

Geologic and Geochemical Evaluation of the Potential for CO₂ Disposal in Deep Saline Aquifers Beneath Ohio

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Introduction

Ohio has abundant reserves of coal and is heavily reliant on coal-fired power plants for electricity. Consequently, it is the second largest producer of CO₂ emissions in the nation. If technology can be developed to manage CO₂ emissions from Ohio's power plants, Ohio's coal reserves could continue to provide a stable energy source for decades to come.

Storage of CO₂ in deep, porous, and permeable sedimentary formations is a promising technology for reducing emissions of greenhouse gases to the atmosphere. Oil and gas reservoirs make strong candidates for disposal sites because their geology is well characterized and they have proven structural or stratigraphic trap geometries that prevent escape of CO₂ to the surface. In addition, injection of CO₂ into depleted reservoirs is a proven method for enhanced oil recovery and can provide economic benefit to offset the cost of disposal. Although oil and gas reservoirs are a sensible first step for sequestration of CO₂ in geologic formations, their total

storage capacity is small compared to storage needs and their distribution is concentrated far from most power-plant sources of CO₂ emissions (Winter and Bergman, 1994; Bergman and Winter, 1995). Ohio's oil and gas reservoirs are concentrated in the eastern part of the state, where coal is mined and many coal-fired power plants are located, but their total storage capacity is estimated sufficient to sequester only a few years of emissions from Ohio's coal generated power plants (Carr, 00). An alternative storage reservoir is needed.

Deep saline aquifers have the largest potential storage capacity for CO₂ because they are wide spread (Bergman and Winter, 1995) and, in contrast to oil and gas reservoirs, may not require special structural and stratigraphic trap geometries (Gunter et al., 1996). Instead, CO₂ can be stored hydrodynamically in the formation waters for tens of thousands of years and longer. In addition, mineral trapping, which involves a series of interactions between the formation mineralogy and CO₂-enriched formation waters, can convert CO₂ to carbonate, an immobile and harmless mineral form that will be stored for millions to hundreds of millions of years.

A number of deep saline aquifers beneath Ohio may be suitable for injection and safe storage of CO₂ (Sass et al., 1998). The Mount Simon, Rose Run, Conasauga, and Kerbel sandstones are all deep permeable aquifers, overlain by thick successions of low permeability carbonate and impermeable shale (Janssens, 1973). These aquifers are deep enough that injected CO₂ would be in a supercritical state. Regional flow is down-dip, and will transport CO₂ away from the surface (Gupta and Bair, 1997; Gupta et al., 1998). However, evaluation of the capacity and integrity of CO₂ storage in these aquifers depends on detailed knowledge of the formation mineralogy and brine composition, the likely mineral-brine-CO₂ reactions, and the rates of the reactions.

Objectives

We have begun an integrated sedimentologic, experimental, and numerical modeling study of expected mineral-brine-CO₂ reactions in Ohio's Rose Run sandstone and overlying carbonate and shale. The Rose Run sandstone is the shallowest of Ohio's deep sandstone units beneath the coal-rich eastern part of the state. It is an active oil- and gas-producing unit, and consequently there is

abundant core and geophysical data available. There is also the possibility that CO₂-injection for enhanced oil recovery could provide economic benefits to offset disposal costs during the development stage of this technique. Later, injection strategies could be expanded to take advantage of the Rose Run's aquifer storage potential.

Our goals are to determine the likely reactions between injected CO₂, formation minerals, and aquifer brines. Because these reactions are sensitive to the details of brine composition, and formation mineralogy, porosity and permeability, geologic study is aimed at characterizing the compositional and textural heterogeneity of the Rose Run sandstone, focusing particularly on areas near large coal-fired power plants and oil and gas reservoirs.

Given good geologic characterization, the principle types of mineral-brine-CO₂ reactions can be relatively well predicted assuming sufficient reaction time to achieve equilibrium conditions. However, the kinetics of mineral-brine-CO₂ reactions remain poorly constrained, and, since fluid flow and fluid rock interactions are dynamic processes, kinematically determined rates of reaction are likely to be crucial in determining the localization of mineral dissolution and precipitation, and the extent of mineral trapping. Rates of mineral-brine-CO₂ reactions relative to rates of fluid sweep through the formation will determine whether or not mineral precipitation plugs the reservoir near the injection site or escapes from the formation prior to reacting. Reaction rates will determine whether or not equilibrium is reached and consequently whether or not equilibrium-based determinations of net reactions are appropriate. Thus, in addition to determining the specific types of mineral reactions expected to occur, our research objectives emphasize development of experimental, field, and numerical modeling techniques to constrain the rates of mineral-brine-CO₂ reactions.

Approach

Our project integrates three approaches aimed at identifying expected mineral-brine-CO₂ reactions and constraining the rates of those reactions.

Geologic Characterization: Surface and sub-surface sedimentologic and petrographic studies are aimed at identifying the main rock types, the details of their mineralogy, and their subsurface spatial relations in order to identify the dominant reactive minerals that are likely to come into contact with CO₂-enriched brines. Based on geologic data, representative samples will be selected for laboratory experiments.

Laboratory Experiments: Experiments with mineral separates and representative Rose Run samples and CO₂-saturated brines will investigate the kinetics of reactions at aquifer pressure and temperature conditions. We have designed an inexpensive pressurized reaction vessel so that multiple experiments can be run simultaneously. Mechanisms for in-line analysis and sampling make it possible to log chemical changes throughout the course of experiments.

Numerical Simulation: Geologic data and experimentally determined reaction rates will be incorporated into geochemical models to predict the capacity for CO₂ storage in the Rose Run sandstone.

Project Description

Geologic Characterization: The Rose Run Formation is a complex unit that is composed of a mixture of both carbonate and siliciclastic lithologies and is heterogeneous at multiple scales (Riley et al., 1993). The aim of the stratigraphic work is to characterize the stratigraphic and compositional heterogeneity of the Rose Run Formation and the overlying aquitard, particularly in the vicinity of selected potential injection sites (i.e. near coal-fired power plants and depleted oil reservoirs).

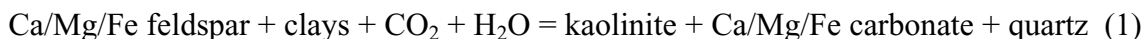
Description and petrographic study of outcrop and core will identify sedimentary facies, or rock units that, owing to deposition in a particular environment, have a characteristic set of properties, such as composition, texture (grainsize, sorting ...), and structure (bed geometries and internal bed characteristics). Depositional models will be developed for how the different

depositional environments were positioned relative to each other in two dimensions at the time of deposition, and how the environments migrated over time to build the third, vertical dimension of the stratigraphic succession. The depositional models will provide the basis for developing geologically reasonable correlations between subsurface geophysical logs and core, and for interpolating between these tie points in order to reconstruct the three-dimensional compositional and textural architecture of the strata in the subsurface. This work is necessary in order to select samples and quantify the volumetrically dominant reactive rock types for more detailed petrographic and experimental study. Reconstruction of the vertical and spatial relations of facies is also important because complex mineral trapping reactions are likely to occur as a consequence of ion exchange across facies boundaries between rock types of different mineralogical composition. In addition, facies controlled permeability and porosity will determine flow paths for CO₂ and brine, localizing flow along boundaries with sharp contrasts in permeability. Experimental and numerical modeling studies of reaction localization along facies boundaries are likely to be important research emphases during the later part of this study or as part of affiliated studies.

Detailed petrography of representative samples is aimed at characterizing mineralogy, texture, and diagenetic history. Some important questions to address include: is there a strong facies or depositional control on diagenesis, or a strong spatial organization to diagenetic fabrics that might aid in reconstructing subsurface composition and permeability. Detailed petrographic studies include pointcounts and image analysis, SEM, electron microprobe, X-ray diffraction, porosity and permeability studies and will be done both before and after experiments in order document changes to mineralogy, texture, porosity, and permeability due to mineral-brine-CO₂ reactions.

Laboratory Experiments: Laboratory experiments will investigate the complex, simultaneous mineral-brine-CO₂ reactions that sequester carbon in both dissolved and solid forms and depend on the formation mineralogy. Reactions with Ca/Mg/Fe-bearing silicate minerals are the most promising for carbon sequestration because these silicates neutralize the added acidic CO₂ and

provide alkali metals that trap the CO₂ through the precipitation of carbonate (Gunter et al. 1997). These reactions can be summarized as (Hitchon et al 1999):



Our approach is to experimentally determine linked dissolution-precipitation rates for a range of mineral-brine systems at aquifer pressures and temperatures. We will incorporate available and experimentally determined reaction-rate data into geochemical models in order to simulate our experiments and thereby test how well our models simulate complex reaction behavior.

First we will consider relatively simple systems to determine net reaction rates for the most important mineral-trapping reactions. For example, we will experimentally determine the rate constant for a simple form of reaction 1, dissolution of Ca-feldspar leading to the precipitation of calcite. We will then broaden our experiments to include studies of the dissolution of clays that also can contribute Ca, Mg, and Fe to precipitate carbonate. Later we will experiment with mineralogically complex natural Rose Run samples. Initially, experiments will be on ground powders in order to minimize fluid transport effects. Ultimately, experiments will use intact rock plugs to include the effects of rock texture and to investigate changes in porosity and permeability as a consequence of dissolution and precipitation.

We have designed a low cost reactor so that multiple reactors can be constructed to run experiments simultaneously. The reactor body consists of a steel tube wrapped in heating tape and insulation and is mobile enough to be easily rocked in order to slosh phases together and maintain uniform mixing. Fittings will seal the ends of the tubing and allow convenient access for placing the crushed rock into the reactor. Valves at either end for allow capture of either brine or CO₂ samples for periodic analyses through the course of the experiment. The details of the reactor and experimental design are explained more fully in a companion paper in this volume (Janda et al.).

Numerical Simulation: Mineralogical and textural data and experimentally determined reactions will be incorporated into thermodynamic and kinetic geochemical models to predict mineral reaction sequences, masses of carbon dioxide sequestration, and the time constraints for the reactions. New model development is not planned for this work. Instead, we will evaluate and adapt existing models to the experimental results, and apply these results to more realistic simulations of the Rose Run under natural conditions and under carbon dioxide injection.

Results

Rocks equivalent to the Rose Run sandstone and surrounding strata are exposed at the surface near Tyrone in western Pennsylvania. Measured sections through the Gatesburg Formation (equivalent to the Conasauga, Kerbel, and Rose Run sandstones) reveal a complex stratigraphy composed of an interbedding of at least 7 major facies, or rock types: dolomudstone; ooid grainstone; stromatolite boundstone; wavy-bedded shale, sandstone, and carbonate; shale; sandy carbonate; and quartz sandstone. These 7 facies can be further subdivided on the basis of sedimentary structure and texture. Clay, quartz sand, and carbonate grains are locally well mixed within single beds. Also, quartz sandstone is locally cemented by carbonate and carbonate ooids are replaced by quartz so that the beds are compositionally and texturally heterogeneous and carbonate and siliciclastic lithologies are mixed at multiple scales.

Five rock cores through the Rose Run sandstone beneath eastern Ohio were measured and described at the Ohio Geological Survey core repository. The cores show the same rock types as the field exposures except that no ooid grainstone or stromatolite boundstone was observed.

Preliminary petrographic analysis and review of the literature indicates very low abundances of Ca-feldspar in the Rose Run sandstone. These low abundances are typical of deep sandstones in the Midwest, which were deposited in stable tectonic environments far from a source of unweathered feldspar. However, several cores from the Rose Run and other deep sandstones, such as the Mount Simon, contain locally abundant glauconite, which may prove important as an

alternative to Ca-feldspar as a source of calcium for mineral trapping of CO₂.

Five computer programs capable of computing multiphase gas-aqueous-mineral equilibria were identified (WATEQ4F, PHREEQC, MINTEQA2, SOLMINEQ88, and the Geochemists Workbench) and evaluated for their suitability for this project. Of these five, MINTEQA2, PHREEQC, SOLMINEQ88, and the Geochemists Workbench also appear to have kinetic capabilities, which can simulate paths of reaction and/or rates of reactions in addition to equilibrium conditions. The features of four of these models are compared in Table 1 and briefly summarized below.

WATEQ4F has several limitations, which prevents its suitability for this project. Gasses cannot be used as inputs to the system, preventing simulation of injection of CO₂ and pressure is fixed at 1 atm. However, its thermochemical database is deemed the most accurate, so most or all the other models use its database. MINTEQA2 was designed for the EPA to simulate contaminant migration in the near surface, so it does not accommodate the necessary temperature and pressure ranges needed for this study. Both of these models were deemed inadequate for this study.

PHREEQC shows promise for application to this problem. PHREEQC allows for the input of various gases (including CO₂) up to a pressure of 1000 bars. However, the model has difficulties converging at higher pressures. The model is easy to use and input data, and allows for the inclusion of minerals in user-defined molar amounts, which will be useful in path-of-reaction calculations at a later date. It is a relatively new model and has received limited application to water-rock problems, but some of the example problems given with the code suggest that it may be an excellent choice for this project.

SOLMINEQ88 has an extensive database and can accommodate the full ranges of temperature, pressure and pCO₂ expected. The model has been applied to these types of water-rock problems by previous workers, so it is likely to be capable of simulating mineral reactions in deep saline

aquifers. Initial examination of the data entry capabilities of the program suggests that there may be difficulties with proper definition of gases; no combination of input parameters caused the pressure of CO₂ to rise significantly. This problem will need to be resolved if this program is selected for further evaluation.

None of the models' databases include data for glauconite, but most allow their input files to be modified. Therefore experimental data for glauconite and other minerals of potential importance for CO₂ sequestration will be added to these models as they become available. As of the writing of this report in February, a prototype of the new experimental apparatus is near completion and ready for testing.

Table 1. Comparison of equilibrium geochemical models. Note that these data are imprecise in many instances because the documentation was inadequate. Many of the data were obtained by examining the source codes, which was sometimes at odds with the documentation. Cited here are the largest values reported or identified for each variable.

Model Name	WATEQ4F¹	MINTEQA2²	PHREEQC³	SOLMINEQ88⁴
Availability	USGS	EPA/IGWMC	USGS	GAMS (commercial)
Language	Fortran	Fortran	C	Fortran
# Lines of code	5380	?	?	50,000
Thermo data	WATEQ4F	WATEQ3	WATEQ4F, MINTEQA2	?
# Elements	34	20	25	28
# Aqueous species	358	484	300	340
# Gases	7 (Output only)	13	8	4
CO ₂ ?	Calculated	Yes	Yes	Yes
# Organics	10	429	0	80
# Redox species	10	20	15	12
# Mineral species	322	557	57	220
Albite?	Yes	Yes	Yes	Yes
Anorthite?	Yes	Yes	Yes	Yes
Ca-Montmorillonite?	Yes	Yes	Yes	Yes
Gamma formula	B-dot, Davies	B-dot, Davies	Ext D-H, B-Dot, Davies	B-dot, Pitzer

Temperature range	0 - 80 °C	0 - 100 °C	0 - 350 °C	0 - 350 °C
Pressure range	1 atm	1 atm	1 - 1000 bars	1 - 1000 bars
Iteration/convergence	Continued fraction	Newton-Raffson	Continued fraction/N-R	Continued fraction
Modify input files?	No	Yes	Yes	Yes
Limitations	pH must be fixed	Carbon system entry?	Trace elements	Entry of gases

- ¹ Ball, J.W. and D.K. Nordstrom 1991. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open-File Report 91-183, 189 pp. (Revised and reprinted August 1992).
- ² Allison, J.D. D.S. Brown, and K.H. Novo-Gradac 1993. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual: U.S. EPA Office of Research and Development, Environmental Research Laboratory, Athens, Georgia, EPA/600/3-91/021.
- ³ Parkhurst, D. L. and C.A.J. Appelo 1999. User's guide to PHREEQC (Version 2) --a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312pp.

Application

Geologic sequestration of CO₂ in deep saline aquifers has potential to be an important technology for greenhouse gas emissions, especially in areas like Ohio that are far from the ocean, have large point-sources of emissions, and relatively little depleted-petroleum-reservoir storage capacity. We are focusing our investigation on a single stratigraphic unit (the Rose Run) in a single location (Ohio), but we have designed our investigative approach to have broad applicability. Rate data from mineral separates can be incorporated into geochemical models to simulate other geologic settings. A focus on obtaining rate data for glauconite and clay minerals that might serve as an alternative source of Ca for mineral trapping of CO₂ has applicability for deep aquifer storage throughout the Midwest, and other locations, characterized by compositionally mature sandstones, deposited in tectonically stable settings. The compositional and textural complexity and heterogeneity of the Rose Run sandstone means that investigations of simple and complex reaction couples and the influence of fluid flow on reactions are essential.

Results of these investigations will have applicability for other geologically complex aquifers as well as simpler ones.

Future Activities

The immediate goal is to test the experimental apparatus and built additional setups so that we can begin a series of simple experiments. Evaluation of the equilibrium models will continue and evaluation of kinetic models will begin with numerical simulations of experimental results.

Geologic characterization will continue with the selection and analysis of representative rock samples for experiments on coupled reactions in mineralogically complex powders.

Long term goals include the incorporation of fluid flow and reactive transport into experiments and numerical simulations. Our initial experimental design is focused on minimizing mass transfer effects so that kinetic reaction rates can be evaluated. However, details of porosity structure and permeability pathways will have a great effect of which reactions are likely to occur by determining which minerals the CO₂ is likely to contact and for how long. Geologic characterization is focused on obtaining both textural and compositional data so that the controls on and influence of fluid flow can be incorporated into the investigations.

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