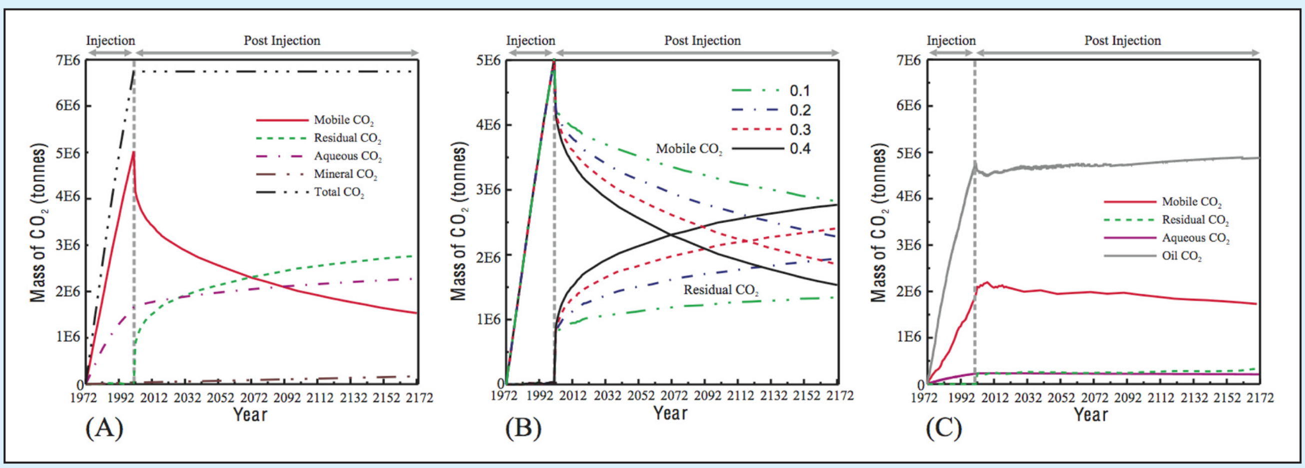


Figure 9. (a) CO_2 trapping mechanisms in brine-only model as a function of time, (b) sensitivity studies of mobile and residual-trapped CO_2 with   in brine-only model, and (c) CO_2 trapping mechanisms in brine+oil model as a function of time.

geostatistical porosity and permeability distributions have been used to upscale these two properties. One of the RCSP models incorporated log-normal distributions and normal distributions for upscaling permeabilities and porosities, respectively. Averaging methods were also used to upscale properties. For example, one RCSP used the harmonic mean for vertical permeability upscaling and the arithmetic mean for upscaling all other properties. Similarly, another of the RCSPs' models featured volume-weighted arithmetic method for porosity upscaling and volume-weighted geometric averaging for permeability upscaling. One RCSP model used an equivalent resistor network model ("renormalization") to upscale permeabilities and volumetric averaging for the porosities. Log-to-grid block upscaling was used in another RCSP model.

In addition to property assignment within grid blocks, dynamic reservoir simulations of CO_2 injection also require a description of the initial state of the system and boundary conditions for solving the partial differential equations. The initial state of the injection formation in various partnership models was site-specific. Many models used hydrostatic pressure gradient to initialize the pressure field, while others used downhole/well pressure measurements. Likewise, where logging data was available, downhole temperatures were used, otherwise, literature values were assumed. Similarly, CO_2-EOR injections used initial conditions (saturation) obtained from history matching the original oil in place (OOIP) and a general understanding of the particular reservoir. For cases where the hydrocarbon reservoir was previously water flooded, brine saturation, pressure and temperature were assigned appropriately. The pressure and temperature in models ranged from 25.9 MPa (3756 psia) and 110 °C (230 °F) to 4.7 MPa (681 psia), 24.5 °C (76 °F).

Similarly, a wide variety of boundary conditions were used in various models to account for the specific geological features at each site. No-flow boundary conditions were relatively common across all models (for example, to represent structural traps), and any fluid flow into the region of interest was appropriately represented by open-boundary conditions (such as an analytical formation, infinite-acting formation, or water-drive in hydrocarbon fields). For the special case of CO_2 injection into coal seams for ECBM, the boundary conditions were either open or had no-flow across interference lines between adjacent well producers.

Midwest Geological Sequestration Consortium: Modeling CO_2 Injection in Unmineable Coal Seams

The modeling used to determine the monitoring well locations with respect to the CO_2 injection well was developed through an iterative process, and closely tied to the field work and test results. At a different site considered during the screening process, permeability of about 50 mD was calculated from the DST of the coal. Because this permeability was higher than previously measured coal permeability in the Illinois Basin, the general purpose model's permeability was updated to 10, 25, and 50 mD, for equivalent coal permeability. Proximity of face and butt cleat monitoring wells to the CO_2 injection well was desired. The requirement was that within 30-60 days of continuous CO_2 injection there was a detectable and measureable change in pressure (with downhole gauges) and gas saturation (post-injection cased hole logging) at the monitoring wells. These thresholds were set at 1 psi pressure and a 10 percent gas saturation.

For the sensitivity study with the updated permeability, well locations were chosen at 150 and 300 ft in each direction. The modeling results indicate that nearly 100% of all scenarios had detectable responses at both wells within 150 ft. If the wells were spaced at 300 ft, only the face cleat well would have an adequate gas saturation increase. So the first two wells were drilled 150 ft apart in the butt cleat direction. DSTs of the Springfield coal at these two wells were below the lowest of the permeability range used in the model. Repeating the sensitivity with the DST based perms showed that the wells needed to be within 100 ft of the injection well. The pilot design plans were changed and the injection well was drilled between the first two wells and the face cleat monitoring well was drilled 100 ft from the injection well. During CO_2 injection, gas composition and pressure was measured at each well to validate the preliminary modeling.

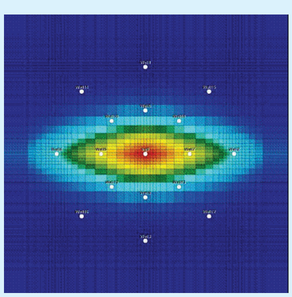


Figure 10. Example of CO_2 saturation for one sensitivity model run showing all face cleat well's (x-direction) with anticipated CO_2 breakthrough. Only the closest butt cleat well locations (y-direction) show breakthrough for this case.

4.3.3 Other Model Design Aspects

Data from all the existing wells within the storage site need to be accounted for, and incorporated into the models, so as to provide the most comprehensive "picture" of the geology, rock, and fluid properties of the site. In addition, data from wells outside of the storage site also should be assessed. Data obtained at a regional scale can be used to establish trends in formation thickness, continuity, and geologic structure, or build a geostatistical model. Property measurement in the same or similar formations can be used to supplement site-specific measurements. Models also need to reflect reality and incorporate properties similar to the downhole environment with the goal of simulating injection rates expected of the planned injection. Any grid reconstruction is also performed at this stage. These aspects are described in the following discussion.

In mature hydrocarbon basins with existing oil/gas production facilities, the simulation models incorporated these wells in specific patterns. Some of these models also included multiple production and/or monitoring wells. In cases where CO_2 injection into saline formations or basalt formations was modeled, typically only the injection well was included in the model.

Consistent with the RCSP goals, the simulations for the validation phase (Phase II) typically involved lesser amounts of CO_2 compared to the larger scale modeling studies (Phase III). The maximum quantity of CO_2 injection modeled for enhanced oil recovery was 1 million tons. The injection of 60,000 tons and 1 million tons of CO_2 was simulated in two other Phase III deep saline formation injection models, respectively. CO_2 injections of 18,400 tons and approximately 105,000 tons were modeled in other Phase III models. Additionally, an injection of 1,000 tons of CO_2 was modeled in a basalt borehole model (further details of the rates, time periods and quantities injected are provided in Table 5).

The time step and simulation time periods are strongly affected by the choice of the simulator, the goals of the simulation, the degree of coupling modeled, the amount of CO_2 injected, and the volume of the model domain. In most deep saline CO_2 injection simulations, the time step was variable or adaptive, with small time steps (of the order of minutes) during CO_2 injection, increasing with the size of the CO_2 plume. Post-injection period simulation time steps were on the order of months to years. Depending on the goals of simulation and the size of the model domain, the simulation time periods varied from at least a hundred years to 1,500 years to model the impact of CO_2 dissolution and mineralization on the CO_2 plume extent.

The simulation time period for the cases involving CO_2 injection into coal seams ranged from a few months to twenty six years, but the maximum time step in all three cases was of the order of months. The time period of simulation could also be set by regulators. For example, as per a request from Washington State, model simulations of CO_2 injection into basalt were performed until the CO_2 plume stopped moving (13 years).

The cases where CO_2 was injected into oil/gas reservoirs (CO_2-EOR, CO_2-Huff 'n' Puff) involved matching the historical field production starting from the field discovery through the waterflooding stage and any tertiary recovery via historical CO_2 injection prior to the simulation. The time steps during the history matching process were larger than those during the simulation and were adaptively varied. The time period of simulations predicting the fate and transport of CO_2 was of the order of hundreds of years to understand processes and parameters of interest to long-term stability of the injected CO_2 (such as area of review [AoR], monitoring design, and trapping mechanisms).

Plains CO_2 Reduction Partnership

Northwest McGregor CO_2 Huff ‘n’ Puff EOR Phase II Pilot Case Study

A CO_2 huff ‘n’ puff (HNP) EOR project was carried out in the E. Goetz #1 well located in the Northwest McGregor field in Williams County, North Dakota. The HNP was one of the Plains CO_2 Reduction Partnership Phase II field validation tests where CO_2 was injected into a fractured carbonate reservoir for the dual purpose of CO_2 EOR and CO_2 storage. The test involved the injection of 440 tons of CO_2 over 2 days and subsequent production from the E. Goetz #1 well following a 2-week soaking period. This HNP test represents one of the deepest operations of this type of EOR ever performed. Geologic modeling and numerical simulations were conducted with the goal to assess the area of review, evaluate CO_2 movement within the injection zone, estimate the impact of CO_2 injection, identify trapping mechanisms, and estimate incremental oil recovery. Another goal of the modeling was to verify and test the effectiveness of the cutting-edge RST and VSPs for use in monitoring.

The workflow for building the static geologic model involved data collection and normalization, petrophysical and facies modeling, and dynamic simulation with history matching (see Figure 11). The small-scale injection model contained only one well, so a larger-scale model containing several wells was built using sequential Gaussian and indicator simulations to determine trends and anisotropy. Then a smaller downscaled injection model was built using discrete and continuous multiple point statistics to model the gradational mudstone to a grainstone sequence common with platform carbonates while using a cropped portion of the large-scale model as a covariable. Through the analysis of core and drill stem test data, it was determined that, to more accurately model the reservoir, a fracture model was needed. This model was constructed using a discrete fracture network (DFN) simulation. The DFN model was then upscaled to the injection grid to produce a heterogeneous dual permeability and porosity model. This dual property model was then exported into the Computer Modeling Group’s Generalized Equation-of-State Model Compositional Reservoir Simulator, and the Computer Assisted History Matching, Optimization, and Uncertainty Assessment Tool was used to adjust the static model’s petrophysical properties, assisting in the history match of the reservoir’s historical production. Finally, the modeling and simulation work was integrated with time-lapse RST and VSP data to accurately account for the injected CO_2 and the produced water, oil, and CO_2.

By following this type of workflow, the complicated nature of the CO_2 HNP was modeled and matched to the monitoring techniques, displaying how this type of a workflow can be applied to other CO_2 storage projects. For the Northwest McGregor HNP test, it is expected that approximately 30% of the CO_2 will be produced back over time and the remaining 70% will be safely stored in the injection zone. The HNP achieved a notable improvement in both oil production and oil cut, proving that EOR operations remain viable, even in deep carbonate reservoirs. The use of HNP techniques on individual wells may be an attractive opportunity for carbon capture and storage by offering an economic beneficial use for CO_2 storage.

Plains CO_2 Reduction Partnership (cont'd)

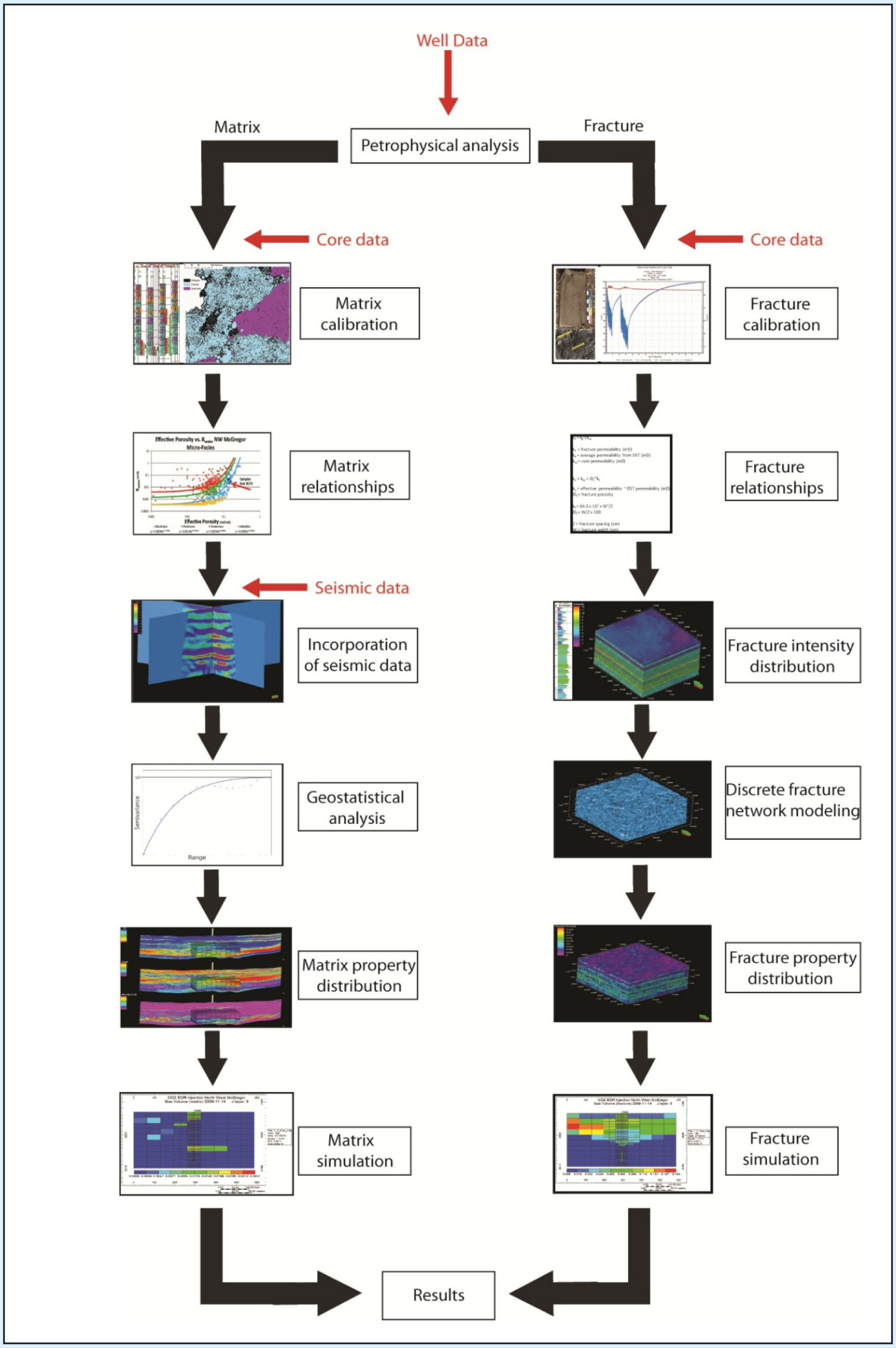


Figure 11. Modeling Workflow for the Northwest McGregor CO_2 Huff 'n' Puff EOR Project.

As outlined in preceding sections, an understanding of the sub-surface transport of injected CO_2, brine, oil, and other phases requires a description of multi-phase flow, thermal, chemical and mechanical processes. A brief summary of the simulation software used by various partnerships is provided in Appendix 3. Several partnerships report that the choice of model simulation software was influenced by previous familiarity with the software and performance in code-comparison studies. Furthermore, the following features were also listed by field project:

- Access
- Ability to model three-phase (oil, saline, CO_2) flows, with an option to simulate coupled geothermal and geomechanical processes
- Performance
- Ability to model multi-phase flow, coupled chemical, thermal and mechanical processes with emphasis on water, CO_2 and salt transport, CO_2 dissolution, and interactions with rock minerals
- Other specific features (such as hysteretic relative permeability and capillary pressure curves)
- Ability to model desorption-influenced reservoirs, which is critical to the injection of CO_2 into coal seams

Reconstruction of the model grid was performed if needed. Local grid refinement or coarsening was used in the some RCSP models. One RCSP model development adopted a two-stage approach. In the first stage, a *basic* COMET3 model was constructed to estimate the plume migration and determine the location of the monitoring well. In the second stage, the CMG-GEM simulator was used for history matching the injection data and plume monitoring during and after CO_2 injection. Simulation results suggested another RCSP model to be too small to act as an infinite reservoir, and alternate boundary conditions were applied.

In addition to grid refinement, model properties were modified either to obtain better matches with historic production data or monitoring data acquired during the CO_2 injection in some cases. For example, the porosities, permeabilities, and relative permeabilities were history-matched to field data in the some RCSP models. Geophysical logs were renormalized for better convergence in other RCSP models..

Simplified models were iteratively refined in the subsequent steps of the modeling process. For example, the history matching process one RCSP model was initialized with a uniform geologic model base case which was subsequently refined to develop a better history match for the final heterogeneous case. Similarly, the history-matching process for another RCSP model initially only involved the CO_2 and CH_4 components. It was subsequently updated by a history match process involving multiple components (CH_4, CO_2, and N_2). Model properties were calculated with the ECO2N (accounting for brine density dependence on dissolved CO_2) equation of state (EOS) instead of the ECO22 EOS in one RCSP model. Further sensitivity studies using multiple injection rates, injection intervals, and initial conditions (temperature, pressure, salinity) were performed in the model simulations to assess their impacts on plume migration.

4.4 Model Evaluation, Calibration, and Modifications

Numerical simulations of CO_2, brine, methane, and oil flows need to be calibrated with any pre-existing field data and evaluated with actual injection data so that stakeholders can gain confidence in their predictive capabilities. The evaluation criteria used by the RCSPs in various models depended on the type of injection, previous field history, whether actual injection had already taken place, the type of monitoring techniques that were deployed in the field, and other variables.

Previous field history (production) data are not generally available for the deep saline injections. Therefore, these saline formations were evaluated by using the injection rates, pressures, downhole temperatures, CO_2 plume migration, the times required for plume stabilization, CO_2 dissolution and the distribution of CO_2 among various phases as the criteria to evaluate and calibrate models. In cases where actual CO_2 injection occurred, the collected injection data were used to calibrate and update the model. Additionally, the one RCSP model was updated using a crosswell seismic study to delineate the CO_2 plume in the subsurface. A basalt pilot model was also evaluated using CO_2 plume extent, velocity, and distribution of CO_2 in the aqueous, mineral and supercritical phases.

On the other hand, fairly extensive historical production data was available for the cases of CO_2 injection into depleted oil/gas reservoirs. In all these cases, the model was evaluated partly based on production- and pressure-history matching, breakthrough times, phase saturation at monitoring wells, and plume geometry from monitoring measurements. However, the parameters varied for calibration were different. For example, porosity cutoffs were varied in one model to match the original oil in place (OOIP), whereas field boundary conditions and other variables such as fracture intensity, fracture permeability, and water saturation were adjusted to match the production and pressure data in another model. The net CO_2 storage from historical EOR operations was matched with field data to calibrate yet another model. The EOR models were not updated with injection/production history data subsequent to the current CO_2 injection phase.

Similar to the cases of CO_2-EOR and CO_2 Huff ‘n’ Puff, history matching was used to evaluate model results in ECBM models. Butt- and cleat-face permeabilities were calibrated with water pressure transient analysis prior to CO_2 injection in one model and history matching the field production data was used to calibrate the second.

4.5 Numerical Simulations and Analyses

4.5.1 Pre-Injection Analyses

The RCSPs’ goals for pre-injection analyses were site-specific. They included both site screening and pilot design. Site screening involves the selection of an optimal site among various candidates, mainly by comparing the storage capacities and the injection rate. Pilot design includes the selection of an optimal injection and/or production and/or monitoring scheme, delineating the area of review (AoR), understanding CO_2 trapping, and estimating incremental oil recovery for the EOR/Huff ’n’ Puff projects. Various simulated outcomes were studied to test the ability of a particular site or pilot design to achieve the goals. These simulated outcomes included:

- Estimation of the volume of CO_2 stored.
- Incorporation of wellbore pressure monitoring to check for injectivity issues.
- Determination of the AoR by the CO_2 plume locations at various times.
- Increased understanding of trapping mechanisms (structural, physical, mineral) by examining the modeled results for CO_2 distribution in the mobile, immobile and dissolved forms, and also quantification of the incremental oil production in the EOR cases.
- Identification of optimal sites for the monitoring wells from the CO_2 plume extent, and breakthrough times in the case of hydrocarbon reservoirs.

Optimal injection schemes were obtained by parameter sensitivity (permeability, well-location, injection pressure, reservoir injection intervals) analyses and economic (net-present value)) analyses. Sensitivity studies help to identify the parameters/processes limiting CO_2 injection rates. For example, in one model, the maximum CO_2 injection rate was limited by the CO_2 tubing perforations and pressures, and not by the properties of the formation. The injection rate was constrained in another model by setting the upper limit of the bottomhole pressure to be the lithostatic pressure. Field measurements were also used to determine optimal injection schemes. Pilot site screening and optimal injection schemes were determined through the oil response results and/or modeling CO_2 breakthrough at individual wells during the simulation.

4.5.2 During-Injection Analyses

At this stage of project development, numerical simulation results were used to assess the performance of the model against expected outcomes (known as model calibration or fine-tuning), for revising any formation properties that may change as a result of CO_2 injection (e.g., brine density, coal swelling) and for the design of the monitoring system. The specific outcomes that were investigated for model calibration and modifications included:

- Monitoring *real-time* or *simulated* pressures at the injection and/or monitoring wells.
- Comparison of injection/production data from model simulations with actual CO_2 injection, and/or hydrocarbon production data.
- Tracking CO_2 migration through estimates of plume geometry and CO_2 phase saturations for monitoring design.

Various partnerships reported changes in the input model parameters, the conceptual model, and the formation properties at this stage. These included:

- The addition of hydraulic fractures
- The modification of relative permeabilities and wellbore skin
- The performance of sensitivity studies, and
- The conducts of case studies on the effects of CO_2 injection rate and the permeability were conducted in another model.

4.5.3 Post-Injection Analyses

The most common goals of post-injection analyses are long–term monitoring of the fate of injected CO_2 (tracking CO_2 plume and anticipating any breakthrough at production or monitoring wells), and prediction of additional oil recovery (in the EOR models). The simulated outcomes used to test whether the model could achieve the goals were:

- Tracking the spatio-temporal movement of the CO_2 plume.
- Estimates of additional oil produced (for the EOR injections).
- Estimates of long-term CO_2 trapping, dissolution, and precipitation (for the deep saline injections).
- Pressure history, phase saturations and CO_2 plume geometries (for risk analysis and long-term monitoring -AoR) Predictions of CO_2 breakthrough times at production and/or monitoring wells.
- Tracking permeability changes with pressure to improve CO_2 injectivity, ECBM production and CO_2 storage (CBM models).

Midwest Regional Carbon Sequestration Partnership: Phase II Michigan Basin Test Site

Model Calibration and Refinement

The MRCSP Phase II Michigan Basin test involved injection of approximately 60,000 metric tons CO_2 in two injection events from February 2008 to March 2008 and February 2009 to July 2009. The site was located in the northern portion of the Michigan Basin, a large, mature sedimentary basin that covers most of Lower Michigan. The CO_2 storage interval included carbonate rock layers at a depth of 3,190 to 3,515 feet, including the porous portions of the Bois Blanc to the Bass Islands Dolomite Formation. The actual interval for injection was within the Bass Islands Dolomite at 3,442 to 3,515 feet, the most permeable section of the storage zone. Little information was available on these formations, because they did not contain oil or gas. Consequently, a test well was drilled to characterize the injection zone prior to injection. The CO_2 storage process was simulated with Subsurface Transport Over Multiple Phases - water, CO_2, salt, energy (STOMP-WCSE).

During this test, the reservoir model was adjusted based on site characterization and monitoring data to better match observations:

- Preliminary reservoir simulations were completed based on regional data to provide guidance for a site characterization program. These simulations input general parameters based on regional data.
- Site specific modeling was completed after a test well was drilled based geotechnical parameters and geophysical logs obtained from the test well. This information was used to establish an appropriate monitoring program, operational guidelines, and risk analysis.
- After injection, the model was calibrated to field monitoring results. The actual injection schedule was input into the model. The model was primarily calibrated to transient pressure and temperature readings measured in the injection well and monitoring well, because these parameters were readily available.
- After additional injection, the model was further adjusted to match CO_2 distribution in the subsurface including geophysical logging, microseismic monitoring, geochemical analysis, and cross-well seismic imaging. This validation process required an additional series of modifications to the model to match the observed CO_2 distribution. In general, the complete suite of monitoring technologies from the Michigan site suggested that the CO_2 moved further upward in the storage zone than the model suggested. Therefore, it was necessary to adjust some of the hydraulic parameters in the CO_2 storage zone such as vertical permeability and porosity matrix.

Midwest Regional Carbon Sequestration Partnership: Phase II Michigan Basin Test Site (cont'd)

The MRCSP Phase II Michigan Basin test highlights the model development process from initial simulation to validation with a suite of monitoring technologies. The storage formation was a carbonate rock, which presented complex reservoir conditions. As more information about the deep rock formation was obtained, the model was updated to determine a more accurate solution. In fact, significant changes were made to the base conceptual model as additional injection was completed and more meaningful monitoring results became available.

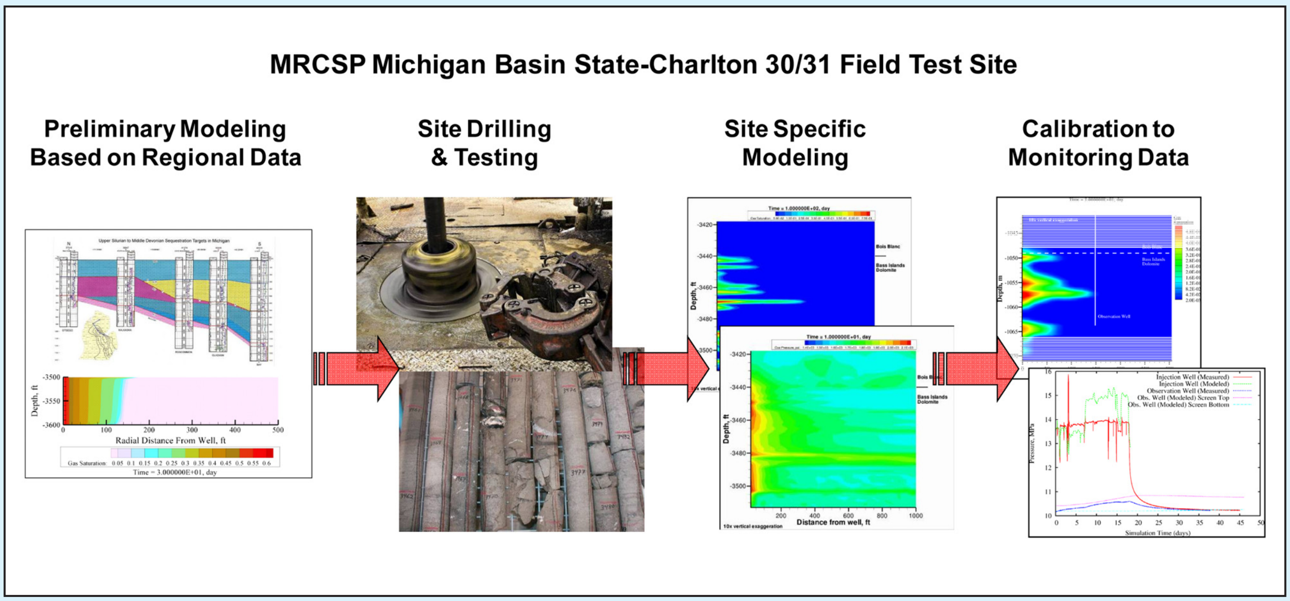


Figure 12. Example of the Modeling Process for MRCSP Michigan Basin Phase II Test Site.

Confining Zone (Caprock) Analysis

Confining Zone (caprock) refers to a lithological sealing sequence or top sealing interval overlying a reservoir lithology, which restricts upward migration of buoyant non-aqueous or overpressured aqueous pore fluid from the reservoir. Confining zones are typically composed of fine-grained rocks with tiny pores, such as mudstones, or relatively non-porous rocks such as evaporites. The confining zone- injection zone couplet constitutes a *trap*, or geologic container capable of both storing and retaining fluids over geologic timescales. In the petroleum industry, traps are categorized as stratigraphic (i.e., reservoir extent is limited due to unconformities or pinch-outs) or structural (rocks are folded with an inverted dome or bowl-shaped confining zone, or faulted) (Schlumerger, 2010); but can also be diagenetic in origin or arise from capillarity contrasts. Traps may also be hydrodynamic, where buoyant migration can be opposed by hydrodynamic potential. These trap concepts are directly applicable to CCS efforts, however it is not clear if a hydrocarbon trap works as efficiently in containing supercritical CO_2 ($scCO_2$). Thus the ability of a proposed confining zone to restrict upward migration of CO_2 directly impacts the success of CCS efforts and some of the inherent risks.

Since the 1950s, the petroleum geosciences have developed conceptual models of how confining zones operate, with sophisticated methods to quantify the ability of confining zones to retain hydrocarbons (Watts, 1987; Weber, 1997; Deckelman et al., 2006). Models have focused on: capillary sealing behavior, permeability and multiphase flow, variation in sealing quality due to sequence stratigraphic controls, mechanical failure, and behavior as faults as conduits or barrier to fluid flow. Characterization methods have been of major importance for exploration and production efforts and include capillary pressure measurements, seismology, core collection and analysis, downhole geophysical tools, and outcrop analogs. Traditional key goals have been to quantify the *sealing capacity*, the height of the hydrocarbon column that can be retained by a particular confining zone, and to predict variations of sealing capacity over the scale of entire reservoirs. It may be advantageous to CCS efforts to refer similarly to confining zone sealing capacity for CO_2.

Due to differences in hydrocarbon and engineered CO_2 storage systems/traps, geologic CO_2 storage has spurred new research on confining zone during the past decade, some aspects of which are discussed below:

- CO_2 has different wetting characteristics than hydrocarbons. This impacts interfacial tension for CO_2/brine/confining zone systems (Chiquet et al., 2007a), which affect capillary breakthrough pressure and multiphase fluid flow. CO_2 – brine-mineral systems typically have lower interfacial tension than hydrocarbon-brine-mineral systems (Chiquet et al., 2007b), which could imply lower breakthrough pressures for CO_2-sealing confining zones compared to hydrocarbon-sealing confining zones.
- Capillary breakthrough pressures for the CO_2/brine/confining zone system are needed to design and implement CO_2 storage. Only limited data in terms of contact angles for confining zone minerals is currently available in the literature, which affects estimation of capillary breakthrough pressures from knowledge of pore sizes (Chiquet et al., 2007a), and it is not clear how these mineral data scale-up to be applicable to reservoir-scale models. Some researchers avoid the need for different knowledge of wettability by performing capillary breakthrough pressure measurements directly on plug samples using CO_2 and brine (Wollenweber et al., 2010).
- CO_2 has enhanced reactivity relative to hydrocarbons, which is evaluated using experiments and numerical modeling (Gaus et al., 2005; Johnson et al., 2005; Gaus, 2010). Modeling efforts assess impacts on porosity, permeability, and fluid flow. Precipitation/dissolution reactions have received more attention than intermolecular interaction that govern sorption or wettability. Dry-out due to injection of anhydrous CO_2 is a concern due to potential crack/fracture formation and other effects, but has not yet been studied in detail (Gaus, 2010).
- Natural, pre-existing fractures or induced fractures are relevant to CO_2 injection activities (Hawkes et al., 2004; Nelson et al., 2009; Rohmer and Bouc, 2010). Of interest are time-dependent processes that may heal or further open fractures due to coupled fluid flow and reactive transport (Gherardi et al., 2007). In spite of their names, confining zone or seals can contain local high permeability features or *seal bypass systems*, which can lead to significant migration of fluids from a reservoir (Cartwright et al., 2007). Identification and characterization of seal bypass systems is still a major research challenge, especially on the regional scale (DOE, 2007).
- Prediction of confining zone properties is difficult due to the heterogeneity of rocks that constitute mudstones. Previous research in the petroleum geosciences has developed useful predictive tools based on sequence stratigraphic methods, which aim to describe variation in sealing capacity due to geologic conditions (e.g., primary depositional environment, burial history, and diagenesis). These methods are being adapted and applied to confining zones at CO_2 storage sites (See Figure 13).

Confining Zone (Caprock) Analysis (cont'd)

- A confining zone that may permit some brine migration, yet serving as a capillary seal for CO_2, may be advantageous for pressure hazard mitigation in reservoirs (Chadwick et al., 2009). So-called waste zones, or lithologic units with transport properties lying somewhere between confining zone and reservoir, may serve in such a capacity.
- Risk assessment in the CO_2 storage community for confining zones has been developing along two lines: 1) One approach is focused on using risk assessment principles for site characterization and selection (Oldenburg, 2008; Oldenburg et al., 2009); and 2) Another approach uses risk assessment to determine what confining zone features and processes will govern the sealing behavior (Rohmer and Bouc, 2010), and which processes are the more significant.

The state of the art for confining zone assessment, thus, focuses on processes occurring at the pore scale which control sealing behavior, but also include analyses of larger-scale bypass features that could lead to significant fluid loss from the reservoir. Time-scales of coupled THMCB processes that operate within and around confining zone lithologies still require examination through natural analogs, laboratory, and numerical modeling, and direct field tests to better constrain potential leakage mechanisms, rates of CO_2 leakage, and coupled dynamic, evolving behavior.

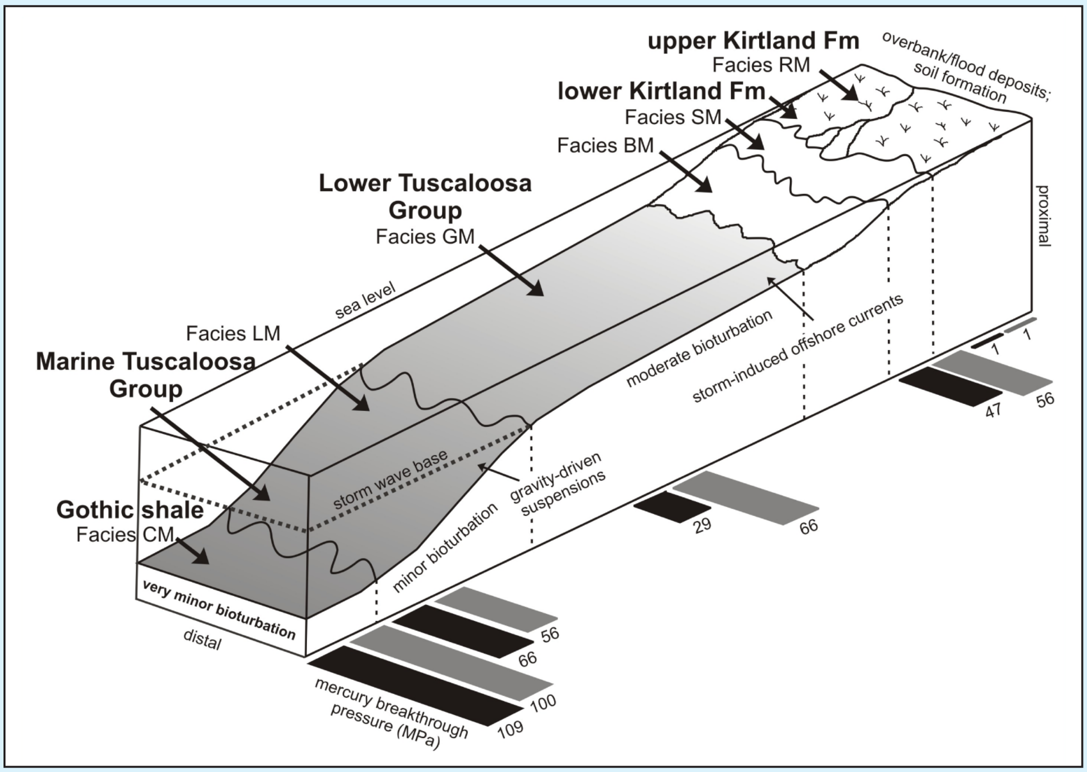


Figure 13. A mudstone facies model annotated with mercury breakthrough pressures and formation or group names of confining zones at Phase II sequestration demonstration sites of the Southeast and Southwest Regional Carbon Sequestration Partnerships (Heath, 2010, modified from Schieber, 1999).

The mercury breakthrough pressure is a measure of the pressure needed to intrude a non-wetting phase into the rocks. These data are used to estimate the CO_2 breakthrough pressures. The black and gray bars represent measurements on two rock samples from the same depth. In general, the distal (towards deeper water) environments, such as that of the Pennsylvanian Gothic Shale in the Paradox Basin, Utah, have high breakthrough pressures due to very small pore associated with small grain sizes. This is largely due to primary depositional environment, but the effects of burial diagenesis cannot be downplayed. More proximal facies have larger pores and more silt, which can lead to very low breakthrough pressures. Other rock types in the study include the Cretaceous Kirtland Formation in the San Juan Basin, confining zone for the SWP Pump Canyon injection site, and the Cretaceous Tuscaloosa Group, confining zone for SECARB's Plant Daniel and Cranfield sites.

4.6 Risk Analysis Methodologies Used by Various RCSPs

The background details of risk analysis, were discussed in Section 2. This section describes the specific approaches used by partnerships at each step of the risk analysis.

4.6.1 Context and Problem Formulation

The process of risk analysis may be initiated by defining the objectives of risk management, or success criteria for a particular project. The roles and responsibilities of various internal stakeholders are identified, and the resources necessary for effective implementation of the risk management plan are allocated. The timing and frequency of risk management steps are defined and any changes to the risk registry or the risk management plan itself are iteratively performed. Any project-specific metrics (frequencies, physical consequences and severities) may also be defined at this stage. Several of the RCSPs incorporated risk analysis methodologies as a first step.

4.6.2 Risk Source Assessment

Subsequently, the technical and programmatic risks of CO_2 injection are identified, typically by using a FEP approach (e.g., BSCSP, PCOR, SWP, and MRCSP). Public databases and site-specific functional analyses were used to prepare a risk register with a list of potential failure modes, causes and consequences. Individual risks may be ranked by frequency and/or severity by an expert panel at this or the subsequent stage. Any potential responses to each risk may also be identified at this stage. Not all partnership models explicitly used the FEP approach for risk identification. For example, (FEP-like) tiered-screening criteria used for the MGSC risk assessment methodology include:

- Type of CO_2 injection (miscible-liquid, immiscible-gas, miscible-supercritical, intermediate).
- Development history of the oil/gas field.
- Location of the well with respect to lakes/ponds, flood plains, homes, major highways.
- Wellbore conditions such as number of zones currently completed in the injector, ability to isolate zones in single wells, type of completions and the recent injection pressure history.
- Qualitative assessment of the geologic/reservoir modeling results (i.e. injection patterns for which oil production and pressure results would be measurable and quantifiable within the planned duration of CO_2 injection).

Similarly, another non-FEP-based general risk assessment approach in the MGSC Phase II operations was to understand potential risks during CO_2 injection by understanding historical operations at the sites and the current operators' role in the day–to-day activities of existing oil fields. Illinois Basin oilfield operators that diligently practice responsible and safe oilfield production protocols were identified. Further, with these operators' cooperation and general pilot descriptions requirements from MGSC, they nominated oilfields or coal sites for consideration for the MGSC pilots, which were further studied qualitatively to understand and minimize project risk.

4.6.3 Risk Characterization

The next step in the risk analysis methodology is a qualitative, semi-quantitative or quantitative characterization or estimation of the risks. Expert inputs were typically elicited at this stage to collate the hundreds of identified FEPs into a more manageable number of prioritized risks to serve as inputs for either risk mitigation or quantitative risk assessment. In the FEP-based approach, project risks were ranked or prioritized (e.g., risks requiring short-term response) relative to one another, and were categorized by the root cause and potential impacts. Furthermore, uncertainties (e.g., risks requiring more analyses/investigations) were also identified at this stage.

Subsequent to the risk identification stage, the probability of occurrence of a particular risk can be either qualitatively or quantitatively determined. In a semi-quantitative approach, the probability of occurrence of a certain risk is obtained via expert panel-inputs. One example of a semi-quantitative approach is the risk pathway analysis methodology used by the MRCSP is to identify and preliminarily assess the key phenomena that mediate the leakage of CO_2 and the CO_2 fluxes and concentrations in each of the environmental media affected due to the leak. Model simulations were used to calculate the migration of CO_2 and its concentration in each of the affected environmental media. The outputs of this analysis are being used as inputs for the consequence and risk assessment calculations, using a risk-matrix approach.

A second example of a semi-quantitative risk assessment methodology is that being used by the PCOR. Using the PCOR risk assessment methodology, the "severity" of CO_2 leaks to the surface and various shallow receptors (USDW and other hydrocarbon mineral resources) were calculated from the consequences of CO_2 leakage using a risk-transfer matrix approach. Further, the frequency of occurrence of a particular risk was assigned by various internal stakeholders and validated by an expert panel. The impacts due to individual risks were then calculated as a product of the severity and the frequency of each risk.

A third example of the application of semi-quantitative risk assessment is Schlumberger's Carbon Workflow process, used by the WESTCARB. The goal of the assessment was to establish a basis for allocating resources for risk reduction, and provide a structure to document and track risk reductions. In this process, risks associated with FEPs were evaluated against pre-defined *project values* on a likelihood-severity scale (i.e. risk matrix approach). Risks were evaluated against health and safety-, financial-, environmental-, research- and industry viability-impact aspects of the project. In the Carbon Workflow process, invited experts (divided into two cohorts comprised of six groups each working on specific project aspects such as air, surface, near surface, subsurface) ranked project-specific, pre-screened (50 to 80) FEPs by project risk. Prior to the ranking, the groups of experts received training on project-specific data and risk assessment methods. For each project value, a wide-range of potential negative impacts was expressed on a five-category severity scale. Similarly, experts were asked to estimate likelihood of negative impact on a five-category scale, based on their expectations relative to an arbitrary standard of "100 similar projects during 100 years". Three estimates for each likelihood and severity, corresponding to a lower bound, best guess and upper bound value were collected to represent approximate confidence measures. Such scales are arbitrary, but provide a consistent basis for comparisons. The product of the likelihood and the severity values was used to compare the FEPs in terms of estimated-risk levels. These expert-elicited inputs were used by a panel to generate key scenarios from higher-ranked FEPs for each aspect of the project. Subsequently, Risk Response Actions (RRAs) for scenarios, grouped in Risk Response Action Groups (RRAGs) were provided to the risk/project manager and assigned to individuals for completion, documentation and periodic-risk review.

In contrast to the semi-quantitative risk assessment tools, quantitative risk assessment tools such as Certification Framework (Oldenburg et al., 2009) used in the WESTCARB, SECARB risk assessments, and CO_2-PENS (Stauffer et al., 2009, Viswanathan et al., 2008, Zhang et al., 2006) used in the BSCSP and SWP risk assessment studies enable the calculation of probabilities and an estimation of the consequences of leakage. As defined in Section 1, risk is a product of the severity and the probability of its occurrence. The purpose of a quantitative risk assessment is to quantify the probability of occurrences of events leading to risks and their impacts. The impacts of CO_2 leaks through abandoned wells, confining zones and faults/fractures are the focus of this discussion.

Two RCSPs are utilizing performance assessment (PA) (based on LANL's CO_2-PENS systems modeling approach) and consequence assessment to quantify risks. As shown in Figure 15, CO_2-PENS is used to predict the probability of CO_2 leaks to other reservoirs, ground water, surface, and atmospheric systems. Similarly, the Certification Framework also predicts the probability of CO_2 leakage into a "compartment", albeit using a different methodology. In addition to these probabilities, evaluation of risk also requires an estimate of the impacts or the severity of a particular event. Risk impacts are evaluated by consequence assessment in the BSCSP and SWP risk assessment methodologies. In contrast, they are estimated based on the concentration or flux of CO_2 in a particular compartment in the Certification Framework. The following discussion focuses on the Certification Framework and CO_2-PENS system modeling.

Estimates of parameter uncertainty, in the form of probability distribution functions (PDFs) are required for quantitative risk assessment. The SWP is employing both experimental design-based methods and Bayesian probabilistic formalisms to estimate parameter uncertainty, as described briefly in Section 2 of this document. A Bayesian probabilistic approach is being used to develop initial PDFs for data gained from previous and ongoing research and field tests. Fully-coupled reservoir/confining zone models are being used as a basis for defining the PDFs for each FEP, as appropriate and the suite of PDFs would be updated with new data as required.

Southeast Regional Carbon Sequestration Partnership

At SECARB's Cranfield "early test" site, the setting is a mixture of what programmatically has been separated into two classes – injection into deep saline formation for storage only and injection into an oilfield for the purpose of EOR. At the Cranfield site four injection wells were drilled into the lower Tuscaloosa D-E sandstones into the downdip "water leg" (saline formation). This is the unit from which injection and production for EOR is underway higher on the anticline, however the downdip wells intersect this unit below the oil-water contact to support the project needs (Figure 14). One of these down-dip saline formation wells was selected as the detailed area study (DAS) for focused monitoring and monitoring studies. Two dedicated observation wells were installed at the DAS to facilitate collection of cross-well data. The DAS serves as the detailed part of the model, where history matching of observed reservoir response to modeled response is underway. Other wells in the oil-bearing zone serve as far-field monitoring points. In a site where monitoring saline formation response to injection is combined with beginning EOR operations in the adjacent oil field, the question arises of the extent to which association with EOR dominates the results. Does risk assessment, modeling, and monitoring inform stakeholders about saline injection or about EOR?

SECARB assessment shows that during the early stages of this project, assessment of reservoir performance at the downdip injectors can be simplified to not explicitly consider the complex aspects of EOR. This simplification takes into consideration assessment of three aspects: (1) compressibility; (2) antecedent conditions, and (3) project evolution. A generic study was conducted into the effect of compressible fluids, in particular a produced gas cap at residual saturation, on performance of injection at the DAS. The results of this study show minimal effects unless the gas cap is very close; the approximately 1,000 foot horizontal distance estimated between the DAS injector and the oil water contact is sufficient that the impact of compressible fluids on the CO_2 plume is negligible. Unique antecedent conditions at Cranfield make this site more like saline storage during the early stages of the project than most EOR. Cranfield field was idle from the end of production in 1966 until the start of injection in 2008, during which time strong natural water drive allowed pressure in the reservoir to return to nearly hydrostatic conditions. This is the same pressure conditions which are found in a saline formation setting, and differ from most EOR operations. Most EOR immediately follows a long period of production and water flood during which fluid compositions and pressures are complexly perturbed; this did not happen at Cranfield. Lastly, the Denbury EOR operations at Cranfield started identically to the conditions at a large saline injection in that injection occurred without production. Denbury uses reservoir-sourced gas lift rather than pumps, so in the period prior to CO_2 breakthrough or significant pressure increase, wells did not produce, and the production aspect typical of EOR is not needed in the model. However, as production increases in the oil zone of the field, it is considered in the model in terms of volumes of equivalent water production.

The risk profile is strongly dominated by the EOR aspects. Risk is managed by the EOR operator under well-known existing commercial processes. Over the long term, pressure is actively managed; observations at this site show that maintaining pressure requires aggressive management to keep pressure up because of open boundaries at the scale of injection. Well completions provide the area of highest risk-management focus and the site will provide early information to the DOE program on this important issue. Modeling and history matching within the EOR part of the field was undertaken in Phase II and CO_2 – oil miscibility had, as expected, a relatively strong impact on flood performance, therefore a modeling project within the oil rim must use a simulator that can deal with the relevant phases. In addition to making possible an early Phase III opportunity at large volume, injection associated with an EOR project increased the speed of permitting, facilitated public acceptance, and reduced infrastructure costs, which allowed a strong focus on the monitoring program.

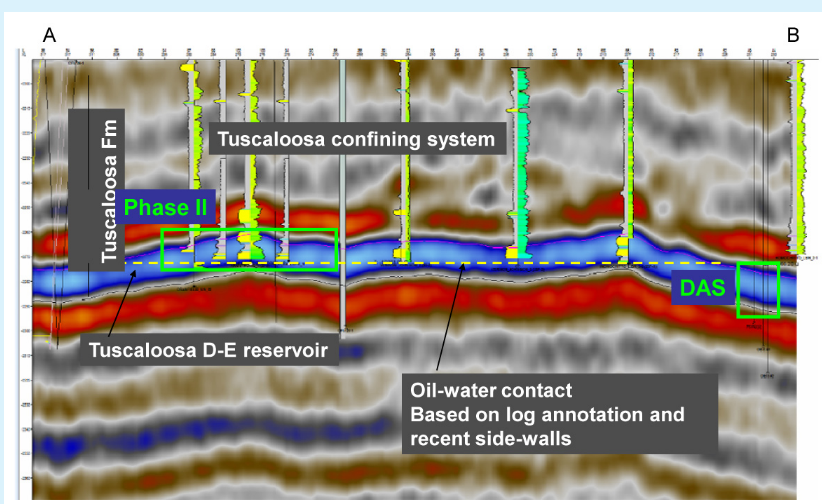


Figure 14. Location of the Phase III Injection Below the Oil-Water Contact.

CO_2-PENS

CO_2-PENS is a system risk analysis model suite using the commercially available GoldSim system programming software. In this architecture, mathematical descriptions of the system can be developed as analytical expressions in GoldSim and, when necessary, as a separate program called by CO_2-PENS via a dynamically linked library. This structure allows detailed simulations of phenomena such as reactive transport of CO_2 and brine within an injection zone. CO_2-PENS can develop a probabilistic description of the aspect of interest using a Monte Carlo simulation approach by feeding various realizations of parameters to the DLL subroutine. LANL has already developed linkages between CO_2-PENS and one of its process-level reactive flow codes (FEHM), and as part of the risk activities in the Southwest Regional Partnership, it is developing linkages to the necessary codes being used to describe the reservoirs at the Gordon Creek and BSCSP field sites, including TOUGHREACT and FLOTRAN. Other linkages currently implemented in CO_2-PENS include ties to Princeton's analytical representation of wellbore release/transport and to PHREEQ-C (to simulate water-CO_2-rock interactions in groundwater reservoirs. The site-specific CO_2-PENS model would be used to calculate probabilities which would be coupled with consequence analysis. The combined risks would then be used to determine overall project risks and also help understand the impacts of uncertainties in various parameters on overall process risks.

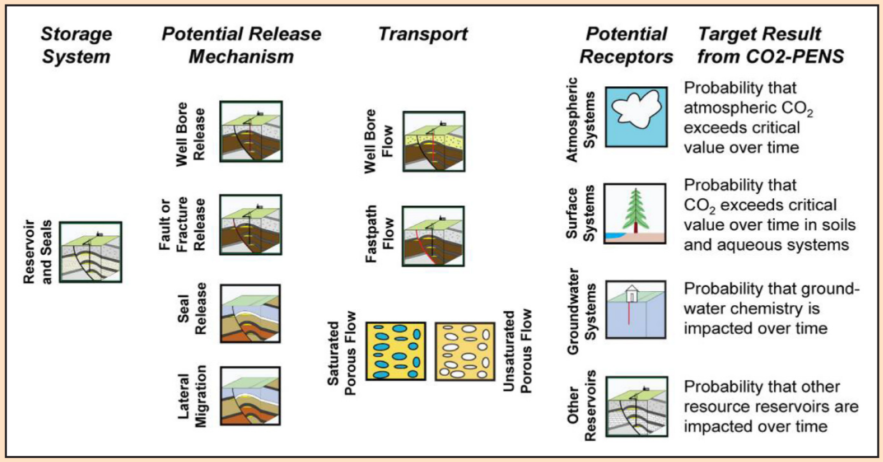


Figure 15. A Schematic Diagram Illustrating the Framework for the CO_2-PENS System Model, which allows a Probabilistic Assessment of Events of Concern.

4.6.4 Risk Management

The ultimate objective of effective risk analysis is to develop an optimized new scope of work that also includes maximum preventive actions to mitigate subsequent occurrences of the risk element(s) in question. The results of qualitative, semi-quantitative, or quantitative risk analyses, provide the basis for developing a comprehensive risk mitigation program.

For example, in the Certification Framework approach, if the CO_2- and/or brine-leakage risks (CLR, BLR) are above the threshold, changes to the injection plan or refinements in site characterization may be made, resulting in decreased CLR/BLR. Additionally, in the CO_2-PENS approach, comprehensive risk assessment would provide insights into the specific FEPs/actions which lead to the risks. This information would be used to identify technologies and approaches that can be deployed to minimize the risks. Mitigation approaches would rely heavily on monitoring and might include:

- Water injection into the reservoir above the primary confining interval to pressurize the formation.
- Water injection into the primary reservoir outside the CO_2 plume to contain the CO_2 and prevent migration.
- Reducing reservoir pressure by venting CO_2 to atmosphere, or by producing brine/water.

In one risk analysis methodology, the results of the qualitative risk pathway analysis were used to develop monitoring and mitigation programs. Monitoring techniques were chosen based on the size and scope of the demonstration. Monitoring results were used to update risk analysis results and assess the long-term security of CO_2 in the subsurface. A mitigation program was developed as a part of the monitoring work plan at the test sites and included features such as automatic shut-off systems for excessive injection pressures, standard oilfield practices for assessing cement bond, casing integrity, and other well materials.

Another RCSP's generalized mitigation plan consisted of identifying potential problems with safety of truck delivered CO_2 to location, operations of CO_2 injection equipment, transportation of CO_2 through an injection

Certification Framework

The Certification Framework (CF) is a simple and transparent methodology to estimate the risks of CO_2 and brine leakage in CCS operations. The CF is a risk-based approach that uses two likelihoods to estimate probability of leakage through wells and faults. The first is the likelihood of intersection of the CO_2 (or brine) source with a conduit. The second is the likelihood of intersection of the conduit and a compartment (which is a collection of vulnerable entities). The various compartments considered in the CF approach (as shown in the Figure 16) are emission credits and atmosphere (ECA), health and safety (HS), near-surface environment (NSE), USDWs, and hydrocarbon and mineral resources (HMR). The product of these likelihoods is the probability of the given source-to-compartment leakage scenario. The risk associated with that leakage is the product of the likelihood of leakage and the impact of that leakage event. In the CF approach, the probability of impacts to various compartments may be calculated using fuzzy rules. Impacts of CO_2 to compartments are evaluated in the CF by modeling and simulation of proxy concentrations or fluxes. The CF does not calculate impacts of CO_2 (or brine) on particular individuals or species within a compartment, as is done for example using exposure and behavior modeling (e.g., McKone, 1993). Instead, the CF assumes that there are agreed upon limits on CO_2 or brine concentrations within the compartment as a whole, or on fluxes into the compartment, that can be established to ensure acceptable impact to the compartment. The numerical value of these limits will be specified in regulations that may vary by country but will presumably be scientifically based, perhaps on natural analogue studies. Whether a concentration- or flux-based limit is appropriate depends on the context and compartment.

The overall work flow of the CF approach is summarized below. External inputs are required to characterize the site and define the reservoir, injection plan, and time frame. These inputs constrain the conditions and properties needed to estimate the CO_2 (source) plume location, footprint size, and pressure perturbation. The estimate can be obtained from a suitably sophisticated reservoir simulation, or from a catalog of pre-computed simulations. Next the CF uses external inputs on wells and faults, typically the plan-view spatial density and depths of abandoned wells and conductive faults. The likelihood of the plume intersecting the conduits is a function of the plume size and conduit spatial density. The output of the reservoir simulation is fed to the conduit flow model to calculate fluxes and/or concentrations within compartments under the assumption that they intersect. Using the externally supplied limits on concentrations or fluxes in the compartments, the value calculated by the CF either exceeds the limit (is an impact) or falls below the limit (is not an impact). The severity of the impact can be calculated by the degree to which a flux or concentration exceeds the limit, e.g., as given by the area between the limit and the flux or concentration curve in a plot of flux or concentration versus time. The risk can then be calculated as the product of the impact severity and the likelihood of the corresponding intersection with conduits (leakage scenario) occurring. Comparing the calculated CO_2 leakage risk (CLR) to the externally provided threshold, the CF determines whether the leakage risk is acceptable. Although written in terms of CLR for brevity, the CF analysis of the brine leakage risk (BLR) follows the same flow process.

The CF approach is being used by WESTCARB and SECARB as a part of their risk assessment studies.

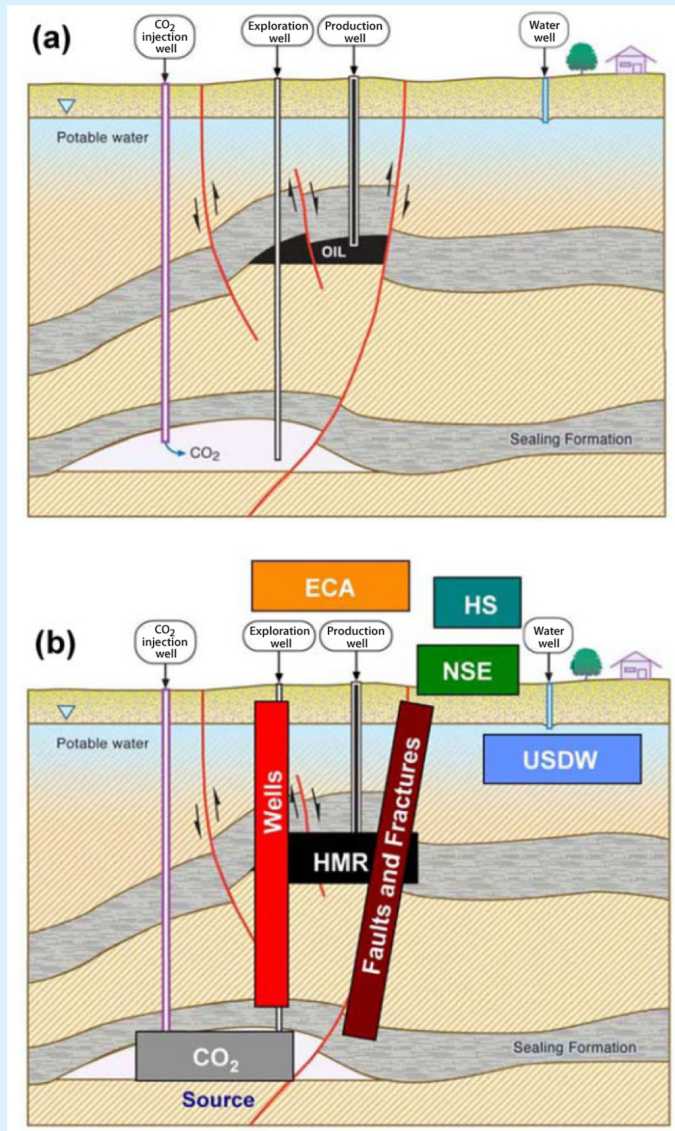


Figure 16. (a) Generic Geologic Cross Section of Potential GCS Site Showing Reservoir and Confining Zones, Faults, Wells, USDW, and Near-Surface and Surface Environments; (b) Generic Cross Section with CF Source and Compartments Overlaid. (Courtesy of WESTCARB)

flowline, operation of injection and production wellbores, and separation of produced fluids through a tank battery. As a result of the rigorous site screening process, the likelihood of operational problems was minimized. Further, the collaboration with reputable oilfield operators further reduced risk and contributed to the mitigation plan to follow commonly used and accepted oilfield practices of that specific operator.

5. Conclusion

The ultimate goal of geologic CO_2 storage is to help reduce the amount of GHG emissions in the atmosphere by ensuring safe, secure, and verified permanent storage in geologic formations. Risk analysis and numerical simulation are critical tools used iteratively in conjunction with site characterization, monitoring, public outreach throughout all of the stages of a geologic CO_2 storage project to help meet these goals. This BPM builds on the experience of the RCSP Initiative and efforts within the research community, notably the IEAGHG R&D Program review of risk assessment guidelines,[8] to develop an approach for utilizing risk analysis and numerical simulation throughout the process of CO_2 storage project site selection, design, operation and closure. Together, risk analysis and numerical simulation are integral to decision-making for CCS project developers, operators, regulators, and public stakeholders. The results from risk analysis and simulation are relevant to decisions made at all stages in a CCS project, from site screening and selection to closure. These analyses need to be routinely undertaken throughout the life of a project and updated as experience and operational data are obtained.

Risk analysis and numerical simulation serve as critical tools in a framework to identify, estimate and mitigate risks arising from CO_2 injection into the subsurface. However, they are used not only to evaluate and quantify risks, but also to optimize monitoring design and facilitate more effective site characterization. Monitoring and site characterization are critical for developing improved models, associated risk analysis and also play a role in accounting and verification. Effective risk communication is key to educating the general public and serves as the basis for obtaining useful feedback from communities. Public outreach and communication is both informed by these activities and also generates input for the analysis, in the form of public views, concerns, and suggestions. All five activities, risk analysis, numerical simulation, site characterization, monitoring, and public outreach, are interdependent. Lessons learned from the RCSP Initiative indicate that all of these activities need to be carried out in an integrated manner.

The manual illustrates the concepts of risk analysis and numerical simulation by describing the experience gained by the DOE Regional Carbon Sequestration Partnerships as they implemented multiple field projects. Successful implementation of geologic CO_2 storage projects will require developers to compare critical criteria among candidate sites including storage capacity, health and environmental safety, economics, local regulatory constraints, monitoring efficacy, and potential ancillary benefits, such as enhanced hydrocarbon production. Risk analysis and numerical simulations will guide this implementation by providing stakeholders (operators, project developers, general public, and regulators) with information to predict the long-term fate of CO_2. It is not intended to be prescriptive but rather shares the experiences and lessons drawn from the risk analysis and numerical simulation activities of the RCSPs. Collectively this experience may serve as a foundation for developing a best practice approach to risk analysis and numerical simulation.

This manual is a companion to several other carbon sequestration best practices documents either recently published or under development within Department of Energy. Subjects for these companion documents include: site screening, selection and characterization; monitoring, verification, and accounting; well construction and closure; public outreach and education; and terrestrial sequestration. For more information on the Sequestration Program or to download a copy of the existing DOE Best Practice Manuals from the Carbon Sequestration Reference Shelf, please visit our website at: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.

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8 IEA GHG Risk Assessment Network, "A Review of the International State of the Art in Risk Assessment Guidelines and Proposed Terminology for Use in CO_2 Geological Storage," Technical Review 2009/TR7, December, 2009.

Appendices

Appendix 1: Brief Summary of Geologic CO_2 Trapping Mechanisms

A1.1 Hydrostratigraphic Trapping

Hydrostratigraphic trapping refers to trapping of CO_2 by low permeability confining intervals. This type of trapping is often distinguished by whether the CO_2 is contained by stratigraphic and structural traps, e.g., similar to oil and gas reservoirs, called static accumulations, or whether it is trapped as a migrating plume in large-scale flow systems, called hydrodynamic trapping. In general, CO_2 is trapped in permeable rock units in which the fluid flow is constrained by upper and lower less-permeable "barrier" lithologies. Such top and bottom confining intervals are often formed by shale or salt units; lateral flow barriers may be due to facies changes or to faults. Faults and fractures may affect fluid flow; in some cases faults/fractures may be sites for preferential fluid flow, whereas in other cases they may inhibit fluid flow. Deep saline units typically have large lateral extents, while oil and gas reservoirs are typically much smaller. Although reservoirs may be classified by the nature of trapping mechanism, the geologic community tends to distinguish them on the basis of lithology (i.e., clastics versus carbonates).

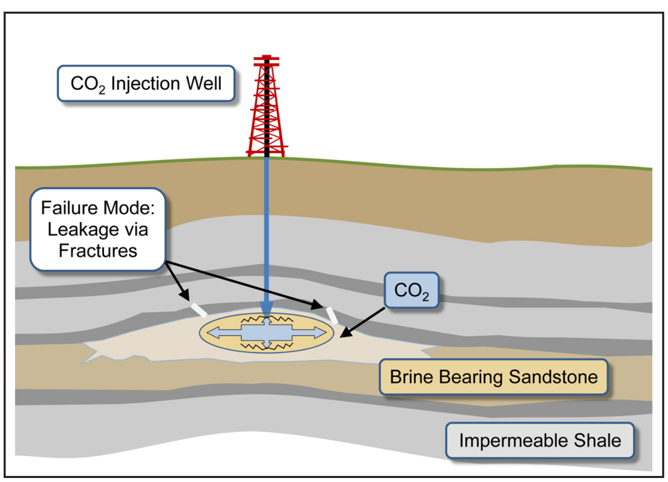

Figure 17. Schematic Example of Hydrostratigraphic Trapping and One of its Failure Modes.

A1.2 Residual Gas Trapping

At the interface between two different fluid phases (such as CO_2 and water), the cohesive forces acting on the molecules in either phase are unbalanced. This imbalance exerts tension on the interface, causing the interface to contract to as small an area as possible. The importance of this interfacial tension in multiphase flow is paramount; the multiphase CO_2-brine-oil-gas flow equations are more sensitive to interfacial tension than many other fluid properties. Interfacial tension may trap CO_2 in pores, if fluid saturations are low. The threshold at which this occurs is called the "irreducible saturation" of CO_2, and is a key concept for defining "residual gas trapping." The magnitude of residual CO_2 saturation within rock, and thus the amount of CO_2 that can be trapped by this mechanism, is a function of the rock's pore network geometry, as well as fluid properties. Geologic conditions that impact the amount of CO_2 trapped as a residual phase include petrophysics, burial effects, temperature and pressure gradients, CO_2 properties (density) under different P-T conditions, and engineering parameters such as injection pressure, induced flow rates, and/or well orientation.

Residual gas trapping is viewed as a secondary mode of storage relative to hydrostratigraphic trapping. Under this assumption, CO_2 would be injected for the purpose of hydrostratigraphic trapping, and residual gas trapping would be an additional process that renders the CO_2 immobile within hydrostratigraphic traps. Such an assumption has implications for evaluating possible failure modes and associated mitigation plans.

A1.3 Solubility Trapping

Perhaps the most fundamental type of trapping is dissolution, or "solubility trapping." First, CO_2 dissolves to an aqueous species:

$$CO_2\ (g) + H_2O \Longleftrightarrow H_2CO_3, \qquad \text{(1) (relatively slow rates)}$$

followed by rapid dissociation of carbonic acid producing bicarbonate and carbonate ions while lowering pH, or:

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad \text{(2a) (relatively fast rate)}$$
$$HCO_3^- \rightarrow H^+ + CO_3^{2-}. \qquad \text{(2b) (relatively fast rate)}$$

This leads to a series of additional reactions and "mineral trapping," discussed in the next section. The amount of storage possible through solubility trapping is limited per unit mass of water, as groundwater (brine) can only dissolve up to a few mol% or less, depending on pressure (P), temperature (T), and salinity. Over large volumes of reservoir, solubility trapping may provide a significant amount of storage.

A1.4 Mineral Trapping

"Mineral trapping" refers to the process of CO_2 reacting with divalent cations to form mineral precipitates in the subsurface. The reactions, especially reaction rates and associated processes that affect rates (e.g., complexation, pH buffering, etc.) are complicated and make estimates of CO_2 storage capacity difficult. However, mineral trapping is assumed to be a relatively safe mechanism that may sequester CO_2 for millions of years.

While mineral trapping may not be permanent, it can certainly render CO_2 immobile for long time scales. The main source of uncertainty with mineral trapping is associated with the kinetic rate coefficients and reaction-specific surface areas of minerals for the many homogeneous and heterogeneous reactions.

A1.5 Description of Failure Modes

A1.5.1 Hydrostratigraphic Trapping Failure Modes

All CO_2 trapping mechanisms have several failure modes. Critical objectives are to ascertain the physical and chemical processes of each failure mode and to minimize uncertainties in the characterization, and potential range of response, of those processes under storage conditions. Major failure modes for hydrostratigraphic trapping include:

1. Unintended migration by pre-existing, but unidentified faults, fractures, or other fast-flow paths (e.g., Figure 16).
2. Unintended migration by stress-induced or reactivated fractures or faults.
3. Unintended migration by reaction-induced breaching of a confining interval.
4. Unintended lateral flow to unintended areas.
5. Catastrophic events (e.g., earthquakes, etc.).
6. Wellbore failure events.

One approach to mitigating several of these failure modes is to select a storage site with multiple alternating confining intervals above the primary (intended) injection zone, sometimes described as stacked reservoirs. However, even when stacked reservoirs are present, other measures must be taken to minimize risk of failure.

Hydrostratigraphic trapping is viewed as the primary mechanism of CO_2 storage in subsurface geologic reservoirs. It is suggested that the other trapping mechanisms, including residual gas trapping, solubility trapping, and mineral trapping, are specific modes of CO_2 storage within hydrostratigraphic traps. As such, the failure mechanisms for hydrostratigraphic trapping are of primary importance. Thus, risk mitigation programs should make quantification of probabilities for hydrostratigraphic trapping failure modes a priority. However, under conditions of a failed hydrostratigraphic trap, it is presumed that leakage from an intended reservoir may lead to CO_2 movement into secondary hydrostratigraphic traps above the target injection / confining zones (e.g., stacked reservoirs), for example; in this case, residual gas trapping, solubility trapping, and mineral trapping all become mechanisms for helping to keep the CO_2 in place in the secondary reservoir. Additionally, if secondary reservoirs have no confining zone or hydrostratigraphic trap (in a strict sense), these other trapping mechanisms may provide an important overall damping of the flux of CO_2 back to the surface. Thus, although hydrostratigraphic trapping is priority, the other trapping mechanisms are still important and uncertainty associated with each must be addressed.

A1.5.2 Residual Gas Trapping Failure Modes

The primary failure mode for residual gas trapping is loss of capillary forces (surface tension) of the pore matrix. Such loss would be due to any process that changes the pore geometry or size or changes the interfacial tension, including compaction, dissolution or precipitation of cements in or around pores, or changing fluid composition. All of these processes require relatively long periods of time, and the risk is low for any of these to occur within timeframes of interest. Additionally, if these processes do occur, the most likely effect will be for CO_2 to dissolve into surrounding brine or to transition to free-phase CO_2. At that point, the CO_2 is subject to the same set of trapping mechanisms for hydrostratigraphic trapping (recall the assumption that the primary goal is hydrostratigraphic trapping, with residual gas trapping as a means of rendering CO_2 immobile within hydrostratigraphic traps).

Significant changes in fluid pressure or temperature throughout the rock unit may change the fluid properties enough to reduce surface tension as well, although this is less likely to occur (low risk), or at the least is easier to monitor.

A1.5.3 Solubility Trapping Failure Modes

The primary failure mode for solubility trapping is exsolution, which would only occur under significant changes in pressure or temperature. As suggested above, the risk of major changes in pressure or temperature in a deep reservoir is low, and monitoring for such changes over time is straightforward. Much like with residual gas trapping, it is assumed that the primary intended storage mechanism for geologic storage will be hydrostratigraphic trapping, with solubility trapping as one mode of storage within hydrostratigraphic traps. Following failure of solubility trapping, the CO_2 is still subject to the failure modes discussed under hydrostratigraphic trapping.

A1.5.4 Mineral Trapping Failure Modes

The primary failure mode for mineral trapping is dissolution of the carbonate minerals that trapped CO_2. This is always a possibility, but much like for exsolution, this would take a great amount of time, and the surrounding brine would need to provide conditions that promote dissolution (e.g., low pH and undersaturated with respect to bicarbonate for carbonate reactions). By monitoring the P-T and fluid composition through time, the status of mineral trapping and failure (dissolution and release of CO_2) can be easily monitored.

Much like with solubility trapping and residual gas trapping, it is assumed that the primary intended storage mechanism for geologic storage will be hydrostratigraphic trapping. Mineral trapping is therefore viewed as a means of rendering CO_2 immobile within hydrostratigraphic traps. Following failure of mineral trapping (dissolution and release of CO_2), the CO_2 is still subject to the failure modes discussed for hydrostratigraphic trapping.

A1.6 Suggested Approach for Quantifying Uncertainty of Trapping Mechanisms and Failure Modes

An approach that includes three key components is suggested: (1) comprehensive integration of previous and ongoing basic research, (2) comprehensive assessment of previous and ongoing field demonstrations, and (3) a program of new laboratory and field testing. All three components are important for identifying gaps in the current state-of-the-art models, for defining and calibrating appropriate phenomenological models, and for quantifying uncertainty of trapping failure modes.

Appendix 2: Risk Assessment Tools

Table 5 provides further details on the specific application of risk analysis tools to projects including the type of assessed risk, inputs to risk analysis, workflow, and outputs from a specific tool.

Table 5. Risk Assessment Tools

Tool	Organization/ Personnel	Goal/ Description	Projects Used/ Conceptual examples	Risks Considered	Methodology family	Impact Categories	Sub-models/ Processes/ Components Considered	Inputs	Workflow	Outputs	Computational /Visualization Tools Used	Reference
Quintessa FEP database	Quintessa	Addresses features, events and processes (FEPs) of the system relevant to long-term safety and performance. Documents the decision-making process	Weyburn, In Salah	FEPs cover technical, operational and programmatic risks	Qualitative, FEP-screened by experts	Includes HSE, casualties, water, air impacts	~200 FEPs grouped into 8 categories	Expert inputs on various FEP categories	Experts participate in workshops to identify and, aggregate FEPs to provide scenarios. A base case scenario (also termed "normal" or "expected evolution" scenario) is defined and alternative "what if?" scenarios for comparison. The FEP database is used either to guide selection of FEPs in the workshop or (more usually) to audit the scenarios produced from "project-specific" FEPs identified in the workshop.	Identifies scenarios to be addressed in system-level models to ensure long-term safety & performance Can be used as an audit tool to evaluate such system models	Quintessa FEP database	Quintessa website Savage et al., 2004
TNO Risk Assessment Methodology	TNO	Demonstrate long-term safety performance of underground CO_2 storage		Technical, Programmatic	Expert-elicited probability and consequence matrices	Include human casualties, environmental risks, groundwater contamination	TNO FEP database & process-level simulations	Site characterization, well characterization, expert inputs on FEPs	1. Assessment basis defined 2. Critical FEPs are grouped into scenarios 3. Experts estimate range and identify probability distribution functions (pdfs) for the parameters of each scenario 4. Monte Carlo (MC) procedure is performed for thousands of input data sets	PDFs of CO_2 plume characteristics from the Monte Carlo procedure (impacted areas, concentrations, fluxes) can be used to calculate impacts (casualties, environmental risks, USDW contamination, etc.)	SIMED II	TNO, Wildenborg et al., 2004
CO_2QUALSTORE guideline	Det Norske Veritas (DNV)	Life-cycle risk-based approach to site selection and qualification Common protocol for *third parties and regulators* to assess safety and reliability of GS Structured basis for decision making	Developed as a part of the Joint Industry Partnership (JIP)	GS life-cycle risks	Qualitative/ Semi-quantitative with "panel" inputs	Multiple categories	Site Screening, Assessment, Selection, Design, Construction, Operation, Closure (transfer-of-responsibility)	Screening, characterization reports, injection and operation plan, storage performance forecast, impact assessment, contingency plans, MVA plans	Structured hazard & safeguard identification ------------- Risk ranking in a "workshop" with the risk matrix approach Risk assessment follows the ALARP (as low as reasonably practicable) principle ------------- Transparent documentation of the iterative risk assessment process	Iterative risk analysis is used to update various operational plans and provide basis for project qualification and regulatory compliance	NA	pages 65-75 of the DNV CO_2QUALSTORE guideline
Carbon Storage Scenario Identification Framework (CASSIF)	TNO	Storage Performance Assessment Both multiple-site screening and single-site certification possible		Technical (containment, effectiveness)	Qualitative, scenario-based	Well, Confining Zone, Fault leakage	Chemical, Mechanical	Expert inputs to FEPQuest, FEPMan 40 questions on basin geometry, reservoir parameters, etc. TNO facilitates *Workshop*	FEPQuest: Expert inputs used to highlight FEPs and identify knowledge gaps ------------- FEPMan: Grouping and pre-selection of FEPs ------------- Workshop: Select Risk Factors, Create Scenarios using mindmapping tools	Consensus on a set of FEP-based scenarios about site-specific risk factors	SQL-based FEP database, VUE for visualizing FEP interactions	Yavuz, F. et al., 2009

Table 5. Risk Assessment Tools (cont'd)

Tool	Organization/ Personnel	Goal/ Description	Projects Used/ Conceptual examples	Risks Considered	Methodology family	Impact Categories	Sub-models/ Processes/ Components Considered	Inputs	Workflow	Outputs	Computational /Visualization Tools Used	Reference
Risk Identification and Strategy using Quantitative Evaluation (RISQUE)	URS	Semi-quantitative technique to estimate both the probability and impact of a set of risk events for multiple projects/ injection sites	Weyburn, CO_2CRC: Otway, Gorgon, BP: In Salah	Technical, Community	Semi-quantitative, expert-elicited probability and consequence matrices	Reservoir Performance Project Viability Community Impacts	Containment, Effectiveness Community safety, amenity & environment	Key Performance Indicators (KPIs) for various impacts Site information Project duration, CO_2 quantity, etc.	Key Performance Indicators (KPIs) used to define baseline to assess impacts to various receptors ------------ Expert panel identifies risk events, probabilities, costs and potential consequence outcomes. ------------ Consequence information used in a simple spreadsheet model with Monte Carlo simulations to generate outputs over a range of confidence limits.	Overall- and impact-wise cost-benefit risk profiles for multiple projects ------------ Ranking of each project against KPIs ------------ A plot indicating where each project falls in the "containment risk index - effectiveness risk index" space	Monte Carlo simulations via Oracle Crystal Ball add-on for MS Excel	Bowden, A. & Rigg, A., 2005; Bowden, A. & Rigg, A., 2004
Screening and Ranking Framework (SRF)	C. M. Oldenburg	Independent assessment of containment/ dispersion potential through numerical evaluation of various attribute properties *(multi-attribute utility analysis)* ------------ Multi-site evaluation to identify site with the least HSE risk	Ventura oil field, Rio Vista gas field	Technical and Community (Health, Safety and Environmental (HSE))	Qualitative, expert-elicited probabilities	Health, Safety and Environment	Primary/Secondary Confinement Attenuation Potential ------------ 1. Long-term potential for primary containment of CO_2 2. Secondary containment potential if 1 fails 3. Attenuation potential if 2 fails	Primary/ secondary/shallow confining zone properties, depths, Injection zone attributes, Information on existing wells, hydrology, faults and topography	Experts assess importance of each property, and assign certainties Spreadsheet uses inputs to generate average assessment and certainties	Overall score for each impact category, average certainty ------------ Graph of average attribute assessment vs. average certainty	MS Excel-based	Oldenburg, C.M., 2006
Certification Framework (CF)	C. M. Oldenburg, S. Bryant, J.-P. Nicot - CCP	Certification of a single site, given adequate characterization data Containment & effectiveness risk only	Kimberlina site, southern San Joaquin valley	Technical (containment, effectiveness)	Quantitative, system-level model, probabilities partly calculated using fuzzy logic	CO_2, brine leakage via wells and faults into "compartments": emission credits & atmosphere, near-surface, health & safety, USDWs and HC/mineral resources	CF Submodels: 1. Injection zone simulation 2. Fault encounter probability 3. Fault connectivity probability 4. Wellbore flow and fault leakage 5. Dense phase atmospheric dispersion	Site characterization, fault population statistics, injection zone, injection rate, time frame, existing wells and faults, limits on CO_2/brine concentrations/ fluxes in each compartment, thresholds on leakage risks	Impacts: modeling & simulation of proxy concentrations or fluxes ------------ Psource-compartment = Psource-conduit * Pconduit-compartment may be calculated using fuzzy rules ------------ CO_2 plume location, size, pressure signal calculated via reservoir simulations or pre-computed simulations ------------ Reservoir simulation results fed to conduit model to calculate flux/concentration of CO_2/brine.	Severity of impact = degree to which flux/ concentration exceeds the limit for a given compartment Risk = (Impact * $P_{source\text{-}compartment}$) ------------ CO_2/brine leakage risk </=/> provided threshold ------------ Injection plan or site characterization modified to decrease risk	TOUGH2, CMG-GEM	Oldenburg, C.M., 2009

Table 5. Risk Assessment Tools (cont'd)

Tool	Organization/ Personnel	Goal/ Description	Projects Used/ Conceptual examples	Risks Considered	Methodology Family	Impact Categories	Sub-models/ Processes/ Components Considered	Inputs	Workflow	Outputs	Computational /Visualization Tools Used	Reference
Vulnerability Evaluation Framework (VEF)	U.S. EPA	Identify conditions leading to increased/ decreased susceptibility to adverse impacts from GS. ------------- Not used for measuring the severity of an outcome, performance assessment or to specify data requirements		Technical (containment, effectiveness, contamination), Community (human health and welfare) Economic	Qualitative	Impacts to human health, atmosphere, ecosystems, USDW, surface waters, and the geosphere	Evaluation Flowcharts 1. Confinement system 2. Injection zone 3. CO_2 stream 4. GS footprint delineation 5. Human health and welfare, atmosphere, ecological factors, GW / surface water, CO_2 spatial area, pressure spatial area 6. Wells 7. Faults	Information on GCS system and geologic attributes of the injection and confining zones : (capillary entry pressures, permeability, travel time, plume lateral extent, wells, faults/ fracture zones, geochemical processes, tectonic activity, geomechanical processes, injectivity, physical capacity)	Spatial area around the injection site in which impacts are evaluated is defined ------------- Input information used in a series of evaluation flowcharts to determine if high/low vulnerability exists for a particular scenario	High/low vulnerability for a particular situation Means to manage the vulnerability indicated VEF can be used to prioritize monitoring and mitigation efforts focused on geologic features and overlying receptors	N.A.	U.S. EPA, 2008
Performance Assessment (PA)	Quintessa	1. Evaluate effectiveness of the system or sub-system relative to some criteria of interest to particular stakeholders. ------------- 2. Allows integration of quantitative, qualitative site information, numerical models, and value judgments by experts in a decision-support framework. ------------- 3. Evidence Support Logic (ESL) and the PA framework can also be used for iterative planning	In Salah, Shell (ESL aspects)	FEPs cover technical, operational and programmatic risks, as required by the context of the assessment	Evidence-support (3-valued) logic (ESL) Distinguishes cases of poor-quality data from uncertain data	Can be implemented so as to consider any impact categories of interest to stakeholders. The decision-support tool based on ESL can be used to analyze decisions and determine implications of information / uncertainties on impacts of concern	1. Online FEP database 2. QPAC-CO_2: modular, general-purpose simulation code 3. TESLA, a decision-support tool which implements ESL and allows development of a hierarchical, logical hypothesis model to provide common structure for all the evidence for/against/ uncertainty corresponding to a root-level hypothesis	Expert definition of a context for the PA Site-specific FEPs Expert evaluation of FEPs Expert definition of performance-relevant hypotheses Expert judgments of evidence for / against each hypothesis mapped on to a numerical scale of 0 to 1 representing evidence for and against (judgments can be based on a wide range of information, including outputs from numerical models)	Define context for the PA FEP analysis and scenario development of a decision tree (also termed a "hypothesis model" using TESLA. Analysis of scenarios or aspects of scenarios using numerical modeling tools, including QPAC-CO_2 Identification of various sources of evidence that corroborate/falsify various sub-hypotheses in the decision tree (including outputs from numerical models) Propagation of evidence through the decision tree to assess the dependability of the root hypothesis	Ratio plots of evidence for/against vs. uncertainty for the overall hypothesis indicate a measure of confidence (ex: for/ against significant chances of leakage from the injection zone) -------------------- Hypotheses where the evidence is uncertain can be re-evaluated at a later stage with new data, including monitoring data	TESLA QPAC-CO_2 Quintessa FEP database	Metcalfe et al., 2009, TESLA User Guide

Table 5. Risk Assessment Tools (cont'd)

Tool	Organization/ Personnel	Goal/ Description	Projects Used/ Conceptual examples	Risks Considered	Methodology family	Impact Categories	Sub-models/ Processes/ Components Considered	Inputs	Workflow	Outputs	Computational /Visualization Tools Used	Reference
Carbon WorkFlow	Schlumberger Carbon Services	Evaluate risks associated with FEPs against project values on a likelihood-severity scale. Establish basis for allocating resources for risk reduction, and provide structure to document and track risk reductions.	WESTCARB Kimberlina Project, CA SCS PurGen Project, NJ Cemex CCS Project, TX Aquistore Project, SK	All Technical and Programmatic risks (project-specific) to project goals and values	Semi-quantitative; FEPs ranked through expert elicitation using a risk matrix approach	Categories designed to suit the project: e.g. HSE, Financial, Technical (Injectivity, Capacity, Containment), Research, Industry stewardship / social acceptance.	1. Risk = Severity (S)*Likelihood (L), each evaluated on categorical scales. 2. Values assigned through working-group consensus, and/or from aggregated "votes" in plenary session. 3. Participants' skill self-evaluation applied as expertise qualification. 4. Workshops structured to promote information sharing and calibration, yet to minimize heuristic pitfalls.	1. List of 50-80 pre-screened FEPs from sources including Quintessa. 2. Aggregate experience of 20-30 internal and external experts. 3. Presentations on project knowns, unknowns, plans, and risks. 4. Mined-data inputs (under development).	1. Invited experts rank FEPs by project risk. 2. Small panel generates key scenarios from higher-ranked FEPs. 3. Broader group provides Risk Response Actions (RRAs) for scenarios. 4. Risk manager creates executable Risk Response Action Groups (RRAGs). 5. RRAGs are assigned to individuals for completion, documentation, and periodic risk-reduction review.	1. List of FEPs ranked by associated risk. 2. List of relevant Scenarios ranked by associated risk. 3. List of Risk Response Actions to be assigned within a project management structure. 4. Format for risk tracking and periodic review.	1. Spreadsheet graphics. 2. Live displays of "votes" and data during workshops.	Hnottavange-Telleen, K., Krapac, I. & Vivalda, C., 2009 -------------------- Hnottavange-Telleen, K., 2010
Oxand Performance & Risk (P&R™) Methodology	Oxand, Schlumberger	Quantify CO_2 leakage through a well for well integrity performance- and risk-assessment Provide initial risk-assessment and mitigation plans to regulators	Ongoing: PCOR	CO_2 leaks/ flow through wellbores	Quantitative Risk matrix evaluation: semi-quantitative	Public acceptance, Financial, Technological, HSE, USDW impacts	• Well leakage: Darcy two-phase flow • Chemical reactions: Cement degradation, carbonation, casing corrosion Likely does not simulate CO_2 injection and plume movement through the target formation to the wellbore	Site characterization, well characterization, cement properties, probability distributions of uncertain parameters	• Risk scenario identification Stochastic simulations to evaluate CO_2 flow along well • Identify targets impacted due to CO_2 leakage • Evaluate risk scenarios from simulation data using a risk matrix • Risks are compared against acceptance limits • Basis for mitigation actions	CO_2 leakage rate, Identification of leakage pathway, Targets impacted identified Risk probability	SIMEO™-STOR	Meyer, V. et al., 2009

Table 5. Risk Assessment Tools (cont'd)

Tool	Organization/ Personnel	Goal/ Description	Projects Used/ Conceptual examples	Risks Considered	Methodology family	Impact Categories	Sub-models/ Processes/ Components Considered	Inputs	Workflow	Outputs	Computational /Visualization Tools Used	Reference
CO_2-PENS	LANL	Comprehensive, systems-level performance assessment of GS based on the Goldsim framework	Ongoing: SWP, Gordon Creek site; Proposed: BSCSP, Kevin Dome; SACROC; Proposed: Otway Basin	Technical, Economic Could be modified to include sub-modules for Community risks	Quantitative, hybrid system-process model	Atmospheric systems, ground water, other reservoirs, HSE	Analytical/ Numerical models for CO_2/brine flow/migration in injection zone, faults, wells, shallow formations, atmosphere	Site characterization, wells/fault characterization, probability distribution of uncertain parameters, thresholds on leakage/capacity/ infrastructure, Data on cost-benefits for various risk events	Site-specific model developed based on available characterization data ------------- CO_2 plume and pressure distribution either calculated through in-built correlations or importing results of detailed reservoir simulations ------------- Goldsim manages data flow across modules & can perform multi-realization stochastic Monte Carlo simulations to generate probabilistic distribution of leakage ------------- Probability distributions of uncertainty for each parameter are coupled to get global uncertainty ------------- Results are used to calculate probability of exceeding thresholds which can be combined with impact analysis	CO_2/brine leakage rates in groundwater formations, shallow formations and to atmosphere; probability of exceeding leak thresholds; CO_2/brine plume in shallow formations; leakage rates through wells, faults and confining zones; Probability distributions of storage capacity and number of injection wells; Stochastic comparisons of the performance of multiple sites	GoldSim	Stauffer, P.H. et al., 2009; Zhang, Y. et al., 2006
Framework for Systems-Level Carbon Storage Risk Assessment	GoldSim Technology Group & LANL	Enhancements to GoldSim: Simulation capabilities/ Scenario comparisons/ Programmatic Risk/Process flow modeling	Under development Prior use of Goldsim: 1. LBNL 2. Alberta 3. Quintessa	Technical, Programmatic	Quantitative, system-level model	Similar to CO_2-PENS	Analytical/ Numerical models	Similar to CO_2-PENS, Added: Deterministic/ probabilistic inputs	Similar to CO_2-PENS	Similar to CO_2-PENS, Added: Sensitivity plots of leakage rates/plume migration	GoldSim	Ian, M., 2010
Comprehensive, Quantitative Risk Assessment Model	Headwaters Clean Carbon Services (HCCS), Marsh Risk Consulting LANL	Quantitative process-/ system-level risk assessment of GS sites with failure effects analyses and risk mitigation cost savings	Under development, to be applied to multiple sites for verification	Surface, Programmatic, Technical (geologic storage-related)	Quantitative	Near-surface, subsurface, community and programmatic impacts	Probabilistic/ Process/System Models	Site characterization, MVA, Risk Mitigation Cost Savings data	Risk identification and characterization Risk modeling (process-level or systems-level) Failure Modes and Effects Analysis (FMEA) using the Risk Priority Number (Probability * Severity * Difficulty of failure pre-detection) Modify MVA, iterate through FMEA to lower the risk priority number	Risk Impacts Cost Savings from Mitigation of Risks	Master-spreadsheet with model components	Lepinski, J., 2010

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Appendix 3. Detailed Description of THMCB Processes Relevant to Geologic CCS Modeling

This section provides brief overviews of the individual aspects of coupled processes relevant to geologic CCS and associated numerical simulation analyses are provided, including thermal, hydrological, mechanical, chemical and biological processes. For sake of brevity, processes are not exhaustively reviewed and generalized versions of governing equations are provided that indicate specific numerical simulation codes that solve the equations used by the RCSPs. For more details about advanced aspects of coupled processes, refer to already published reviews in the literature (e.g. Valentine et al., 2002).

A3.1 Hydrologic and Thermal Processes

Numerical modeling of basin scale groundwater flow and transport processes involves solving the appropriate mass, momentum, and energy conservation equations. Appendix X provides more detailed information on these equations. (Bethke, 1985; Bredehoeft and Norton, 1990; Garven, 1995; McPherson and Garven, 1999). De Marsily (1986) and Person et al. (1996) provide detailed summaries of the fundamental conservation laws used to analyze regional scale flow and transport. For this report, generic (simplified) expressions of multiphase flow associated with CO_2 storage in saline formations are provided:

$$\text{water} \quad \nabla \cdot \left(\frac{\rho_w k_{rw}}{\mu_w} \overline{\overline{k}} \left\{ \nabla p_w - \rho_w \vec{g} \right\} \right) = \phi \frac{\partial (s_w \rho_w)}{\partial t} \qquad \text{Eq. 1}$$

$$CO_2 \quad \nabla \cdot \left(\frac{\rho_{CO_2} k_{rCO_2}}{\mu_{CO_2}} \overline{\overline{k}} \left\{ \nabla p_{CO_2} - \rho_{CO_2} \vec{g} \right\} \right) = \phi \frac{\partial (s_{CO_2} \rho_{CO_2})}{\partial t} \qquad \text{Eq. 2}$$

$$\text{Note} \quad s_w + s_{CO_2} = 1 \qquad p_c = p_{CO_2} - p_w \qquad p_c = p_c(s_w)$$

and thermal energy, or the heat transport equation:

$$\nabla \cdot (\overline{\overline{E}} \nabla T) - (\rho c \vec{q}) \cdot \nabla T = [\rho c \phi + \rho_S c_S (1 - \phi)] \frac{\partial T}{\partial t} \qquad \text{Eq. 3}$$

where:

$\vec{q}$	Darcy velocity
$\overline{\overline{k}}$	permeability tensor
k_{rw}	relative permeability for water
k_{rCO_2}	relative permeability for CO_2
μ	fluid viscosity
p	fluid pressure
p_c	capillary pressure
s	fluid saturation
ρ	fluid density
$\vec{g}$	gravitational acceleration
ϕ	porosity
t	time
E	thermal conductivity-dispersion tensor
T	Temperature
c	specific heat of water
c_S	specific heat of solid mass (rock)

All three equations are coupled through their common dependence on fluid properties and the Darcy velocity. A necessary addition to this set of equations for multiphase flow is constitutive relations for capillary pressure as a function of saturation and relative permeability-saturation relations. Popular examples of this are developed by van Genuchten (1980). Doughty (2007) discusses hysteresis in capillary pressure curves, which has important consequences for residual trapping of CO_2.

To illustrate the coupling of processes, a common form of the coupled fluid and heat flow governing equation is:

$$\nabla \cdot K_r \nabla T - \rho_f C_f \vec{q} \cdot \nabla T = -\rho_r C_r \frac{\partial T}{\partial t} \qquad \text{Eq. 4}$$

where ρ_f is fluid density, K_r is thermal conductivity of the saturated porous rock, C_f is fluid heat capacity, C_r is rock heat capacity, and ρ_r is the density of the saturated porous rock (Stallman, 1960; Domenico, 1977). This and other forms of the governing equation for coupled groundwater and heat flow are typically solved numerically, using finite difference or finite element methods (e.g., Remson, et al, 1971; Pinder and Gray, 1977; Huyakorn and Pinder, 1983). Smith and Chapman (1983) provide a detailed review of research applications of coupled heat and groundwater flow.

A number of two- and three-dimensional numerical codes for simulating coupled groundwater and heat flow have been developed recently. Pruess (1999) developed TOUGH2 as a geothermal reservoir simulator using the integrated finite difference method (Narasimhan and Witherspoon, 1976). TOUGH2 was specifically designed to simulate coupled heat and multiphase fluid transport in porous and fractured media. The integrated finite difference method permits construction of 3D, irregular meshes, and the solvers included are robust for many applications, including non-geothermal applications. The equation of state (EOS) package is written as an independent module, and a variety of different EOS modules are available for different applications. For CCS, the module ECO2N (Spycher and Pruess, 2005; Pruess and Spycher, 2007) treats supercritical CO_2, water, and NaCl; EOS7C (Oldenburg et al., 2004) treats supercritical CO_2, CH_4, water, and brine; and EOSM (Pruess, 2004) treats supercritical, gaseous, and liquid CO_2, along with water and NaCl. TOUGH has been tested and compared with several other geothermal reservoir simulators (Pruess and Wang, 1984; Moridis and Pruess, 1992; Oldenburg and Pruess, 1994), and is currently used by many researchers, especially in the geothermal community. It has also been benchmarked against a suite of other codes for CCS problems (Pruess et al., 2004).

In addition to the need to couple multiphase flow, heat transfer, reactive transport and geomechanical processes, robust model development also requires accurate characterization of the component (CO_2, water, sodium chloride (for the case of saline formation injections)) transport properties across a large range of temperatures and pressures (Schnaar and Digiulio, 2009). Such thermophysical properties, including mutual solubility effects, control the amount of CO_2 that may dissolve into brine and therefore affect the ultimate fate of the sequestered CO_2. However, accurately representing these properties over a range of temperatures and pressures is non-trivial. For example, the equation of state (EOS) package for TOUGH2 is written as an independent module, and a variety of EOS modules are available for different applications in the TOUGH-family of codes. For CCS, the module ECO2N (Spycher and Pruess, 2005; Pruess and Spycher, 2007) treats supercritical CO_2, water, and NaCl; EOS7C (Oldenburg et al., 2004) treats supercritical CO_2, CH_4, water, and brine; and EOSM (Pruess, 2004) treats supercritical, gaseous, and liquid CO_2, along with water and NaCl. TOUGH has been tested and compared with several other geothermal reservoir simulators (Pruess and Wang, 1984; Moridis and Pruess, 1992; Oldenburg and Pruess, 1994), and is currently used by many researchers, especially in the geothermal community. It has also been benchmarked against a suite of other codes for CCS problems (Pruess et al., 2004).

Many other coupled groundwater and heat flow numerical models have been developed and applied by different researchers for modeling research specific to thermal processes, and although they are not CCS-focused, they provide good examples of research problems faced by the geologic CCS community. For example, Garven and Freeze (1984a,b), Bethke (1985a, 1985b, 1986), Bethke and Marshak (1990) and Garven et al. (1993) developed and applied 2-D models of groundwater and heat transport to evaluate topographic recharge as a driving mechanism of fluid flow in the formation of Mississippi Valley Type ore deposits and associated thermal anomalies. Deming and Nunn (1991) and Deming (1992) also used coupled groundwater and heat flow numerical models to challenge the previous authors' results. Raffensperger and Garven (1995a,b) used a reactive transport model along with coupled groundwater and heat flow to evaluate formation of uranium deposits, with free convection as a driving mechanism of flow. Burrus and Audebert (1990) modeled thermal and compaction processes in the Gulf of Lions, and Person and Garven (1989, 1994) and Wieck et al. (1995) used a similar modeling approach to examine other rift basins. Burrus et al. (1993) used coupled groundwater and heat flow equations along with separate phase generation, expulsion and flow of hydrocarbons to reconstruct basin evolution and associated hydrocarbon migration histories in the Northern Viking Graben. Many sophisticated models of coupled single-phase groundwater and heat flow, with unique and clever applications, are found in the literature, and serve as good examples of modeling practice.

More recently, Han et al. (2010) used coupled process numerical models to evaluate non-isothermal processes and heat transport associated with geologic CO_2 storage, including Joule-Thomson effects, heat of CO_2 dissolution and H_2O vaporization/dissolution, effective heat capacity, dry-out processes and other non-equilibrium thermal processes. Figure 18 illustrates these fundamental thermal processes (Han et al., 2010).

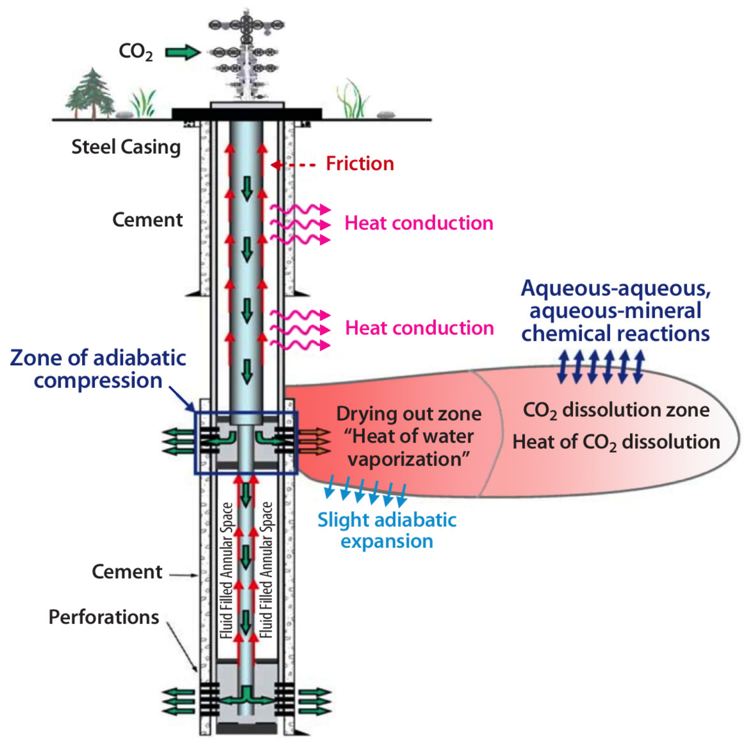

Figure 18. Potential Thermal Processes during CO_2 Injection for Geologic Storage.
(Reprinted from Han et al., 2010, with permission from the American Geophysical Union)

Other numerical simulation codes in use by the RCSPs for specific evaluation of thermal aspects of geologic storage include FLOTRAN, STOMP, TOUGH2, and others (Table 6).

Table 6. Simulation Codes in Use by the RCSPs

	BSCSP	MGSC	MRCSP	PCOR	SECARB	SWP	WESTCARB
ABACUS						●	
CMOST				●			
CO_2-PENS	●					●	
COMET		●			●	●	
COMSOL						●	
Eclipse	●			●	●	●	
FEHM						●	
GEM-GHG				●	●	●	
GC Workbench	●	●	●	●			
GMI - SFIB							
GOPHAST				●			
HYDROTHERM				●			
IMEX				●			
MASTER							
NEFLOW-FRACGEN							
NUFT	●	●					
PFLOTRAN						●	
PHAST				●			
PHREEQC		●	●	●			
PSU-COALCOMP							
STARS				●			
STOMP			●				
TOUGH2 (aka as TOUGH+)		●			●	●	●
TOUGH-FLAC							●
TOUGHREACT		●				●	●
VIP		●					

● = Indicates Corresponding Model Implemented by RCSP

A3.2 Geomechanical Processes

In broadest terms, geomechanical processes include effects of fluid pressure, elastic and non-recoverable deformation, fracture opening and closing, and larger-scale faulting. Coupling geomechanics and other processes in CCS reservoir models is mainly through fluid pressure and the effects of deformation on absolute and relative permeability. This coupling between hydrologic and mechanical processes may be examined in two ways: (1) the sole effect of fluid pressure on mechanical response (effective stress), and (2) the effects of mechanics (strain and stress) on the hydrologic response, especially via permeability modification. Both of these coupling pathways can be equally important. However, one or both are often ignored in analyses of geologic CCS and other applications. Many conditions or situations call for simplification in the form of neglecting one direction of this coupling. For example, the transient-groundwater flow equation (Eqs. 1 and 2) assumes that deformations are small and reversible (i.e., elastic deformation) and that permeability remains unaltered Numerical models of coupled hydrologic-geomechanical processes are vital for evaluating competing geologic CCS risk FEPs such as overpressures, leakage through *in situ* fracture networks, fracture generation, and induced seismicity.

Poroelastic Approach

The theory of linear poroelasticity (Biot, 1941) provides a framework for coupled hydrologic-geomechanical simulation analysis.). For porous media, general expressions describe the coupling between fluid flow:

$$S_\sigma\left[\frac{B}{3}\frac{\partial\sigma_{kk}}{\partial t}+\frac{\partial p_{ex}}{\partial t}\right]=\frac{1}{\mu}\nabla.\overline{\overline{k}}\nabla p_{ex} \quad \text{Eq. 5}$$

and mechanical equilibrium:

$$\nabla^2\left(\sigma_{kk}-4\eta p_{ex}\right)=-\frac{1+\nu}{1-\nu}\nabla\cdot\vec{F}; \quad \text{Eq. 6}$$

where:

S_σ	three-dimensional specific storage
B	Skempton's coefficient
σ_{kk}	mean stress
p_{ex}	pore pressure in excess of hydrostatic
μ	fluid viscosity
$\overline{\overline{k}}$	permeability tensor
η	poroelastic stress coefficient
ν	drained Poisson's Ratio
$\vec{F}$	body force per unit volume

Coupling between these equations is explicit because pore pressure appears in both equations, as does mean stress (or volumetric strain). Two-dimensional versions of these equations were solved numerically by Ge and Garven (1992) to analyze the coupling among stress, rock deformation, and fluid pressure. The differential form of the 2-D equilibrium relation for poroelastic media may be expressed as:

$$\frac{\partial}{\partial x}\left[C_{11}\frac{\partial u}{\partial x}+C_{12}\frac{\partial v}{\partial z}-P\right]+\frac{\partial}{\partial z}\left[C_{33}\left(\frac{\partial u}{\partial z}+\frac{\partial v}{\partial x}\right)\right]=X \quad \text{Eq. 7}$$

$$\frac{\partial}{\partial x}\left[C_{33}\left(\frac{\partial u}{\partial z}+\frac{\partial v}{\partial x}\right)\right]+\frac{\partial}{\partial z}\left[C_{21}\frac{\partial u}{\partial x}+C_{22}\frac{\partial v}{\partial z}-P\right]=Y \quad \text{Eq. 8}$$

where X and Y are body forces in the x- and y- cartesian coordinate directions, u is displacement in the x-direction, v is displacement in the y-direction, and C_{ij} are material coefficients including Young's modulus and Poisson's ratio. Note that such a 2-D formulation neglects one direction of tectonic stresses (e.g., vertical). Ge and Garven (1992) also utilized a constitutive relationship between stress and strain introduced by Biot (1941):

$$\varepsilon=\frac{1}{E}\left[(1+\nu)\overline{\overline{\sigma}}-\nu(Tr(\overline{\overline{\sigma}})\overline{\overline{1}})\right]+\frac{P}{3H}\overline{\overline{1}} \quad \text{Eq. 9}$$

and also added a stress change rate as a source term to the groundwater flow, with volumetric strain (ε) related to stress and fluid pressure by the bulk compressibility:

$$\frac{\partial \varepsilon}{\partial t} = -\alpha\left(\frac{\partial \sigma_t}{\partial t} - \frac{\partial P}{\partial t}\right). \qquad \text{Eq. 10}$$

In these equations, *X* and *Y* represent applied tectonic stresses, E_Y is Young's modulus, ν is Poisson's ratio, is the incremental stress tensor, *H* is Biot's (1941) pressure modulus, and is the identity tensor. Solutions to these linear poroelastic equations, when coupled with the single- or multi-phase fluid-flow equations, provide estimates of physical displacement of a model domain (e.g., strain), and the converse fluid pressure effects associated with stresses imposed by injection, such as that in a geologic CCS injection well. For a more detailed discussion of this poroelastic formulation, its solution using a finite element method, and applications to coupled fluid pressure and rock deformation, refer to Ge and Garven (1992), McPherson and Garven (1999) and Person et al. (1996).

Inelastic Deformation

Irrecoverable or inelastic deformation involves any non-elastic deformation including time independent (plasticity) and time dependent (creep) mechanisms. Relevant for CO_2 injection and subsurface storage are inelastic deformations induced by injection-related overpressures; a stress-sensitive reservoir can respond to fluid pressure increases by localized fracture or fluid pressure decreases (mean stress increases) by pore collapse. Such effects can be described by cap-plasticity models in commercially available codes like ABAQUS™ and FLAC3D™. Relevant for clay-bearing confining zones are multi-phase phenomena like dry-out, and matrix suction, as well shrink/swell deformations due to clay mineral reactions. In this way shale confining interval deformation can be strongly coupled to multiphase flow, thermal effects, and chemical reactive transport (Borja, 2004).

Fracture generation, opening and closing of pre-existing fracture networks, induced wellbore damage, and the potential for induced seismicity are all domains where the coupling of fluid flow and geomechanics is relevant for CCS operations. State regulations for injection wells may apply for certain CCS operations, and set limits on injection rates to prevent wellbore damage that are a function of local stress conditions and petrophysical properties for injection horizons. Code development for hydrofracture generation is a topic of current research, especially for unconventional shale gas resources, and CCS operations and regulators can benefit from this work. NETL's FRACGEN™ software is an example of such an effort.

A3.3 Chemical Processes

As field tests of geologic CO_2 storage advance in size and scope, numerical simulation models also increase in complexity, including increases in resolution (denser grids) and coupling of additional processes (THMCB). Perhaps the most computationally-intensive process is reactive transport, because addition of even a single reaction in the set of governing equations adds multiple variables and associated degrees of freedom. Consequently, most reservoir simulators apply relatively coarse grids to injection problems, often becoming too coarse to capture the fine-scale reaction fronts and chemical gradients that arise in subsurface engineering scenarios. Methods for using different grids, or using nesting or adaptive grids, have been explored and may be necessary for coupled multiphysics codes, given the disparate size and time scales among THMCB processes for CCS operations. Chemical modeling for CCS can take several forms, and ideally should include a multitude of chemical and transport processes. Some examples of chemical processes include aqueous speciation, dissolution/precipitation, microbial-mediated redox reactions, ion-exchange between solutions and minerals, surface chemical reactions occurring at phase interfaces (i.e. surface complexation, sorption), the effects of these processes on porosity and permeability, coupling with mechanical effects (e.g. water-assisted creep and crack growth; fracture healing, clay mineral swelling). Further, transport processes involved in multiphase reactive flow include advection, dispersion, and multicomponent diffusion. Because of these inherent complexities, time and length scales under consideration, reactive buffering capacity (e.g. of gases and minerals), limitations on thermodynamic and kinetic data for the system in question, options for model validation, geochemical and biological processes to include, and what can be excluded from consideration, should all be considered when choosing a model.

At its simplest, geochemical modeling of multicomponent systems calculates the speciation of an interstitial aqueous solution and/or gas (or supercritical phase) at equilibrium and determines the saturation state of a suite of minerals and/or gases with respect to that solution and/or gas. Given an analytical suite of concentrations of elements, speciation/solubility codes distribute moles or masses of the elements amongst discrete chemical species existing in solution at equilibrium at the temperature, pressure, and chemical conditions of interest. Codes that perform these tasks use one or more methodologies for dealing with the thermodynamics of aqueous solutions and gases, and thus activity coefficients, and are applicable to more or less fixed ranges in pressure, temperature, and ionic strengths (i.e. salinity) of solutions. These include (with increasing ionic strength), the Debye-Huckel or extended Debye-Huckel formulation, the B-dot method, and finally the Pitzer formulation applicable to concentrated brines (Wolery, 1992; Bethke, 1996).

More complex spatial and temporal dependent geochemical reaction transport models can be classed variously as inverse or forward; batch or transport; equilibrium, non-equilibrium, or "partial local equilibrium". Nearly all reaction-transport codes in use today for multicomponent spatial-temporal modeling use the partial local equilibrium approach, wherein homogeneous reactions such as aqueous speciation (most of which occur with rates faster than milliseconds) are taken at equilibrium, and heterogeneous reactions such as mineral-water dissolution/precipitation are kinetically mediated. This reduces the number of partial differential equations to those only for the primary species. Most simulators utilize thermodynamic databases for the chemical species of interest, and include equilibrium constants at various temperatures, some from 0 °C to as high as 300 °C. Crawford (1999), Steefel et al. (2005) and MacQuarrie and Mayer (2005) have recently reviewed reactive transport modeling.

Most reactive transport codes couple fluid flow (pressure) with heat flow (temperature) and multicomponent, heterogeneous and homogeneous chemical reactions in multiple spatial dimensions. Multiphase species reaction and advective and diffusive transport in gas and liquid are sometimes included. Lichtner et al. (1996) provides a comprehensive overview of generalized governing equations.

Numerical Formulation of Chemical Reactions and Continuity

Chemical species are partitioned among aqueous, gaseous, or mineral phases. To account for mass transfer between each of these phases, most reactive transport codes (RTCs) assume that a set of independent aqueous species (primary species, or *components*) can fully describe the chemical system. Implementation of continuity in this manner requires the casting of chemical reactions in terms of different sets of species, including primary or basis species. The number of primary species (N_p) is defined as the difference between the total number of species (N) and the number of reactions within the system (N_R):

$$N_p = N - N_R \qquad \text{Eq. 11}$$

The prescribed primary species within a system must be represented within the aqueous phase. Gases, other aqueous species and mineral species are defined within the secondary species. Each secondary species (in the gas/liquid and aqueous phases) is expressed as the product of a reaction involving only other primary species. In other words, each secondary species is represented as linear combinations of the set of primary species. The mass transport of these chemical species can be modeled using equilibrium reactions (mass action equations) or kinetic rate relationships. The classification of chemical species simplifies the modeling, because only the concentrations of primary species (components) need to be "solved" in the reactive modeling workflow. The concentrations of secondary species can be obtained by linear combinations of the primary species as discussed above.

Mass Transport Equations

In its simplest form, a mass transport equation embodies the solute flux entering and exiting a representative elemental volume (REV), and accounts for the change in the solute concentration within the REV, along with any contributions from chemical reactions occurring within the elemental volume. Following the formulation of the mass transport equations presented by Lichtner (1985), a generalized form of the mass transport equation for multicomponent system (solid-liquid) in saturated-porous media is:

$$\frac{\partial}{\partial t}(\phi C_j) + \nabla \cdot \vec{J}_j = -\sum_{m=1}^{M} \nu_{ji}^{m} I_m - \sum_{i=1}^{N_{rev}} \nu_{ji}^{rev} I_i^{rev} \qquad \text{Eq. 12}$$

for the j^{th} primary species with concentration , where is porosity, is the total concentration for the j^{th} primary species, is the flux of the j^{th} primary species, is the total number of minerals reacting within the system, is the reaction rate for the m^{th} mineral, and is the matrix of stoichiometric reaction coefficients of the chemical reactions (represented by linear combinations of the primary species). This can be generalized for multiphase fluid systems such as supercritical CO_2-brine.

Note that in Eq. 13, the flux J_j can have advective (Darcy flow), diffusive or dispersive components. Coupled transport phenomena may require complex multicomponent treatments using a matrix of diffusion coefficients. On the other hand, simple, uncoupled Fickian diffusion may also be considered. The Darcy velocity (advective contribution to the flux) of a given phase in turn, is defined as a function of the intrinsic permeability of the porous medium, dynamic viscosity, density and pressure of the fluid phase. The reaction rate is expressed per unit volume, and therefore, the volume fraction of the m^{th} mineral in the system can be correlated to its reaction rate and specific volume. Because heterogeneous reactions result in precipitation or dissolution, with concomitant changes to the system porosity, the porosity may be calculated after each time step and updated over the domain and mass transport equations applied again to keep total porosity full coupled. Such a relationship between porosity of the system and mineral volume fractions of reacting minerals creates a coupling between the chemical and hydrologic regimes.

Under the local-equilibrium assumption, concentrations for aqueous complexes may be calculated through a mass action equation:

$$C_i^{rev} = K_i \gamma_i^{-1} \prod_{j=1}^{N} (C_j \gamma_j)^{v_{ji}} \qquad \text{Eq. 13}$$

where is the specific equilibrium constant for the equilibrium reaction, γ_i, γ_j are the activity coefficients of the aqueous complexes (i) and primary species (j), respectively, is the total number of reactions, and γ_{ji} is the stoichiometric reaction coefficient for the reaction in question.

Mass action equations that describe mineral reactions are similar to the aqueous reacting solute species, but concentrations are not obtained through these equations if the activities of minerals are set equal to unity. Mineral mass action equations may be written as:

$$K_m \prod_{j=1}^{M} (C_j \gamma_j)^{v_{jm}} = 1 \qquad \text{Eq. 14}$$

where is the equilibrium constant for the heterogeneous mineral reaction m, is the total number of heterogeneous mineral reactions, and is the stoichiometric reaction coefficient for the m^{th} mineral reaction. In summary, the mass transport equation, any mass-action equations, fluid fluxes, and porosity coupled to chemical reactions describe the transport of solute species in a multicomponent reactive system, and are implemented in various mathematical forms in many reactive-transport codes.

Reaction Kinetics

Solving these transport equations (Eq. 13) requires effective reaction rates for kinetically controlled reactions, specifically both homogeneous reactions and heterogeneous reactions. Relevant time-dependent homogeneous reactions, for which reaction kinetics need to be explicitly accounted for, include conversion of dissolved CO_2 or carbonic acid, or certain microbial-mediated reactions. Similarly, heterogeneous reactions which are rate-controlled include the interactions of water with silicates, carbonates and sulfates. In the case of aqueous species, homogeneous reaction rate (I_i^{rev}) is represented as the difference between the forward- and backward-reaction rates. Heterogeneous precipitation-dissolution reactions involving mineral species are represented in multiple forms, the simplest of which involves the kinetic rate constant k_m, specific surface mineral surface area s_m, and the degree of disequilibrium of the reaction (A_m or reaction affinity), which in turn is related to the ion activity product (Q_m). For further mathematical treatment, refer to the simplified expressions for homogeneous and heterogeneous reaction rates provided by Lichtner et al. (1996). In the case of heterogeneous reactions, more complex functions of the ion activity product are determined from experiment, especially for ionic solids like carbonates and sulfates, which have faster reaction rates than silicates and could be potentially important phases for CCS. A recent review of forms of mineral-water reaction rate laws is found in Palandri and Kharaka (2004).

Perhaps the most uncertainty associated with reactive transport stems from lack of robust kinetic parameters, especially kinetic rate constants (k_m) and specific mineral surface areas (s_m). These parameters are difficult to measure in the laboratory, and their use at the field-scales incurs even more uncertainty. Furthermore, rates measured in the laboratory may be significantly different from field measurements. Nevertheless, many effective reactive transport simulators are now available, and over the past decades some notable reactive transport study was accomplished.

For example, one of the first comprehensive analyses of reactive transport in the context of geologic CCS was performed in 2001. Johnson et al. (2001) developed a reactive transport simulator (NUFT) that explicitly coupled multi-phase flow processes and kinetically-controlled geochemical processes. Initial modeling work consisted of simulating the well characterized CO_2 injection site at Statoil's North-Sea Sleipner facility. Objectives of this modeling study included general fate and transport of injected CO_2, determination of CO_2 partitioning between trapping mechanisms, analysis of the confining zone, and effects of prograde (active-injection) and retrograde (post-injection) regimes of geologic storage. Researchers of the Sleipner CO_2 injection site investigated basic parameters including porosity, permeability, pressure, temperature, brine composition, and mineralogy of the target formation (Utsira Sandstone) and adjacent formations. The modeling efforts utilized SUPCRT92 (Johnson et al., 1992) for thermodynamic data, and activity coefficients were corrected using the Debye-Huckel formulation.

Specific surface area for most minerals was estimated by assuming idealized spherical grains of various diameters dependent upon the grain size of the specific formation. All simulations carried out adopted the same prograde and retrograde storage regime with an injection rate of 10^4 metric tons-CO_2 per year for 10 years and then a continuous linear decreasing function to zero metric tons-CO_2 per year over three months with a retrograde period of 9.75 years thereafter. Results of this study forecasted that approximately 85% of injected CO_2 mass would remain in place and migrate as an immiscible supercritical fluid phase, while 15% would dissolve into formation waters, and less than 1% would precipitate as carbonate minerals. It was also shown that only mineral trapping was enhanced during retrograde storage and plays an important role in the migration of immiscible CO_2. Results suggested that precipitation of minerals and associated reduction of permeability increases the integrity of the confining zone and creates a positive feed-back loop for increasing residence times of separate-phase CO_2. These conclusions cannot be confirmed easily, but ongoing studies utilizing measured data along with updated models of the Sleipner site will likely yield some degree of validation.

Many other studies of geologic CCS that utilized reactive transport were completed since the Johnson et al. (2001) project. Refer to the special issue of *Chemical Geology* edited by Oelkers and Schott (2005) for further studies of geochemical aspects of CO_2 storage. In 2003, the RCSP's began their characterization phase (Phase 1), but in the subsequent validation (Phase II) and deployment (Phase III) phases, reactive transport modeling has become a staple among analysis tools. Simulation packages that couple reactive transport to other processes include FLOTRAN, STOMP, TOUGHREACT, GEM-GHG, and others (Table 3). Reactive transport simulation analysis results are summarized briefly in sidebars throughout this document, and reviewed in detail in the individual RCSP case studies.[9] Also refer to Gaus et al. (2005; 2008), Oelkers et al. (2008), and Gaus (2010) for a detailed review of geochemical process modeling associated with geologic CCS.

A3.4 Biological Processes

Research into the specific conditions in which microbial processes play a role affecting geologic CCS is needed to better understand the THMCB couplings governing the transport and ultimate fate of injected CO_2. The activities of microorganisms can have a considerable chemical and physical impact on subsurface environments. In the context of geologic CCS, cellular and extracellular biomass production can clog pores in the subsurface, leading to decreased permeability (Taylor et al., 1990). Microorganisms can also affect permeability by driving mineral dissolution and precipitation.

[9] http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.

One area of current research is focused on examining potential microbiological and mineralogical changes resulting from CO_2 injection which may cause altered porosity and permeability in the injection or confining zones. Biofilm-forming organisms, such as *Shewanella frigidimarina* can endure exposure to supercritical CO_2 and may create a confining zone for the CO_2 by decreasing the permeability (Mitchell et al., 2009). Kandianis et al. (2008) suggest that microbial biomass acts as a catalyst to precipitate $CaCO_3$ in advection-dominated systems, which may lead to a decrease in the porosity, which has the potential to alter the ultimate fate and transport of CO_2 in the injection formation. Similar studies on "biomimetic" carbonate precipitation using carbonic anhydrase enzymes which catalyze the rates of CO_2 hydration are reported by Bond et al. (2002). On the other hand, biofilm dissolution, and carbonate and other mineral dissolution caused by microbial-mediated pH changes may cause the porosity to increase, potentially adversely affecting CO_2 storage and groundwater quality if they increase the risk of migration from the confining zone.

One fundamental approach to model the microbial response and its coupling with the geochemical changes consists of coupling mineral kinetics (Wilkin and Digiulio, 2010), and adsorption (Dzombak and Morel, 1990) with the kinetics of microbial metabolism (Jin and Bethke, 2005) in microbiological-geochemical models such as Geochemist's Workbench (Bethke, 2009). Examples of heterotrophic redox reactions catalyzed by microorganisms in the presence of acetate are shown in Table 6.

Table 7. Heterotrophic Oxidation-Reduction Reactions of Electron Donors (with Acetate Ions as an Example) Catalyzed by Microorganisms in the Environment

Function	Example Chemical Equation	ΔG_r^{oa} (kj/mol)
Oxygen Respiration	$CH_3COO^- + 2\,O_2(aq) \leftrightarrow 2\,HCO_3^- + H^+$	-838
Nitrate Reduction	$CH_3COO^- + H^+ + NO_3^- + H_2O \leftrightarrow 2\,HCO_3^- + NH_4^+$	-536
Manganese Reduction	$CH_3COO^- + 7\,H^+ + 4\,MnO_2$(pyrolusite) $\leftrightarrow 2\,HCO_3^- + 4\,H_2O + 4\,Mn^{2+}$	-805
	$CH_3COO^- + 15\,H^+ + 4\,Mn_2O_3$(bixbyite) $\leftrightarrow 2\,HCO_3^- + 8\,H_2O + 8\,Mn^{2+}$	-1002
Iron Reduction	$CH_3COO^- + 15\,H^+ + 8\,Fe(OH)_3 \leftrightarrow 2\,HCO_3^- + 20\,H_2O + 8\,Fe^{2+}$	-673
	$CH_3COO^- + 15\,H^+ + 4\,Fe_2O_3$(hematite) $\leftrightarrow 2\,HCO_3^- + 8\,H_2O + 8\,Fe^{2+}$	-451
	$CH_3COO^- + 15\,H^+ + 8\,FeOOH$ (goethite) $\leftrightarrow 2\,HCO_3^- + 12\,H_2O + 8\,Fe^{2+}$	-473
Sulfate Reduction	$CH_3COO^- + H^+ + SO_4^{2-} \leftrightarrow 2\,HCO_3^- + H_2S(aq)$	-88
Acetotrophic Methanogenesis	$CH_3COO^- + H_2O \leftrightarrow HCO_3^- + CH_4(aq)$	-15

[a]Standard state Gibb's free energy values for each reaction (ΔG_r^o) were obtained from the Lawrence Livermore National Laboratory thermodynamic database (Delany and Lundeen, 1990).

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