Evaluation of the impact of CO_2, aqueous fluid, and reservoir rock interactions on the geologic sequestration of CO_2, with special emphasis on economic implications

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Abstract

Lowering the costs of front-end processes in the geologic sequestration of CO_2 can dramatically lower the overall costs. One approach is to sequester less-pure CO_2 waste streams that are less expensive or require less energy to separate from flue gas, a coal gasification process, etc. The objective of this research is to evaluate the impacts of an impure CO_2 waste stream on geologic sequestration using both reaction progress and reactive transport simulators. The simulators serve as numerical laboratories within which a series of computational experiments can be designed, carried out, and analyzed to quantify sensitivity of the overall injection/sequestration process to specific compositional, hydrologic, structural, thermodynamic, and kinetic parameters associated with the injection fluid and subsurface environment.

Introduction

The costs of separation, capture and compression of CO_2 from point sources, e.g., coal-fired power plants, have been estimated to account for 75% of the total cost of a geologic sequestration process. Obviously, lowering the costs of the front end processes can dramatically lower the overall costs. One approach to lower cost is to permit a waste stream to be less than pure CO_2. The evaluation of the impacts of this impure CO_2 waste stream on geologic sequestration is the goal of this project.

The 3 primary candidate formation/reservoir types suggested for geologic sequestration (oil and gas reservoirs, coal beds and deep saline formations) all contain associated formation aqueous phases. Oil fields under active EOR (enhanced oil recovery) may have additional (foreign) water used in flooding. Although CO_2 injected as part of a geologic sequestration effort may initially behave as an immiscible phase, it can chemically react with water to form carbonic acid and then further react with or form mineral phases once it has dissociated into bicarbonate or carbonate aqueous species. This interaction of CO_2 with water is the ultimate basis for the geologic sequestration processes of solubility trapping (as carbonate aqueous species) and mineral trapping (as carbonate minerals). It is essential, therefore, to have a good understanding of the effect of CO_2 injection on aqueous and mineral phase chemistries, as well as the physics of flow involving immiscible fluids.

Only a handful of directly relevant experiments and supporting geochemical modeling have been done to date (e.g. (Czernichowski-Lauriol *et al.*, 1996; Gunter *et al.*, 1997; Sass *et al.*, 2000)). These preliminary studies keyed on the impact of elevated CO_2 fugacity on mineral dissolution and precipitation. They drew some general inferences from their results relating to dissolution of carbonate cements and the potential for both carbonate and silicate mineral formation with the accompanying impact on porosity/permeability. These inferences relate directly to injectivity issues, as well as to the long term performance of geologic sequestration owing to solubility and mineral trapping. However, these early studies did not begin to assess the direct or indirect impact of waste stream contaminants (NO_x, SO_x, H_2S, etc.) on injectivity and long term performance. More recently, modeling efforts have begun to investigate the impact of waste stream contaminants (Gunter *et al.*, 2000). These impacts must be evaluated in order to optimize front end processes (separation, capture and compression) and lower costs.

Objectives

The specific project goals are:

1. Identify and quantify the impact of waste stream contaminants (NO_x, SO_x, H_2S, etc.) on injectivity. This will permit definition in composition space of allowable concentrations of contaminants (i.e., upper limits) and provide criteria for injection optimization.

2. Identify and quantify the post-injection (longer term) chemical behavior of CO_2 in the presence of contaminants. This will permit evaluation and prediction of the long term performance of geologic sequestration of CO_2 as a climate control process.

Approach

Thermodynamic/kinetic geochemical models and reactive transport simulators provide powerful tools for evaluating the impact of waste stream contaminants on injectivity and long term performance. We foresee the need to use a variety of computational models to fully explore the range of conditions and types of processes taking place during CO_2 injection and to account for the impact of contaminants in the waste stream. Chemical models such as EQ3/6 (Wolery *et al.*, 1990) and REACT (Bethke, 2000), which include both equilibrium speciation/solubility capability and mineral dissolution-precipitation kinetics in a batch mode, will be needed to

predict the major chemical effects of the processes. This approach will allow us to evaluate mineral phase stability and aqueous speciation through equilibrium calculations, to estimate potential impacts on injectivity resulting from the generation of excess porosity or conversely loss of porosity due to formation of clay minerals, and to evaluate the potential for and rate of scale formation in extraction wells in a combined EOR/CO_2 sequestration project. In addition, the models allow one to estimate the total amount of CO_2 that may be sequestered, as well as providing information on how the relative rates of mineral reactions affect the efficiency of the process in terms of the amount of carbon tied up as carbonate minerals. Analysis using this approach will allow us to identify a range in permissible waste stream compositions for CO_2 disposal in terms of rock type, pore fluid chemistry (formation water or EOR injectate), and T-P conditions at a specific site.

Coupling a chemical model with simplified fluid flow using GIMRT/OS3D (Steefel, 1998) will allow us to explore the results of injection into heterogeneous rock formations where mineralogical changes along the probable flow path can be accounted for. We need to progress beyond the batch mode calculations done to this point by the earlier work. The reactive transport approach is essential for calculating the spatial distribution of porosity change, since reaction products tend to be distributed along a flow path. More detailed analysis of two phase flow (water and supercritical CO_2) can be provided using transport simulators such as NUFT (Nitao and Buscheck, 1991), where now the greater mobility of the less dense and lower viscosity CO_2 fluid can be explicitly accounted for. In addition, the multiphase flow simulators, when combined with reactive chemistry, can explicitly take into account the dissolution of CO_2 into the aqueous phase. Finally, we see the need to use both natural analogues (e.g., the CO_2 trapped at the Bravo Dome (Pearce *et al.*, 1995)) and ideal physical models (e.g., plug flow reactors (Johnson *et al.*, 1998)) to benchmark the results obtained using reactive transport simulators. We envision that the research program outlined here will allow us to better design and optimize the separation, capture and compression process and ultimately allow us to predict the results of CO_2 injection at actual field sites. Our goal is to define an acceptable set of limits in each contaminant concentration for each reservoir type, thereby realizing cost savings.

Preliminary Results

The simulations began with simple batch-type reactions that simulate titration of an equilibrated reservoir rock/water system with a gas phase that starts off pure CO_2 and has SO_2 (or H_2S or NO_2) incrementally added to it. Various approaches to simulating mineral or gas buffering of fO_2 (where f = fugacity) were investigated and compared to simulations in which fO_2 was unbuffered or in which redox reactions were switched off completely. We then constructed a series of simulations in which the batch-type reactions were perturbed by periodically flushing out the aqueous phase and permitting the evolved reservoir rock system to re-equilibrate with the "fresh" aqueous phase. This is a "rock-centered", pseudo-flow-through simulation. In this paper we will not present results from these first two types of preliminary simulations.

Both of these initial types of simulations are pure thermodynamic calculations: no reaction kinetics are invoked. We then constructed a series of simulations that are equivalent to the first batch-type (closed system) reactions, but this time including dissolution kinetics for all of the mineral phases present in the reservoir rock and assuming a composition and modal abundance appropriate for a feldspathic sandstone containing clay and carbonate with and without an Fe-bearing phase. The precipitation of secondary phases in these simulations was assumed to be instantaneous, i.e., we did not explicitly consider precipitation kinetics. However, if chemical conditions change in a way that causes the initial reactant minerals to precipitate, their precipitation rate is determined by the same kinetic rate law that governed their dissolution. In these simulations reaction progress is first allowed to proceed for a time period of 30 years, appropriate for a real CO_2 sequestration process, and then for a time period of 500 years, to investigate continued reaction and sequestration.

The simplified, generic reservoir rocks were defined as follows. The feldspathic sandstone reservoir consisted of: 88.5% quartz, 9% K-feldspar, 1% calcite, 1% siderite and 0.5% muscovite. The siderite is added to the mix as a proxy for solid solution of Fe in the calcite. The muscovite is added as a proxy for all clay-like phases, e.g., illite. The carbonate reservoir consisted of: 49.25% calcite, 49.25% dolomite and 1.5% siderite. The simulations are defined in terms of 1 kg of water in a rock/water system with 33% porosity. The simplified brine composition consists of 0.7 m NaCl. The brine is first equilibrated with a gas phase consisting of

80 b CO_2 and some amount of a contaminant gas (H_2S, SO_2 or NO_2). The exact amount of the contaminant gas added to the gas mix was arbitrarily set to an amount required to produce a very acidic (pH ~1 in the case of SO_2 and NO_2, pH ~ 3 in the case of H_2S) aqueous solution. The simulations then essentially titrated in the reservoir rock components at rates appropriate for their dissolution kinetics. While the reactions proceed, two approaches were used w.r.t. continued equilibration of the aqueous phase with the gas phase. In order to investigate the extreme conditions very near the injection point, the runs proceeded with the gas phase always in equilibrium with the aqueous fluid. This maintains very acidic conditions throughout the run. In other simulations the gas phase was initially equilibrated with the aqueous fluid, but then the system was isolated from the gas phase as reaction with the rock progressed. This would be conceptually equivalent to following a packet of water that moves away from the injection point and is no longer in continuous contact with the gas waste stream.

Because the simulations consider the impact of adding acid anhydride gases, we used a dissolution rate law that explicitly accounts for acid catalysis of the mineral dissolution kinetics. Dissolution rate constants and reaction order with respect to H^+ activity are used for each mineral. We ran the simulations at a reservoir temperature of 60ºC (e.g., the Rangely Field under CO_2 flood was at 56ºC, (Bowker and Shuler, 1991)) and the rate constants were calculated using the appropriate activation energy for each mineral.

As an example of the results obtained, we now describe a simulation of the reaction of a brine that was initially equilibrated with a gas phase consisting of 80 b CO_2 and 10 b H_2S that is then allowed to react with the feldspathic sandstone reservoir in isolation from that gas phase. Note that this high H_2S fugacity is not unlike that present in a waste stream produced in a coal gasification process. In this simulation we have assumed that in the short-term redox disequilibria will pertain, so effectively, all redox reactions are turned off. This means, for example, that dissolved H_2S remains H_2S and does not oxidize to SO_4^{2-}. The initial fO_2, while low (log fO_2 = -55, approximately equivalent to initial buffering by hematite-siderite), is still just high enough that at redox equilibrium all the H_2S would convert to SO_4^{2-}. The results after 30 years of reaction are presented in Fig. 1, while the results after continued reaction in the same system after 500 years are presented in Fig. 2.

Notice that in this simulation (Fig. 1) the reservoir rock carbonate minerals (calcite and siderite) react rather quickly with the dissolved CO_2, raising the pH until the carbonate minerals are essentially equilibrated with the resulting solution. The existing carbonate minerals are not sequestering the CO_2 in this case. The only form of sequestration at this point is the CO_2 present in dissolved form in solution. From this point forward in the calculation the principal reaction involves dissolution of the K-feldspar at the still slightly acid pH of approximately 4.8. However, the Al released from the K-feldspar combines with Na from the brine and dissolved CO_2 to form the mixed hydroxycarbonate mineral dawsonite. This new secondary mineral is sequestering CO_2 via mineral trapping. The silica released from the dissolving K-feldspar is precipitated as the silica polymorph chalcedony, as well as going into growth of additional quartz. Notice that the absolute abundance of quartz is so much larger than the other minerals that we have not plotted it. It grows in linearly at a rate determined by it's kinetic rate law, increasing in volume from 1804 cm^3 to 1808 cm^3 after 30 years and to 1832 cm^3 after 500 years. The chalcedony and dawsonite both grow in at a rate determined by the dissolution rate of the K-feldspar.

The dissolved silica in the simulation (Fig. 2) maintains a steady-state concentration reflecting the sum of the processes: K-feldspar dissolution, quartz and chalcedony precipitation. After 10 years or so, the K-feldspar approaches equilibrium with the solution and stops dissolving. After this point, the chalcedony starts dissolving at a rate determined by quartz growth until after 90 years it is completely consumed. Quartz keeps growing and lowers the dissolved silica to the point that K-feldspar starts dissolving again, allowing more dawsonite to form, sequestering more dissolved CO_2. Note that the pH also increases slightly at the point that the chalcedony disappears, allowing additional calcite to precipitate, also sequestering more dissolved CO_2. By the end of the run at 500 years, quartz is only slightly supersaturated and it's rate of growth has slowed considerably. The CO_2 concentration in solution decreases from more than 1.3 m to less than 0.9 m after 500 years.

This simulation illustrates several important points. First, the minerals that may prove important in sequestering CO_2 may not be the obvious ones, i.e., calcite, dolomite, siderite, magnesite and the like. Second, the mineral trapping of CO_2 is a long-term, on-going process that will evolve as solution chemistry evolves over time and minerals evolve in response to the fluid chemistry changes.

Many other similar calculations have been made for the matrix of conditions mapped out by the 2 generic reservoir mineral types, the 3 contaminant gases, conditions of fixed gas fugacity or isolation from the gas phase during reaction, various initial O_2 fugacities depending upon assumptions concerning the likely mineral/solution buffers, and finally, assumptions concerning redox equilibria or disequilibria during the simulations. These will be described in more detail in the presentation.

Future Activities

Guided by the reaction progress (full chemistry, no flow) modeling that we have completed up to this point, we will next begin simplified 1-D and 2-D reactive transport (chemistry and flow) calculations using GIMRT and NUFT. We have recently added a CO_2 Equation of State capability to these codes (Johnson *et al.*, 2000).

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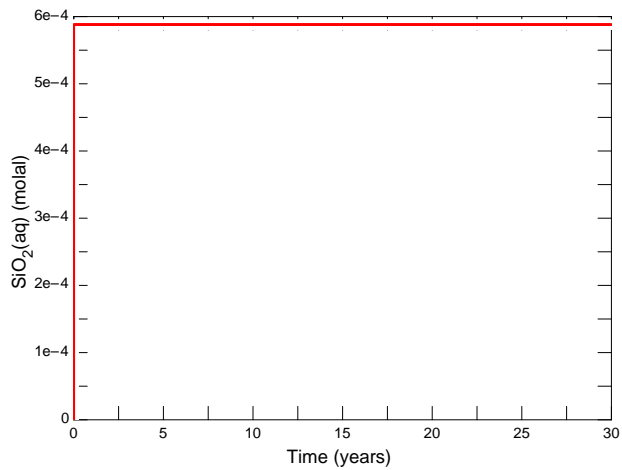
Fig. 1

Fig. 2