EXPERIMENTAL DESIGN APPLICATIONS FOR MODELING AND ASSESSING CARBON DIOXIDE SEQUESTRATION IN SALINE AQUIFERS

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DISCLAIMER

ABSTRACT

This project was a computer modeling effort to couple reservoir simulation and ED/RSM using Sensitivity Analysis, Uncertainty Analysis, and Optimization Methods, to assess geologic, geochemical, geomechanical, and rock-fluid effects and factors on CO_2 injectivity, capacity, and plume migration. The project objective was to develop proxy models to simplify the highly complex coupled geochemical and geomechanical models in the utilization and storage of CO_2 in the subsurface. The goals were to investigate and prove the feasibility of the ED/RSM processes and engineering development, and bridge the gaps regarding the uncertainty and unknowns of the many geochemical and geomechanical interacting parameters in the development and operation of anthropogenic CO_2 sequestration and storage sites. The bottleneck in this workflow is the high computational effort of reactive transport simulation models and large number of input variables to optimize with ED/RSM techniques. The project was not to develop the reactive transport, geomechanical, or ED/RSM software, but was to use what was commercially and/or publically available as a proof of concept to generate proxy or surrogate models.

A detailed geologic and petrographic mineral assemblage and geologic structure of the doubly plunging anticline was defined using the USDOE RMOTC formations of interest data (e.g., Lower Sundance, Crow Mountain, Alcova Limestone, and Red Peak). The assemblage of 23 minerals was primarily developed from literature data and petrophysical (well log) analysis. The assemblage and structure was input into a commercial reactive transport simulator to predict the effects of CO_2 injection and complex reactions with the reservoir rock. Significant impediments were encountered during the execution phase of the project. The only known commercial reactive transport simulator was incapable of simulating complex geochemistry modeled in this project. Significant effort and project funding was expended to determine the limitations of both the commercial simulator and the Lawrence Berkeley National Laboratory (LBNL) R&D simulator, TOUGHREACT available to the project.

A simplified layer cake model approximating the volume of the RMOTC targeted reservoirs was defined with 1-3 minerals eventually modeled with limited success. Modeling reactive transport in porous media requires significant computational power. In this project, up to 24 processors were used to model a limited mineral set of 1-3 minerals. In addition, geomechanical aspects of injecting CO_2 into closed, semi-open, and open systems in various well completion methods was simulated. Enhanced Oil Recovery (EOR) as a storage method was not modeled.

A robust and stable simulation dataset or base case was developed and used to create a master dataset with embedded instructions for input to the ED/RSM software. Little success was achieved toward the objective of the project using the commercial simulator or the LBNL simulator versions available during the time of this project. Several hundred realizations were run with the commercial simulator and ED/RSM software, most having convergence problems and terminating prematurely. A proxy model for full field CO_2 injection sequestration utilization and storage was not capable of being developed with software available for this project.

Though the chemistry is reasonably known and understood, based on the amount of effort and huge computational time required, predicting CO_2 sequestration storage capacity in geologic formations to within the program goals of ±30% proved unsuccessful.

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1 EXECUTIVE SUMMARY

The United States Department of Energy National Energy Technology Laboratory (USDOE/NETL), for the purposes of this report will be referred to as NETL, funded Fusion Petroleum Technologies, Inc. (FPTI), doing business as (dba) Fusion Reservoir Engineering Services, Inc. (FRESI), [†] to demonstrate the applicability of Experimental Design and Response Surface Methodology (ED/RSM) under the Carbon Capture Utilization and Storage program (CCUS). The project was a computer modeling effort to couple reservoir simulation and ED/RSM using Sensitivity Analysis (SA), Uncertainty Analysis (UA), and Optimization Methods (OM), to assess geologic, geochemical, geomechanical, and rock-fluid effects and factors on CO_2 injectivity, capacity, and plume migration.

The project objective was to develop proxy models to simplify the highly complex coupled geochemical and geomechanical models in the utilization and storage of CO_2 in the subsurface. The bottleneck in this workflow is high computational effort of simulation models and large number of input variables to optimize.

The US DOE RMOTC (Rocky Mountain Oilfield Testing Center) Teapot Dome site seismic and reservoir data targeting the Crow Mountain aquifer is used as a realistic surrogate or analog to evaluate the feasibility of the proposed methods. This project builds on and extends the knowledge base of a previous DOE project DE-FE-0001111, awarded to FPTI. [1]

The project was originally divided into three phases, namely Phase I, Phase II, and Phase III over two Budget Periods. The goals were to investigate and prove the feasibility of the ED/RSM processes and engineering development, and bridge the gaps regarding the uncertainty and unknowns of the many geochemical and geomechanical interacting parameters in the development of anthropogenic CO_2 sequestration and storage sites.

The original proposed objective of Phase I developed the basis for realistic geoscience foundation for reservoir simulation studies in the various project tasks and demonstrate the feasibility of using ED/RSM to engineer, design, and develop CO_2 sequestration sites in deep saline aquifers. This was to be accomplished by evaluating and expanding upon a realistic reservoir model recently developed by FPTI for DOE, namely DE-FE0001111, based on the Crow Mountain saline aquifer at the DOE Teapot Dome RMOTC site.

A detailed geologic and petrographic mineral assemblage was defined for the RMOTC formations of interest. The assemblage of 23 minerals was primarily developed from literature data and petrophysical analysis. The assemblage was input into a reactive transport simulator to predict the effects of CO_2 injection of a complex reservoir, and tracking and monitoring the reactions with the reservoir rock. Enhanced Oil Recovery (EOR), as a storage technique for anthropogenic CO_2 was not modeled in this project.

[†] A wholly owned subsidiary of Sigma Cubed Inc.

1.1 Phase I: Reservoir Modeling and Simulation

An ED/RSM study starts with a robust and stable simulation dataset or base case file. The base dataset is used to create a master dataset. The master dataset is the modified base case with embedded instructions that instructs the ED/RSM software where and how to substitute different input parameter values at runtime. After a number of simulation runs a proxy or objective function can be calculated. A robust and stable base case must be developed.

Phase I objectives were to develop a baseline reservoir model used in other phases particularly for the proof-of-feasibility study and for the development of the methodology of ED/RSM. A reservoir modeling grid was populated with geologic parameters representing lateral and vertical permeability variations and variable mineralogy distributions. The grid was integrated with a commercial reactive transport simulator. The concept was to simulate injection of pure CO_2 into vertical and multilateral horizontal well configurations and evaluate the reservoir performance and integrity (injectivity and capacity of closed, partially closed, and open systems) using the currently available reservoir modeling and simulation tools in the industry.

Phase I incorporated standard reservoir modeling concepts to accomplish the necessary detailed petrophysical studies, load data in appropriate software, and develop the static reservoir models and geocellular gridding and base dataset for dynamic simulation models used in Phase II and III. The simulation goals were to study the performance effects of: (1) impurities in the injected stream on reservoirs and seals; (2) rock types (e.g., dolomite and sandstone, etc.), (3) petrophysical parameters; (4) geochemical effects of injected gas on brine and rock interactions; (5) structural effects, e.g., vertical layering and areal permeability; and, (6) well type configuration, construction, and placement.

Initially the modeling effort was to utilize the structured model developed for the targeted formation, e.g., Crow Mountain (refer to Figure 1, page11). However, because of difficulties with the reactive transport simulator, a more simplified layer cake model was used with the approximate areal and volumetric dimensions of the structured model and defined rock characteristics (refer to Figure 2, page 11 and Figure 3, page 12). The full block model (17x73x100 cells) was used for simulating while injecting CO_2 in closed, open, and semiopen reservoirs.

1.1.1 IMPEDIMENTS:

Phase I had significant impediments, as the commercial reactive transport simulators were incapable of simulating complex geochemistry to be modeled in this project. Significant effort and funding were expended to determine the limitations of both the commercial simulator and the Lawrence Berkeley National Laboratory (LBNL) R&D simulator.

As originally proposed, the project was to use a commercially available reactive transport reservoir simulator. At the start of the project, only one commercially available code was known to exist. However, as the software was used, severe limitations were discovered regarding its capability to accomplish the simulation on the complex geochemistry of the project associated with CO_2 injection in brine aquifers.

Working with the software vendor, we expended a great effort attempting to model the realistic complex reservoir defined for this project. The vendor concluded the geochemistry problem was

greater than a user issue and the solution would require software adjustments. A follow-up with the vendor in the late seventh quarter indicated they were working the issue, but a near future resolution would not be available, primarily due to the perceived lack of a market driver. Lacking a workable commercial simulator created a considerable challenge in accomplishing the project objectives.

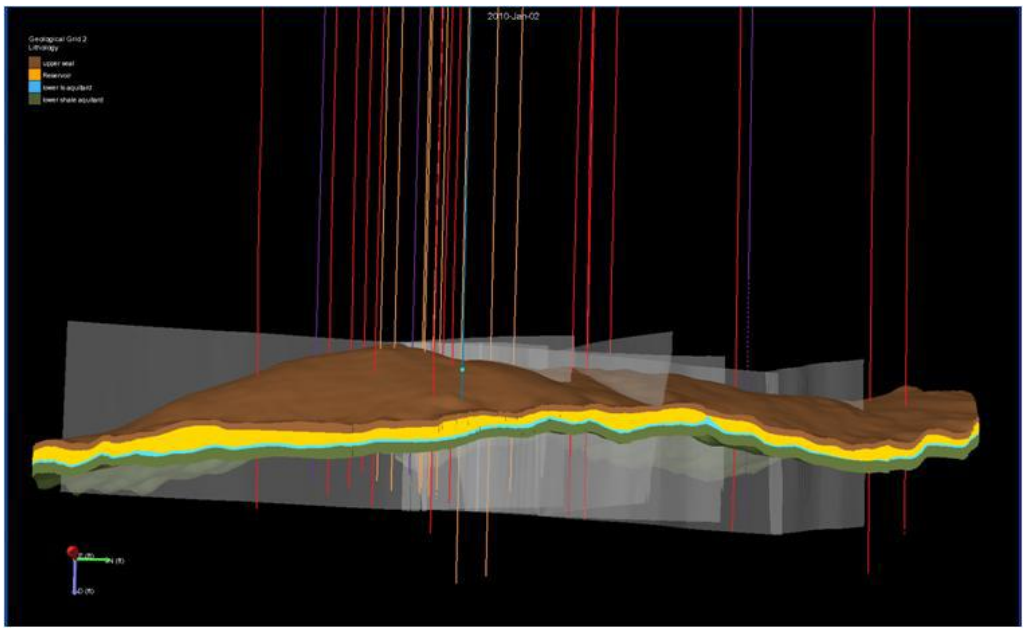

Figure 1: Targeted formations, e.g., Lower Sundance (brown), Crow Mountain (yellow), Alcova (blue), and Red Peak (green).

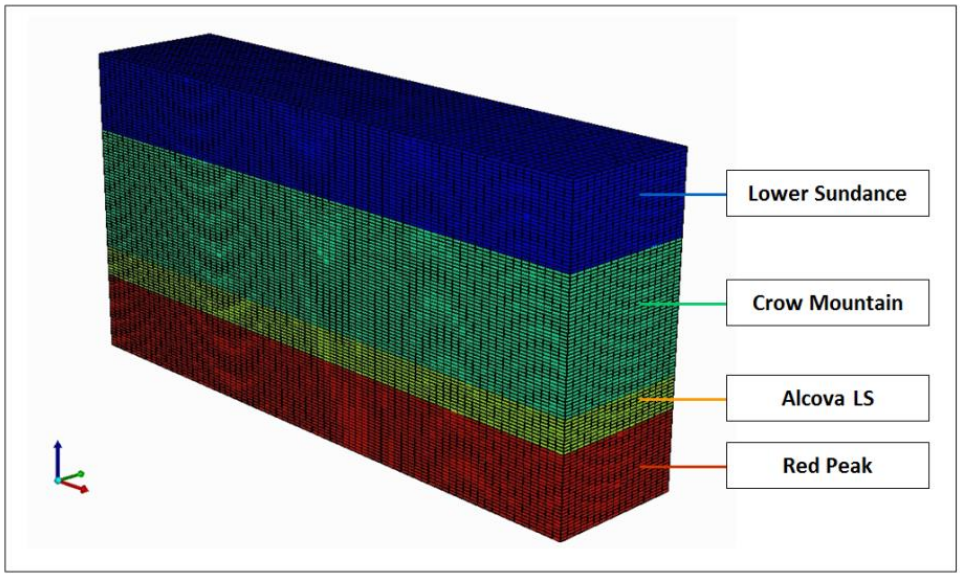

Figure 2: Simplified block model 73x17x100 cells.

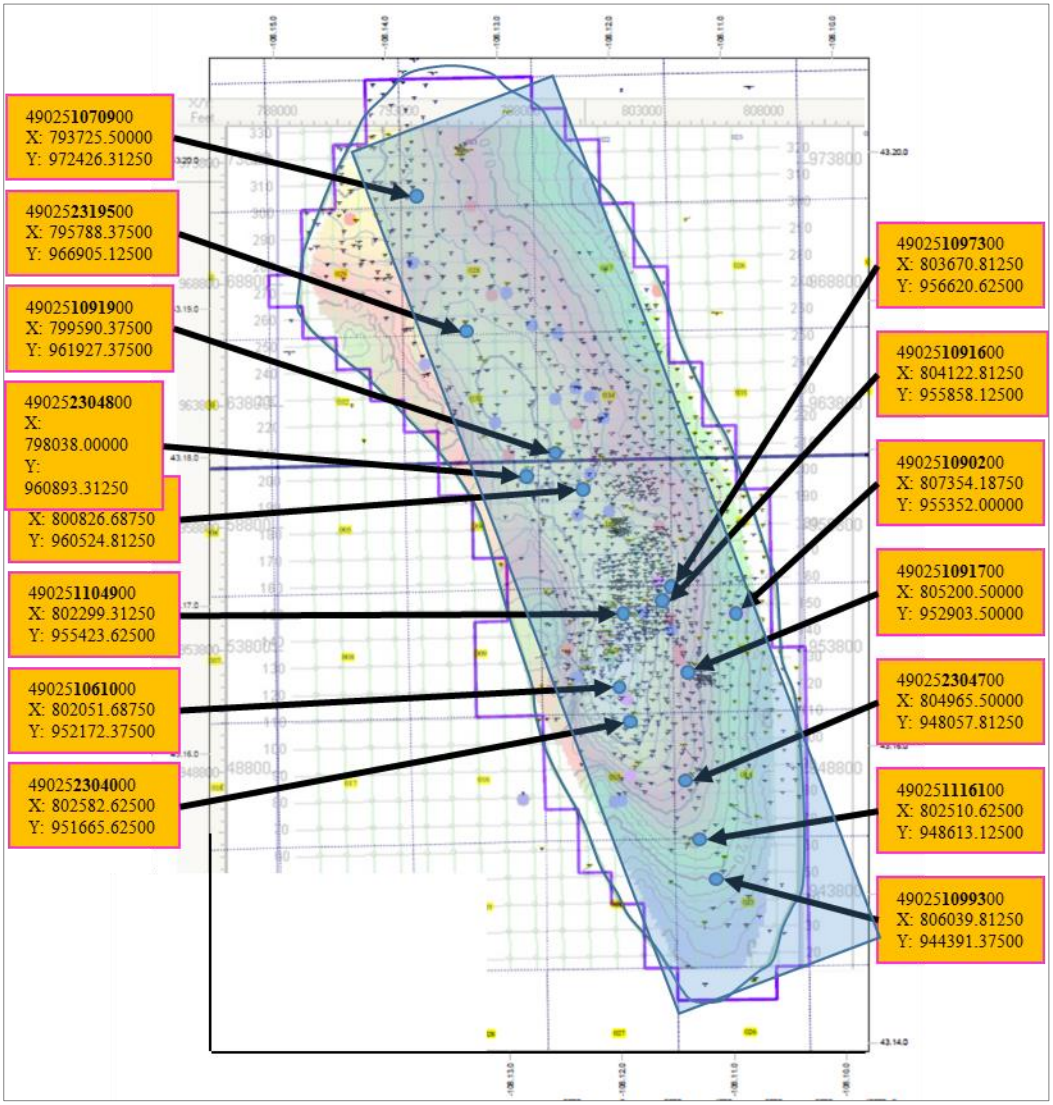

Figure 3: Layer Cake and RMOTC areal approximation.

The reactive transport simulation is a very numerically stiff problem. This seems to be especially true for a mineral assemblage that has a large number of minerals and thus a very large number of reactions, as was the case for this project. The vendor reactive transport simulator had only the kinetic reactive model for all reactive pathways, which is conceptually, fundamentally and mathematically correct, but creates modeling difficulties because of the difference in reactive time scales of the reaction systems (conflict of correct science with nuances of numerical simulation software development and run time execution).

The vendor continues to improve the geochemistry module incorporating the equilibrium modeling with the kinetic modeling, so the time scale conflict is mitigated and the science and physics of reactive flow transport in porous media is honored. The concept is fairly well published, so the

science is known, yet a software package to honor and couple the science principles and avoiding the time scale and numerical conflicts is a difficult problem.

1.1.2 Simulation Efforts

The simulation effort is a critical effort in this project and a reactive transport simulator is a required tool to accomplish the objectives of this project. The original commercial reservoir simulator had difficulty converging with the coupled geochemistry transport module engaged. Injecting CO_2 in a reservoir without modeling the geochemistry is fairly easily completed and has been achieved in the previous project (DE-FE-000111), as well as this project. To our knowledge there is only one commercial simulator available that has incorporated and truly coupled the transport model with the geochemistry and the parallel computation architecture required to model CO_2 sequestration chemistry transport in porous media and integrated with an experimental design module required for this project.

Due to this critical tool failure a change in the approach away from a commercial reactive simulation tool required to accomplish the tasks of the project was evaluated. A number of publically available high level research type software (e.g., TOUGHREACT (LBNL), CRUNCHFLOW (LBNL), PFLoTran (LANL, et al.)) could accomplish this effort, but would not allow the feasibility study as directly as the commercial reactive transport coupled with an ED/RSM software.

A change to the project schedule in the fifth quarter was implemented. Tasks were incorporated to add LBNL code, e.g., TOUGHREACT v1.2.1, TOUGH2, TOUGH2-MP, and iTOUGH2 in the project. Additional tasks to parallelize the code and integrate into FPTI GeoPRO database engine and geocellular static reservoir model (CRYSTAL™) were added, as well. The overall objectives would be the same, but the scope requirement of using a commercial simulator was replaced with the LBNL TOUGH2 programs. The LBNL TOUGH2 programs would be integrated with the FPTI software platform recently completed under DE-FE-0001111. This required substantial task revision to make the TOUGHREACT v1.2.1 capable of accomplishing the ED/RSM primary objective of this project.

At the end of the seventh quarter we determined this effort would take significant specialized resources not available during the project, and have a high risk of being unsuccessful. The resources required to properly develop a fully coupled reactive transport model with parallel software architecture for use in a full field scale ED/RSM study was determined to be unrealistic and unachievable under the current monetary and resource constraints of the project. A re-evaluation of the direction of the project was undertaken in the eighth quarter, and a focused but limited effort using the nonparallel TOUGHREACT in the eighth and ninth quarters was employed.

Toward the end of the extended BP1, the project Principle Investigator (PI), attended the 2012 TOUGHREACT and TOUGH2 symposium and training sessions to become acquainted with the TOUGHREACT code, as well as the community using the codes. There was a focused, yet limited effort attempting to accomplish limited successful geochemistry modeling with TOUGHREACT in the ninth quarter. Three alternatives were evaluated and the decision was made to modify the project tasks, incorporating additional geomechanical concepts, implementing a hydraulic

stimulation and completion study, and limiting the geochemistry evaluation of the project. The reactive transport simulation technology would require considerable development outside the scope of this project.

A very fast reservoir simulator having the capability of coupling geochemistry reactive flow was necessary to accomplish the efforts proposed in this project. Thus, a parallelized integrated chemically reactive transport reservoir simulator would be required. The simulator must be integrated with an ED/RSM to obtain the objective functions and primary tasks of the project. In addition, creating a reactive simulator was not within the scope, schedule, and resources of this project. Developing another reactive transport simulator was not a prudent approach with the other software available albeit seemingly limited as they are to achieving the projects goals.

Significant effort and resources were employed for the planning and task modification of the project for geomechanics and hydraulic fracturing. A considerable effort was expended to run the layer cake RMOTC geochemistry model in TOUGHREACT v1.2.1. Utilizing the current commercial and R&D reactive transport simulators with realistic complex mineral rock assemblages and structure, has proven intractable for full scale field modeling efforts and achieving the goal of the ED/RSM analogs. Note, a new version of TOUGHREACT v3.0-OMP has been implemented as of June 2014. This parallel version of TOUGHREACT was unavailable during the execution portion of this project. As of the writing of this report (11.12.14), a new version of the commercial reactive reservoir simulator has also been released.

1.2 Budget Period 2

The tasks for BP2 were modified to stay within the same purpose and scope of the original proposed project. In BP2 most tasks associated with geochemistry were eliminated and focus shifted to emphasize geomechanics, viz. completions, stimulations, well configurations, and other engineering and planning requirements for implementing CO_2 utilization and storage in the subsurface.

BP2 emphasized the development of geomechanical modeling tools to aid in the design and efficient operations of injecting CO_2 into oil and gas wells though EOR processes were not modeled. In BP2, the project was initially incorporated as an important and integral segment of an internally funded Sigma Cubed Inc. initiative, SUPERNOVA, to build a sophisticated integrated completion and asset management product to aid in the design, placement, and completion of oil and gas wells.

Integration of a stimulation and geomechanics software with a reservoir simulator was envisioned as part of the project in BP2 and was a significant part of the Sigma Cubed Inc. SUPERNOVA project. The SUPERNOVA Sigma Cubed Inc. initiative, was to build a sophisticated integrated completion and asset management product to aid in the design, placement, and completion of oil and gas wells. This part of SUPERNOVA was reprioritized and postponed due to resource allocations and other company priorities.

1.2.1 Scope of Work for BP2

- Develop an integrated communication method and platform for static reservoir model CRYSTAL, and dynamic reservoir simulator RESSIM, with a geomechanical simulator STIMSIM
- Incorporate discrete natural fractured network modeling capability in RESSIM and STIMSIM
- Evaluate dynamic fluid flow in the reservoir and the migration of the CO_2 plume, due to vertical and lateral heterogeneity, pressure migration, fault, and seal integrity, due to discrete natural fractures during injection of fluid into a reservoir for intentional or nonintentional rock stress failure
- Investigate the effects of complex structure in the CO_2 sequestration process on plume migration in a brine aquifer
- Evaluate the use of multilateral horizontal wells versus vertical or single lateral wells, and stimulated and non-stimulated wells on the potential of CO_2 capacity, injectivity, and trapping mechanisms

1.2.2 Simulation in Budget Period 2

The full block model (17x73x100 cells) developed earlier in the project to model the geochemistry was used to develop modeling efforts to incorporate geomechanics, while injecting CO_2 in closed, open, and semiopen reservoirs. Initially, all geochemistry was taken out of the simulation models. However, to account for proper pH and other water chemistry (e.g., effects on CO_2 solubility), limited mineralogy was put back into the model. Three minerals, specifically calcite, anorthite and kaolinite, were modeled again using a block layer cake model.

The model was changed to reflect the four geologic rock units of Sundance, Crow Mountain, Alcova Limestone, and Red Peak formations. Each modified rock unit has a defined relative permeability model taken from Bennion and Bachu literature work [2,3,4,5] on CO_2 water system in tight sandstones, shale, and carbonates, specific to that rock type. The four rock units were defined to have the three minerals with varying amounts of calcite per unit, but zero anorthite and kaolinite, as opposed to other models developed in BP1, with 23 minerals. Laterally, each layer is defined with the same permeability and porosity, but vertically each layer is different.

Incorporating even the limited chemistry creates convergence difficulty and/or reasonable run times using a single processor or core. Incorporating a realistic block model with geomechanics and limited geochemistry requires use of parallel computer code architecture in the reservoir simulator. Parallel threading using the commercial code reservoir simulator requires the use of additional software licensed from the vendor referred to as "parallel tokens."

The use of the parallel code is expensive and takes significant effort to fine tune the parallel partitions and other numerical constraints. Eventually, a successful runtime of 13.3 hours with 24 cores was achieved. Using one mineral, calcite, a base case simulation was successfully accomplished in approximately 9.7 hours.

With considerable aid from the reservoir simulator vendor, limited success was achieved in reducing the run times using parallel threading. The base case was optimally tuned to run on 8,

16, and 24 cores to achieve a sufficient speed, so the sensitivity and optimization modules in the commercial ED/RSM software could run an adequate number of cases to develop a proxy model.

Changing the numerical formulation state of the system from fully implicit to explicit-adaptive-implicit scheme, a surprisingly 9.4 fold speedup to approximately one (1) hour was achieved using 24 cores or processors for the block model. Generally, due to the stiffness of the reactive simulation, the explicit models have difficulty converging and the fully implicit models are required to maintain proper material balance and/or convergence. [6] Modeling three minerals did not increase the amount of time for a successful run using an explicit-adaptive-implicit model. However, attempting to use the structured model and one mineral, or the layer cake model with 23 minerals, were not successful regardless of the numerical approach.

1.2.3 Rock Physics Modeling

In many cases there is very limited well log data available to develop geomechanical properties for a particular area or well. The concept was to create pseudo-logs with correlations and extrapolated data (via kriging, etc.) for use in field studies, reservoir and data analytics. We used twenty-four permutations of six types of logs; Gamma Ray (Gr), SP/resistivity, Density, Neutron, and Acoustic. A software we called "quick look petrophysics" was developed using a rule-based log processing of five rules to calculate the geomechanical properties and stress in the rock using well logs. In addition, a well blocking technique was developed.

1.2.4 Geomechanical and Completion Modeling

Geomechanical properties, determined from the quick look well log petrophysical analysis program, were loaded into the reservoir simulator. The mechanical and reservoir properties (porosity and permeability) were then geostatistically populated to all grid blocks in the model using kriging techniques. Density maps from well logs and geomechanics (parameter) maps, e.g., Poisson's ratio and Young's modulus, were geostatistically distributed using Gaussian Geostatistical simulation. Due to software limitations, the complete mapping of rock properties by geostatistical distribution was grouped into 1500 rock types, corresponding to different Young's modulus and Poisson's ratio combinations. A mapping between these representative rock types and grid blocks were used to populate the geomechanical grid in the commercial transport simulator.

Initial reactive transport simulation software run times with geomechanics increased from the optimized reactive transport of approximately 30+ minutes to approximately six hours, using 24 cores. The geomechanics module in the current version of the coupled reactive transport and geomechanics model does not allow Poisson's ratio and Young's modulus to be input for each individual cell, nor does it have parallel capability for the geomechanics module. The parallelizing of the geomechanics module may be added in an upcoming 2014 release.

1.2.4.1 Fracturing of the reservoir due to injection of CO_2

A base model for vertical injection wells in a single-porosity model was developed. The base model is used for input into the commercial ED/RSM module to develop sensitivity and optimization simulation runs. Many of the simulation runs from the ED/RSM using the master

dataset for vertical injection wells had convergence issues even though the initial master dataset ran successfully. Thus, the ability to compute the objective functions was unsuccessful.

Dendritic fractures can be implied, if microseismic data and analysis are completed during injection. The dendritic fracture model is inferred to be a more realistic assumption than the conventional planar fracture assumption. A symmetrical distribution of fractured cells was considered around the vertical wells.

Fractured reservoirs are composed of two distinct systems, namely the rock matrix and interbedded or discrete fracture network. Fluid flow in structured porous media (nonfractured and fractured rocks) can be described using a variety of dual-porosity, dual-permeability, multi-porosity, and/or multi-permeability models.

In this study, a number of fracture type models were attempted, as follows:

1. Planar fractures
2. Dendritic fractures
3. Multi-stage horizontally fractured wells
4. Multi-stage horizontally fractured wells with zipper fractures
5. Dual-porosity model with no active fractures
6. Dual-porosity model with active fractures everywhere
7. Dual-permeability model with active fractures in Crow Mountain layer
8. Single-porosity models with local grid refinement around vertical and horizontal wells to simulate improved permeability resulting from hydraulic fractures
9. Dual-porosity models with MT (Matrix Block) option to allow communication between injected fluid and matrix

Unfortunately, few of these models ran successfully to the end of the injection period and the following observation period. Primarily due to the protracted time these models took to complete (in the order of 5-7 days), numerical instabilities resulted in improper run terminations.

Overall, approximately 100+ different realizations were created and tested, but a limited number (approximately a dozen) successfully ran to completion.

1.3 Conclusion, Achievements, Program Benefits

There were two program goals addressed in project DE-FE-0004510:

1. Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness.

2. Support industry capability to predict CO_2 storage capacity in geologic formations to within ±30 percent.

Successful demonstration of the modeling effort would illustrate proxy type models could be developed to rapidly, cost effectively, and efficiently perform technical assessments of major engineering and scientific issues considered to be critical in the design, implementation, and

operation of a saline aquifer CO_2 sequestration storage site. The project was unsuccessful proving the feasibility of this benefit.

1. The industry continues to lack a fast commercial reactive transport simulator capable of complex reservoir geochemistry coupled with a geomechanical simulator.

2. A limited number of minerals (<3) were modeled with publically available reactive transport simulators during the project lifecycle. The maximum number of minerals that can be effectively modeled with a reactive transport simulator is unknown; however, from the current work and published literature the limit estimation is < 5-8.

3. The industry is making progress in building robust reactive transport simulators; however, with no market driver the progress and acceptance of a coupled reactive transport and geomechanics model will be exceptionally slow.

4. EOR is helping create a market for anthropogenic CO_2. However, the concept of utilization and storage of anthropogenic CO_2 for EOR is a different chemical process than the geochemistry modeled in this project. The lifecycle of EOR projects using CO_2 is relatively short-term (measured in decades) compared to the lifecycle of a sequestration project (measured in centuries). Predicting recovery factors for EOR has a high value to the oil and gas industry; but, predicting CO_2 interactions with rocks for typical current CO_2 type floods for enhanced oil and gas recovery, has minimal economic value.

5. Geomechanical modeling simulation is fairly well defined, and a market driver primarily in completions of shale oil and shale gas reservoirs in the oil and gas industry is accelerating the development of a coupled geomechanical transport simulator.

6. A proxy model for full field CO_2 injection sequestration was not capable of being developed with software available for this project.

7. Based on the amount of effort and huge computational time required, predicting CO_2 sequestration and/or storage capacity in geologic formations to within 30% is doubtful unless the new releases of the commercial reactive transport software used in this study, TOUGHREACT v3, and PFLoTRAN can provide the ED/RSM input to develop the proxy models and verify output. Additional testing of the new releases is needed.

2 INTRODUCTION

NETL funded FPTI (dba FRESI)† to demonstrate the applicability of Experimental Design and Response Surface Methodology (ED/RSM), to develop proxy models to rapidly, cost effectively, and efficiently perform technical assessments of major engineering and scientific uncertainties critical to design, implement, develop, and operate a saline aquifer CO_2 sequestration/storage site. The project is a computer modeling effort incorporating deterministic and ED/RSM using Sensitivity Analysis (SA), Uncertainty Analysis (UA), Optimization Methods (OM), Experimental Design (ED) modeling, and Response Surface Methods (RSM), to assess geologic, geochemical, geomechanical, and rock-fluid effects and factors on CO_2 injection, capacity, and plume migration.

The project objective is to develop proxy models to simplify the highly complex coupled geochemical and geomechanical models in the utilization and storage of CO_2 in the subsurface. The bottleneck in this workflow is high computational effort of simulation models and large number of input variables to optimize.

The US DOE RMOTC (Rocky Mountain Oilfield Testing Center) Teapot Dome site seismic and reservoir data targeting the Crow Mountain aquifer is used as a realistic surrogate or analog to evaluate the feasibility of the proposed methods. This project builds on and extends the knowledge base of a previous DOE project DE-FE-0001111, awarded to FPTI. [1]

2.1 Project Objectives

The overall project goal is to develop and demonstrate the efficacy of using proxy models that integrate what is known and bridge what is unknown or uncertain, in the design and operation of CO_2 storage and utilization sites. Proxy analogs are a fast calculation of how the many geologic, rock, and fluid properties interact in unison (rather than separately) to govern plume migration, injectivity, and reservoir capacity. Encompassing the current state of the science and art of reservoir simulation, the goal is to better quantify expectations and improve understanding and insight in the estimation of capacity, prediction of optimized injectivity, and improved injection well designs, by using ED/RSM methods and the resulting proxy models or algorithms.

The key goals in this project were fourfold: 1) Evaluate the fluid flow in a candidate reservoir as it pertains to migration of the CO_2 plume, due to vertical and lateral heterogeneity, relative permeability effects and changes due to dissolution of the rock, pressure migration, fault distribution, and seal integrity; 2) Evaluate the use of multilateral horizontal wells, as opposed to vertical or single-lateral wells; 3) Model the competing thermodynamic and chemical factors in saline aquifers on the geologic formation and caprocks, by injecting impurities associated with the CO_2 gas stream, and tie all these aspects together by; 4) using a commercial third-party reactive transport simulator coupled with ED/RSM software to develop and evaluate the capability of creating fast surrogate models for CO_2 utilization and storage.

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2.2 Management of Project

2.2.1 Approach

A realistic analog reservoir model, previously developed by FPTI for DOE (DE-FE-0001111) [1], based on the Crow Mountain saline aquifer at the DOE Teapot Dome RMOTC site was used and modified, as necessary, for this project. The RMOTC site was chosen because suitable publically available 3-D seismic, reservoir, and well data for the site was available, and CO_2 sequestration baseline work has been completed at the site by FPTI and is readily available. FPTI applied high-end seismic imaging and reservoir analysis tools, thereby deriving a seismic rock physical model of the reservoir, incorporating well information, defining the formation geopressure distribution, and overall reservoir characterization. From the seismic and rock physics analysis, a reservoir model was defined and used to simulate injection and further develop realistic development strategies incorporating well completions, effects of rock-fluid interactions, and vertical and lateral heterogenic effects.

To setup a realistic framework for the methodology, an analog reservoir was characterized and geologic and geophysical structure defined (the earth model), including faulting and petrophysical attributes using geostatistical analysis to gain an understanding of the effects of facies changes, rock type variations, areal and vertical distribution of rock types, layering, vertical permeability variations, and high and low lateral permeability streaks, all of which can create baffles and barriers to flow.

The computer modeling effort in this project incorporated the concept of "seismic through simulation" to characterize a reservoir and capture the geological structure effects on CO_2 fluid flow. The strategy was to use as much of the detailed earth model in the reactive transport simulator as possible. The purpose of the simulation would analyze how variations of a well construction (e.g., multilateral well type) and geologic variations influence plume migration, storage capacity, and injectivity. The proposed modeling efforts used FPTI proprietary seismic technology, a third-party geocellular model, and limited use of CRYSTAL geocellular modeling software (acquired by FPTI parent company in an additional merger after project award), integrated with a third-party reactive transport reservoir simulator and ED/RSM software.

The intent was to couple geochemistry with an analysis of how well construction variations affect plume migration, capacity, and injectivity. The data associated with the DOE/RMOTC Crow Mountain saline aquifer (all publically available and in FPTI possession) was used. All data came from previously published or existing petrophysical and mineralogical analysis of well logs and limited core data. Though the RMOTC field has been well studied, Crow Mountain, as a saline aquifer for CO_2 injection, provides a well-defined analog for general storage analysis and should provide an adequate dataset to develop the methodology proposed herein.

The project was originally divided into three phases, namely Phase I, Phase II, and Phase III over two Budget Periods. The goals were to investigate and prove the feasibility of the ED/RSM processes and engineering development, and bridge the gaps regarding the uncertainty and unknowns of the many geochemical and geomechanical interacting parameters in the development of anthropogenic CO_2 sequestration and storage sites.

2.2.2 Challenges and Difficulties

As originally proposed, the project was to use a commercially available reactive transport reservoir simulator. At the start of the project, only one commercially available code was known to exist. However, as the software was used, severe limitations were discovered regarding its capability to accomplish the simulation on the complex geochemistry of the project associated with CO_2 injection in brine aquifers.

Working with the software vendor, we expended a great effort attempting to model the realistic complex reservoir defined for this project. The vendor concluded late in the fifth quarter the geochemistry problem was greater than a user issue and the solution would require software adjustments. A follow-up with the vendor in the late seventh quarter indicated they were working the issue, but a near future resolution would not be available, primarily due to the perceived lack of a market driver. Lacking a workable commercial simulator created a considerable challenge in accomplishing the project objectives.

Other avenues were explored to accomplish the project, which relied primarily on using the DOE/LBNL TOUGH2 series of codes. However, using the LBNL codes proved unsuccessful. At the time, the TOUGHREACT codes available to the public (version 1.2.1) did not have parallel architecture, or were very slow for the required many multiple simulation runs required to define the proxy models. Limited success was achieved with the commercial reactive transport reservoir simulator at the end of the project, after multiple software version releases by the vendor.

In addition, FPTI (and FRESI) was purchased and merged into Sigma Cubed Inc. The organizational change caused a redirection of company strategy, and because of the reactive transport simulation challenges, the project was redirected away from geochemistry and more into geomechanical impacts of CO_2 injection at the beginning of Budget Period 2 (BP2). The overall project scope in BP2, which was to develop proxy models of CO_2 injection into brine or mature oil and gas reservoirs, remained the same.

Initially in BP2, the project was to be an integral part of an internal initiative called SUPERNOVA. However, that initiative was soon redirected and the project was subsequently moved outside of SUPERNOVA. The third-party reservoir simulator still had considerable challenges. The geomechanical module of the reservoir simulator did not have parallel architecture, and was inefficient in modeling the geomechanical and completion aspects of the project.

The combination of organizational changes causing strategy redirection and the lack of functional software created difficulty in achieving project objectives.

2.3 Background

2.3.1 NPR-3 RMOTC Teapot Dome - Analog Realistic Reservoir

The Naval Petroleum Reserve No. 3 (NPR-3) commonly referred to as the Teapot Dome field (refer to Figure 4, page 22) is operated by the U.S. Department of Energy (DOE), through the

Rocky Mountain Oilfield Testing Center (RMOTC). At the writing of this report, the RMOTC was being divested for privatization through a public bid offering.

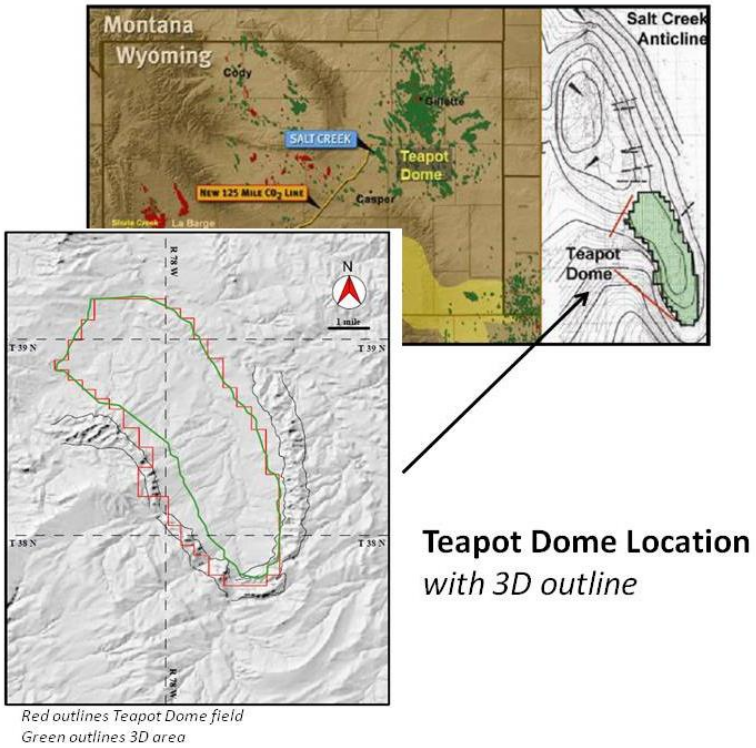

Figure 4: Geographical location of Teapot Dome with lease.

NPR-3 is located in the southwest portion of the Powder River Basin, 35 miles north of Casper, Natrona County, Wyoming. Production from the Teapot Dome commenced in the 1920's and was shut-in approximately 1923, after the Harding Administration Teapot Dome scandal. There was sporadic limited production from NPR-3 until 1976, when full development activities began, following the effects of the first Arab oil embargo. NPR-3 has nine (9) productive horizons with the Shannon, Steele, and Niobrara Shales, Second Wall Creek, and Tensleep formations being the most productive. The stratigraphy of the Teapot Dome is illustrated in the geologic column displayed in Figure 5, page 24.

The extent of the Crow Mountain reservoir does not end at the boundaries of the RMOTC NPR-3 lease. The geographic expanse of the Crow Mountain formation is not exactly known; however, outcrop petrographic studies defining the lithology in northwest Wyoming have been accomplished. There appears to be pinchouts and structural unconformities in Crow Mountain and its surrounding formation.

Lying between oil and gas reservoirs in the RMOTC lease boundaries, the data for analysis of the Crow Mountain aquifer was primarily a vestige of activity to define the oil and gas horizons and producing capabilities in the boundaries of the RMOTC NPR-3 Teapot Dome. In the boundaries

of the DOE NPR-3, the Crow Mountain formation or reservoir is considered a brine aquifer for oilfield waste water disposal. The Crow Mountain formation has been reported to produce significant amounts of oil in several anticlines in the Big Horn and Wind River basins of northwestern and north central Wyoming, outcrops near Ten Sleep and Dubois, Wyoming, and near the southeastern end of the Washakie Range.

FPTI previously processed the Teapot Dome 3-D seismic data and evaluated geological, petrophysical, and engineering information, and all RMOTC data available [1] focused on Crow Mountain. There is limited petrophysical data across the Crow Mountain aquifer in the Teapot Dome (RMOTC) area. Three wells are completed in Crow Mountain and used for water disposal. More than 33 wells penetrate to the lower horizons, primarily targeting the Tensleep oil producing formation. Fourteen of the wells penetrating Crow Mountain have sonic logs and were evaluated with the density neutron logs to estimate rock and fluid properties.

For this study, the entire aerial extent of the Teapot Dome property was utilized. Initially, in the first quarter of the project, the petrophysical data was re-evaluated and determined that quality and quantity of the available petrophysical data was not sufficient to further delineate mineralogy and lithological facies definition of Crow Mountain and immediate surrounding rock from the well log data. Thus, any detailed petrographical or mineralogical and geochemical data would necessarily come from the literature, either directly or by analogy to similar types of rocks and lithology. Fortunately, there has been a significant amount of petrographical and stratigraphic work accomplished in the decade 1960-1970.

The targeted Crow Mountain reservoir for this study is contained in the lease boundaries of the NPR-3. Though the formations and reservoirs in the NPR-3 lease have been well studied, Crow Mountain as a saline water repository for anthropogenic CO_2, has not been extensively studied for CO_2 sequestration or storage. The complex structure, lack of hydrocarbon producing potential, and available seismic and reservoir data, make the Crow Mountain formation a favorable analog for a realistic and general analysis for CO_2 storage in a confined brine aquifer. Other formations in the NPR-3 site, primarily oil producing strata in the Tensleep and Dakota (Frontier) formations, have been evaluated for CO_2 EOR/Sequestration, but the Crow Mountain reservoir has not been evaluated to any extent.

Picard, et al [7,8,9] presented several works in the 1960's and 1970's, with additional current works reported in Cavaroc [10] on the petrography and stratigraphy of the Red Beds of the Triassic Chugwater Group in northwestern and south central Wyoming. The work of Picard and others provide a basis for the petrography (mineralogy assemblages) and stratigraphy used in this study. The Crow Mountain, Alcova, and Red Peak are members of the Chugwater Group.

2.3.2 Teapot Dome Geology and Structure Overview

The Teapot Dome is a large northwest-southeast trending, highly faulted, doubly plunging, basement-cored, Laramide-age asymmetrical anticline. [11] The anticline is an extension of the larger Salt Creek anticline to the north. The structure drops much more rapidly on the west flank than on the east side of the structure. For most of this study, the entire aerial extent of the Teapot Dome property is utilized.

The Chugwater Group (Triassic) in ascending order, consists of the Red Peak, Alcova Limestone, Crow Mountain Sandstone, and Jelm or Popo Agie formations. With the exception of Alcova Limestone, which is a marine limestone, the remainder of the Chugwater Group is primarily red mudrock interbedded with very fine to medium grained sandstone. [12] Crow Mountain is thought to be of tidal flat to shallow marine origin. [12] In the RMOTC Teapot Dome area (central Wyoming), the Jelm or Popo Agie formations are disconformable, and the Crow Mountain formation of the Chugwater Group is overlain by the Sundance formation (Jurassic).

The Red Peak consists of silty claystone to sandstone and has casts of salt, mud cracks, and raindrop impressions, indicating tidal flat to nearshore marine depositional environments, and underlays the Alcova and Crow Mountain formations [13]. The origin of other units, consisting of continuous sandstone or claystone units, is much less certain. However, continuous sandstones observed near Alcova Reservoir have irregular bedding that may be sabkha (coastal salt flat) related. Other units exposed near Dubois, Wyoming, have distinct channel forms [13]. In the current project model, the Red Peak is defined as the lower aquitard or seal. The top fifty feet are modeled in this project. Refer to Figure 5, page 24.

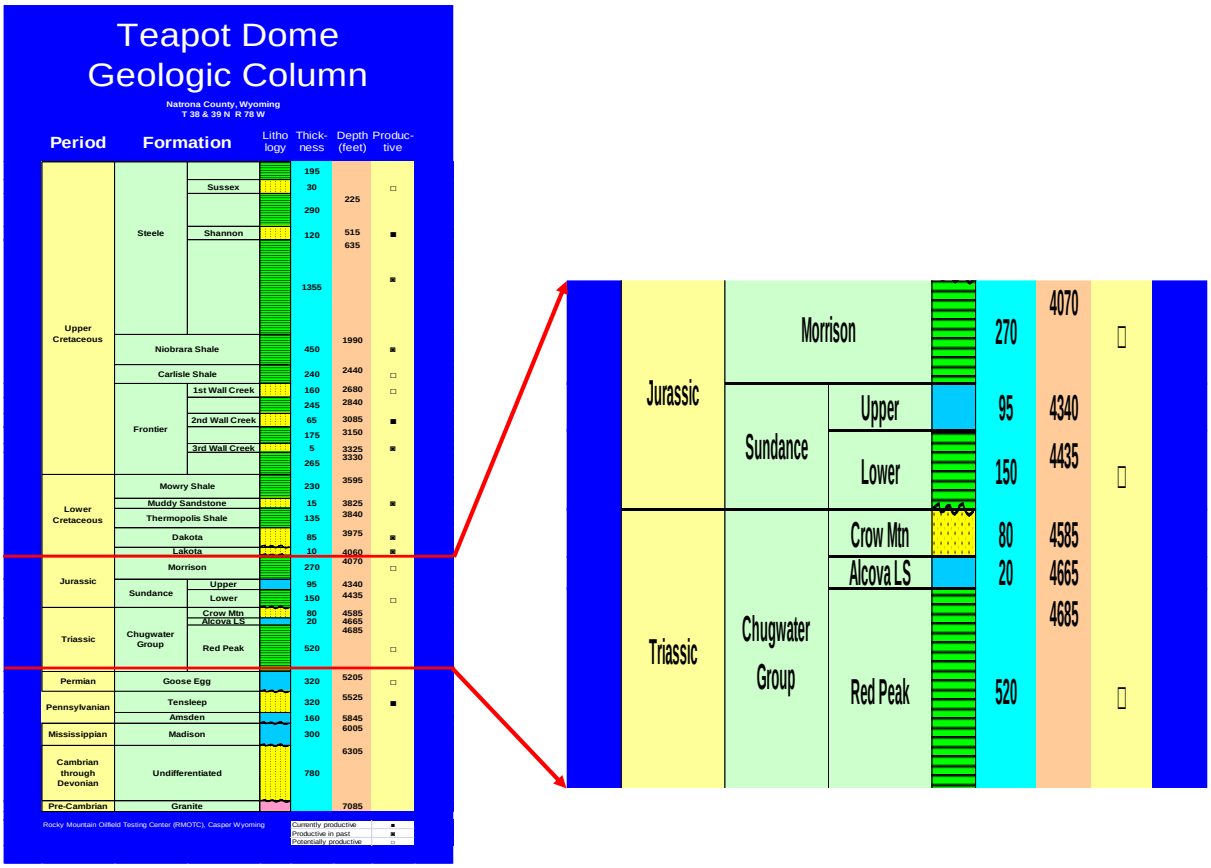

Figure 5: Geologic Column of the Teapot Dome field displaying the Triassic Crow Mountain saline aquifer and surrounding formation.

The Alcova Limestone consists of marine limestone and dolomite, and contains minor mollusks and abundant algal structures. The unit is a minor reservoir that produces hydrocarbons from fractured limestone with no primary porosity at Big Sand Draw field [13]. The Alcova has a thickness ranging from over 20 feet in the southeastern and central portions of the field, to a few feet in the northwest portion of the NPR-3, where it eventually pinches out.

Above the Alcova is a well lithified Upper Triassic sandstone formation called Crow Mountain. Crow Mountain is characterized by fine to medium grained, crossbedded sandstone, and has produced approximately 2 million barrels of oil with associated gas in the Beaver Creek, Pilot Butte, Poison Spider, Rolff Lake, Sheldon Northwest, and Steamboat Butte fields, Wyoming. These fields are west and southwest of the RMOTC NPR-3 site. Crow Mountain is considered a minor reservoir. [13] Crow Mountain is the targeted reservoir to simulate CO_2 sequestration for this project.

For the project, the Lower Sundance formation is defined as the upper aquitard and possible seal to the CO_2 injected into Crow Mountain. In general, the Sundance formation is approximately 200 to 550 feet thick in the RMOTC area. We are modeling the lower 50-foot section immediately above Crow Mountain. The overall formation consists of interbedded sandstone and siltstone, with some limestone and shale deposited in marine to eolian environments. [13] Some strata are glauconitic (iron potassium phyllosilicate) and highly fossiliferous. [13] The unit may be effectively sealed off from Phosphoria generated oil in the western half of the Wind River Basin by anhydrite beds in the underlying Gypsum Spring formation. Approximately 3.5 million barrels of oil have been produced from the Sundance formation at Bolton Creek, Poison Spider, Schrader Flats, and Spindletop fields, all located at the extreme eastern margin of the Wind River province where the Gypsum Spring anhydrite beds are not present [13] (west and southwest of the NPR-3 Teapot Dome area).

Though the formations surrounding Crow Mountain, e.g., Red Peak (below) and Sundance members (above) have considerable clay compositions, they are not considered impermeable shale aquitards or aquicludes. These silty claystones would conventionally be considered a shale, but these rocks cleave in more sub-conchoidal to conchoidal fractures and exhibit poor fissility [7], and are not defined as a true shale, which generally cleave along planes in thin sheets.

2.3.3 Petrophysical Data

Petrophysical data across the Crow Mountain aquifer is limited. Three wells are completed in Crow Mountain (primarily used as disposal wells) and over 33 wells penetrating to the lower horizons primarily targeting the Tensleep oil producing formation. Fourteen of the wells penetrating Crow Mountain have sonic logs and were evaluated with the density neutron logs to estimate rock and fluid properties. There is one known core taken over Crow Mountain in well 34-CMX-10 (API number 49-025-10929-00), and one Drill Stem Test (DST) in the same well. The DST was not analyzed for any reservoir characteristics for this project. The sparsity of available petrophysical data makes satisfactory rock and fluid flow characteristics in Crow Mountain and immediately neighboring rock difficult to establish.

2.3.4 Simple Geochemical Model-DE-FE-0001111

A simple geochemical model using three mineral components and a simple single relative permeability model was initially developed to simulate injection of 1 million scf per day of CO_2 in each of two simulated wells in the structured reservoir modeled in DE-FE-0001111 project. There were significant challenges getting the reactive reservoir simulation model to run with the structured model with very limited number of mineral reactions. CO_2 was simulated injecting into the reservoir for 30 years, with soak time of 1000 years. Computation time took over two weeks with one four-core processor. A method to reduce the significant computation time would certainly prove beneficial, and was one of the impetus for the current project (DE-FE-0004510). The concept of developing proxy models or equations would allow more efficient and optimized methods of determining operating parameters for CO_2 injection sites.

DE-FE-0001111 simulation model used six aqueous reactions and three mineral components, with seven aqueous components H^+, Ca^{++}, Al^{+++}, $SiO_2(aq)$, HCO_3^-,CO_3^{--}, and OH^-. The mineral components were anorthite ($CaAl_2Si_2O_8$), a calcium rich feldspar, calcite or calcium carbonate ($CaCO_3$), and kaolinite, a common clay mineral ($Al_2Si_2O_5(OH)_4$) prevalent in sandstone rocks. The volume fraction of rock input in the model was anorthite 0.0088, calcite 0.0088, and kaolinite 0.0176, with the remainder considered or assumed inert. There are a number of other minerals that may be used from the commercial reactive transport reservoir simulator database. Three of the most common and prevalent minerals were selected for initial runs for the DE-FE-0001111 project. The six equilibrium reaction equations are:

$$CO_2\ (aq) + H_2O \rightleftharpoons (H^+) + (HCO_3^-)$$

$$(CO_3^{--}) + (H^+) \rightleftharpoons (HCO_3^-)$$

$$(OH^-) + (H^+) \rightleftharpoons H_2O$$

$$\text{Anorthite} + 8\ (H^+) \rightleftharpoons 4\ H_2O + (Ca^{++}) + 2\ (Al^{+++}) + 2\ SiO_2\ (aq)$$

$$\text{Calcite} + (H^+) \rightleftharpoons (Ca^{++}) + (HCO_3^-)$$

$$\text{Kaolinite} + 6\ (H^+) \rightleftharpoons 5\ H_2O + 2\ (Al^{+++}) + 2\ SiO_2\ (aq)$$

The equilibrium reaction equations define the chemistry during the injection of the CO_2 and the subsequent dissolution and deposition during the shut-in periods. However, since the primary purpose of DE-FE-0001111 was to inject CO_2 and determine the capability to monitor the plume using synthetic seismic, additional chemistry was not advisable since the more complex the chemistry the more computer resource time is required. The parameters used for the aqueous phase chemical equilibrium reaction equations and mineral dissolution and precipitation reactions define the mineral reaction system and are determined from the commercial equation-of-state software. Mineralization of CO_2 is possible with providers of Ca^{++}, Mg^{++}, and Fe^{++}. The actual physical process takes a long time. Henry's law solubility model was used to calculate the solubility of CO_2 in water. The reservoir simulation section of the final report [1] for DE-FE-0001111 is reproduced in Appendix A.

3 RESULTS AND DISCUSSIONS

3.1 Reservoir Static Model Base

The objective of Phase I was to develop a baseline reservoir model to be used in other Phases, particularly for developing the Proof-of-Feasibility and the methodology of experimental design and response surface processes. A reservoir modeling grid was populated with geologic and geomechanical parameters. These parameters defined lateral and vertical permeability variations and variable mineralogy distributions, and were integrated with a commercial reactive transport simulator.

The concept was to simulate injection of pure CO_2 into vertical and multilateral horizontal well configurations, and evaluate the reservoir performance and integrity (injectivity and capacity of closed, partially closed, and open systems) using currently available industry tools. The majority of the development of the static structured modeling work was accomplished in a previous project DE-FE-0001111. [1]

Phase I incorporated standard reservoir earth modeling concepts into a base dataset for dynamic reactive simulation models used in Phases II and III. To accomplish this, the necessary detailed petrophysical and mineralogy data was loaded into earth modeling software to develop the static reservoir models and geocellular gridding necessary for the base dynamic reactive simulation models.

The Teapot Dome geological structure (horizons and faults), as defined in the previous project, was based on the interpretation of 3-D seismic time data and converted to depth using FPTI in-house time-to-depth conversion process and well ties. The depth seismic cube, well tops, faults, and horizons were then imported to the JewelSuite™ geocellular earth modeling software.

Fourteen faults and four horizon surfaces (Crow Mountain, Alcova, Dakota, and Tensleep) were interpreted from seismic data and correlated to formation tops using ten wells that penetrated Crow Mountain. Six of the interpreted faults extended above and below the Crow Mountain formation (refer to Figure 6). The Dakota formation is approximately 650 feet above the Crow Mountain formation, and Tensleep approximately 840 feet below Crow Mountain. Sundance forms a caprock of approximately 245 feet of silty, limestone-dolomitic claystone, and Red Peak forms the lower seal of approximately 520 feet of claystone (refer to Figure 5, page 24). In the NPR-3, the Dakota and Tensleep formations both produce hydrocarbons, while Crow Mountain is an aquifer currently used as a brine disposal formation. The surfaces of the two horizon tops for Red Peak and Sundance were developed by copying the Crow Mountain surface and creating a parallel surface snapped to the Sundance formation tops. The surface of Red Peak was developed similarly using the interpreted Alcova surface. The surfaces fit the seismic cube well.

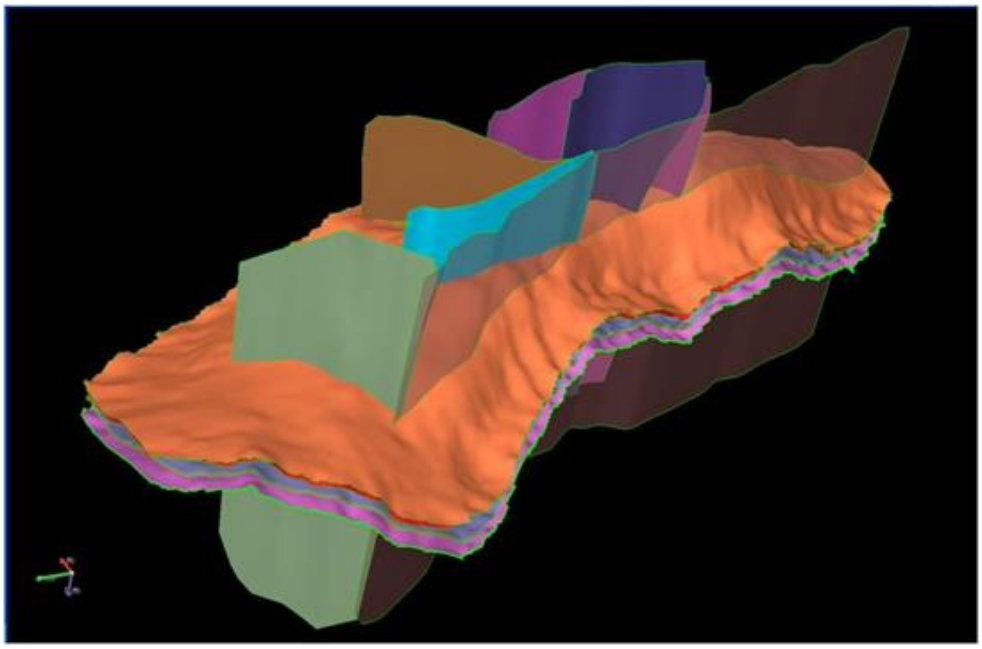

Figure 6: Six Interpreted Faults

3.1.1 Permeability Determination

Critical reservoir parameters used to determine reservoir rock and fluid flow characteristics for engineering analysis and simulation is the absolute and effective permeability. They are usually obtained by core analysis and then scaled appropriately to develop a porosity and permeability relationship, to relate porosity and reservoir resistivity from well logs and estimate water saturations and permeability of the reservoir at the appropriate scale.

The data from the one core in the Crow Mountain reservoir was used to generate a cross plot of core permeability versus core porosity. The cross plot data was compared with published correlations to estimate the permeability strictly from log data. The Timur correlation was determined to fit the data fairly well. Based on the limited data, and the fact there is such sparse core data available, using a correlation to estimate the permeability based on porosity and irreducible water saturation, is justified.

The Timur Correlation [14,15] is given in equation (1), presented in modified form as equations (2) and (3), and used to calculate permeability from ten logs penetrating Crow Mountain, based on effective porosity from the neutron density logs:

Where irreducible water saturation was calculated using a simple approximation, as given by equation (3):

$$k = 0.136 \frac{\emptyset_{eff}^{4.4}}{S^2{}_{wirr}} \quad (1)$$

$$k = \left(100 \frac{{\emptyset_{eff}}^{2.25}}{S_{wirr}}\right)^2 \quad (2)$$

$$S_{wirr} = \frac{0.065}{\emptyset_{NDe}} \quad (3)$$

The following definitions apply:

k	Permeability (md)
$\emptyset_{eff}$	Effective porosity
S_{wirr}	Irreducible water saturation
$\emptyset_{NDe}$	Effective Porosity determined from neutron density log cross plot with shale correction applied[1]

An empirical correlation for a measured core and permeability relationship was completed where core had been gathered from the upper 30 feet of the Crow Mountain formation on one well (refer to Figure 7 page 31 - Figure 9, page 32). The Timur correlation approximated the permeability sufficient for the purposes of this project, considering the limited core data available. The time and project scope did not allow for separate zonal calibration of core porosity and core permeability relationships. None of the core measurements appeared to be conducted at reservoir pressures, so if analyzed based on core data available in other zones, the core relationship could be misleading.

The Timur correlation was developed for clean sands, which should be valid for the relatively clean Crow Mountain sandstone. However, for the project scope we extended the use of the Timur equation without modification or justification, to calculate permeability in shaley areas and in limestone and dolomite formations. Generally, the Timur correlation, as well as other correlations used to determine permeability, are calibrated with more core data, production data, and pressure transient data, to ensure the values are representative of the permeability of the particular formation. The magnitude of shale permeability calculated using the Timur correlation indicates it is consistent with published laboratory conductivity and permeability of shale.

At the time of this project, there was little known work regarding correlations for shale permeability. Some Research & Development (R&D), regarding shale gas mechanism is proceeding in the scientific community. Efforts to evaluate the conductivity of shale have been accomplished and recently published. Shale and seal permeability can range over many orders of magnitude. Reported shale permeability ranges from 0.1 to 10^{-8} md. [16] Hart, et al, [17] recently measured the permeability of the shale aquitards in the Maquoketa formation in Wisconsin, and found the permeability range from 1.8 x 10^{-6} to 4.1 x 10^{-4} md, while other researchers [18] measured smaller values over a wider range, between 0.01 to 10^{-8} md. Blasingame [19] documents the

[1] In this case $\emptyset_{NDe}$ is the shale corrected porosity calculated from the total porosity from a typical neutron density cross-plot. The shale volume used to adjust the total porosity is equal to the bentonite volume plus the shale volume (Neutron$_{Shale}$ = 12-14% Density$_{Shale}$ = 2.44 to 2.46 g/cc and S_{wirr} is the water saturation irreducible estimate.

progression of technology for the evaluation and characterization of low permeability reservoir systems. He remarks the estimation of shale permeability remains difficult and the work of Neuzil [18] focuses less on specific values of shale permeability and more on "regions" shown on a plot of porosity versus logarithm of permeability. Blasingame suggests this perspective is useful in understanding that shales and clays have high porosity and low permeability, and some predictability in terms of trends.

The use of a power law model for estimating permeability in shaley sands using porosity and shale volume has been suggested. This method is somewhat similar to the Timur correlation, in that ultimately a power law (or modified power law) relation is obtained. We used this technique to estimate the effective porosity by reducing the total porosity based on the shale volume, and used the effective porosity to calculate the permeability for modeling the Crow Mountain aquifer in this project.

3.1.2 Mineralogy Estimates

3.1.2.1 Lithology from well logs

Working with a ten well log subset, a limited mineralogy study was completed. The purpose was to determine if the general lithology encountered in the Teapot Dome area could be modeled with the available data. Based on mud log cutting descriptions, we were able to establish a model that represents the major lithology types of Crow Mountain and surrounding formations. Because log quality was generally satisfactory, the model demonstrated robustness, in that we were able to accomplish the lithology representation with minimal iterations and in considerably less time than typical multi-mineral analysis. The multi-mineral representation of the rocks from well logs helps to develop a facies distribution model of the impact on flow and geochemical reactions during the injection and storage of CO_2. Refer to Figure 8, page 32, Figure 10, page 33, and Figure 11, page 34. Figure 11 illustrates an example of the lithology from one of the wells. Though the lithology is important, reactive transport simulation requires a quantitative analysis of the mineral composition, so reaction equations can be defined.

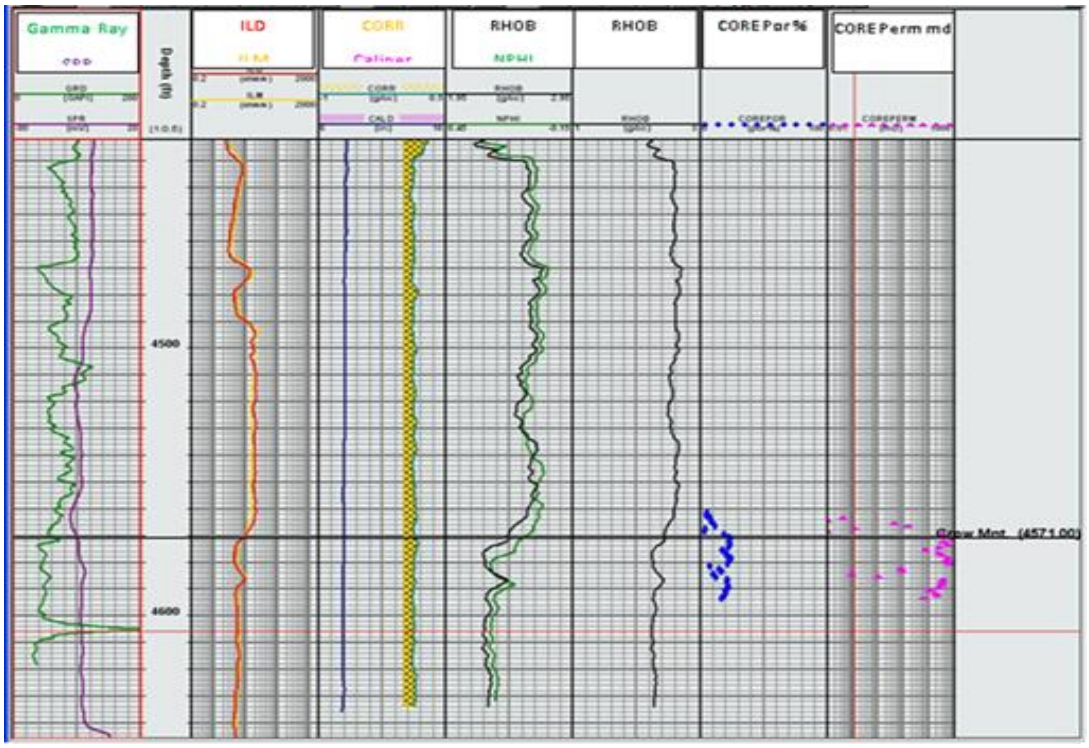

Figure 7: The 34-CMX-10 (API Number 490251092900) well has core data in the upper 30 feet of the Crow Mountain formation. The core porosity (blue points) and core permeability (pink points) are illustrated in the last two tracks.

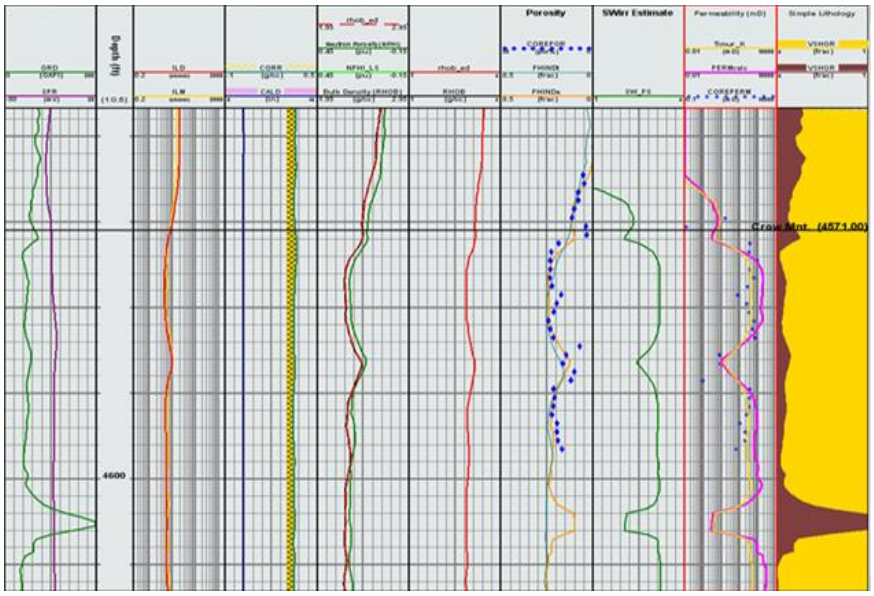

Figure 8: The Timur curve (yellow) in the last track appears to be a better fit than the pink statistical fit to measured porosity and permeability core data (blue points).

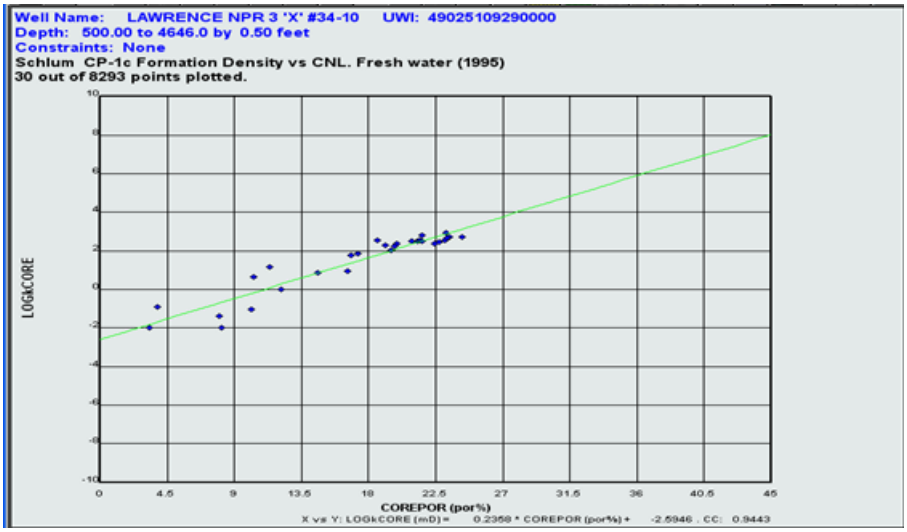

Figure 9: Core relationship for Crow Mountain: $k = 10^{(0.23568\phi_{core} - 2.5946)}$.

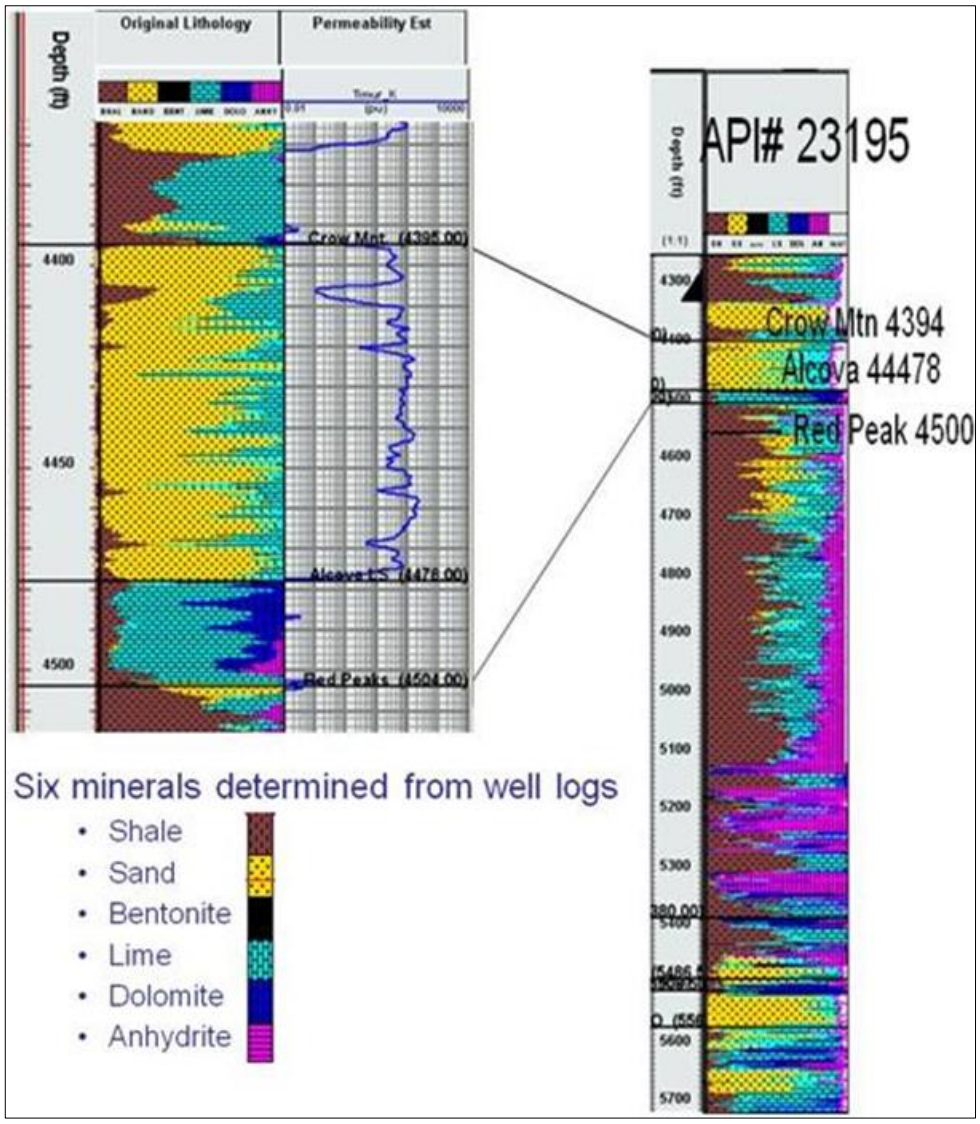

Figure 10: Limited mineralogy study example from well logs.

Eight of the ten wells used for the mineralogy study indicate the lithology of the Chugwater Group in Figure 11, page 34. The arrangement of the wells shown in Figure 11 is not in any particular pattern or order (e.g., no specific cross-section is depicted). The wells were hung on the top of Crow Mountain measured depth. The purpose of the illustration is to show the Crow Mountain lithology and surrounding formations. Crow Mountain is moderately clean sandstone, but it has stringers of calcium carbonate with bentonite clays present. The Sundance formation above the Crow Mountain shows considerable "liminess" with some areas having sandy permeable stringers.

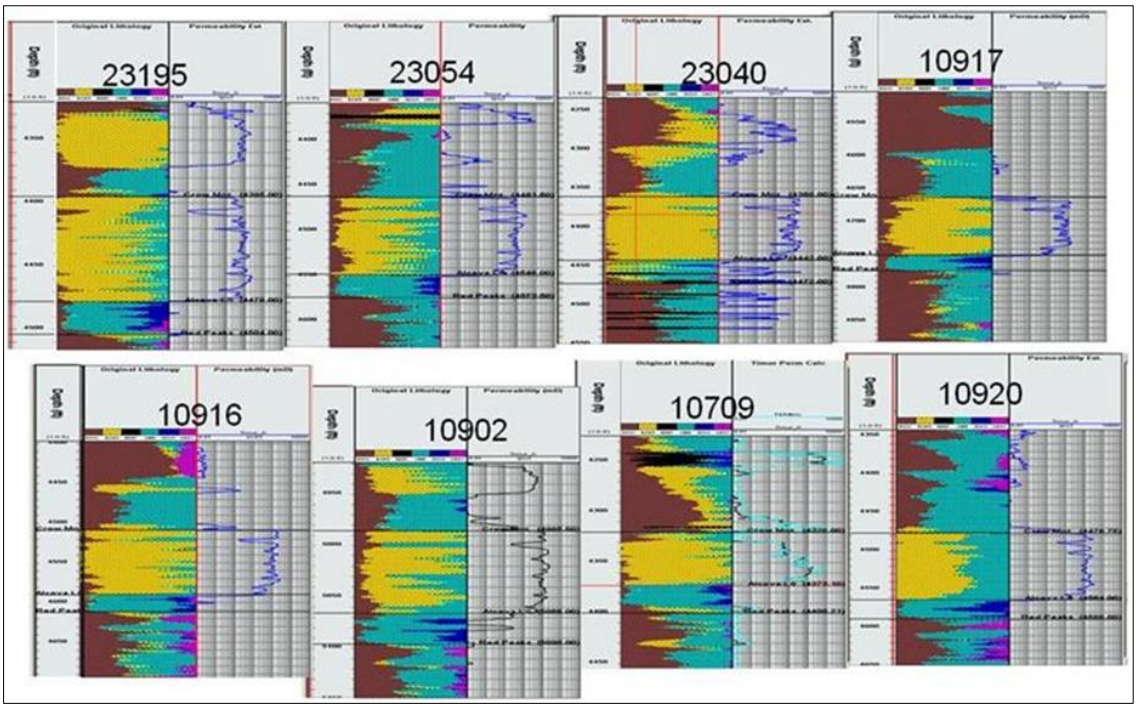

Figure 11: Eight of the ten wells used for the mineralogy study illustrates the lithology of the Chugwater Group across the RMOTC lease. Note, the order of the wells does not depict any specific cross-section in the reservoir.

3.1.2.2 Mineralogy from Petrographic Studies

Mineral assemblages for the rock types of the four reservoirs were defined for the model, Red Peak claystone, Alcova Limestone, Crow Mountain Sandstone, and Sundance. Crow Mountain is the primary targeted formation to simulate injection of CO_2 for aquifer sequestration purposes. Using previously discussed FPTI petrophysical analysis efforts, combined with literature petrographic data, rock type geochemical assemblages were defined, as well as an equilibrated water composition for the four rock types in the model. Dr. M. Dane Picard's decade(s) of petrographical work [7,8,9] in the Chugwater Red Beds of Wyoming was used with the FPTI petrophysical mineral analysis to define the initial rock type assemblages.

Previous work by the FPTI petrophysicist using log analysis identified six lithological components of the Chugwater Group and Lower Sundance (sand (quartz), bentonite (clays), limestone, dolomite, anhydrate, and shale) in the modeled area of the Chugwater members and a portion of the overlying Lower Sundance formation. [1] For purposes of reactive transport simulation, more detailed actual mineral compositions of the rock are required, and as stated earlier, subsurface petrophysical data availability and analysis are limited in the Chugwater Group (Crow Mountain aquifer) in RMOTC. A substantial amount of qualitative and considerable amount of quantitative surface outcrop petrographic data has been presented in the literature (refer to Dr. Piccard's work, previously referenced). This data combined with the log data is used to define the rock assemblages necessary to develop a petrographic model. Though not a particularly unique model

of this specific reservoir, the petrographic model was input to a reactive transport simulator to simulate the complex fluid-rock reactions associated with injecting CO_2 into the Chugwater Group, specifically the Crow Mountain reservoir.

Table 1, page 36, shows the initial rock assemblage developed from the qualitative and quantitative analysis of published work. Picard [7] presented a calculation for normative minerals for Red Peak, which aided in developing an assemblage for that particular formation. The other analyses were primarily point counts of principal rocks of various minerals to determine percentage composition and rock classification by grain size distribution. The detailed grain size analysis presented in a petrographic study could be used to help determine a representative reactive surface area for each mineral in the defined mineral assemblage model. [20]

The initial assemblage in Table 1 is viewed as an unstable assemblage as some of the minerals, such as chalcedony and quartz cannot be in chemical equilibrium, and much of the iron and clay components, as described by Picard, are authigenic sediments and may or may not be an equilibrated assemblage. The assemblage was developed from Picard's outcrop petrographic layering analysis and areal extent causing localized petrographic data, and we are averaging the analysis over an extended area, as well as going from surface to subsurface. A detailed mineralogy and petrographic interpretive analysis was not the intent for this project. However, a reasonably realistic rock definition (assemblage) of the reservoir is required to accomplish a reasonable simulation analysis of CO_2 sequestration in a complex rock type using coupled geochemical reactive transport simulation, as proposed in this project.

One point to note, is equilibrium may not exist between pore fluids and minerals. [21] Many potential reservoir rocks contain a range of minerals that may react at very different rates. The reservoir or aquifer may be in steady state composition, but not in equilibrium, as fluids migrate albeit at very small rates. Some reactions, such as congruent dissolution proceed until the reacting mineral is in equilibrium with the pore fluid (proceeds stoichiometrically between solid and dissolved solute). Some minerals may dissolve incongruently where the composition of the solute in the pore solution does not match that of the solid. The incongruent reactions may involve unstable reactants that never attain equilibrium with the pore fluid, resulting in mineralogical transformation over time. [21] For example, the dissolution of albite to form gibbsite.

$$NaAlSi_3O_8(s) + H^+ + 7H_2O \Rightarrow Na^+ + Al(OH)_3(s) + 3H_4SiO_4 \quad (4)$$

The United States Geological Survey (USGS), computer program PHREEQC (pH-REdox-EQuilibrium) was used to establish the low temperature aqueous chemical equilibrium composition of the minerals and water. This is necessary to define the actual geochemical makeup of the reservoir in the coupled geochemical and transport simulator.

3.1.3 Additional Static Reservoir Model

The original static reservoir model was built in JewelSuite in DE-FE-0001111 project. [1] JewelSuite has the functionality, though limited at the time of use, to integrate various commercial reservoir simulation software with the developed static reservoir model. Faults, horizons, and surfaces were initially preferred to be integrated into the reservoir simulation; however, at the time

of use, the software lacked this integration functionality. The static model for the DE-FE-0001111 project was sufficient to analyze the plume development and its evolution and migration, but not sufficient for this DOE project (DE-FE0004510).

Table 1: Original Rock Assemblage gleaned from Picard's Petrography publications and FPTI Petrophysical (log) mineral analysis in wt. %.

Mineral Name	Chemical Formula	density g/cc	Lower Sundance wt%	Crow Mountain wt%	Alcova LS wt%	Red Peak wt%
Albite	$NaAlSi_3O_8$	2.61569	6.1	5.88	0.00	8.78
Anhydrite	$CaSO_4$	2.96338	1	0.02	1.08	9.17
Anorthite (plagioclase)	$CaAl_2Si_2O_8$	2.76029	0	0.00	0.00	2.86
Calcite (Auth Carb)	CaCO3	2.70995	40.00	12.45	62.12	12.10
Chalcedony (Chert)	SiO_2	2.64829	0.5	1.37	2.06	1.17
Chamosite-7A (Chlorite)	$(Fe^{2+},Mg)_5Al(AlSi_3O_{10})(OH)_8$	1.61455	1.8	3.86	0	0.00
Dolomite (Auth Carb)	$(CaMg)(CO3)_2$	2.86496	18.10	12.45	13.08	12.50
Hematite	Fe_2O_3	5.27559	0.8	2.87	0	0.80
Hydroxylapatite ***	$Ca_5(PO_4)_3(F,Cl,OH)$	3.14738	0	0.00	0	0.30
Illite (clay)	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	2.76307	1	7.25	1.08	12.10
Ilmenite	$FeTiO_3$		0	0.30	0	0.60
K-Feldspar (Orthoclase)	$KAlSi_3O_8$	2.55655	0.8	3.27	0.00	1.43
Magnetite	$FeO{\cdot}Fe_2O_3$	5.20078	0	0.30	0	0.60
Muscovite (Mica)	$KAl_2(AlSi_3O_{10})(F,OH)_2$	2.8307	0.8	1.90	0.00	2.60
Pyrite	FeS	5.01115	0	0.00	0	0.10
Quartz	SiO_2	2.64829	29.1	47.47	20.59	33.72
Tourmaline (Use Schorl)	$NaFe^{2+}{}_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$	3.244	0	0.60	0.00	1.18
Secondary Reactions						
Dawsonite	$NaAlCO_3(OH)_2$ (used as an antiacid)	2.42825				
Fayalite	Fe_2SiO_4	4.39269				
Goethite	α-FeO(OH)	4.26771				
Gypsum	$CaSO_4$	2.3051				
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.59405				
Magnesite	$MgCO_3$	3.00929				
Siderite	$FeCO_3$	4.04667				
Smectite-high-Fe-Mg		3.00777				

Through a company merger, FPTI (now Sigma Cubed Inc.) acquired access to a static reservoir model called CRYSTAL. CRYSTAL has the capability to glean additional reservoir information from the seismic data not typically produced in post-processing seismic analysis. In a single environment, CRYSTAL provides the tools necessary to improve the seismic resolution, to run volumetric curvature, to image all faults, run deterministic and stochastic inversions, apply spectral imaging to define lithology, build complex subsurface structural frameworks, generate reservoir properties using geostatistics and neural networks, upscale the reservoir models to any grid size, all while maintaining the geologic features and planned optimal well trajectories.

An additional external merger caused the loss of the alliance to use JewelSuite for the project. Therefore, an earth model was built in CRYSTAL using the previously interpreted surfaces and faults. The CRYSTAL model used the neural network internal to CRYSTAL to develop the

reservoir lithology. JewelSuite had the capability to do facies modeling, but not with neural networks. CRYSTAL could model the lithological facies, as defined by the six components in the FPTI log analysis, but could not model complex mineral compositions at the time of use in this project. Moreover, CRYSTAL does not have the capability to export grid and cell attributes directly into the reservoir simulator.

3.2 Reactive Transport Simulation

Reactive transport modeling studies were to evaluate the simultaneous effects on the performance of: (1) impurities in the injected stream on reservoirs and seals; (2) rock types (e.g., dolomite and sandstone, etc.); (3) petrophysical parameters; (4) geochemical effects of injected gas on brine and rock interactions; (5) structural effects (vertical, e.g., layering and areal permeability); and, (6) well type configuration, construction, and placement.

The simulation effort was a critical effort in this project and a reactive transport simulator was a required tool to accomplish the objectives of the project. To our knowledge, there was only one commercial simulator available that had incorporated and truly coupled the transport model with the geochemistry and parallel computation architecture required to model CO_2 sequestration chemistry transport in porous media, and integrated with an experimental design module required for the project. There are a number of publically available, high level research software that could accomplish most of the project efforts (e.g., TOUGHREACT (LBL), CRUNCHFLOW (LBL), PFLoTran (LANL, et al.)). However, the R&D software would not allow the feasibility study as directly as the third-party commercial reactive transport simulator and ED/RSM software. In addition, the research software would not be a software code a typical Engineer would use to accomplish the design of a CO_2 utilization and storage site.

An evaluation of the geochemical transport models in the literature indicates some are equilibrium models and do not model kinetic rate reactions. TOUGHREACT, CRUNCHFLOW, and PFLoTran have the capability to model equilibrium and kinetic rate reactions. However, many of these simulators and others discussed in the literature are not parallelized, which limits size of the model complexity, as in our case, resulting in long execution times.

TOUGH-2 transport model has been parallelized, but TOUGHREACT has not been parallelized. An advantage of TOUGHREACT is that it can handle both equilibrium and kinetic rate reactions simultaneously, as can CRUNCHFLOW and PFLoTran. Most of the models in the literature are not capable of the sensitivity, optimization, and uncertainty modeling integration required for the ED/RSM portion of the study. The commercial reactive transport simulator has the advantage of parallelization (at additional cost), as well as integration of the sensitivity analysis, optimization, and uncertainty assessment required for the ED/RSM portion of the project (again, at additional cost). Many of the R&D codes do not have these extensibilities (even at additional cost).

One program in the LBL TOUGH2 series could possibly do the sensitivity and optimization required in this study. *i*TOUGH2 was developed for inverse modeling and parameter estimation, sensitivity analysis, and uncertainty propagation analysis. *i*TOUGH2 is based on the TOUGH2 simulator for non-isothermal multiphase flow in porous media, but has not yet been parallelized. PFLoTran is a newer effort by a number of the US DOE national labs (led by Los Alamos National Laboratory (LANL)), to develop a robust, massively parallelized model for multiscale subsurface

processes that have wide ranges of spatial scales of several orders of magnitude, and time scales of seconds or less to millions of years. Though they exist, they are not in the commercial realm, are cumbersome to use, and require substantial interaction and support software. There are commercial codes available to do ED/RSM, but they are not directly integrated with a reservoir simulator with the geochemistry coupling.

3.2.1 Initialization of the Reservoir Simulator

A reservoir simulator needs to start from a state as close to equilibrium as possible to maintain proper material balance and avoid convergence and other problems during the simulation. The initialization of a reservoir simulation model for a specific reservoir(s) can prove difficult, and is particularly challenging when two or more phases are initially present. Current reservoir simulators have various models to aid in establishing the initial equilibrium of the pressure and saturations for each cell. Initially, in our reservoir model for CO_2 sequestration, the reservoir was defined as a single phase, e.g., 100% water. To avoid any problems with the pressure and saturation equilibrium distributions, a gas/water model with a gas/water interface (Gas Water Contact or GWC) outside of the targeted reservoirs, and the simulator establishes an initial equilibrium saturation and pressure distribution. Above the GWC is all gas and below is 100% water. However, this does not establish the geochemical equilibrium for the rock assemblage and pore water in the coupling of the geochemistry and transport.

3.2.1.1 Reservoir Temperature

The reservoir temperature in Crow Mountain based on temperature gradient, varies from a minimum of 170°F to 194°F, with an average of 178°F. The gradient was determined from temperature recordings on logs in Dakota (163°F at 3800 feet) and Tensleep (190°F at 5500 feet). The gradient is calculated internally in the simulator, and each cell temperature is populated according to its respective depth from the gradient.

3.2.1.2 Reservoir Pressure

The initial pressure for each reservoir block was developed using a specific gravity of sea water of 1.03, and an average surface elevation of 5218 feet above sea level, and is a close approximation to the vertical equilibrium models assuming a water saturation of 100%.

3.2.1.3 Geochemistry

A geochemical equilibrium model was developed for each of the four types of rock regions defined in our model. The USGS PHREEQ geochemical modeling software was used to establish an equilibrated water chemistry and mineral assemblage, initially using the water analysis produced from the Sundance, Crow Mountain, Alcova, and Red Peak formations and the defined mineral assemblages for each of the four rock types.

Table 2, page 39, illustrates the water analysis in various modeled formations taken from various locations in Wyoming. The water analyses are not sufficiently detailed to provide equilibrium data with the specific mineral data of each of the four rock types. The water data is more qualitative than quantitative, but provides a starting point of the possible composition and pH of the typical formations water. The water source depth is not readily available, and except for the data from a RMOTC DST, is primarily from the Green River Basin southwest of NPR-3.

Using PHREEQC, the initial water analysis and initial mineral composition were equilibrated for each formation or region, using a batch equilibration model. The resulting equilibrated output of the mineral assemblage and water analysis for each formation is presented in Table 3, page 40, and Table 4, page 41, respectively. Zero mineral concentrations are the secondary reactions and input to allow the simulator to generate the necessary equilibrium and kinetic chemical information to ascertain additional transfer of minerals across the formation boundaries, as well as mineral trapping due to CO_2 injection and dissolution of the primary mineral assemblage. For example, the minerals that have values in Table 3, page 40, are the primary minerals and have the potential of both reacting and precipitating.

Table 2: Produced water analysis in targeted formations from various locations.

	Chugwater formation		Crow Mtn		Alcova****	sundance**
	mg/liter	mg/liter	mg/liter	mg/liter	mg/liter	mg/liter
	#1*	#2 **	DST #2 sampler ***	DST #2 BTM ***		
pH	7.2		7.05	8.44	8.1	7.5
conductance (µS/cm)	1640					
specific res (ohm-meters)			0.87	0.87		
Hardness (as CaCO3)	1000					
Calcium (Ca)	277	47	265	220	46	75
Magnesium (Mg)	78.8	26	49	49	43	31.5
Potassium (K)	2.21		50	44	52	
Sodium (Na)	28.7	2160	3123	3087	1091	5880
Iron (Fe)			present	present		
Alkalinity (as CaCO3)	184					
Bromide (Br)	0.08					
Bicarbonate (HCO3)		2090	378	366	549	2980
Carbonate			0	84		
Chloride (Cl)	9.2	2110	2600	2500	780	5720
Flouride (F)	0.3					
Hydrogen Sulfide			Absent	Absent		
Silica (SiO2)	15.1					
Sulfate (SO_4^{2-})	776	231	3600	3420	1021	970
Dissolved Solids	1420	5600	9874	9584	3375	16900
NaCl			8025	7853		
Available groundwater determination Technical memorandum						
WWDC Green River Basin Water Plan II 2007-2009 August 2010 Deith E. Clarey Et al. David Copelan and Meg Ewald Eds						
* from Wyoming state geologic survey Appendix 4C Green River basin water plan						
**Wyoming State Geologic survey Appendix 5C Green River Basin water Plan						
*** From DST Felix and Scisson 345-X-10 11/21/1979						
**** USGS water database Freemnot county swabb 26-270 ft Federal #3 4901320070 10/12/1970						

3.2.1.3.1 Thermodynamic and Kinetic Data

The general rate law is used for kinetically controlled mineral dissolution and precipitation. [22,23]

$$r_m = A_m k_m \left[1 - \frac{Q_m}{K_{eq,m}}\right] \quad (5)$$

Table 3: Mineral Assemblage in Equilibrium with Water output from PHREEQC bulk volume % basis.

	Molecular Weight g/g-mole	density g/cc	Lower sundance	Crow Mtn	Alcova LS	Red Peak
Albite	262.223	2.61569	0.057369	0.05275	0.000609	0.080925
Anhydrite	136.1376	2.96338	0.006898	0	0.009836	0.07835
Anorthite	278.2093	2.76029	0	0	0	0
Calcite	100.0892	2.70995	0.366271	0.110839	0.613739	0.128782
Chalcedony	60.0843	2.64829	0	0	0	0
Chamosite-7A	341.7688	1.61455	0	0	0	0
Dawsonite	143.9951	2.42825	0	0	0	0
Dolomite	184.4034	2.86496	0.153892	0.098897	0.122498	0.09455
Fayalite	203.7771	4.39269	0	0	0	0
Goethite	88.8537	4.26771	0	0	0	0
Gypsum	172.168	2.3051	0	0	0	0
Hematite	159.6922	5.27559	0.007008	0.020676	3.3E-13	0.00294
Hydroxylapatite	502.3214	3.14738	0	0	0	0.002387
Illite	383.9006	2.76307	0	0	0.008656	0
K-Feldspar	278.3315	2.55655	0	0	0	0
Kaolinite	258.1603	2.59405	0.006254	0.005434	1.29E-05	0.022018
Magnesite	84.3142	3.00929	0	0	0	0
Magnetite	231.5386	5.20078	0	0	0	0
Muscovite	398.308	2.8307	0.021256	0.088406	0.001112	0.097353
Pyrite	119.967	5.01115	0.000383	0.000122	0	0.000308
Quartz	60.0843	2.64829	0.275762	0.447104	0.229072	0.339845
Siderite	115.8562	4.04667	0	0	0	0
Smectite-high-Fe-Mg	418.0803	3.00777	0.005517	0.020684	1.4E-11	0.051532

Where r_m is the rate, A_m is the specific reactive surface area (in m^2/m^3 or m^2 per m^3 of bulk rock volume), Q_m is the activity product of mineral reaction *m* and $K_{eq,m}$ is the chemical equilibrium constant for mineral reaction *m*. The quotient $\frac{Q_m}{K_{eq,m}}$ is the saturation index and indicates how far the mineral is from equilibrium with pore fluid and whether the pore fluid is undersaturated or supersaturated. The equilibrium constant, reaction rate constant, and specific reactive surface area are assimilated from the literature.

Table 4: Water equilibrium for each modeled formation of interest.

	initial	Lo Sundance	Crow Mtn	Alcova	Red Peak
pH	7.05	7.351835221	7.433680378	8.016824928	7.325966
H+	1.12E-07	4.45E-08	3.68E-08	9.62E-09	4.72E-08
Na+	0.12970	0.08180	0.06631	0.01767	0.08709
Al3+	1.37E-27	9.25E-18	4.56E-18	9.23E-20	1.13E-17
SiO2 (aq)	1.65E-25	0.0005708	0.0005708	0.0005708	0.0005708
Ca2+	0.004232	0.007336	0.002985	0.029580	0.008380
SO42-	0.028020	0.011770	0.000006	0.000000	0.010780
Fe2+	4.21E-10	5.47E-08	9.57E-08	7.04E-14	6.25E-08
Mg2+	0.000493	0.000264	0.000111	0.001068	0.000300
Fe3+	4.03E-18	5.98E-24	2.94E-24	5.98E-26	7.31E-24
HPO42-	1.62E-18	1.66E-18	1.90E-18	8.82E-19	7.32E-09
K+	0.001191	0.000041	0.000033	0.000009	0.000043
HS-	2.59E-18	2.74E-07	5.18E-07	0.00E+00	2.61E-07
Cl-	0.072760	0.071590	0.072280	0.073470	0.081170
values in molality moles/kg H2O					

3.2.1.3.2 Brief Review of Reactive Surface Area

Surface area represents a key scaling parameter for studying the kinetics of mineral dissolution used to extrapolate from the atomic scale to the laboratory and field scales. Reactive surface area is an essential parameter in the derivation of universally applicable rate laws for mineral dissolution. The literature reports data primarily from BET (Brunauer-Emmett-Teller) adsorption test specific surface area tests.

The BET approach determines sorption isotherms for a gas (generally nitrogen), and measures the entire surface in a sample regardless of its mineralogical composition. However, this approach is not applicable for reactive minerals present as a minor component of sediments. The units are converted from area per mass to area per volume, using the density of the mineral. The result can be significantly large and unreasonable, as the specific surface area is not the correct reactive area for minerals in a natural setting. Actual reactive surface areas in natural mineral reservoir settings are largely unknown, but have been determined smaller by several orders of magnitude than laboratory mineral surface area measurements suggest [24]. For this reason, many past works have estimated the initial reactive surface area from available geometric data on the size and shape of mineral grains in porous media. [24] Calculated by relatively simple mathematical expressions that do not require a high level of accuracy, given the large variability of the parameter in natural systems. Moreover, the initial surface area can be calibrated during the course of reactive transport simulations.

Using a simple geometric method for calculating surface area has been suggested and used for the last two to three decades. The reactive surface area is estimated based on a simple cubic packing of spherical grains of radius *r*. The cubic arrangement has a side measurement of 4*r* and a volume

of $(4r)^3$ with a total of 8 spheres, each having a r radius and a volume of $\frac{4\pi r^3}{3}$, and a spherical surface area of $4\pi r^2$. Thus, an estimated reactive surface area A_m calculated by dividing the area of the spheres by the volume of the cube as: [24]

$$A_m = \gamma_m \frac{0.5}{r} \tag{6}$$

where r is the average grain size of the mineral.

An effective surface area has been suggested [24] using the following:

$$A_{meff} = \gamma_m \left(\emptyset_m A_{SS_m} \rho_m 1000 + \bar{A}_m \right) \tag{7}$$

where A_m is the effective reactive surface area of minerals (m^2 mineral per m^3 porous medium), γ_m is the fraction of the mineral surface area in contact with the reactive phase (usually water), $\emptyset_m$is the volume fraction of the mineral, A_{SS_m} is the specific surface area of the mineral (m^2/g), ρ_m is the density of the mineral (kg/m^3), and the factor 1000 converts from kg to g. $\bar{A}_m$ is the precursor surface area (m^2 mineral per m^3 porous medium). The precursor is defined [23] as:

> "A stable secondary mineral, which would otherwise be difficult or impossible to nucleate at low temperatures because of its high critical supersaturation for heterogeneous nucleation may circumvent this problem by making use of a more soluble precursor with a lower interfacial energy. A precursor phase is usually amorphous or poorly crystalline, and it may have a chemical composition distinct from that of the final stable mineral Kinetic Data for Project."

As illustrated in Table 5, page 43, many of the specific reactive surface areas for the minerals of interest are quite large. Specific surface areas from literature are typically determined by the BET method. Sheet clays have internal areas that may or may not be available to the fluid for reaction activity. The surface areas from the literature are primarily compiled from specific surface areas, and need to be adjusted to define a more realistic view of natural mineral reactivity of the reservoir. Some recent work uses the same values from previous efforts and are primarily arbitrarily modified values. The A_m for minerals that are not known are typically assigned values of minerals in the same group or classification that have a published value. This is an ongoing research topic and beyond the scope of this project. Based on a review of the current state of science, incorporating Picard's petrographical review and grain sizing method, as previously defined, may be an appropriate direction to determine the specific reactive surface areas of the four formations of this project.

The extreme scaling of the reactive surface area from laboratory to actual field implementation, and the limited and variable nature of the data in the field environment (reservoir conditions and different rock formations, even in the same reservoir) probably reduce the precision and accuracy by orders of magnitude for the reactive surface area value. This is especially in evidence, since a "true" value is difficult to obtain in a mixed mineral system.

Table 5: Kinetic Data for Dissolution and Precipitation Reactions

Mineral Name	Chemical Formula	Reaction	Molecular Weight g/g-mole	density g/cc	Surface area: SSA or RSA value from Literature with other units: value	Surface area: SSA or RSA value from Literature with other units: units	Surface area: Literature RSA values with m2/m3	Surface area: calc m2/m3	Rate Constant log 10(ka) mole/m2*s	Activation Energy Ea J/mole	References
Albite	$NaAlSi_3O_8$	$+4H^+=(Na^+)+(Al^{3+})+3SiO_2(aq)$	262.223	2.61569	9.1	cm2/g		2366	-10.16	65000	xu spycher sonnethal, et al [25]
					98	cm2/g		25480	-9.69	59770	xu,Apps,Pruess 2005 [26]
Anhydrite	$CaSO_4$	$=(Ca^{2+})+(SO_4^-)$	136.1376	2.96338	1.44	m2/g		4276800			Ticknor and Saluja 1990 [27]
									-3.19	14300	USGS compilation of rate parameters [28]
					7.89E-02	m2/g		234333	-7.38		Gaus, Azaroual Sleipner paper [29];4.1 (±0.7) × 10–9 mol cm–2 s–1
Anorthite (plagioclase)	$CaAl_2Si2O_8$	$+8(H^+)=4H_2O+(Ca^{2+})+2(Al^{3+})+2SiO_2(aq)$	278.2093	2.76029			88		-12	67830	SPE 109739 [30];SPE89474 [31]
					98	cm2/g		26803	-3.5	16600	USGS compilation [28]; same area as albite
					9.1	cm2/g		2488.85			
Calcite (Auth Carb)	$CaCO_3$	$+(H^+)=Ca^{2+}+HCO_3^-$	100.0892	2.70995			88		-8.79588	41870	SPE 109739 [30];SPE89474 [31]; xu apps and Pruess [32]
					0.043	m2/g		116530			
Chalcedony (Chert)	SiO_2	*$SiO_2(aq)$*	60.0843	2.64829			*7128*		*-13.9*	*87500*	*SPE 109739 [30];SPE89474 [31];xu apps and Pruess* [32]
Chamosite-7A (Chlorite)	$(Fe^{2+},Mg)5Al(AlSi_3O_{10})(OH)_8$	$+ 10 (H^+) = 2 (Fe^{2+}) + SiO_2(aq) + 2 (Al^{3+}) + 7 H_2O$	341.7688	1.61455				3136	-11.11	88000	USGS [28]
							88		-9.2218	41870	SPE 109739 [30];SPE89474 [31]
Dolomite (Auth Carb)	$(CaMg)(CO_3)_2$	$+2H^+=Ca^{2+}+Mg^{2+}+2HCO_3^-$	184.4034	2.86496	9.1	cm2/g		2593.5	-3.187	52200	xu spycher sonnethal, et al [25]
							88		-9.2218	41870	;xu apps and Pruess [32]
					9.8	cm2/g		2793	-2.991	20900	xu,Apps,Pruess 2005 [26]
Hematite	Fe_2O_3	$+6H^+=2Fe^{3+}+3H_2O$	159.6922	5.27559	12.9	cm2/g		6785.4	-9.38	66200	xu spycher sonnethal, et al [25]
					12.9	cm2/g		6785.4	-10.397	62760	xu,Apps,Pruess 2005 [26]
									-9.39	66200	USGS compilation [28]
Hydroxylapatite ***	$Ca_5(PO_4)_3(F,Cl,OH)$	$+ 4 (H^+) = 5 (Ca^{2+}) + 3 (HPO_4^{2-}) + H_2O$	502.3214	3.14738	100	m2/g		316000000	-4.29	250000	USGS [28]
Illite (clay)	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	$+8H^+=5H_2O+0.6(K^+)0.25(Mg^{+2})+(Al^{+3})+3SiO_2(aq)$	383.9006	2.76307			26400		-14	58620	SPE 109739 [30];SPE89474;xu apps and Pruess [32]
					151.6	cm2/g		41690	-11.36	62760	xu,Apps,Pruess 2005 [26]
Ilmenite	$FeTiO_3$		151.73	4.72					-8.35	37900	USGS [28]
K-Feldspar (Orthoclase)	$KAlSi_3O_8$	$4H^+=2H_2O+(K^+)+(Al^{3+})+3SiO_2(aq)$	278.3315	2.55655			176		-12	67830	orthoclase;SPE89474 [31]
							176		-12	67830	xu apps and Pruess [32]
					10	cm2/g		2560	-9.44	51830	xu,Apps,Pruess 2005 [26]
									-10.06	51700	USGS compilation [28]
Magnetite	$FeO{\cdot}Fe_2O_3$	$+ 8 (H^+) = (Fe^{2+}) + 4 H_2O + 2 (Fe^{3+})$	231.5386	5.20078	12.9	cm2/g		6643.5	-8.59	18600	USGS [28] area set to that of Hematite
Muscovite (Mica)	$KAl_2(AlSi_3O_{10})(F,OH)_2$	$+ 10 (H^+) = 6 H_2O + (K^+) + 3 (Al^{2+}) + 3 SiO_2(aq)$	398.308	2.8307	0.25	m2/g		707500			Kline and Fogler Che Engr Sc 1981
Pyrite	FeS	$+ H_2O = (Fe^{2+}) + 1.75 (HS^-) + 0.25 (SO_4^{--}) + 0.25 (H^+)$	119.967	5.01115	12.9	cm2/g		6462.9	-10.397	62760	xu,Apps,Pruess 2005 [26]
									-7.52	56900	USGS Compilation [28]
Quartz	SiO_2	$SiO_2(aq)$	60.0843	2.64829			7128		-13.9	87500	SPE89474 [31]
							7128		-13.9	87500	xu apps and Pruess [32]
					9.8	cm2/g		2581.32	-13.89	87500	xu,Apps,Pruess 2005 [26]
Tourmaline (Use Schorl)	$(NaFe^{2+})_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$		1,053.38	3.244					-3.8		USGS [28]
Secondary Reactions											
Dawsonite	$NaAlCO_3(OH)_2$ (used as an antiacid)	$+ 3 (H^+) = (Na^+) + (Al^{3+}) + (HCO_3^-) + 2 H_2O$	143.9951	2.42825							
Fayalite	Fe_2SiO_4	$+4H^+=2(Fe^{2+})+SiO_2(aq)+2H_2O$	203.7771	4.39269	2300	cm2/g		1009700	-4.8	94400	USGS compilation [28]; used Olivine SSA taken from Brantley and Mellot [33]
Goethite	α-FeO(OH)	$'+3H^+=2Fe^{3+}+2H_2O$	88.8537	4.26771	200	m2/g		7.60E+08	-7.94	86500	USGS compilation [28]
Gypsum	$CaSO_4$		172.168	2.3051							
							17600		-13	62760	SPE 109739 [30];SPE89474 [31]; xu apps and Pruess [32]
					10-70	m2/g					Specific Surface Carter, Mortland, Kemper A Soc Agronomy 1986 [34]
Kaolinite	$Al_2Si_2O_5(OH)_4$	$6H^+=5H_2O)+2(Al^{3+})+3SiO_2(aq)$	258.1603	2.59405	17.5	m2/g		4.55E+07	-11.9 to -12.88		Nagy, Blum, Lasaga AJS 1991 [35]at 80C
					151.6	cm2/g		39416	-11.36	62760	xu,Apps,Pruess 2005 [26]
									-11.31	65900	USGS compilation [28]
Magnesite	$MgCO_3$	$+(H^+)=(Mg^{2+})+HCO_3^-$	84.3142	3.00929	9.1	cm2/g		2730	-6.37	23500	xu spycher sonnethal, et al [25]
					9.8	cm2/g		2940	-2.3595	18980	xu,Apps,Pruess 2005 [26]
Siderite	$FeCO_3$	$+(H^+)=(HCO_3^-)+Fe^{3+}$	115.8562	4.04667			88		-9.2	87500	SPE 109739 [30]
							88		-9.22	41870	;xu apps and Pruess [32]
					9.1	cm2/g		3603.6	-3.187	36100	xu spycher sonnethal, et al [25]
					9.8	cm2/g		3880.8	-2.991	20900	xu,Apps,Pruess 2005 [26]
Smectite-high-Fe-Mg		$+ 8 (H^+) = 0.5 (Fe^{2+}) + 3.5 SiO_2(aq) + 0.2 (Fe^{3+}) + 5 H_2O +$ ' $1.25 (Al^{3+}) + 0.1 (Na^+) + 0.025 (Ca^{2+}) + 0.2 (K^+) + 1.15 (Mg^{2+})$	404.1991	2.90791	151.6	cm2/g		35626	-11.36	62760	xu,Apps,Pruess 2005 [26]

One of the major emphases of this project is the experimental design and response surface methodology (sensitivity and optimization concepts), which may develop some insight in determining the "more correct" values to apply in this particular reservoir for the reactive surface and other critical parameters.

The thermodynamic equilibrium data and reaction rate data in Table 5, page 43, were used as listed, though uncertainty exists. Many of the thermodynamic data were taken from DOE PNNL-19766.[36] The rate constants of a specific reaction can be dependent on the environment (e.g., pH and activity of the system). Temperature dependence of the rate constants is defined by the Arrhenius-like expression of the transition state theory, as follows:

$$k = k_{T_{ref}} exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (8)$$

Where E_a is the activation energy, k_{TRef} is the rate constant at T_{ref}, which is generally at 25°C (298.15 K), and T_{ref} is in the Kelvin scale.

3.2.1.4 Rock-Fluid Data Relative Permeability Data

The reservoir model has four rock units (Sundance, Crow Mountain, Alcova Limestone, and Red Peak formations). Initially, the 100 layers with two-foot thicknesses were defined with each layer having a constant permeability, porosity, mineral, and water composition, and only one rock type was defined with a single relative permeability curve. However, the fact is each facies or lithology has different fluid rock interactions, particularly in the tight shale. As the model was developed, each rock unit was defined with a specific relative permeability analogized from the literature.

Through a series of papers, Bennion and Bachu[2,3,4,5] published rock-fluid interaction data on the CO_2/brine system in a variety of potential sequestration zones in Western Canada. Represented in these publications are drainage and imbibition relative permeability data for various lithologies, namely intergranular sandstone, carbonates, shale, and anhydrite rocks. Capillary pressure data is not published in Bennion and Bachu work, other than by plot images. The relative permeability curves in Figure 12, page 45, are modified to extend endpoints to k_r=1 for each phase. Initially, each layer in the model was defined with the same permeability and porosity for each layer, though each layer is different vertically. Later, the block model was modified in the simulator, by importing well logs and geostatistically populating the simulation grid cells with the porosity and permeability, along with the geomechanical properties.

3.2.2 Impediments and Actions to Rectify Reactive Simulation

Phase I had significant impediments, as the commercial reactive transport simulators were incapable of simulating complex geochemistry to be modeled in this project. Significant effort and funding were expended to determine the limitations of both the commercial simulator and the Lawrence Berkeley National Laboratory (LBNL) R&D simulator.

Most studies published using the commercial simulator that we used, either have not used the geochemistry (GHG aka Greenhouse Gas) portion of the simulator, or have used the dataset or

subdata set of the Sleipner rock assemblage. Other complex rock assemblages do not seem to have been evaluated with the commercial simulator we used.

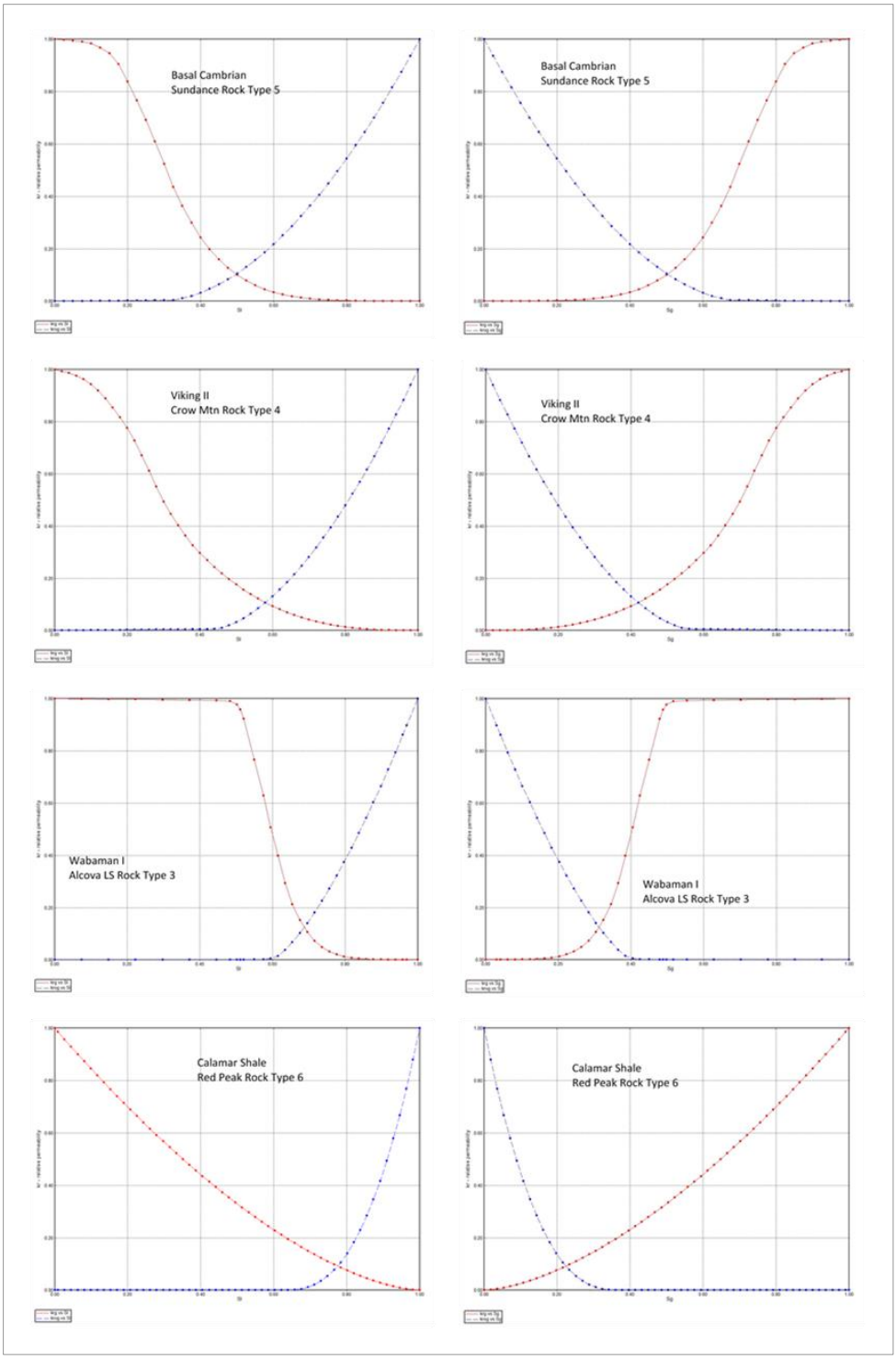

Figure 12: Relative permeability curves for each rock type modified from Bennion and Bachu published data [2,3,4,5].

3.2.2.1 Layer Cake Modeling

Previously, in project DE-FE-0001111, the simulation of CO_2 injection into the RMOTC Teapot Dome using the realistic complex (double plunging anticline) structure and very limited concentration of three mineral example components, was achieved with difficulty. One million cubic feet per day of CO_2 was simulated injected into each of two wells for 30 years using the commercial reservoir simulator.

Believing the structural complexity was creating material and convergence problems, a simplified "layer cake" model was developed (refer to Figure 13, page 46) without any structure or faulting as a preliminary modeling effort, and included the 23 mineral assemblage (14 primary and 9 secondary minerals). The porosity and permeability parameters were the average of each individual layer in the realistic original model. The block model originally had one geologic rock unit with the permeability, porosity, three minerals, relative permeability, and water composition in 100 layers. Aerially and volumetrically, the model is approximately the same as the RMOTC bounded reservoir, as illustrated in the map comparison in Figure 14, page 47. The cell dimensions were the same.

The “layer cake” model had difficulty converging, as well. Thus, a simplified model analogous to a pseudo 2-D model (3-D model 1 cell wide) was developed, which did not solve the problem, as the simulator did not converge. The second simplified model was developed by uplayering to 50 layers and approximately 3650 cells (73x1x50). The mineral and water input was equilibrated to ensure initial geochemical and material balance equilibrium.

Significant effort was expended working with the vendor to determine the cause of the difficulty in getting the model to converge and run as designed. A hypothesis proposed the geochemical complexity of the reservoir, the number of rock types, and some kinetic parameter value inputs to the simulator, may have caused part of the problem.

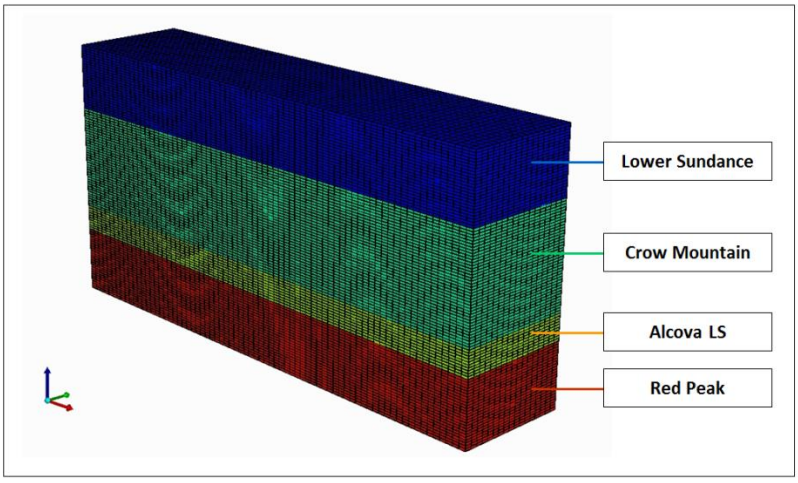

Figure 13: Simplified Block Model 73x17x100 to develop preliminary understanding of complex reactive transport at RMOTC.

After consulting with the vendor and the Alberta Research Council (ARC) experts on reactive fluid flow transport, and several teleconferences between the vendor, FPTI, and ARC, the vendor concluded a significant problem existed with the coding of the reactive geochemistry aspect of their commercial GHG software. A solution would not be realized for several months moving into month sixteen of the project.

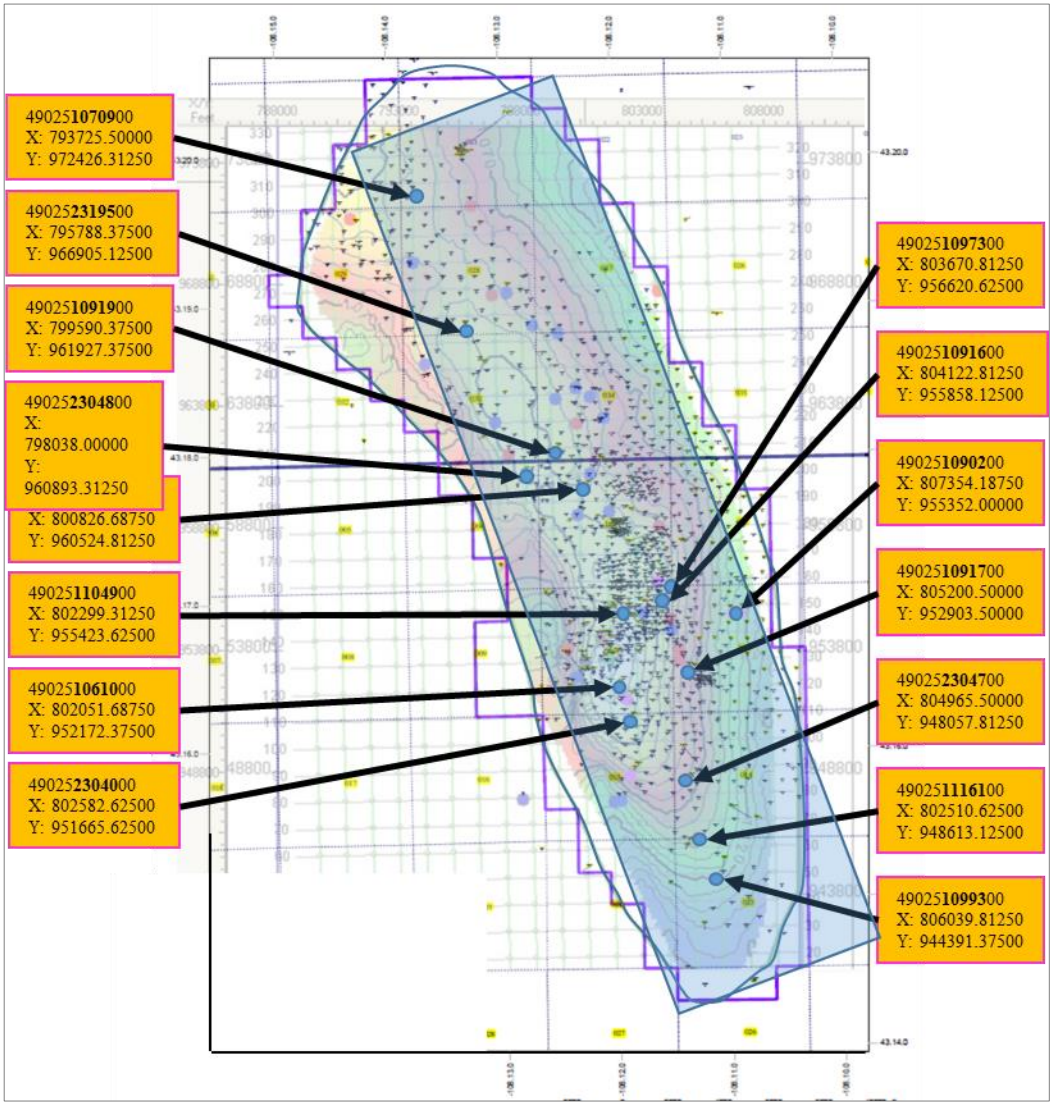

Figure 14: Layer Cake and RMOTC areal approximation.

Some reactions may be fast enough that they are considered equilibrium reactions. This is the case for carbonate calcite reactions. The reactive transport simulation software used was a rate limited model, meaning if the reactions are fast, i.e., equilibrium controlled, the time steps are automatically reduced to very small values $<10^{-10}$ days, and can cause problems with other reactions that are rate limited and result in nonconvergence of the software. Very fast reactions and very slow competing reactions can create oscillations, which may intensify if a number of competing and simultaneous reactions are occurring.

Simultaneous (near or local) equilibrium and kinetically controlled equilibrium are not implemented in the commercial simulator at this time. We have requested it be implemented. A workaround is to reduce the fast reaction rate magnitudes to be more in line with those of the slow reaction rates. This is incorrect chemistry and physics, but is a "trick" to try and get the kinetic rate simulation model to work as currently available. Precipitation effect may not be impacted, but the rate of dissolution could be in error. However, changing the magnitudes did not seem to have any positive effect on developing a solution to the problem.

A very fast reservoir simulator having the capability of coupling geochemistry reactive flow, is required to accomplish the tasks proposed in this project. Moreover, the task of creating such a simulator is not within the scope, schedule, and resources of this project.

To accomplish 3-D and 4-D reactive transport reservoir simulation for field studies and applying experimental response surface methodology, as proposed in this project, would require massively parallelized multi-component reactive fluid flow and geochemical transport simulator, integrated with a parameter estimation, sensitivity, and uncertainty program.

3.2.2.2 Use of LBNL TOUGHREACT Code

During the sixth quarter, we initiated a change in the project to accommodate inclusion of the TOUGH2 products from LBNL, e.g., TOUGHREACT, TOUGH2-MP, and iTOUGH2. The change was not to alter the goals or objectives of the project, but would require resource adjustments, and additional scheduling and budgetary risk.

- TOUGH2 - is a general-purpose numerical simulation program for multidimensional fluid and heat flows of multiphase, multicomponent fluid mixtures in porous and fractured media. The capabilities available through TOUGH2 are quiet diverse

- TOUGH2-MP - is a massive parallel version of the TOUGH2 code designed for computationally efficient parallel simulation of isothermal and nonisothermal flows of multicomponent, multiphase fluids in one, two, and three-dimensional porous and fractured media

- TOUGHREACT - TOUGHREACT was developed by LBNL as a comprehensive nonisothermal, multicomponent reactive fluid flow and geochemical transport simulator to model subsurface multiphase fluid and heat flow, solute transport, and chemical reactions, and can be applied to many geologic systems and environmental problems, including geothermal systems, diagenetic and weathering processes, subsurface waste disposal, acid mine drainage remediation, contaminant transport, CO_2 disposal in deep saline aquifers, groundwater quality, and other geochemical transport in porous media and fractured rocks. TOUGHREACT is developed by introducing reactive geochemical transport into the framework of the existing multiphase fluid and heat flow code TOUGH2 V2

- *i*TOUGH2 - is a program for parameter estimation, sensitivity analysis, and uncertainty propagation analysis. The program is based on the TOUGH2 reservoir or subsurface fluid transport simulator for nonisothermal multiphase flow in porous and fractured media

The LBNL programs have been well tested in various aspects of CO_2 sequestration, as well as other geochemical and subsurface transport physical systems. The TOUGH software simulators were to be integrated in the FPTI proprietary GeoPRO software platform. However, to effectively implement the integration for the benefit of this project and Carbon Capture Utilization and Storage (CCUS) program, these codes would require parallelization. TOUGH2 and *i*TOUGH2 have been parallelized, but at the time, TOUGHREACT had not. Note, a new version of TOUGHREACT v3.0-OMP [37] has been implemented as of June 2014. This is a parallel version of TOUGHREACT, but was not available during the execution portion of this project.

The three primary data input files for TOUGHREACT, namely flow.inp, solute.inp, and chemical.inp, were developed.

- flow.inp - mainly introduces the rock properties, time-stepping information, geometric grid information, initial and boundary conditions, and data related to a multiphase fluid flow simulation defined in TOUGHREACT. Moreover, the file is used to make the mesh or grid and initialize the reservoir in a separate initial run

- solute.inp - defines tolerance limits, convergence criteria, input parameters for reactive transport, and output criteria

- chemical.inp - defines the geochemical system, e.g., the mineralogy for each rock type and number of minerals, and type of aqueous component species, minerals, gases, and sorbed species considered in the simulation. The initial composition of water and minerals in each zone or domain is defined

In addition, a thermodynamic database is required that defines the reaction stoichiometry, disassociation constants, and regression of the equilibrium constants for the minerals and components to be modeled in the geochemical system. For the simulation of CO_2 sequestration in an aquifer, the ECO2N equation-of-state was used and required a file called CO2TAB, which is a table of properties (e.g., density, viscosity, and specific enthalpy) of pure CO_2 as a function of pressure and temperature. The values are obtained during the simulation by means of bivariate interpolation. The table is provided with ECO2N, which reads the table and provides the data to the simulator. CO2TAB has a valid temperature and pressure range of $3.04°C \leq T \leq 103.4°C$ and $1 \text{ bar} \leq P \leq 600 \text{ Bar}$.

The inputs to build a 3-D layer cake model (no structure or faulting) in TOUGHREACT for the RMOTC Crow Mountain field were initiated during the seventh quarter. Most of the parameter inputs have been developed previously in attempting to use the commercial reactive transport simulator. The van Genuchten [38,39] capillary pressure and relative permeability parameters model was developed for the four reservoir rock lithologies (Sundance - tight siltstone/mudstone; Crow Mountain - sandstone; Alcova - limestone/carbonate; and Red Peak - tight siltstone/shale) as inputs to the TOUGHREACT reactive transport simulator. The capillary pressure and relative permeability data for the CO_2/brine systems published by Bennion and Bachu [2,3,4,5] for similar types of rock, were used as analogies for this project, since no CO_2/brine data was available for each specific rock type in the RMOTC formations.

Table 6, page 50, displays the parameters of the analogous rock in the Bennion and Bachu works compared to the same parameters in the respective RMOTC formations used in this effort.

Table 7, page 50, displays the van Genuchten relative permeability parameters. Table 8, page 51, is the capillary pressure parameters inputs for TOUGH2v2 from the published relative permeability data of Bennion and Bachu [4]. The capillary pressure was back calculated using the RETC (RETention Curve) [39] software utilizing the relative permeability data. The threshold pressure published in Bennion and Bachu works was used to set the initial saturation pressures (refer to Table 6 , page 50) in the RETC software. The RETC software then generated synthetic capillary pressure curves, which were visually verified with Bennion and Bachu published capillary pressure images. Thus, consistent capillary pressure and relative permeability curve data parameters could be input into the reservoir simulator (refer to Table 8, page 51).

Table 6: Comparison of average project RMOTC rock parameters with analogous Bennion and Bachu formations.

	porosity	Sl perm (m^2)	perm md	B&B anology	Type of Formation	porosity	Sl perm (m^2)	perm md	Threshold Capillary Pressure (kPa)
sundance	0.0517	1.59E-17	0.01619	Basal Cambrian	sandstone	0.117	7.99E-17	0.081	31.9
crow mtn	0.159	1.50E-14	15.23	Viking II	sandstone	0.198	2.14E-14	21.72	3.5
alcova	0.0312	1.65E-18	0.001671	wabamum I	carbonate	0.079	1.78E-17	0.018	493.6
Red Peak	0.0307	1.54E-18	0.001557	calmar	shale	0.039	2.90E-21	2.94E-06	72,827.0

Table 7: van Genuchten relative permeability parameters for input to TOUGH2v2, based on Bennion and Bachu published data for analogous lithologies for CO_2/brine system.

	VG model Relative perm parameters				
	rp1 (λ)	Rp(2)Slr	RP (3)Sls	Rp(4) Sgr	analogy
sundance	0.9750361	0.294	0.999	0.001	Basal Cambrian
crow mtn	0.99503	0.426	0.999	0.001	Viking II
alcova	0.9948777	0.594937	0.959	0.041	wabamum I
Red Peak	0.958173	0.666154	0.9999	0.0001	calmar

Table 8: van Genuchten capillary curve parameters for input to TOUGH2v2, based on Bennion and Bachu published data for analogous lithologies for CO_2/brine system.

	VG model Cap Pressures curves parameters					
	CP(1) λ=m	Cp(2) Slr	CP (3) 1/Po Pa^{-1}	CP(4) Pmax Pa	CP(5) Sls	analogy
sundance	0.43185	0.2929	0.000243	52975.7934	1	Basal Cambrian
crow mtn	0.8823619	0.425758	0.097745	22672.9748	1	Viking II
alcova	0.994801	0.59481	1.53E-05	67,309	0.9618987	wabamum I
Red Peak	0.957926	0.664872	1.02E-07	15,935,806	1	calmar

The full field model is currently gridded with 108,188 cells (68x37x43). The most current version of TOUGHREACT available for this project from the USDOE Office of Scientific and Technical Information (OSTI), was v1.2, which was not designed for the large number of cells required for this large field engineering study. The most current version of TOUGHREACT during this project was found to be v2.0 from LBNL, at a cost of $30,000, plus the cost of equations of state necessary for specific modeling efforts. LBNL no longer supplies OSTI with the current version of the TOUGH products. LBNL did modify the t2f file in TOUGHREACT v1.2.1 to read and write large grids (up to 999,999 grid blocks) and provided it for our use. The large number of grid blocks was necessary to allow the larger grid mesh model defined for this project (approximately 108,000 cells).

LBNL personnel were successful in running the model on the TOUGHREACT version 2.0, for flow only. However, running on v1.2.1 became a challenge for us and LBNL. A successful simulation run (flow only) injecting ~1MM cuft/day of CO_2 into the Crow Mountain target reservoir for thirty years and then soaked for seventy years (100 years total) was accomplished in approximately 5.12 hours (18431 seconds). Note, this does not include any geochemistry, meaning only advective flow of CO_2 into the reservoir was modeled using TOUGHREACT. However, this achievement was capable with the commercial code, as previously discussed in this report.

To facilitate a faster turnaround, the 3-D grid mesh was reduced to 430 cells with the vertical layering in the z kept the same, e.g., z=43, y=2, x=5. The reservoir or cell pressures increased beyond the limit of the CO_2 database file for calculating the CO_2 properties in the ECO2N equation-of-state. The increase in pressure was due to modeling a closed system. One way to overcome the pressure challenge is to make some of the boundary cells very large in volume, thus forcing the system to emulate a constant pressure system, e.g., a Dirichlet boundary condition. However, this could cause material balance errors. There is no approach in the versions of TOUGH products we were using to emulate a constant bottom hole injection pressure (limit the pressure of injection) and let the rates adjust to the physics of the reservoir and grid pressures, other than using a high volume boundary condition.

We also attempted to use CO2TAB3.f to generate a CO2TAB property database with higher pressure than 60MPa. However, the new generated table was not accepted for input by TOUGHREACT. In discussions with LBNL, no one had tried to use this method, since Pruess developed the code to make a table of CO_2 properties and could not guide us regarding what exactly was wrong and why the CO2TAB3.f would not generate a table at higher pressures acceptable to the TOUGHREACT code. Attaining the high pressure (>60Mpa or ~8700psi) is realistically improbable for this particular formation, since it would likely fracture before exceeding this pressure. However, the 60MPa (8700psi) is not an unreasonable value for moderate to deep horizons, which limits the use of ECO2N. High pressures will be a challenge with closed systems without any removal of fluid or external flow system, as the compressibility of the water is not enough to keep the pressure below the rock fracture limit value. The full system modeled or reservoir (108,000+ cells approximately) seemed to be large enough; therefore, the water compressibility was sufficient to keep the pressure below the limit of 60MPa in the CO2TAB file.

Using the Dirichlet boundary conditions allows the smaller section of the reservoir to be modeled at constant pressure with faster simulation run times. Changes were made to the chemistry input files, so the chemistry models would converge. This was a learning process to adapt the proper input for the number of water species and minerals of the system and constraints for TOUGHREACT input. Simulating only the flow for the smaller section and Dirichlet boundary conditions proved successful for the most part. Modeling the injection of CO_2 or other fluids into a formation or reservoir is not a particularly thwarting challenge to simulate, regardless of the simulator used. The geochemistry modeling proved to be a persistently arduous challenge.

The thermodynamic database file DATABASE1 and CHEMICAL.inp were changed for the current problems to reflect the four specific formations of different lithologies (Lower Sundance (tight mudstone/siltstone with carbonate), Crow Mountain (sandstone ~15 md with carbonate cement), Alcova (tight limestone), and Red Peak (tight mudstone/siltstone). The sandstone/mudstones have clays and polysilicates, along with iron containing compounds that make them a "red bed" rock type. Iron compounds are important in CO_2 sequestration, as other studies have suggested [40].

Formations containing iron minerals have higher potential for sequestering CO_2. Unfortunately, there are convergence problems with both the oxidized form of iron (Fe^{+3}) and the reduced iron form (Fe^{+2}), which can create convergence problems, depending on the mineral and component initially defining the system. Taking out mineral components that generate or use Fe^{+3} as a reactant (e.g., smectite with high iron and magnesium content, and pyrite, etc.) for this project, leaves an assemblage similar to that modeled with TOUGHREACT in examples published by LBNL. The difference is this project is a 3-D Cartesian system with four rock domains, and the published example is a less complex 1-D and 2-D radial system with a single rock domain.

The only geochemically Cartesian gridded model successfully run with TOUGHREACT in this project is a reduced mesh 3-D model (215 cell grid mesh 1x5x43) with a Sequential No Iteration Approach (SNIA), which is a fully explicit reaction source term. The simulation run took nearly nine hours to complete for 30 years of CO_2 injection and 70 years of soak. Using the same input, grid, etc., and a sequential iterative approach in TOUGHREACT 1.2.1, the simulation ran for over

35 days and only simulated 0.2857 years. The step size increased very slowly. The initial conditions for both the runs were the same.

A 1-D and 2-D radial model (258 cells 6x43) was developed with the four rock domains, as modeled and discussed in the 3-D Cartesian model. The model ran without CO_2 injection, but in reactive transport sequential iterative approach for nearly 32 days and never properly terminated.

Evaluation to parallelize the TOUGH2 code during the seventh quarter concluded that parallelizing the current TOUGHREACT code (version 1.2.1) would take significant specialized resources that were not available, and the effort would have a high risk of not being successful in the time period and budget remaining in the project. The resources required to properly develop a fully coupled reactive transport model with parallel software architecture for use in a full field scale ED/RSM study would be unrealistic and unachievable under the resource constraints of the project. At the 2013 and 2014 DOE/NETL Carbon Storage R&D Project Review Meeting, a separate project DE-FE-0000988 reported the successful development of a parallelized reactive transport simulator, based on the TOUGH2 simulators. [41] Unfortunately, this was too late for use to test or utilize in the DE-FE-0004510 project.

3.3 Geomechanics Modeling

3.3.1 Modification to Project Approach

As discussed in previous sections of this report, the primary simulation effort was to use a commercial third-party 3-D reactive transport simulator to model the geochemical effects on CO_2 injection. In addition, well placement and completion design impact on injectivity, capacity, and plume migration of injected CO_2 in a brine aquifer or depleted oil and gas reservoir was modeled. As the reactive transport simulation software was applied, severe limitations were discovered regarding its capability to accomplish the simulation on complex geochemistry models associated with CO_2 injection in brine aquifers.

Three alternatives were considered and evaluated to continue the project into BP2.

1) Modify the project to focus on geomechanical modeling, with limited, if any, geochemistry modeling, concentrating on completion techniques and impacts of injection of CO_2.

2) A second approach evaluated was to reduce the scope of the ED/RSM and build a model with TOUGHREACT (without parallel software architecture) reducing the number of sensitivity and optimization evaluations, since a single parameter change could take several days or weeks to run without parallel architecture.

3) The third approach evaluated was to use a 3-D "pseudo reactive transport model" using a hydrochemical thermodynamic model incorporated into a transport model. In these model types, each cell is treated as a batch reactor for each time step.

    a. Hydrochemical models do not reveal the reactive pathways, reaction rates, or the effects of competitive reactions. They are not true reactive transport models, even though kinetics are part of the models. The results are the end points of the reactions, but do not reveal the

actual reactive pathways. These models are used as chemical scaling models in the oil and gas industry, as well as the environmental applications of surface and subsurface aquatic systems.

b. The hydrochemical models presuppose the establishment of chemical equilibrium and mass balance. The assumption of equilibrium in natural systems is generally not true, particularly where reactions are dominated by kinetics or catalyzed by microorganisms or precipitation of certain minerals. [42] Note, different reaction pathways and competing pathways resulting in a similar mineral speciation, numerical dispersion, or oscillations can create sources of errors when using finite difference or finite element numerical methods, while modeling mass transport. These errors can be reduced or eliminated utilizing numerical stability methods. These facts make this alternative of limited value in developing a proxy model to accomplish the goals and purposes of this project.

The tasks in BP2 were modified to stay in the same purpose and scope of the original proposed project, but eliminated most of the geochemistry and focused on geomechanics, completions, stimulations, well configurations, and other engineering and planning needs for implementing CO_2 utilization and storage in the subsurface. The geochemistry effort was reduced to move into the primary strategy direction of BP2, continue to model CO_2 injection, and how well placement and completion design would impact injectivity, capacity, and plume migration of injection of CO_2 in a brine aquifer or depleted oil and gas reservoir.

BP2 emphasized the development of geomechanical modeling tools to aid in the design and efficient operations of injecting CO_2 into oil and gas wells. In BP2, the project was initially incorporated as an important and integral segment of an internally funded Sigma Cubed Inc. initiative, SUPERNOVA, to build a sophisticated integrated completion and asset management product to aid in the design, placement, and completion of oil and gas wells.

A geomechanical reservoir tool (stimulation simulator (STIMSIM)) was intended to be coupled with a commercial reservoir transport tool (reservoir simulator (RESSIM)) to develop a method of seamless input and output from an integrated wellbore and reservoir simulation software tool with a static geocellular reservoir model. The integration of various wellbore stimulation, dynamic, and static reservoir simulation tools would allow the evaluation of impacts of fractures on the engineering of injection well configuration, construction, and placement on the CO_2 injectivity, capacity, plume migration, and seal integrity in a CO_2 utilization and storage site.

In addition, sensitivity and optimization analysis could be accomplished using the following:

- rock types (e.g., dolomite, sandstone, shale, etc.)
- petrophysical parameters, particularly relative permeability model effects
- structural and mechanical characteristic effects (vertical, e.g., layering, areal petrographic, petrologic, and stress controls on fluid flow
- impact and risk of fracturing on CO_2 injectivity and capacity on CO_2 utilization and storage

Integration of a stimulation and geomechanics software with a reservoir simulator was envisioned as part of the project in BP2 and was a significant part of the Sigma Cubed Inc. SUPERNOVA

project. This part of SUPERNOVA was reprioritized and postponed, due to resource allocations and other company priorities.

3.3.1.1 Scope of Work for BP2

- Develop an integrated communication method and platform for static reservoir model CRYSTAL, and dynamic reservoir simulator RESSIM, with a geomechanical simulator STIMSIM

- Incorporate discrete natural fractured network modeling capability in RESSIM and STIMSIM

- Evaluate dynamic fluid flow in the reservoir and the migration of the CO_2 plume, due to vertical and lateral heterogeneity, pressure migration, fault, and seal integrity, due to discrete natural fractures during injection of fluid into a reservoir for intentional or nonintentional rock stress failure

- Investigate the effects of complex structure in the CO_2 sequestration process on plume migration in a brine aquifer

- Evaluate the use of multilateral horizontal wells versus vertical or single lateral wells, and stimulated and non-stimulated wells on the potential of CO_2 capacity, injectivity, and trapping mechanisms

3.3.2 Rock Physics Modeling

Rock physics modeling was a task established in BP2 to produce a standard set of reservoir properties using whatever logs are available. In many cases, there is very limited well log data available to develop geomechanical properties for a particular area or well.

The concept was to create pseudo-logs with correlations and extrapolated data (via kriging, etc.) for use in field studies, reservoir, and data analytics. We used 24 permutations of six types of logs, namely Gamma Ray (Gr), SP, Resistivity, Density, Neutron, and Acoustic. Assuming a combination of these logs will give 24 permutations or combinations of the logs. An example of the work flow is illustrated in Figure 15, page 56, and Figure 16, page 57.

Petrophysical calculations and rock physics modeling was completed using "Quick Look Petrophysics." "Quick Look Petrophysics" was developed, using a rule-based log process of five rules to calculate the geomechanical properties and stress in the rock using well logs (refer to Figure 17 (Left), page 59). Quick Look Petrophysics is a specialized well log analysis package that was created for internal use at Sigma Cubed Inc. and tailored towards the needs and requirements of this project. In addition, a well blocking technique was developed (refer to Figure 17 (Right), page 59).

Automated log analysis starts by blocking well logs in cascading order. A maximum deviation tolerance of 20% in each 30 feet interval is used as the blocking criteria. Initial blocking is completed on Gamma Ray logs, followed by compressional sonic velocity and density logs. The

relative volume of shale in each block, V_{Shale} is calculated using the linear Gamma Ray index method:

$$I_{GR} = \frac{GR_{log} - GR_{min}}{GR_{max} - GR_{min}} \tag{9}$$

$$V_{shale} = I_{GR} \tag{10}$$

Where

GR_{log}: Value of Gamma Ray in the interval of interest
GR_{max}: Maximum observed value of Gamma Ray in the complete interval
GR_{min}: Minimum observed value of Gamma Ray in the complete interval
I_{GR}: Gamma Ray Index
V_{Shale}: Relative volume of shale in the interval of interest

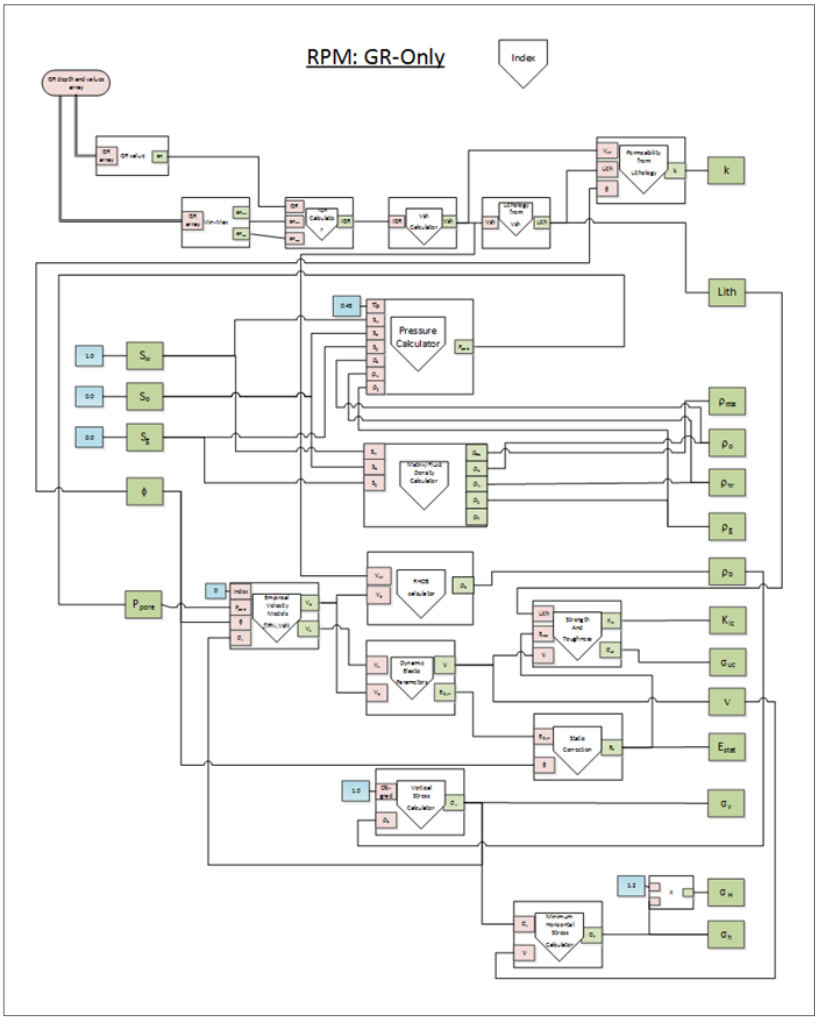

Figure 15: Example of Gr only.

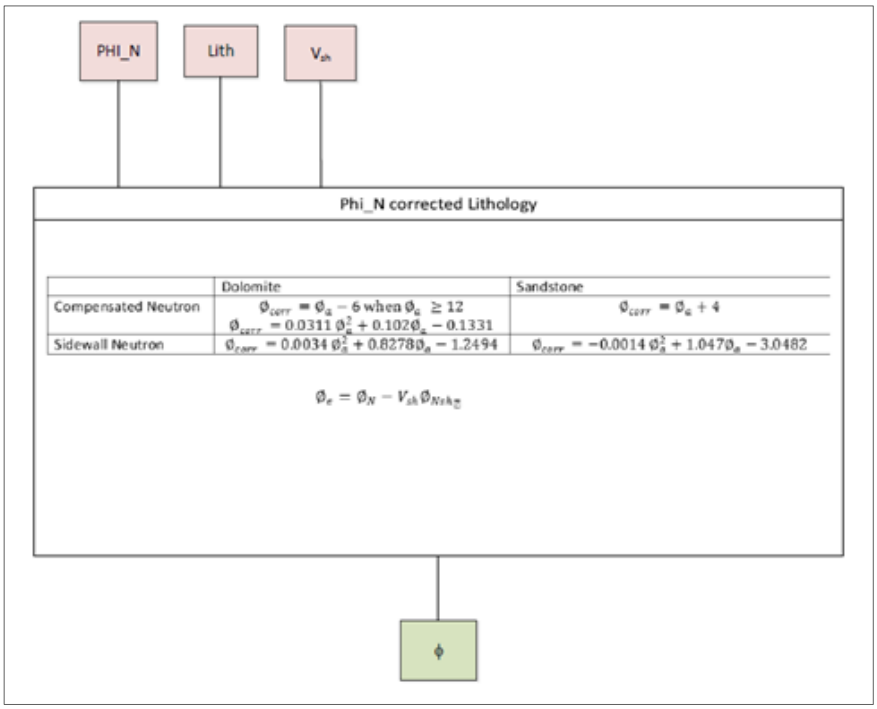

Figure 16: Neutron corrected lithology.

Since compressional sonic velocity measurements were completed in a limited number of available well logs, the Tosaya and Nur[43] velocity model (refer to equations 11 and 12) was used to estimate the sonic velocity in each interval.

$$V_p = 5.8 - 8.6\emptyset - 2.4V_{Shale} \tag{11}$$

$$V_s = 3.7 - 6.3\emptyset - 2.1V_{Shale} \tag{12}$$

Where

V_p: *Compressional Sonic Velocity,* $\frac{m}{sec}$
V_s: *Shear Sonic Velocity,* $\frac{m}{sec}$
$\emptyset$: *Porosity*

Sonic velocities were then used for calculation of Young's modulus, E, and Poisson's ratio, ν:

$$E = \frac{\rho V_s^{\,2}\left(3V_p^{\,2} - 4V_s^{\,2}\right)}{V_p^{\,2} - V_s^{\,2}} \tag{13}$$

$$\nu = \frac{{V_p}^2 - 2{V_s}^2}{2\left({V_p}^2 - {V_s}^2\right)} \quad (14)$$

Where

E: Young's modulus, GPa
ν*: Poisson's ratio*
ρ*: Rock density* $\frac{kg}{m^3}$

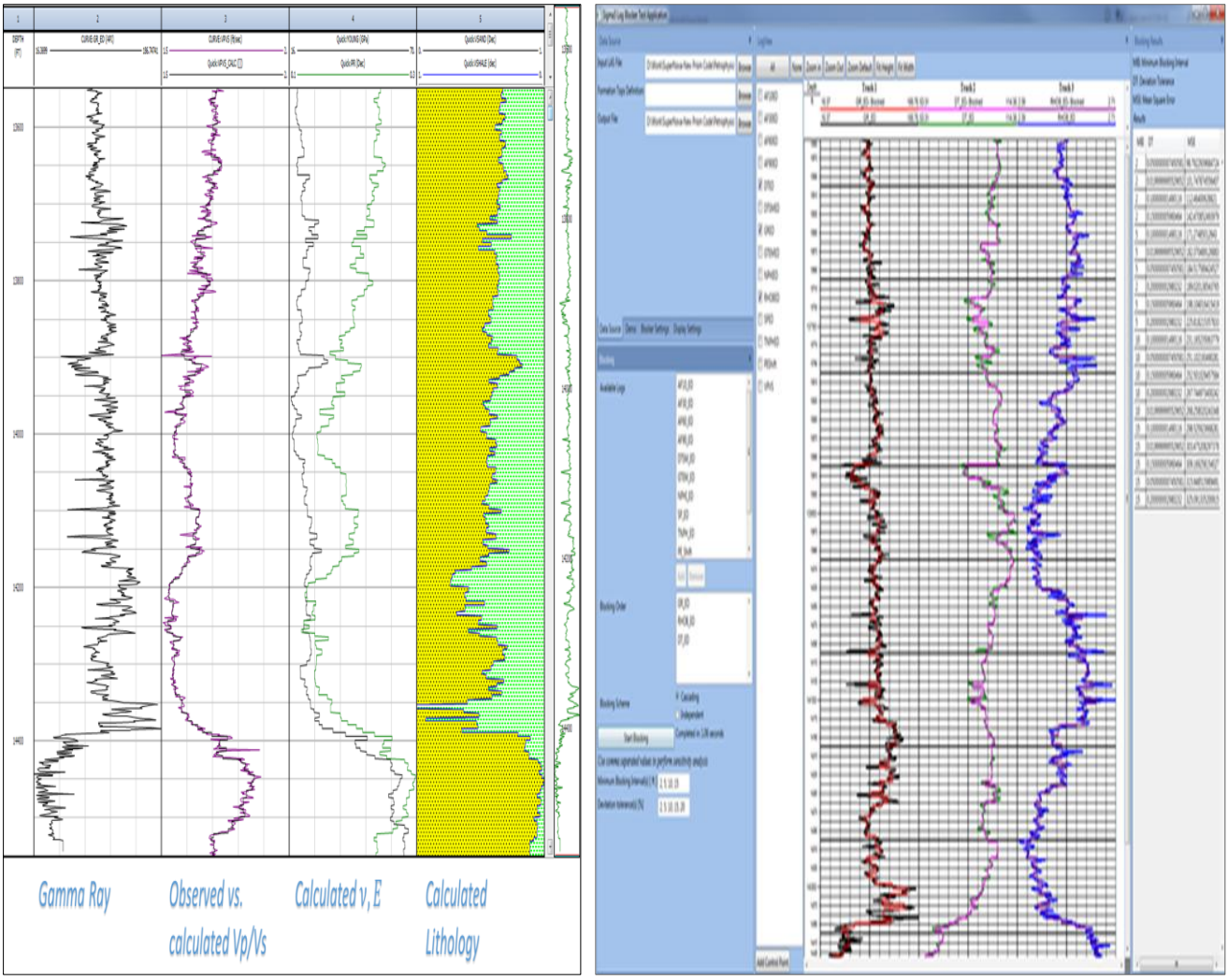

Figure 17: Left is geomechanics from well logs. Right is well log blocking example.

3.3.3 Simulation Efforts

An ED/RSM study starts with a previously completed simulation dataset or file base case. In this project, the base dataset is used to create the master dataset for the commercial ED/RSM software. All previous tasks and efforts to characterize the reservoir define the parameters of the base dataset, which must be stable and running with no convergence problem. The master dataset is the modified base case with embedded instructions that tells the ED/RSM software where to substitute different input parameter values at runtime. A limited number of simulation runs will determine the parameters that should be varied in subsequent studies and over what range. Once the sensitivity study is completed, the optimization studies are used to produce optimal field development plans and operating conditions that will produce either a maximum or minimum value for objective functions.

3.3.3.1 Base Layer Cake Model

The full block model (17x73x100 cells) developed earlier in the project to model the geochemistry was used to develop modeling efforts to incorporate geomechanics, while injecting CO_2 in closed, open, and semiopen reservoirs. Initially, all geochemistry was taken out of the simulation models. However, to account for proper pH and other water chemistry (e.g., effects on CO_2 solubility), limited mineralogy was put back into model. Three minerals, namely calcite, anorthite and kaolinite, were modeled again using a block layer cake model. The model was changed to reflect the four geologic rock units of Sundance, Crow Mountain, Alcova Limestone, and Red Peak formations, but still had 100 layers. Each modified rock unit has a defined relative permeability model taken from Bennion and Bachu literature work [2,3,4,5] on CO_2 water system in tight sandstones, shale, and carbonates, specific to that rock type. The four rock units were defined to have the three minerals with varying amounts of calcite per unit, but zero anorthite and kaolinite, as opposed to other models developed in BP1, with 27 minerals. Laterally, each layer is defined with the same permeability and porosity, but vertically, each layer is different.

The dissolution and precipitation of calcite reaction affects the pH by introducing or removing CO_3^-. The water salinity affects the dissolution, location, shape, size, and phase of secondary minerals. CO_2 solubility in brine increases with pressure and diminishes with increasing temperature. [44] The greater the brine salinity, the less CO_2 will dissolve into it, as implied in Figure 18, page 60.

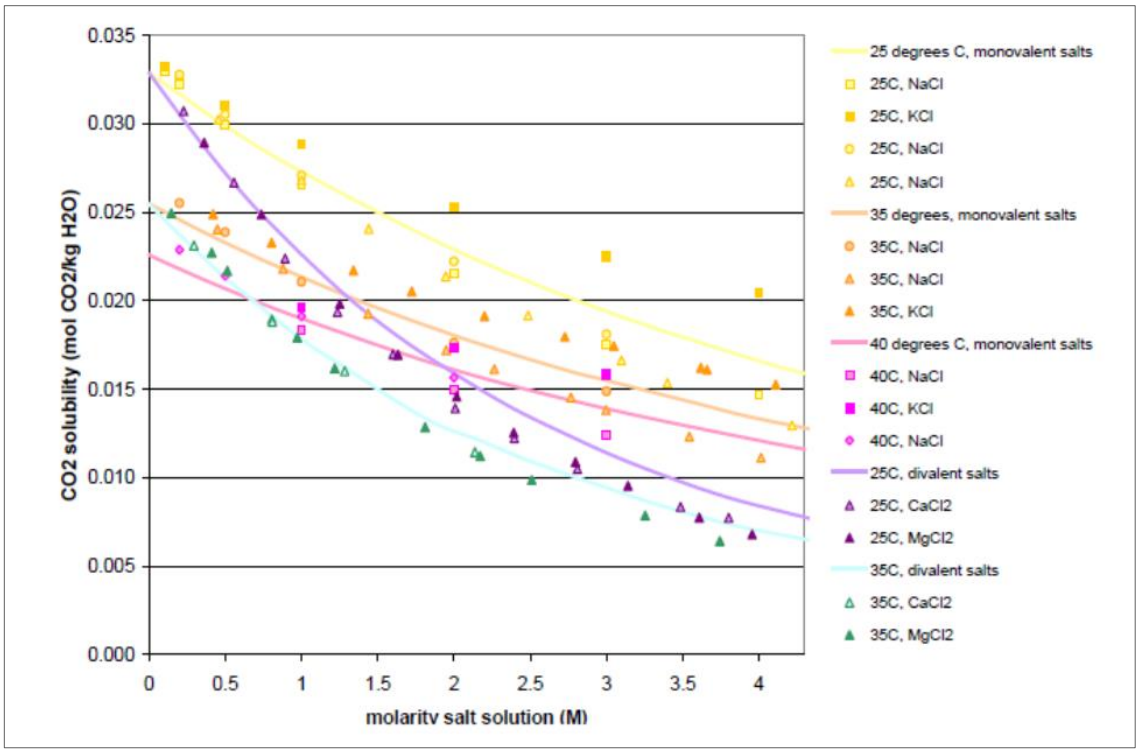

Figure 18: CO_2 solubility as a function of salt molarity at 1 atm pressure from Hangx [44].

With no chemistry considered at all and four rock units with different rock-fluid interactions (i.e., relative permeability considerations) for all rock units, both the closed and open models ran to completion with minimal difficulty, though some time steps could be small, i.e., tenths of days. By modifying different convergence criteria and constraints, the run time can be reduced to 5-6 hours compared to previous run times of over 40 hours. However, this in itself is a trial and error art, and the convergence is very sensitive to any changes in the model definition.

Incorporating even the limited chemistry creates difficulty in getting models to converge and/or run with reasonable run times using a single processor or core. To incorporate a realistic block model with geomechanics with limited geochemistry, requires the use of parallel computer code architecture in the reservoir simulator. To accomplish parallel threading using the commercial code reservoir simulator requires the use of additional software licensed from the vendor referred to as "parallel tokens."

Using two parallel tokens allows the use of eight cores initially resulting in 4.3 days computational time, with loose convergence tolerances in a semiopen system with limited chemistry of three minerals (kaolinite, anorthite, and calcite). The loose tolerances decrease the run times, but can create instabilities and cause particular runs to cut the time step until the minimum time step is reached and the run "crashes" or aborts.

With considerable aid from the reservoir simulator vendor, limited success was achieved in reducing the run times using parallel threading. The base case was optimally tuned to run on 8, 16, and 24 cores to achieve a sufficient speed, so the sensitivity and optimization modules in the commercial ED/RSM software could run an adequate number of cases to develop a proxy model.

The vendor provided significant input to optimize the model run time. The vendor has released several versions of the reactive simulator since the start of this project. These releases had limited impact on reducing the convergence issues in running the complex simulations required in this project. Initially, an optimum run time of approximately 12 hours was developed late February 2014 using eight cores. Additional parallel token licenses were obtained, so 24 cores could be used to run the model. The model tuned and optimized to run over eight cores failed to run over 24 cores, due to the parallel partitioning setup.

Additional optimization for the 24 cores achieved a best run time of 47,844 seconds (13.29 hours, or 0.55 days) compared to the best run time using eight cores of 61,526 seconds (17.09 hours, or 0.712 days). These are the best run times achieved for the layer cake limited chemistry modeled system. Since the run time using eight cores was a very reasonable speed, three parallel runs could be accomplished simultaneously, using the same 24 cores with a 29% increase in the run time per run. Unfortunately, when the geomechanics model is added, the run time increases considerably.

Reducing the mineral composition to one mineral, i.e., calcite, reduced the run time to 9.7 hours, using 24 cores. In addition, the numerical formulation state of the system was changed from fully implicit to explicit-adaptive-implicit model, and surprisingly achieved a 9.4 fold speedup to approximately one hour, using 24 cores or processors for the block model. The speedup was surprising because generally with geochemistry the explicit models have difficulty converging and the fully implicit models are required to maintain proper material balance. The material balance

error increased from 2.3E-5% to 3.8E-4%. Note, the run time is for a single mineral component (calcite) and seven aqueous components with a four-rock type reservoir.

Testing on a model with three minerals and seven aqueous components did not indicate a significant increase in run time nor convergence problems. Additional modification to the model inputs, viz., maximum operating bottom hole pressure to 3500 psi, reducing the injection flow rate to 86 MCFD, changing the maximum time steps to 365 days, decreased the simulation run time to just over 35 minutes for a single mineral and 36.8 minutes for three minerals.

Subsequent runs with 23 minerals using the layer cake model and 24 cores, with some of the initial mineral and component concentrations being zero in some of the horizons, created significant problems starting the simulation and proved unsuccessful. In addition, based on the capability to get a fast simulation run using the full layer cake model with one mineral and 24 cores, a similar simulation run was attempted using the original RMOTC structure model and 24 cores, but was unsuccessful.

3.3.3.2 Distributed Attribute Base Case Model

Geomechanical properties determined from the quick look well log petrophysical analysis program were loaded into the reservoir simulator. The mechanical and reservoir properties (i.e., porosity and permeability) were then geostatistically populated to all grid blocks in the model using kriging techniques (refer to Figure 19, page 63). Density maps from well logs and geomechanics parameter maps, i.e., Poisson's ratio and Young's modulus, were geostatistically distributed using Gaussian Geostatistical simulation. Due to software limitations, the complete mapping of rock properties by geostatistical distribution was grouped into 1500 rock types, corresponding to different Young's modulus and Poisson's ratio combinations (refer to Figure 19 C, D). A mapping between these representative rock types and grid blocks were used to populate the geomechanical grid in the commercial transport simulator.

Initial reactive transport simulation software run times with geomechanics increased from the optimized reactive transport of approximately 30+ minutes to approximately six hours, using 24 cores. The geomechanics module in the current version of the coupled reactive transport and geomechanics model does not allow Poisson's ratio and Young's modulus to be input for each individual cell, nor does it have parallel capability for the geomechanics module. The parallelizing of the geomechanics module may be added in an upcoming 2014 release.

This basically means the finite difference reactive transport module of the commercial reactive transport simulator is parallelized, but the finite element geomechanics module is not, at the writing of this report. Thus, the modeling of the geomechanics is a bottleneck to modeling complex geology, as defined in this project. The current version of the geomechanic coupled reservoir simulator will only allow defined rock types to have a specific Poisson's ratio and Young's modulus. This is a substantially tedious endeavor to build and define each rock type for each cell.

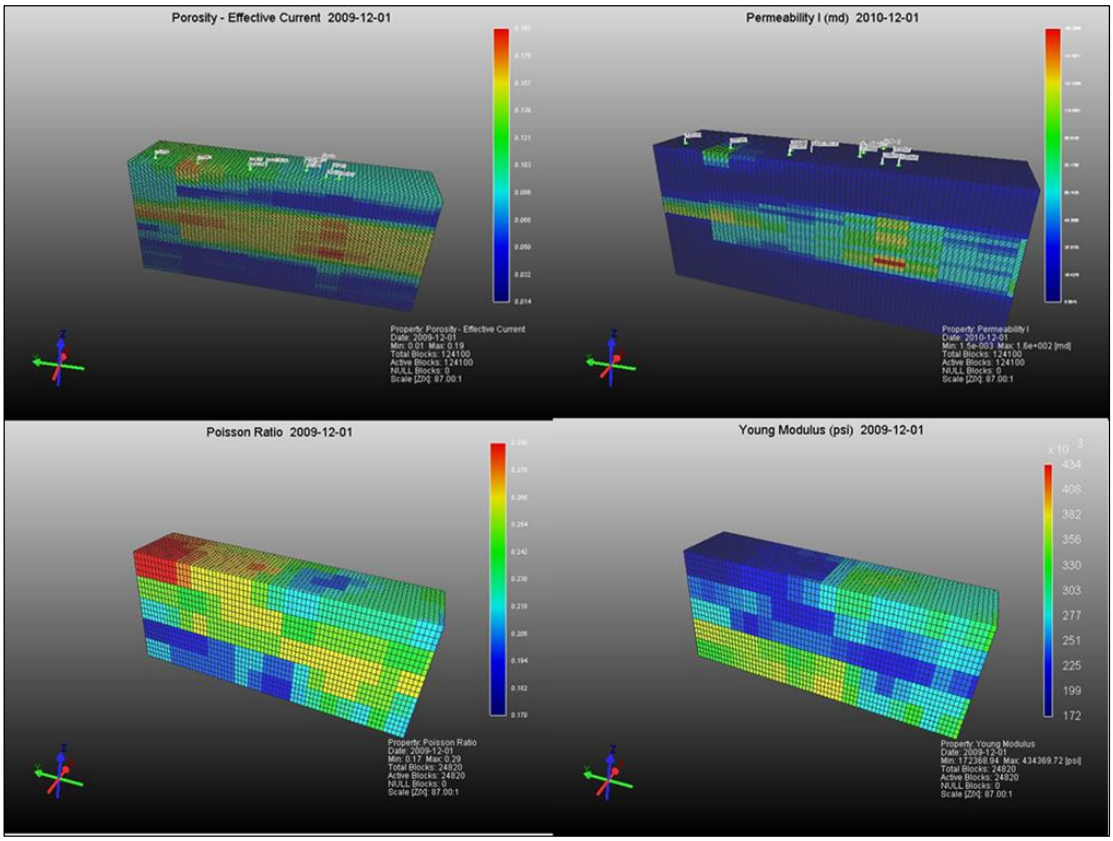

Figure 19: Geostatistical distribution of reservoir and geomechanical properties.

3.3.3.3 Well Completion Modeling

To accomplish the project objectives of how well placement and completion design would impact CO_2 injectivity and capacity, a number of scenarios of multilateral horizontal injection wells were simulated and compared to vertical and horizontal single lateral injection wells.

3.3.3.3.1 Conventional Planar Fractures in Vertical Injection Wells

A base model for vertical injection wells in a single-porosity model was developed. The base model is used for input into the commercial ED/RSM module to develop sensitivity and optimization simulation runs. Many of the simulation runs from the ED/RSM using the master dataset for vertical injection wells, had convergence issues even though the initial master dataset ran successfully. Thus, the ability to compute the objective functions was unsuccessful.

Fractures were extended in the direction of assumed intermediate horizontal stress that was implied by the direction of the existing faults in the region. The prevailing stress regime was assumed to be constant in the region. Figure 20, page 64, illustrates the planar fractures in the northwest-southeast direction around CO_2 injection wells 1 and 2.

Due to software limitations simulating hydraulic fractures, the following two approaches were implemented to model fractures:

a. The reservoir was considered to be single-porosity with fractures being present around the vertical injectors in a planar fashion. This approach was pursued to study the effects of change in effective stress on the fractures during the course of CO_2 injection. Although the most realistic approach, the practical limits of the simulator, in terms of numerical stability and acceptable run time, prevented investigation of this model.

b. A wizard in the simulator was used to create a region of increased permeability around the fractured region. A value of effective fracture permeability was assumed and applied to the extent of fracture half-length, as a gradient that eventually equaled the matrix (unfractured rock) permeability. Although the simplest approach to model fractures, the simulator limitations, in terms of numerical stability and acceptable run time, prevented investigation of different fracture permeability.

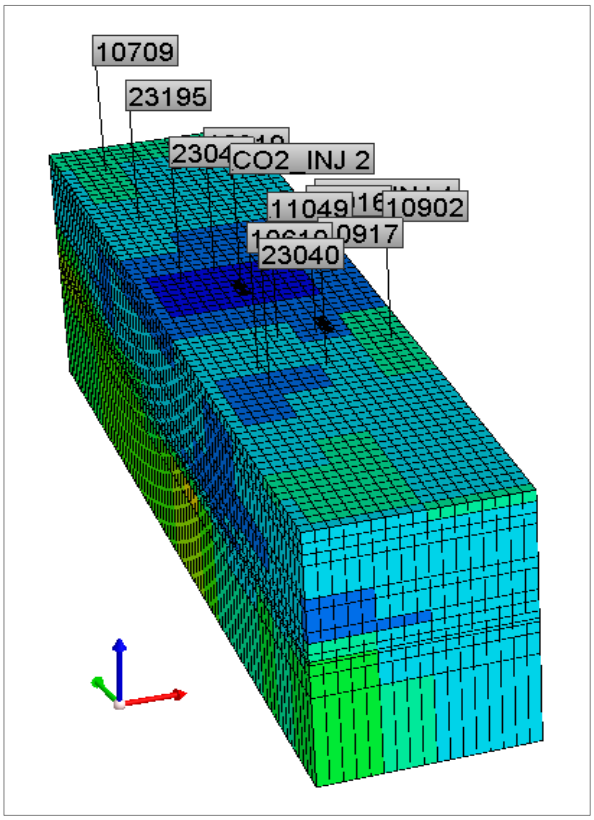

Figure 20: Planar fractures around vertical injection wells.

3.3.3.3.2 Dendritic Fractures in Vertical Wells

Dendritic fractures can be implied, if microseismic data and analysis is completed during injection. The dendritic fracture model is inferred to be a more realistic assumption than the conventional

planar fracture assumption. A symmetrical distribution of fractured cells was considered around the vertical wells. Figure 21, page 65, illustrates the fracture spacing around vertical CO_2 injection wells 1 and 2, which represent the presence of dendritic fractures. As observed in simpler cases, the dendritic model suffered from numerical stability, but was able to progress until the end of the designated 50-year simulation life cycle.

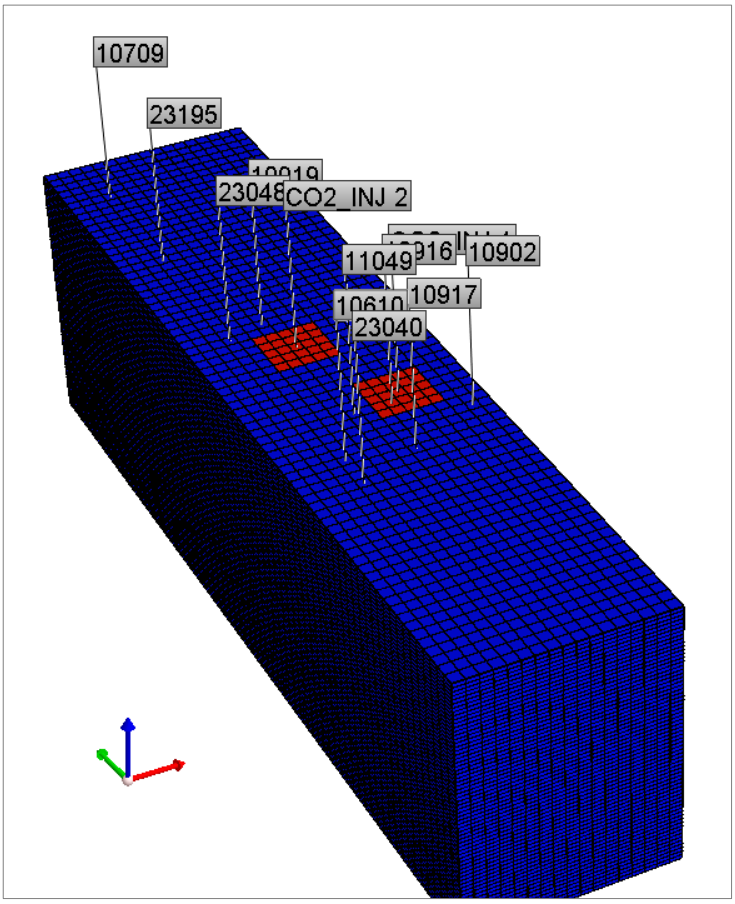

Figure 21: Fracture spacing around vertical injection wells 1 and 2 represent dendritic fractures.

3.3.3.3.3 Hydraulically Fractured Horizontal Injection Wells

Three horizontal wells were also created in the model and fractured in a multi-stage, toe to heel fashion with interconnected fracture planes (refer to Figure 22, page 66). Due to the size limitations in the model previously mentioned, assumptions for the northwest-southeast direction for intermediate horizontal stress direction were ignored and the wells were assumed drilled in the direction of minimum horizontal stress, which was assumed to be northwest-southeast. Thus, the hydraulic fractures that resulted from the treatment were assumed to be in the east-west direction. To simulate the toe to heel fracturing, perforations were applied only in the location of fracture planes.

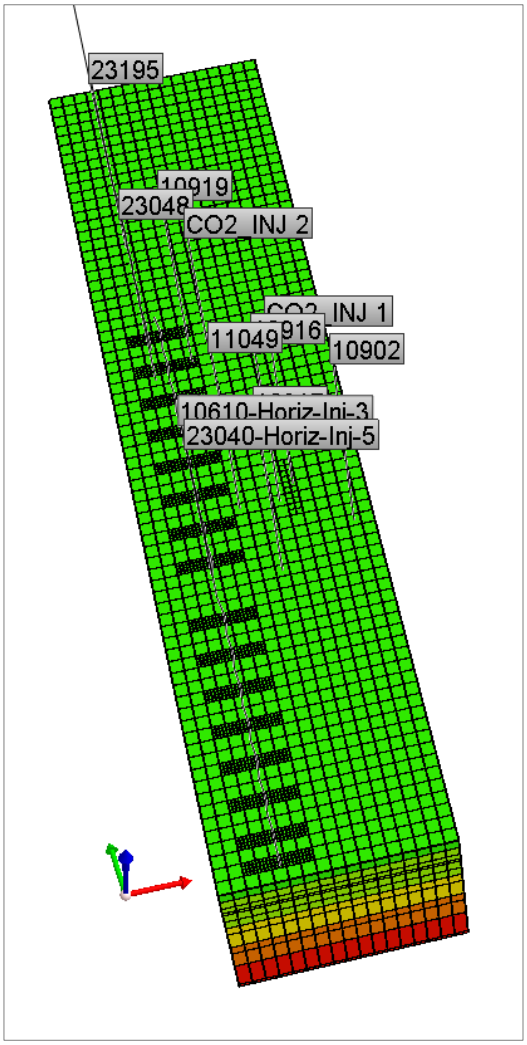

Figure 22: Horizontal wells 3 and 5 displaying the multi-stage fractures.

As in the vertical well fracturing simulation, due to software limitations simulating hydraulic fractures, the following two approaches were implemented towards modeling fractures:

a. The reservoir was considered to be single-porosity with fractures being present around the vertical and horizontal injectors in a planar fashion. This approach was pursued to study the effects of change in effective stress on the fractures during the course of CO_2 injection. Although the most realistic approach, the practical limits of the simulator, in terms of numerical stability and run time, prevented investigation of the model.

b. A wizard in the simulator was used to create a region of increased permeability around the fractured region. A value of effective fracture permeability was assumed and applied to the extent of fracture half-length, as a gradient that eventually equaled the matrix (unfractured rock) permeability. Although the simplest approach to model fractures, the simulator

limitations, in terms of numerical stability and acceptable run time, prevented investigation of different fracture permeability.

3.3.3.3.4 Fractured Reservoir Models

Fractured reservoirs are composed of two distinct systems, namely the rock matrix and interbedded or discrete fracture network. Fluid flow in structured porous media (nonfractured and fractured rocks) can be described using a variety of dual-porosity, dual-permeability, multi-porosity, and/or multi-permeability models. Dual-porosity and dual-permeability models both assume the porous medium consists of two interacting regions, wherein one is associated with the inter-aggregate, macropore, or fracture system, and one is comprised of micropores (or intra-aggregate pores) inside the rock matrix. While dual-porosity models assume fluid in the matrix is stagnant, dual-permeability models allow for fluid flow in the matrix, as well. In a dual-porosity system, hydrocarbons are produced only through the fracture network, though reservoir fluid can flow from the matrix to the fracture. In a dual-porosity/dual-permeability system, flow into the wellbore can occur from both the rock matrix and the fracture. Simulations with a dual-permeability model indicate a few discrete fractures can have a major influence on plume geometry. [45]

A number of fracture type models were attempted in this study, as follows:

1. Planar fractures
2. Dendritic fractures
3. Multi-stage horizontally fractured wells
4. Multi-stage horizontally fractured wells with zipper fracs
5. Dual-porosity model with no active fractures
6. Dual-porosity model with active fractures everywhere
7. Dual-permeability model with active fractures in Crow Mountain layer
8. Single-porosity models with local grid refinement around vertical and horizontal wells to simulate improved permeability resulting from hydraulic fractures
9. Dual-porosity models with MT (Matrix Block) option to allow communication between injected fluid and matrix

Unfortunately, few (if any) of these models would run successfully to the end of the injection period and the observation period following. Primarily due to the protracted time it took for these models to complete (in the order of 5-7 days), numerical instabilities resulted in improper terminations of the run.

Overall, approximately 100+ different realizations were created and tested, but only a dozen, or so, were completed in a reasonable fashion.

3.4 Project Accomplishments

- BP1
  - Baseline Reservoir Model defined
  - Detailed Reservoir Characterization Model defined
  - Detailed Rock Mineralogy and Assemblage defined
  - Commercial third-party reactive transport simulator tested
- BP2

- Rock Physics Concepts Workflow created
- "Quick Look" Petrophysics Analysis software created
- Simplified well bore simulator developed
- Layer Cake Base Reservoir Model successful
  - Limited Geochemistry (1-3 minerals)
  - Geomechanics Model implemented
  - Reasonable Base Model run times
- Distributed Base Reservoir Block Model developed
- A number of well completion simulation scenarios were run
  - Modeled wells were in fractured and nonfractured reservoirs using vertical and horizontal completion methods
  - All fractured reservoir models used a dual-permeability simulation technique
- Numerical stability created difficulty in accomplishing objectives using the coupled geochemistry and geomechanics, and just geomechanics. Upscaling improved the simulations to run to completion, but the upscaled models presented unusual behavior as to the fluid escaping to upper layers above the targeted zone

4 CONCLUSIONS

4.1 Key Findings and Lessons Learned

1. The industry continues to lack a fast commercial reactive transport simulator capable of complex reservoir geochemistry coupled with a geomechanical simulator.

2. A limited number of minerals (<3) were modeled with publically available reactive transport simulators during the project lifecycle. The maximum number of minerals that can be effectively modeled with a reactive transport simulator is unknown; however, from the current work and published literature the limit estimation is < 5-8.

3. The industry is making progress in building robust reactive transport simulators; however, with no market driver the progress and acceptance of a coupled reactive transport and geomechanics model will be exceptionally slow.

4. EOR is helping create a market for anthropogenic CO_2. However, the concept of utilization and storage of anthropogenic CO_2 for EOR is a different chemical process than the geochemistry modeled in this project. The lifecycle of EOR projects using CO_2 is relatively short-term (measured in decades) compared to the lifecycle of a sequestration project (measured in centuries). Predicting recovery factors for EOR has a high value to the oil and gas industry; but, predicting CO_2 interactions with rocks for typical current CO_2 type floods for enhanced oil and gas recovery, has minimal economic value.

5. Geomechanical modeling simulation is fairly well defined, and a market driver primarily in completions of shale oil and shale gas reservoirs in the oil and gas industry is accelerating the development of a coupled geomechanical transport simulator.

6. A proxy model for full field CO_2 injection sequestration was not capable of being developed with software available for this project.

7. Based on the amount of effort and huge computational time required, predicting CO_2 sequestration and/or storage capacity in geologic formations to within 30% is doubtful unless the new releases of the commercial reactive transport software used in this study, TOUGHREACT v3, and PFLoTRAN can provide the ED/RSM input to develop the proxy models and verify output. Additional testing of the new releases is needed.

4.2 DEFE0004510 Relevancy to the Aims of the CCUS Program

There were two program goals addressed in project DE-FE-0004510:

1. Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness.

2. Support industry capability to predict CO_2 storage capacity in geologic formations to within ±30 percent.

Successful demonstration of the modeling effort would have illustrated that proxy type models could have been developed to rapidly, cost effectively, and efficiently perform technical assessments of major engineering and scientific issues considered to be critical to the design, implementation, and operation of a saline aquifer CO_2 sequestration storage site. The project was unsuccessful proving the feasibility of this benefit.

The project was proposed as a proof of concept and feasibility study that the industry has the capability to accomplish the above two program goals by using a commercial reactive transport simulator and develop simpler and faster design models namely proxy equations or model using ED/RSM techniques. The concept could not be positively demonstrated as feasible at this time as the industry does not have a reactive transport simulator capable of providing the complex geochemistry reactive transport modeling coupled with the ED/RSM software to produce the proxy models. This could be a burden to typical design and efficient operations of a full field scale CCUS process outside of an R&D government subsidized operation.

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LIST OF ACRONYMS AND ABBREVIATIONS

1-D	one dimension (dimensional)	GR_{min}	Minimum observed value of Gamma Ray in the complete interval	R&D	Research and Development
2-D	two dimension (dimensional)	i.e.	*id est*, in effect, namely, in other words, that is	RESSIM	acronym or "nom de guerre" for REServoir SIMulator in SUPERNOVA
3-D or 3D	three dimension (dimensional)	Inc.	Incorporated	RETC	RETention Curve software developed by USEPA
4-D	four dimension or dimensional	I_{GR}	Gamma Ray Index	r_m	reaction rate for mineral m
A_m	reactive surface area for mineral *m* (m^2 mineral per m^3 porous medium)	*i*TOUGH	LBNL software for OM, SA, UA, based on TOUGH2	RMOTC	Rocky Mountain Oilfield Testing Center
$\tilde{A}_m$	precursor surface area (m^2 mineral per m^3 porous medium)	J	Joules	RSA	Reactive Surface Area
API	American Petroleum Institute	k	permeability	RSM	Response Surface Methods (Methodology)
aq	aqueous	k_a	rate constant	SA	Sensitivity Analysis
ARC	Alberta Research Council	$K_{eq,m}$	chemical equilibrium constant for mineral react m	scf	standard cubic foot (feet)
A_{ssm}	specific surface area of mineral (m^2/g)	kg	kilogram	SP	Spontaneous Potential
BET	Brunaur-Emmet-Teller adsorption test for specific surface area	k_r	relative permeability	SSA	Specific Surface Area
BP1	Budget Period 1 or first budget period	k_{Tref}	rate constant at reference temperature	STIMSIM	acronym or "nom de guerre" for STIMulation SIMulator in SUPERNOVA
BP2	Budget Period 2 or second budget period	l	liter	SUPERNOVA	code name for Sigma Cubed Inc. internal project
cc	cubic centimeter	LANL	Los Alamos National Laboratory	S_{wirr}	Irreducible water saturation
CCUS	Carbon Capture Utilization and Storage	LBNL	Lawrence Berkeley National Laboratory	TM (™)	Trademark
cm	centimeter	LS	Limestone	TOUGH2	simulator for nonisothermal multiphase flow in porous and fractured media developed by LBNL
CO_2	Carbon Dioxide	m	meter	TOUGH2-MP	Massively Parallel (MP) version of TOUGH2
dba	doing business as	m^2	square meter	TOUGHREACT	LBNL porous media reactive transport program
DST	Drill Stem Test	m^3	cubic meter	T_{ref}	reference temperature
E	Young's modulus, GPa	*m* (subscript)	mineral	UA	Uncertainty Analysis
E_a	Activation energy (J/mole)	MCFD	thousand cubic feet per day	(US)DOE	(United States) Department of Energy
ECO2N	LBNL equation-of-state software for CO_2 water systems	md	millidarcy	USEPA	United States Environmental Protection Agency
ED	Experimental Design	mg	milligram	USGS	United States Geological Survey
e.g.	*exempli gratia*, example given, for example	MT	keyword in commercial reactive transport software matrix block	viz.	*videlicet* (*videre licet*), that is, namely, to wit
EOR	Enhanced Oil Recovery	NETL	National Energy Technology Laboratory	V_{shale}	Relative volume of shale in the interval of interest
FPTI	Fusion Petroleum Technologies, Inc.	NPR-3	Naval Petroleum Reserve No. 3	γ_m	fraction of mineral surface are in contact with the reactive phase
FRESI	Fusion Reservoir Engineering Services, Inc.	OM	Optimization Methods	μS	micro second
g	gram	PFLoTRAN	open source, massively parallel subsurface flow and reactive transport code	ν	Poisson's ratio
GeoPRO	Proprietary Internal Database	PHREEQC	USGS computer program pH-Redox-Equilibrium written in C+	ρ	density (mass/volume)
GHG	Greenhouse Gas	PMP	Project Management Professional	ρ_m	density of mineral (kg/m^3)
g-mole	gram mole	PMP	Project Management Plan	φ_{core}	core porosity
GR	Gamma Ray	PNNL	Pacific Northwest National Laboratory	φ_{eff}	effective porosity
GR_{log}	Value of Gamma Ray in the interval of interest	Q_m	activity product of mineral reaction *m*	φ_m	volume fraction of the mineral
GR_{max}	Maximum observed value of Gamma Ray in the complete interval	r	radius (grain radius)	φ_{NDe}	effective porosity from neutron density log cross plot with shale correction applied

APPENDICES

APPENDIX A RESERVOIR SIMULATION DEFE0001111

Most reservoir simulators are designed based on no flow boundary conditions that basically predefine a system as closed. This works well for estimation of oil and gas reserves, and reservoir analysis, especially where there is more than one immiscible phase. However, for CO_2 sequestration, orders of magnitude smaller permeability are required to create a seal, and aquifers may not be considered a locally closed system.

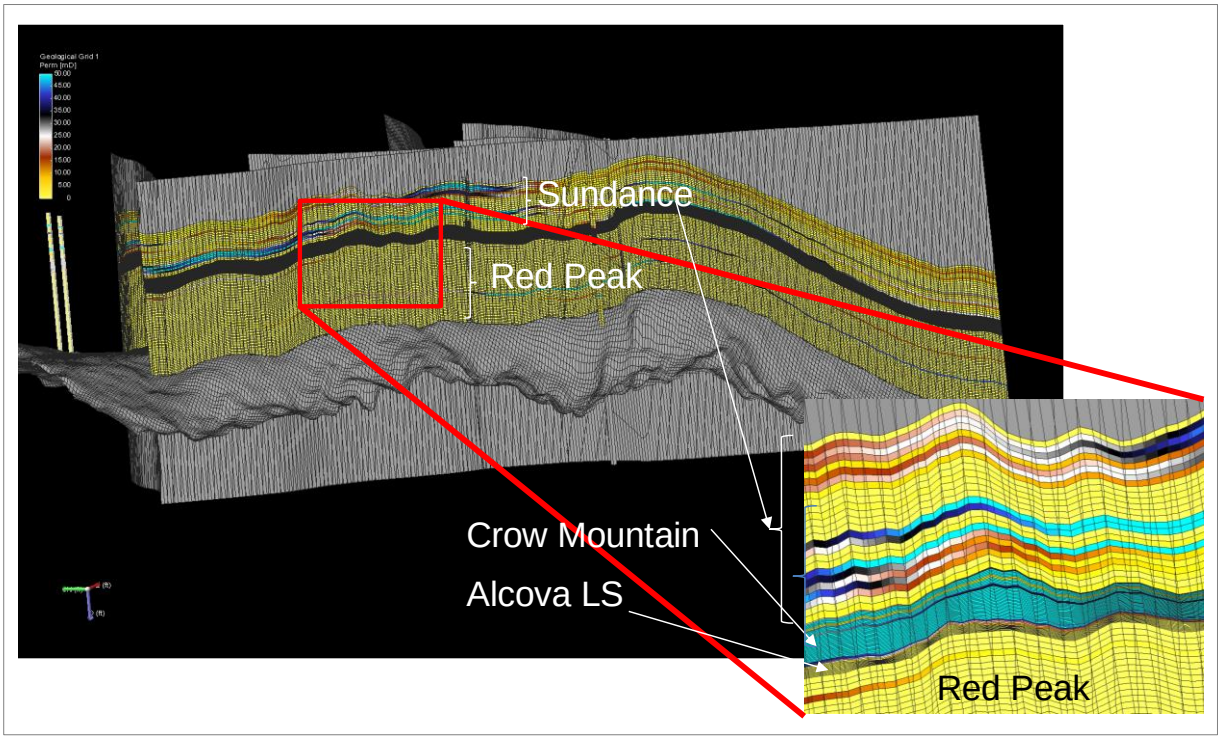

Figure 23: Permeability property along the main fault. The figure displays all red peak structure. Note, the indication of high permeability stringers in the upper and lower seal structures, and low permeability stringers in the upper Crow Mountain unit.

Closed systems may not offer sufficiently large capacity to sequester any reasonable amount of CO_2. For a single phase system of water and gas to flow, it is not necessarily impeded by the pay cut off definitions for uneconomic oil and gas development. Single phase fluids do not encounter significant restriction to movement in porous media, until very low permeability or capillary restrictive conditions exist, generally due to more than one immiscible phase present in the system. Water can hydraulically flow through very "tight" (micro and even nano darcy range) reservoir rocks albeit very slowly. Seal permeability above 10^{-18} m^2 (10^{-3} md) behave as open systems, while systems below 10^{-19} m^2 (10^{-4} md) exhibit closed system behavior [46]. Most aquifers would be too large aerially to be modeled as a closed system, if the aquitards (seals) surrounding the aquifers are included in the modeling effort and the vast lateral extension of an aquifer was included.

As an example, the fresh water Ogallala aquifer covers 174,000 square miles in portions of eight states. Though this is a fresh water aquifer and is not suggested as a target for CO_2 sequestration, its expanse indicates just how large aquifers may be. Multiple phases in a reservoir rock retard the nonwetting phases from readily flowing, but aquifer rock can be considered water wet and water flows less impeded than other nonwetting phases, e.g., defining CO_2 to be a nonwetting phase.

- Most reservoirs are initially bounded by competent caprock that is sealing
- There exists a pressure differential across the caprock
- During injection phase, when the pressure drop becomes sufficiently large, the seal provided by the caprock may be breached, and flow across the breach in the caprock may occur

However, since the pressure drop across the caprock may be driven higher by external influences (though fluid can now move across it), further seal degeneration could occur, resulting in progressively larger outflow.

Appendix A.1 Reservoir Simulation Model

The grid of the reservoir simulation model was populated with the porosity and permeability determined from the logs and the Timur correlation. The 3-D images in Figure 24, page 78, illustrate the heterogeneity and layering of different permeability, and infer possible transmissivity variations and barriers to flow both horizontally and vertically.

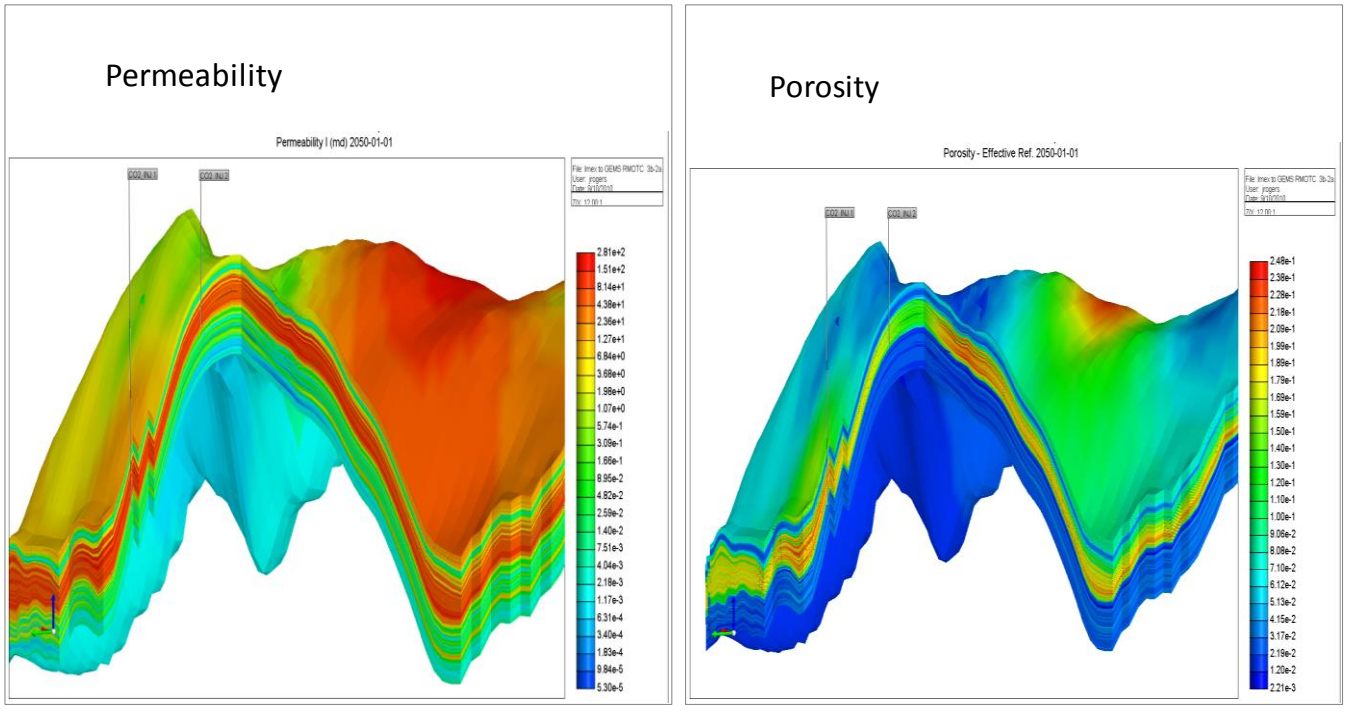

Figure 24: Left is a cutaway view of permeability parameter model in the Teapot Dome by Timur correlation. The vertical scale is overemphasized. Right is a cutaway of Teapot Dome showing porosity map of Crow Mountain and surrounding reservoir.

Appendix A.1.1 Infinite System

In order to emulate an open or infinite reservoir system, the cells in the outer pillars of the grid system had a pore volume multiplier of 10^6 applied to each cell (refer to Figure 25, page 79). Applying the multiplier resulted in a large total pore volume of approximately 1.092 $x10^{15}$ cubic feet. Moreover, assuming a 200 feet height for the reservoir of interest (50 feet of sandy/shale/siltstone above Crow Mountain, 80 feet of Crow Mountain aquifer, 20 feet of Alcova limestone/dolomite, and 50 feet of shale/claystone in Red Peak) an area of 5.45 x 10^{12} square feet, or approximately 195,400 square miles is calculated. For comparison, the area of Wyoming is 97,814 square miles. The magnitude of the area may seem somewhat unrealistic as Crow Mountain and its parent geologic member outcrop in northwestern Wyoming, and may in fact be substantially smaller, if truly hydraulically bounded as some have suggested. However, the model provides an axiom to define Crow Mountain as an open system and a proxy to mimic a fairly constant pressure realization for sequestering CO_2 in the Crow Mountain aquifer. The simulation grid consists of 256,632 blocks, of which 124,331 are active and 132,301 have pinchout characteristics, e.g., pore volumes small enough to cause high transmissibility with the neighboring cells and cause convergence problems or cells outside of the reservoir model.

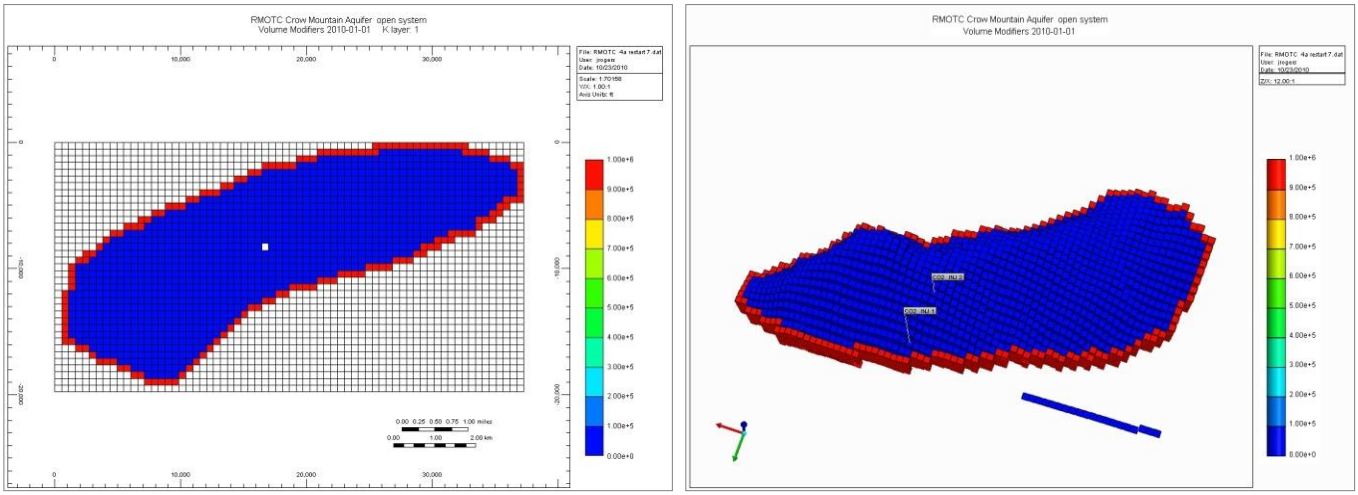

Figure 25: Left is a 2-D aerial view of the input grid. Right is a 3-D view of the input grid. Note, red cells indicate the cells that have large multipliers to emulate an open (infinite) reservoir.

Appendix A.1.2 Simulation of CO_2 Injection

Simulated supercritical CO_2 injection into Crow Mountain was through two wells. Injection well 1 was placed close to the Teapot Dome boundaries on the south end of the east edge of the field, away from the main fault line and at one of the lowest areas in the reservoir. Injection well 2 was placed up dip of injection well 1, but not quite at the apex of the anticlines or higher structures prevalent in Teapot Dome. Both wells had rates of 1MM cuft/day (total of 2 MM cuft/day for approximately 106 tons per day and a total of approximately 1.2 MM tons of CO_2). Both wells were completed in the bottom ten feet in layers 50-55. Each layer in the model is approximately two feet thick.

Preliminary simulation evaluations indicated gravity segregation seems to be a prevailing mechanism in CO_2 injection in Crow Mountain, due to the structural nature of the Teapot Dome formations. Figure 26, page 81, shows four snapshots of layer 22 (slightly above the top of Crow Mountain) at various times during the injection of carbon dioxide. Layer 22 shows the largest plume accumulation of CO_2 during the injection. The accumulation is under a layer of dolomitic claystone above the Crow Mountain aquifer. Figure 27, page 82, is a cross-section or cutaway view displaying the gravity segregation as the CO_2 accumulated at the higher apexes of the aquifer. The CO_2 does not diffuse laterally, but appears to flow vertically very rapidly in the immediate injection blocks and then flows below the low permeability layers at the top of Crow Mountain to the apex of the anticlines where the gas concentrates due to gravity. Though there is some lateral convective flow along the longitudinal axis during injection of the reservoir, the primary flow is in the southwest as a result of gravity segregation and density differences of the dense supercritical CO_2 and water. The dense gaseous phase flows along a less permeable layer, but the CO_2 still indicates penetration in the upper "seal" as is illustrated in the "fence diagrams" of the different time realizations in Figure 28, page 83.

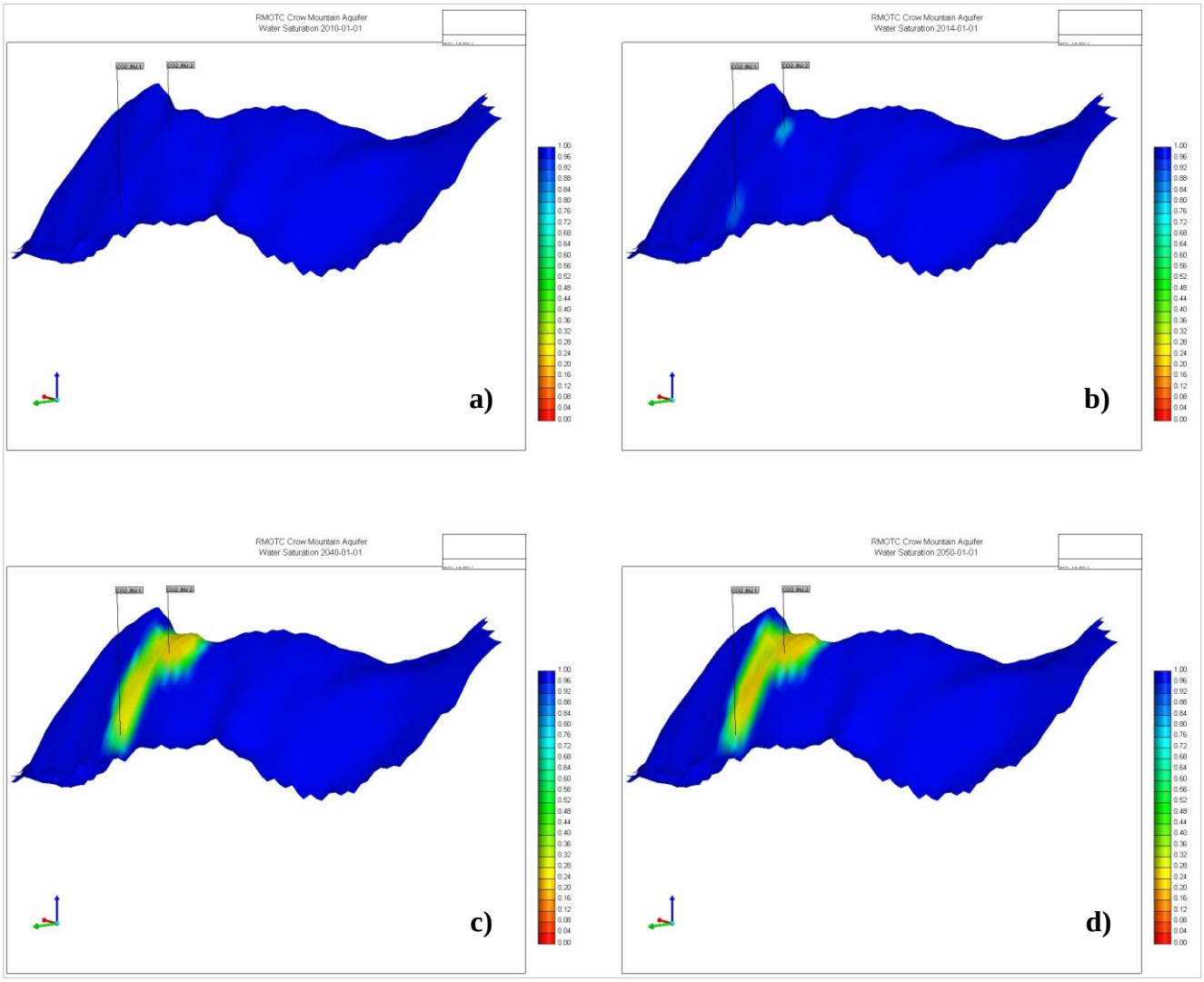

Figure 26: a) Start of injection, b) 4 years after injection, c) end of injection 2040, and d) after a 10-year soak. The images illustrate a single layer at the top of Crow Mountain.

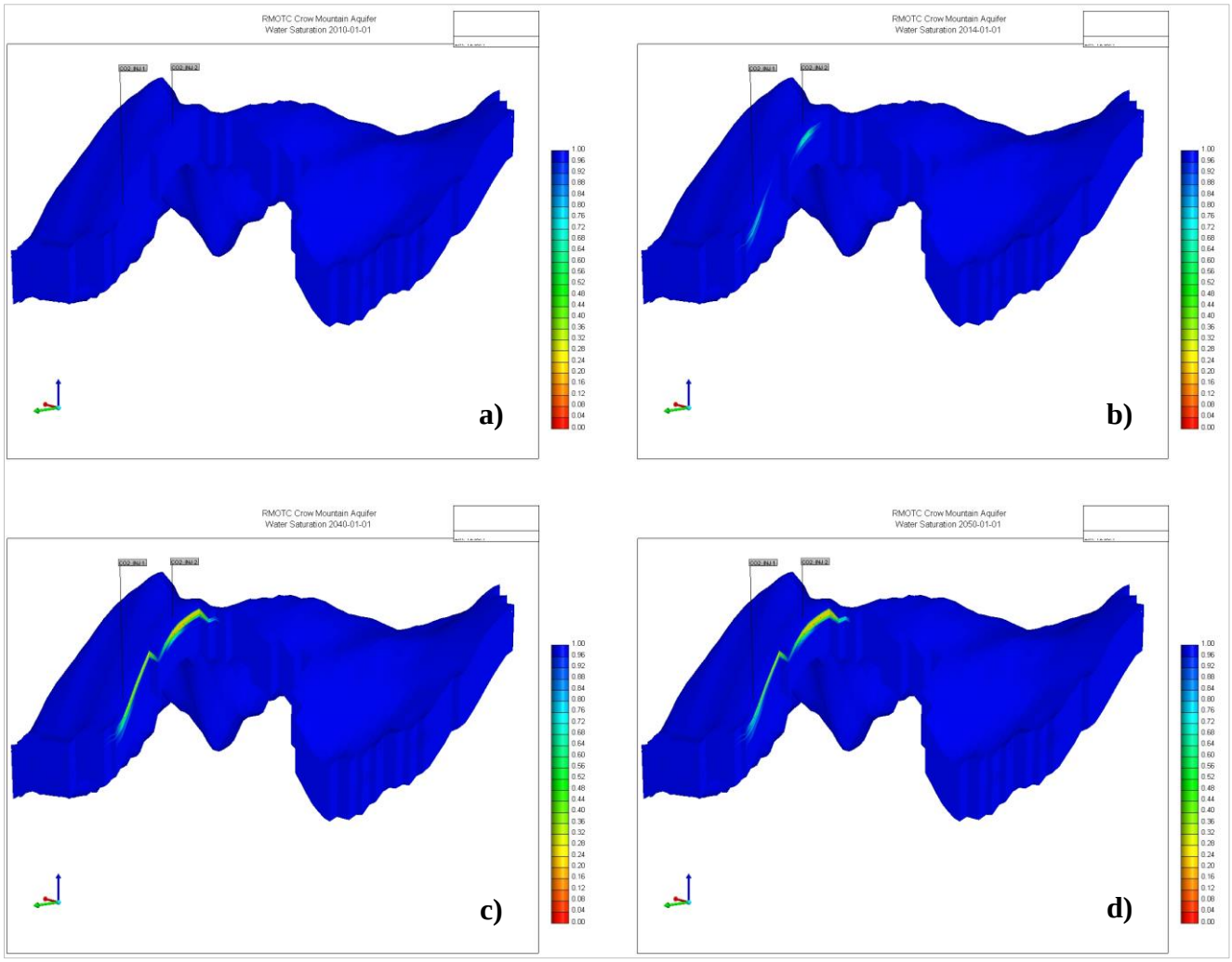

Figure 27: a) Start of injection, b) 4 years after injection, c) end of injection 2040, and d) after a 10-year soak and equilibration time.

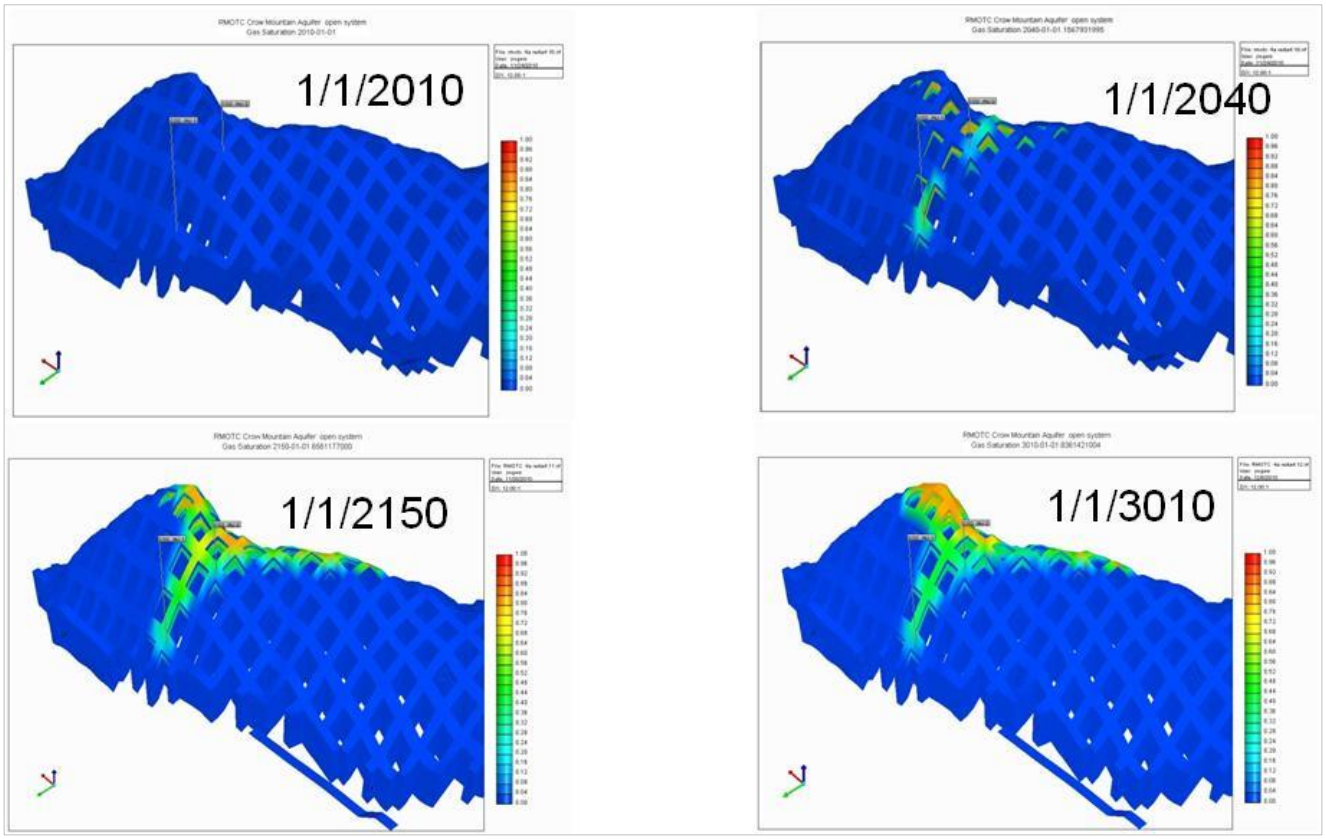

Figure 28: 3-D "fence diagrams" of the gas saturation from the reservoir simulation of CO_2 injected into Crow Mountain. The injection simulation started 1/1/2010 and injection ceased 1/1/2040, 30 years later. Note, the gas continues to displace vertically, as well as in the two lateral directions after injection ceases.