Award Number: DE-EE0002764 **Awarded to:** Regents of the University of Minnesota

Research Title: Recovery Act: An Integrated Experimental and Numerical Study: Developing a Reaction Transport Model that Couples Chemical Reactions of Mineral Dissolution/Precipitation with Spatial and Temporal Flow Variations.

Principal Investigator: Martin Saar

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Executive Summary

A total of 12 publications and 23 abstracts were produced as a result of this study. In particular, the compilation of a thermodynamic database utilizing consistent, current thermodynamic data is a major step toward accurately modeling multi-phase fluid interactions with solids. Existing databases designed for aqueous fluids did not mesh well with existing solid phase databases. Addition of a second liquid phase (CO2) magnifies the inconsistencies between aqueous and solid thermodynamic databases.

Overall, the combination of high temperature and pressure lab studies (task 1), using a purpose built apparatus, and solid characterization (task 2), using XRCT and more developed technologies, allowed observation of dissolution and precipitation processes under CO2 reservoir conditions. These observations were combined with results from PIV experiments on multi-phase fluids (task 3) in typical flow path geometries. The results of the tasks 1, 2, and 3 were compiled and integrated into numerical models utilizing Lattice-Boltzmann simulations (task 4) to realistically model the physical processes and were ultimately folded into TOUGH2 code for reservoir scale modeling (task 5).

Compilation of the thermodynamic database assisted comparisons to PIV experiments (Task 3) and greatly improved Lattice Boltzmann (Task 4) and TOUGH2 simulations (Task 5). PIV (Task 3) and experimental apparatus (Task 1) have identified problem areas in TOUGHREACT code. Additional lab experiments and coding work has been integrated into an improved numerical modeling code.

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1. An integrated experimental and numerical study: Developing a reaction transport model that couples chemical reactions of mineral dissolution/precipitation with spatial and temporal flow variations in CO_2/brine/rock systems

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- Subcontractors and Participating Organizations: [none]

2. Project Objectives and Purpose

- The overarching objective of this project is the modification of a numerical simulator (TOUGH2) to allow coupling of experimentally observed chemical interactions between supercritical carbon dioxide (CO_2) and enhanced geothermal system (EGS) reservoir rocks with spatial and temporal variations in pore/fracture geometries and in associated permeability and flow fields. These chemical interactions are predominantly mineral dissolution/precipitation reactions that are likely heterogeneously distributed and time-dependent.
- This project will result in a numerical simulator (modified version of TOUGH2) that can adjust porosity and permeability fields according to experimentally observed chemical fluid-rock interactions (mineral dissolution/precipitation) under realistic conditions likely found when supercritical CO_2 is injected into geothermal reservoirs for heat energy extraction. The simulator can thus help determine if CO_2 injection into EGS brines will cause clogging of pore spaces or dissolution of host rocks with potentially detrimental consequences to heat extraction. As a result, this simulator will play a critical role when assessing long-term sustainability of geothermal energy utilization in enhanced and natural geothermal systems. The simulator can also be used to evaluate long-term CO_2 sequestration potentials. The project applies to the DOE Geothermal Technologies Program's Multi-Year Research, Development, and Demonstration (MYRDD) plan as the research furthers the development and commercial operation of an enhanced geothermal system (EGS) resource through investigation of Topic 14 of FOA DE-PS36-09GO99018. In particular, the study addresses issues related to geothermal reservoir sustainability. The goal of "Reservoir Sustainability," as outlined in MYRDD's Technical Plan, is to "Develop the ability to manage EGS reservoirs for maintenance of reservoir lifetime and productivity." Our study addresses the two tasks listed in Table 4.29 (Page 75) of MYRDD's "Reservoir Sustainability" section, i.e., "Stimulation and management of created reservoir" and "Maintaining fluid flow and reservoir lifetime." These tasks are achieved via the approach listed in Table 4.29 entitled "Improve understanding of rock-fluid geochemistry for scale and dissolution prediction."

3. Technical Barriers and Targets

- Standard chemical models that assume homogeneously mixed components, local equilibrium, and evenly distributed pore structures cannot be applied to reactive transport models. Instead, this study will conduct physical experiments involving the actual fluids (brine, supercritical CO_2) and solids (various likely reservoir rocks) under realistic pressure and temperature conditions. An additional complication results from an inconsistency between aqueous and solid phase thermodynamic databases. Reconciliation of the liquid and solid phase databases was a key hurdle before any geochemical modeling could proceed. These experiments are then utilized to include mineral dissolution/precipitation processes and related permeability changes into

TOUGH2 reservoir scale modeling of conditions that are likely found when supercritical CO_2 is used in EGS.

4. Technical Approach

Task 1: Laboratory Experiments – Conduct laboratory experiments with supercritical CO_2, brine, and rocks resembling CO_2 injection into enhanced geothermal systems (EGS) to generate mineral dissolution and/or precipitation reactions under realistic pressure-temperature-chemistry conditions.

Task 2: Solid Characterization – Characterize in two and three dimensions the spatial and temporal distribution of mineral dissolution and precipitation processes employing X-ray tomography, SEM imaging, and Microprobe analysis.

Task 3: PIV Experiments on multi-phase flow through porous media – To allow simulation and parameterization, of the processes observed under Tasks 1 and 2 using a lattice-Boltzmann (LB) method (Task 4), we will conduct particle image velocimetry (PIV) experiments with analogue materials resembling supercritical CO_2, brine, and porous rocks. PIV provides fluid flow vector field time series which can be directly compared to LB simulation results.

Task 4: Lattice Boltzmann code development – Develop new, and modify existing, lattice-Boltzmann (LB) multiphase-multicomponent fluid flow simulators that allow numerical modeling of chemical fluid-rock interactions in complex pore, fracture, and conduit openings without the need to know permeabilities a-priory if the exact pore space geometry is given (e.g., by X-ray tomography – Task 2). LB simulations can be used to test reaction laws and compare results with physical experiments (Objective 1). LB simulations also serve to determine permeability tensor fields of the samples which can later, as a function of chemistry/temperature/pressure/time conditions be included (as empirical parameterized equations) into TOUGH2 (Task 5). Permeability variations, in turn, cause variations in flow fields.

Task 5: TOUGH2 modification – Combine previous objectives to achieve the overall objective of including parameterized equations of permeability changes (as a function of temperature, pressure, chemistry, time) into TOUGH2, the standard code used for multiphase-multicomponent flow modeling in CO_2 and geothermal systems.

5. Technical Accomplishments:

Task 1 Laboratory Experiments – The recently published paper in *Environmental Science & Technology* documents our experiments with arkosic sediment (Luhmann et al. 2013). This paper describes a previously undocumented CO_2 trapping mechanism, where CO_2 may be trapped in large accumulations due to grain reorganization. We have conducted experiments on lithified cores of arkose and dolostone. We have observed secondary clay precipitation on K-feldspar grains that produces minimal permeability change during arkose experiments and extensive dissolution during dolomite experiments, where the rate of permeability increase depends on flow rate. We added separators to our system this summer, which has permitted us to conduct experiments using brine. Runs with basalt samples from the Idaho National Laboratory that have appropriate permeability have been completed. During this last quarter several samples were re-run to replicate and confirm hypotheses. Publications have been completed and submitted for review. Additional sample runs are being conducted as time allows and the experimental set up remains operable.

Task 2 Solid Characterization – Core samples representative of typical deep basin aquifers collected and analyzed. X-Ray Computed Tomography (XRCT) results for arkose samples from Task 1 analyzed.

Comparison of XRCT results with SEM and EDS to analyze chemical composition. Observed losses in permeability shown to be clay precipitation on K-feldspar grains. We have completed XRCT scans of starting carbonates and basalts and are conducting scans of post experimental carbonate samples. In preparation for our geochemical modeling for Tasks 4 & 5, we have retrieved thermodynamic properties of aqueous species and utilized these thermodynamic properties to produce a geochemical thermodynamic data set that is internally consistent with respect to both mineral phases and aqueous species. The paper has been published in Geochimica et Cosmochimica. With the aid of DBCreate (Kong et al., 2012), the derived data set can be applied to geochemical systems from 0 to 1000 C and 1 to 5000 bars using reactive transport codes such as TOUGHREACT and GWB. Additionally, we have calculated reactive surface area of rock grains from 3D XRCT imagery obtained both at UMN and the Advanced Photon Source at Argonne National Laboratory. These surface area calculations are one of the vital parameters required to upscale measurements of reactive transport from the laboratory scale to the reservoir scale. Recent work includes measurement of porosity by Helium pycnometer for comparison and calibration of XRCT porosity determinations.

Task 3 PIV Experiments on multi-phase flow through porous media – We have developed a test facility and obtained volumetric, time-evolving velocity measurements and visualizations for a data set involving drop coalescence in the absence and presence of solid bodies. Measurements of particle velocities in multi-phase, three dimensional flow for drop motion through circular pores have been performed. We are currently running tests on multi-fluid phase flow through pores in support of LB simulations. Time resolved velocity fields have been captured using Particle Image Velocimetry (PIV). Over the past year, we completed experiments examining the effect of pore edge geometry, surface wettability, orifice-to-drop diameter ratio (d/D), and drop Bond number on drop motion through a circular orifice. Results from high speed imaging and PIV have been compared to results from numerical simulations using an immiscible, two-color BGK lattice-Boltzmann method performed under similar test conditions.

Task 4 Lattice Boltzmann code development – Development of a 3D simulation for 2-phase fluid movement incorporating results from Task 3. Prepared code to compare GPU and CPU simulation methods and conducting simulations. A FORTRAN 90/95 DBCreate package has been refined and a paper about the DBCreate package has been accepted by Computers & Geosciences. Validated simulations using LBHydra (a software package using lattice Boltzmann method) for multiphase flow have been conducted, which include parameter calibration (gravity in lattice units) and flow simulation of droplets through an opening. The results are close to the experimental observations of Ellen's group (Task 3). Further experimental validations have been performed on contact angle of CO2 in brine on different mineral substrates including quartz, biotite, and dolomite. The three-phase contact angle for various pressure, temperature, pH, and mineral conditions is a critical input parameter for the lattice-Boltzmann fluid flow simulations and has been integrated with Lattice Boltzmann code.

Task 5 TOUGH2 modification – Integration of current thermodynamic data, from Task 2, into TOUGH2 thermodynamic database. A numerical study using TOUGH2/EOS7 has been conducted to investigate the effects of permeability heterogeneity on density-driven convection during CO2 dissolution storage in saline aquifers. This work serves as a method to evaluate the ability of CO2 being transferred into the aqueous phase of a formation with a given heterogeneous permeability. TOUGH2-MP is in development. An evaluation of the reactive transport model, TOUGHREACT, to predict experimental results from arkosic sandstones (Task 1) has identified problem areas. A numerical study using TOUGH2/ECO2N to investigate the effects of CO2 exolusion on the reduction of permeability in heterogeneous porous media is being conducted. An additional post-doc researcher was hired to assist with Tasks 4 and 5. Simulations with modified code have been run.

6. Discussion:
A total of 12 publications and 23 abstracts were produced as a result of this study. In particular, the compilation of a thermodynamic database utilizing consistent, current thermodynamic data is a major step toward accurately modeling multi-phase fluid interactions with solids. Existing databases designed for aqueous fluids did not mesh well with existing solid phase databases. Addition of a second liquid phase (CO2) magnifies the inconsistencies between aqueous and solid thermodynamic databases.

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7. Cost Share Status: Cost sharing funds were spent on equipment and supplies purchased as specified in grant proposal. Cost sharing funds nearly completely expended working with financial staff to close out project.

8. Schedule Status: Project is on schedule. Milestones in thermodynamic database compilation have been reached. Results from Tasks 1, 2, and 3 have helped refine improvements in Lattice-Boltzmann and TOUGH2 code development. Work continues on Task 4 and 5 with a new NSF grant allowing further TOUGH2 code modifications and now comparison with Schlumberger Eclipse software.

9. Changes: No changes in approach or aims of project.

10. Problems or delays: None.

11. Key personnel: Three post-doctoral candidates and one graduate student worked in coordination with PIs.

12. Products and technology transfer:

A) Publications

Tutolo, B.M., A. Schaen, M.O. Saar, and W. E. Seyfried, Jr. 2015. Implications of the redissociation phenomenon for mineral-buffered fluids and aqueous species transport at elevated temperatures and pressures. Applied Geochemistry 55:119-127. DOI: 10.1016/j.apgeochem.2014.11.002.

Tutolo, B.M., A.J. Luhmann, X.-Z. Kong, W.E. Seyfried Jr., and M.O. Saar. 2015. CO2 sequestration in feldspar-rich sandstone: the importance of solution composition and saturation state. Geochimica et Cosmochimica Acta 160:132-154. DOI: 10.1016/j.gca.2015.04.002.

Tutolo, B.M., X.-Z. Kong, A.J. Luhmann, W.E. Seyfried Jr., and M.O. Saar. 2015. High performance reactive transport simulations examining the effects of thermal, hydraulic, and chemical (THC) gradients on fluid injectivity at carbonate CCUS reservoir scales. International Journal of Greenhouse Gas Control 39:285-301. DOI: 10.1016/j.ijggc.2015.05.026.

Luhmann, A.J., X.-Z. Kong, B.M. Tutolo, N. Garapati, B.C. Bagley, M.O. Saar, and W.E. Seyfried, Jr. 2014. Experimental dissolution of dolomite by CO2-charged brine at 100 ºC and 150 bar: Evolution of porosity, permeability, and reactive surface area. Chemical Geology 380: 145-160. DOI: 10.1016/j.chemgeo.2014.05.001.

Tutolo, B. M., A. J. Luhmann, X. Z. Kong, M.O. Saar, and W.E. Seyfried Jr. 2014. Experimental observation of permeability changes in dolomite at CO2 sequestration conditions. Environmental Science & Technology. DOI: 10.1021/es4036946.

Tutolo, B.M., X.-Z. Kong, W.E. Seyfried Jr., and M.O. Saar. 2014. Internal consistency in aqueous geochemical data revisited: applications to the aluminum system. Geochimica et Cosmochimica Acta 133:216-234. DOI: 10.1016/j.gca.2014.02.036.

Kong, Xiang-Zhao, B.M. Tutolo, and M.O. Saar. 2013. DBCreate: A SUPCRT92-based Program for Producing EQ3/6, TOUGHREACT, and GWB Thermodynamic Databases at user-defined T and P. Computers & Geosciences 51:415-417. DOI: 10.1016/j.cageo.2012.08.004.

Luhmann, A.J., X.-Z. Kong, B.M. Tutolo, K. Ding, M.O. Saar, and W.E. Seyfried, Jr. 2013. Permeability reduction produced by grain reorganization and accumulation of exsolved CO_2 during geologic carbon sequestration: A new trapping mechanism. Environmental Science & Technology 47:242-251. DOI: 10.1021/es3031209.

Randolph, J.B., and **M.O. Saar** 2011. Combining geothermal energy capture with geologic carbon dioxide sequestration. Geophysical Research Letters 38:L10401(1-7). DOI: 10.1029/2011GL047265

Randolph, J.B. and **M.O. Saar** 2011. Coupling carbon dioxide sequestration with geothermal energy capture in naturally permeable, porous geologic formations: Implications for CO2 sequestration, Energy Procedia 4:2206-2213. DOI: 10.1016/j.egypro.2011.02.108.

Saar, M.O. 2011. Review: Geothermal heat as a tracer of large-scale groundwater flow and as a means to determine permeability fields, special theme issue on Environmental Tracers and Groundwater Flow, editor-invited peer-reviewed contribution, Hydrogeology Journal, 19:31-52, DOI: 10.1007/s10040-010-0657-2.

Bordoloi, A.D. and Longmire, E.K. 2012. Effect of neighboring perturbations on drop coalescence at an interface. Phys. Fluids 24:062106. DOI: 10.1063/1.4729815.

Tutolo, B.M., A.J. Luhmann, X.-Z. Kong, W.E. Seyfried Jr., and M.O. Saar 2014. CO2 sequestration into feldspar-rich sandstone: the importance of solution composition and saturation state. Abstract H12B-02 presented at the 2014 Fall Meeting, AGU, San Francisco, Calif., 15-19 Dec.

Saar, M.O., B.M. Tutolo, X.-Z. Kong, A.J. Luhmann, and W.E. Seyfried, Jr. 2013. Carbonic acid reactions with reservoir minerals and associated permeability field changes during CO2-based geothermal energy extraction. New Zealand Geothermal Workshop Conference, 18-21 Nov.

Tutolo, B.M., X.-Z. Kong, M.O. Saar, and W.E. Seyfried Jr (2014) Using high performance computing to examine the effects of thermal gradients in carbonate CCUS reservoirs. GSA Abstracts with Programs 46(6).

Kiesel, T., B.M. Tutolo, A.J. Luhmann, and W.E. Seyfried, Jr. 2014. Experimental evaluation of glauconitic sediments for in-situ carbon sequestration. Geological Society of America Annual Meeting Abstracts with Programs, Vol. 46, No. 6, p. 817.

Tutolo, B. M. and W.E. Seyfried Jr. 2014. High Resolution Characterization of Porosity and Permeability Evolution during Serpentinization. Abstract 2526. Goldschmidt Conference, Sacramento, CA, 8-13 June 2014.

Luhmann, A.J., B.M Tutolo, X.Z. Kong, M.O. Saar, W.E. Seyfried Jr. 2014. Hydrothermal flow-through experiments of basalt alteration: Exploring feedbacks between reactive transport processes. Abstract 1535. Goldschmidt Conference, Sacramento, CA, 8-13 June 2014.

Tutolo, B.M, A.J. Luhmann, X. Kong; M.O. Saar; W.E. Seyfried Jr. 2013. Experimental observation and numerical simulation of permeability changes in dolomite at CO2 sequestration conditions. AGU Fall Meeting San Francisco, CA. Abstract H12C-04.

A.J. Luhmann; X. Kong; B.M. Tutolo; M.O. Saar; W.E. Seyfried Jr. 2013. Experimental observations of dolomite dissolution in geologic carbon sequestration conditions. AGU Fall Meeting San Francisco, CA. Abstract V41A-2752.

N. Garapati; J. Randolph; M.O. Saar. 2013. Analysis of Geologic Parameters on the Performance of CO2-Plume Geothermal (CPG) Systems in a Multi-Layered Reservoir. AGU Fall Meeting San Francisco, CA. Abstract H51D-1216.

Saar M.O., X-Z. Kong, B.M. Tutolo, A.J. Luhmann, and W.E. Seyfried Jr. 2013. Fluid-Mineral Reactions during CO2-Based Geothermal Energy Extraction. Presented at Goldschmidt Meeting Augsut 25-30, Florence, Italy. Mineralogical Magazine, 77(5) 2108.

Tutolo B.M., A.J. Luhmann, X-Z. Kong, M.O. Saar, and W.E. Seyfried Jr. 2013. Developing Speciation Codes and Thermodynamic Data for Non-Isothermal and Non-Isobaric Systems: Applications to CO2 Sequestration. Presented at Goldschmidt Meeting Augsut 25-30, Florence, Italy. Mineralogical Magazine, 77(5) 2368.

Bordoloi, A.D. and Longmire, E.K. 2013. Parametric study of drop motion through an axisymmetric orifice. 8th International Conference on Multiphase Flow, Jeju, Korea.

Luhmann, A.J., X.-Z. Kong, B.M. Tutolo, M.O. Saar, and W.E. Seyfried, Jr. 2012. Physical and chemical processes affecting permeability during geologic carbon sequestration in arkose and dolostone: Experimental observations. 2012 Fall Meeting, AGU, San Francisco, Calif., 3-7 Dec.

Kong, X.-Z., B.M. Tutolo, A.J. Luhmann, M.O. Saar, and W.E. Seyfried, Jr. 2012. Characterization of permeability fields and fluid flow through rock core during CO_2 sequestration. 2012 Fall Meeting, AGU, San Francisco, Calif., 3-7 Dec.

Tutolo, B.M., A.J. Luhmann, X.-Z. Kong, M.O. Saar, and W.E. Seyfried, Jr. 2012. Linking pore-scale chemical processes to continuum-scale flow properties: An experimental and theoretical reactive transport approach. 2012 Fall Meeting, AGU, San Francisco, Calif., 3-7 Dec.

Luhmann, A.J., B.M. Tutolo, X.-Z. Kong, K. Ding, M.O. Saar, and W.E. Seyfried, Jr. 2012. Permeability change from CO_2 injection: Experimental considerations. 2012 Goldschmidt Meeting, Montreal, Canada, 24-29 June.

Tutolo, B.M., A.J. Luhmann, X.-Z. Kong, M.O. Saar, and W.E. Seyfried, Jr. 2012. Evaluating permeability change due to altered pore geometry in CO_2 sequestration systems. 2012 Goldschmidt Meeting, Montreal, Canada, 24-29 June.

Randolph, J.B. and **M.O. Saar** 2010. Coupling geothermal energy capture with carbon dioxide sequestration in naturally permeable, porous geologic formations: A comparison with enhanced geothermal systems, Geothermal Research Council Transactions 34:433-438.

Bordoloi, A., Longmire, E.K. 2012. Effects of surface wettability and edge geometry on drop motion through an orifice. American Physical Society, 65th Annual Meeting, San Diego, Nov 2012.

Bordoloi, A. D., Longmire, E. K., Kong, X. and Saar, M. O. 2011. Investigation of drop motion through circular orifices, American Physical Society Division of Fluid Dynamics, 64th Annual Meeting, Baltimore, 2011.

Kong, X. and M.O. Saar 2011. Effects of permeability heterogeneity on density-driven convection during CO2 dissolution storage in saline aquifers, AGU 2011 Abstract H21C-1121.

Tutolo, B.M., W.E. Seyfried and M.O. Saar 2011. An assessment of thermodynamic database effects on reactive transport models' predictions of permeability fields, AGU 2011 Abstract H51C-1216.

Luhmann, A.J., K. Ding, M.O. Saar and W.E. Seyfried 2011. Effects of small-scale chemical reactions between supercritical CO_2 and arkosic sandstone on large-scale permeability fields: An experimental study with implications for geologic carbon sequestration, AGU 2011 Abstract H51G-1261.

B) & C) Internal twiki site set-up to facilitate collaboration between PI's and their research groups.
No **D)** Technologies, **E)** Invention/Patents or **F)** Other products developed.