Mathematical Models as Tools for Probing Long-term Safety of CO₂ Storage

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1. Introduction

Subsurface reservoirs being considered for storing CO_2 include saline aquifers, oil and gas reservoirs, and unmineable coal seams (Baines and Worden, 2004; IPCC, 2005). By far the greatest storage capacity is in saline aquifers (Dooley et al., 2004), and our discussion will focus primarily on CO_2 storage in saline formations. Most issues for safety and security of CO_2 storage arise from the fact that, at typical temperature and pressure conditions encountered in terrestrial crust, CO_2 is less dense than aqueous fluids. Accordingly, CO_2 will experience an upward buoyancy force in most subsurface environments, and will tend to migrate upwards whenever (sub-)vertical permeable pathways are available, such as fracture zones, faults, or improperly abandoned wells (Bachu, 2008; Pruess, 2008a, b; Tsang et al., 2008). CO_2 injection will increase fluid pressures in the target formation, thereby altering effective stress distributions, and potentially triggering movement along fractures and faults that could increase their permeability and reduce the effectiveness of a caprock in containing CO_2 (Rutqvist et al., 2008; Chiaramonte et al., 2008). Induced seismicity as a consequence of fluid injection is also a concern (Healy et al., 1968; Raleigh et al., 1976; Majer et al., 2007). Dissolution of CO_2 in the aqueous phase

generates carbonic acid, which may induce chemical corrosion (dissolution) of minerals with associated increase in formation porosity and permeability, and may also mediate sequestration of CO_2 as solid carbonate (Gaus et al., 2008). Chemical dissolution of caprock minerals could promote leakage of CO_2 from a storage reservoir (Gherardi et al., 2007). Chemical dissolution and geomechanical effects could reinforce one another in compromising CO_2 containment. Additional issues arise from the potential of CO_2 to mobilize hazardous chemical species (Kharaka et al., 2006), and from migration of the large amounts of brine that would be mobilized by industrial-scale CO_2 injection (Nicot et al., 2008; Birkholzer et al., 2008a, b).

Site characterization and selection, and careful design of the CO_2 storage operation, will have sought to minimize such concerns (Birkholzer and Tsang, 2008; Gibson-Poole et al., 2008; Doughty et al., 2008). However, given natural imperfections of geologic media, and the enormous scale at which CO_2 storage would have to be carried out to make a noticeable impact on atmospheric emissions (Orr, 2004; Pacala and Socolow, 2004), it seems likely that some CO_2 will escape from the primary storage formation (Pruess, 2008). Concerns with leakage include keeping the CO_2 out of the atmosphere, protecting valuable groundwater resources from CO_2 intrusion and possible mobilization of hazardous trace elements (Wang and Jaffe, 2004; Apps et al., 2008; Zheng et al., 2008), avoiding negative impacts on other subsurface resources and uses, and avoiding detrimental effects at the land surface. The various processes of concern with respect to storage safety may occur on a large range of space and time scales, from pore level to regional, and from seconds to millennia. The multi-scale nature of the problem poses great challenges for modeling (BRN, 2007).

Key to successful modeling is a sound understanding of the underlying physical and chemical processes, and their mathematical formulation in a set of "governing equations." For applications to CO_2 injection, storage and migration scenarios, these equations must be complemented with constitutive equations for physical and chemical properties of the interacting gaseous, liquid, and solid media. For site-specific applications, we require hydrogeologic parameters for the host formations, such as porosity, absolute and relative permeability, and others, which usually will display considerable internal variability ("heterogeneity"), as well as scale dependence. The presence of heterogeneity on multiple scales poses difficult challenges for site characterization and flow modeling alike.

Mathematical models can be constructed in different ways, and for different objectives. Models can be designed to approximate and simplify real-world systems by focusing on a few features that are deemed to be especially important. On the other hand, models can be built to include comprehensive process descriptions and to represent in great detail the (known or hypothesized) variability of hydrogeologic conditions and actual injection operations at specific field sites. Simplified, approximate models have certain advantages. They can emphasize specific features and mechanisms, and may often admit analytical or semi-analytical solutions. This facilitates insight into relevant processes and parameters, and may allow to reach broad and robust conclusions. Detailed and comprehensive site-specific models on the other hand must be implemented through numerical simulators that are capable of representing real-world heterogeneity, and the interplay of many interacting processes on different scales. This will require partitioning of the flow domain into a large number of subdomains or "grid cells," on the order of one million or more (Zhang et al., 2007; Birkholzer et al., 2008b; Yamamoto et al.,

2008). Highly spatially resolved models can provide a much more detailed and quantitative outlook on the behavior of flow systems, but the many interacting processes and parameters, and the complexity of data inputs and outputs, pose severe challenges for computation as well as for comprehension of model results. The choice of modeling approach will depend on the objectives of the modeling study. For example, a feasibility assessment of a certain proposed containment mechanism for CO_2 may use rather different conceptualizations and mathematical approaches than a model designed to assess the storage capacity and guide injection operations at a specific site.

Another important aspect of mathematical models relates to regulatory requirements for CO_2 storage, which are in formative stages in different countries (Collord, 2006; Wilson and Gerard, 2007; Wilkinson, 2008). Regulations must be based on a rational, process-based understanding of CO_2 behavior in the subsurface (Tsang et al., 2002, 2008). Mathematical models are a chief source of such understanding, informing regulators about what is practical and feasible; at the same time, it is evolving regulations that will influence or even determine the needs and objectives that must be met by mathematical models. This feedback calls for a flexible approach of "learning by doing."

The next section will summarize the main modeling challenges for demonstrating the safety of CO_2 storage. This will be followed by a review of recent modeling applications and challenges on issues of central importance to CO_2 storage, including (1) fluid pressurization and brine displacement by CO_2 injection, (2) the long-term fate of stored CO_2, and (3) containment of CO_2 beneath a caprock, and leakage through fractures, faults, and open wellbores. Selected

references to the published literature are given to enable readers a more in-depth pursuit of the issues addressed in this book chapter.

2. Coupled processes: a challenge for mathematical models

Large-scale injection of CO_2 into subsurface reservoirs will induce a complex interplay of coupled processes of multiphase flow, chemical and mechanical interactions between fluids and rocks, and heat transfer. These processes will determine the short-term injection performance of a CO_2 storage system as well as the long-term fate of injected CO_2. The individual physical and chemical processes and mechanisms affecting the fate of CO_2 in the subsurface are well understood "in principle," based on extensive geoscientific and engineering experience with oil, gas, and geothermal reservoirs, in which similar processes are taking place. However, in practice it is quite challenging to construct accurate models even for a basic process such as CO_2 displacing brine in a well-characterized porous medium in the laboratory, with known initial and boundary conditions. This is largely due to the complicated scale- and history-dependence of relative permeability and capillary pressure behavior of two-phase mixtures of water and CO_2 (Juanes et al., 2006; Bachu and Bennion, 2007; Doughty, 2007). Applications to geologic CO_2 storage systems face additional hurdles, because subsurface flow systems can only be partially characterized and known, introducing significant uncertainty into mathematical models. Even for idealized, hypothetical systems in which all hydrogeologic parameters are prescribed, modeling of CO_2 storage faces difficult challenges due to

(1) processes that occur over a broad range of space and time scales, with constitutive parameters that are scale-dependent, and

(2) non-linear feedbacks between different processes.

We will proceed here with a general overview of modeling challenges posed by multi-scale behavior and non-linear feedbacks. Specific examples of modeling approaches developed to address these issues will be given in Sec. 3.

CO_2 injected into a saline aquifer will initially be present primarily as a free and mobile non-aqueous and non-wetting phase, which for convenience we will refer to as gas. Over time, CO_2 may be transferred to different storage modes: it may become partially trapped by capillary forces, some of it may dissolve in the aqueous phase, and eventually, over longer time scales that may extend to hundreds or thousands of years, some of the dissolved CO_2 may react with formation minerals to form solid carbonates. The progression from free gas to trapped gas, dissolution in the aqueous phase, and sequestration in solid minerals is very desirable, as CO_2 is becoming less mobile during this process, so that permanence and security of CO_2 storage are increased (IPCC, 2005).

Injection of CO_2 into saline aquifers will cause significant fluid pressure increases over very large areas that typically may be two orders of magnitude larger than the extent of the CO_2 plume (Pruess et al., 2003; Birkholzer et al., 2008a). Fluid pressurization may induce movement on faults and fractures that could enhance the porosity and permeability of permeable pathways, and may compromise caprock integrity. Such effects could be amplified by dissolution of formation minerals and wettability changes induced by CO_2 (Chiquet et al., 2007a). Non-isothermal effects during CO_2 injection and storage are usually minor, except for leakage scenarios where expansion of CO_2 migrating to shallower horizons can give rise to very strong Joule-Thomson cooling (Katz and Lee, 1990; Skinner, 2003; Pruess, 2005). Boiling of liquid

CO_2 into gas may occur when stored CO_2 leaks upward into sub-critical pressure and temperature regimes, and would be accompanied by strong cooling from latent heat ffects (Pruess, 2008b). Capabilities exist to model the individual processes of fluid flow, chemical and mechanical interactions between rocks and fluids, and heat transfer. Much current research is devoted to more comprehensive modeling of couplings and feedbacks between different processes that may induce strong non-linearities with both self-enhancing and self-limiting features on different space and time scales.

3. Ilustrative modeling applications

In this section we discuss models that involve a range of spatial scales relevant for CO_2 storage. We begin with a regional perspective that addresses environmental impacts under conditions where several CO_2 storage projects would be conducted simultaneously in a sedimentary basin. As will be seen, pressurization of saline aquifers from CO_2 injection could induce brine flow effects over distances of several 100 km, with potential impacts on freshwater aquifers. We then address the long-term fate of CO_2 plumes from individual storage projects, that are expected to reach linear dimensions of order 10 km (Pruess et al., 2003). This is followed by a discussion of CO_2 leakage along faults, fracture zones and wellbores, which may involve important flow processes on scales as small as 1 m.

3.1 Fluid pressurization and brine displacement

The amounts of CO_2 that would need to be injected and stored underground to make a noticeable impact on atmospheric emissions are very large. Anthropogenic releases of CO_2 into the atmosphere are currently almost 30 Gt (billion metric tonnes) per year. At typical *in situ*

densities of stored CO_2, the corresponding fluid volume would be about eight times larger than current world oil production. This means that geologic storage of just 15 % of the CO_2 that due to human activities is currently released into the atmosphere would require a fluid handling system larger than world oil. A CO_2 storage project at a large coal-fired power plant of 1,000 MWe generating capacity will over a typical lifetime of 30 years generate a subsurface plume with linear dimensions of order 10 km or more (Pruess et al., 2003). Pressurization of displaced brine by more than 1 bar, corresponding to a hydraulic head of 10 m, would occur over a region with dimensions of order 100 km.

Figure 1 shows schematically the large-scale subsurface impacts that will be experienced during and after industrial-scale injection of CO_2. While the CO_2 plume at depth may be safely trapped under a low-permeability caprock within an anticlinal structure, the footprint area of the region with elevated pressure in the storage formation is much larger than the footprint area of the plume. The environmental impact of large-scale pressure buildup and related brine displacement depends mainly on the hydraulic connectivity between deep saline formations and the drinking water aquifers overlying them. One concern would be a storage formation that extends updip to form a drinking water resource used for domestic or commercial water supply (Bergman and Winter, 1995; Nicot, 2008). If there is direct hydraulic communication, CO_2 storage at depth could impact the shallow portions of the aquifer, which may experience water table rise, changes in discharge and recharge zones, and changes in water quality. Even if separated from deep storage formations by low-permeability seals, freshwater resources may be hydraulically communicating with deeper layers, and the pressure buildup at depth would then provide a driving force for upward brine migration. Interlayer pressure propagation and brine

leakage may occur, for example, if high-permeability conduits such as faults and abandoned boreholes are present (see Sec. 3.3, below). Pressure may also propagate in a slow, diffuse process if the sealing layers have a relatively high permeability (Birkholzer et al., 2008a).

Concerns about large-scale pressure buildup and brine migration caused by industrial-scale CO_2 sequestration have been raised as early as the 1990s (van der Meer, 1992; Bergman and Winter, 1995; Gunther et al., 1996). Since then, less emphasis has been placed on evaluating large-scale pressure changes and understanding the fate of the native brines that are being displaced by the injected CO_2. Most research into geologic storage of CO_2 has instead focused on evaluating the hydrogeological conditions under which the injected volumes of CO_2 can be safely stored, addressing issues such as the long-term efficiency of structural trapping of CO_2 under sealing layers. Regional estimates of storage capacity for CO_2 sequestration have often been based on simple calculations of the fraction of the total reservoir pore space available for safe trapping of CO_2 (Bradshaw et al., 2007; USDOE, 2007), implying an underlying assumption of "open" formations from which the native brine can easily escape laterally and make room for the injected CO_2. However, recent modeling studies have suggested that environmental concerns related to large-scale pressure buildup may be the limiting factor in carbon dioxide sequestration capacity (e.g., Zhou et al., 2008; Nicot, 2008; van der Meer, 2008).

From the standpoint of fluid dynamics, brine pressurization and migration is a much simpler process than two-phase flow of water-CO_2 mixtures. The challenge for mathematical modeling is not in fundamental process issues, but rather in obtaining a sufficiently detailed and realistic characterization of large subsurface volumes, to be able to place meaningful limits on

quantities and pathways for brine migration. Nicot (2008) employed a single-phase flow model to simulate the regional-scale brine flow processes in response to hypothetical future CO_2 sequestration in Texas Gulf Coast Basin, approximating the injection of CO_2 by adding equivalent volumes of saline water. Direct comparison of the single-phase flow model with a more complex simulation suggested that the far-field procceses can be represented reasonably well without accounting for local two-phase and variable density effects (Nicot et al., 2008).

Other studies have attempted to evaluate regional-scale impacts together with local CO_2-water flow processes, in one single model. Unless idealized geologic settings are considered (Birkholzer et al., 2008a), the need for large model domains combined with non-linear local flow phenomena requires novel grid designs with appropriate spatial resolution, and efficient high-performance computing techniques. Yamamoto et al. (2008) evaluated the impact of CO_2 storage on regional groundwater flow in Tokyo Bay, Japan. Their 3-D model covered an area of 60×70 km^2 and was discretized into approximately 10 million gridblocks, with extensive local grid refinement around the ten CO_2 injection wells. The model was run on the massively-parallel Earth Simulator (http://www.jamstec.go.jp/esc/index.en.html), a supercomputer with 5120 CPUs that is among the fastest available to Earth scientists worldwide. Birkholzer et al. (2008b) developed a regional-scale 3-D model for the Illinois Basin with an area of 240,000 km^2, that included local mesh refinement and more than one million gridblocks. To illustrate the methods used and results obtained from such large-scale high-performance models, we shall present the Illinois Basin model in more detail below.

The Illinois Basin region has annual CO_2 emissions of over 300 Mt (million metric tonnes) from fixed sources, primarily from large coal-fired power plants (USDOE, 2007). The primary target for CO_2 storage in the area is the Mount Simon Sandstone, a deep saline formation with proven seals, good permeability and porosity, as well as sufficient thickness (Figure 2). With a large (estimated) storage capacity (USDOE, 2007), the Mount Simon is expected to host multiple sequestration sites, based on the current portfolio of industrial point sources and the projected future developments. In northerly direction, the saline formation extends updip to form a freshwater aquifer in southern Wisconsin. Thus, there is concern about potential degradation of freshwater resources due to pressure buildup and brine displacement in response to future deployment of CO_2 sequestration in the area. An important objective in the setup of the large-scale numerical model for the Illinois Basin was to predict simultaneously (1) the basin-scale environmental impacts (i.e., pressure buildup and brine displacement) of projected future CO_2 storage scenarios involving multiple injection sites, and (2) the detailed plume-scale phenomena at individual CO_2 injection sites and their interaction.

The model domain for the Illinois Basin covers an area of roughly 570 km by 550 km (Figure 2). It includes a core area that is suitable for CO_2 storage, as well as a far-field area with important groundwater resources where environmental impacts need to be assessed. The core area was selected based on the favorable geological setting, sufficient thickness and depth, and proximity to gas storage fields as well as to various large anthropogenic CO_2 sources. In vertical direction, the model comprises the Mt. Simon Sandstone as well as the overlying shale unit and a portion of the underlying granite bedrock. A three-dimensional unstructured mesh was constructed with progressive mesh refinement in the core injection areas to capture details of

two-phase flow and spatial variability, using grid refinement down to 20 m in the horizontal and 10 m in the vertical direction. A hypothetical carbon sequestration scenario was modeled that assumes twenty individual sequestration sites (spaced about 30 km apart) within the core area. At each site, the assumed annual CO_2 injection rate is 5 Mt for an injection period of 50 years.

Illustrative model results showing the characteristics of individual CO_2 plumes after 50 years of continuous injection are presented in Figure 3. The maximum size of CO_2 plumes, on the order of 6 to 10 km, is much smaller than the lateral distance between different injection sites, suggesting that merging of plumes would only occur after very long times (hundreds of years or more), if at all. The close-up view in the vertical cross section highlights the variability of CO_2 saturation and how it relates to the internal layering and permeability differences within the Mt. Simon. In addition to the local heterogeneity structure, CO_2 plume shapes are affected by the thickness of the Mt. Simon and the slope of the structural surfaces, while pressure interference from neighboring injection sites has very little effect on plume shape. The details of CO_2 saturation evident in Figure 3 emphasize the importance of local mesh refinement to resolve smaller-scale processes, such as structural trapping from internal layering or enhanced dissolution due to spatial heterogeneity.

Figure 4 shows the simulated pressure buildup (in bar) at the top of the Mt. Simon at 10, 50 (end of injection period), 100, and 200 years after start of injection. While the maximum pressures are not a concern with respect to geomechanical damage and caprock integrity, the pressure buildup from individual storage locations has obvious implications for neighboring sites. After 10 years, a continuous region with pressure buildup of 10 bar or more has evolved in

the core injection area, indicating strong pressure interference between different storage sites located at distances of 30 kilometers or more. Such interference may suggest a hierarchical approach to regulating CO_2 injection, that would start with a regional assessment of storage capacity and a general permit for a region, prior to permitting individual sites (Nicot and Duncan, 2008). With respect to the far-field impact of CO_2 injection and storage, pressure changes may propagate as much as several hundred kilometers away from the core injection area. Moderate pressure buildup (up to 2.0 bar at the top of the Mt. Simon) is observed after 50 years of injection in northern Illinois, where valuable and heavily used freshwater aquifers overlie the Mt. Simon and Eau Claire. Such pressure changes may have some impact on groundwater recharge and discharge regimes in these freshwater aquifers. In comparison with the magnitude and extent of pressure buildup, the changes in salinity experienced in the subsurface as a result of brine displacement are very small, posing no direct threat to groundwater quality. However, salinity issues could become a concern if deep saline water from the Mt. Simon was pushed upward into overlying aquifers via localized pathways, such as transmissive faults or open boreholes, which are currently not included in the model (see Sec. 3.3, below). After CO_2 injection ends, the pressure buildup in the core injection area reduces quickly to moderate values around 5-10 bar, while the far-field pressure response initially continues to increase and expand (compare the 50 and 100 year frames in Figure 4). The system then progresses slowly towards an equilibrated state, with pressures eventually returning to hydrostatic conditions, long after the end of the injection period.

The simulation results discussed above are for a hypothetical future injection scenario in which one-third of the total CO_2 emissions from large point sources in the Illinois Basin are

captured and stored. The total injected mass of CO_2 after 50 years is 5,000 Mt, which is about one sixth of the lower bound of the estimated storage capacity (USDOE, 2007) for the Mt. Simon Sandstone in the Illinois Basin. If the CO_2 injection were to continue at the assumed injection rate for 250 more years, to fully utilize the estimated storage capacity, the pressure buildup would be much stronger and extend over a larger area than seen in Figure 4. This suggests that estimates of storage capacity, if solely based on effective pore volume of suitable formations, may have to be revised downward, based on assessments of pressure buildup and environmental impacts. It should be noted that the Illinois Basin study discussed here is preliminary, and considerable uncertainty regarding the large-scale geological model needs to be acknowledged. Further site characterization efforts are underway, and model predictions of environmental impacts may change as more details for future storage scenarios are being developed.

3.2 Long-term fate of injected CO_2

When injected into a saline aquifer, supercritical CO_2 forms a separate non-aqueous fluid phase, that for convenience we refer to as "gas." At typical subsurface conditions for terrestrial CO_2 storage projects, the *in situ* density of the gas phase will be less than the density of the aqueous phase, generating a buoyancy force that will drive CO_2 towards the top of the permeable interval. CO_2 storage would be made into formations that have a suitable caprock of low permeability to contain the CO_2, and injection pressures would be limited so as not to exceed the capillary entry pressure of the caprock (Krooss et al., 2004; Chiquet et al., 2007b; Bachu and Bennion, 2007; Gibson-Poole, 2008). However, as CO_2 spreads beneath the caprock, containment could be compromised if (sub-)vertical permeable pathways with low or vanishing entry pressures were encountered, such as fracture zones and faults, or improperly abandoned

wells. Upward buoyancy force could be avoided if CO_2 were injected into deep-sea sediments at an ocean depth of more than 3,000 m, as this would place CO_2 at temperature and pressure conditions that would make it more dense than aqueous phase, thus removing concerns about upward leakage (House et al., 2006). However, storage of CO_2 in deep-sea sediments faces great technical and economic challenges, chief among them the difficulty and cost of (1) operating CO_2 injection in more than 3,000 m water depth, and (2) transporting the CO_2 from land-based sources to deep-ocean injection sites. There is no evidence that these challenges can be overcome in practice, and in the remainder of this section we will focus on issues relating to terrestrial CO_2 storage only.

CO$_2$ injected into terrestrial saline aquifers will over time become partially trapped by capillary force, rendering it immobile and reducing concerns about leakage. This is due to the well-established fact that in two-phase (gas-liquid) flow, the relative permeabilities of the phases depend not only on their saturation (i.e., the fraction S of pore volume occupied by a phase), but also on the path by which this saturation was reached. Supercritical CO_2 injected into an aquifer acts as a non-wetting (nw) phase, and is mobile (non-zero relative permeability) already for very small saturations S_{nw}. However, when aqueous phase reinvades pore space previously occupied by non-wetting phase, the latter becomes immobile or "trapped" at a finite "irreducible" saturation $S_{nw,ir}$, which may be of the order of 20 %, and increases with the maximum non-wetting phase saturation that had been reached during prior CO_2 invasion. CO_2 trapped in this way cannot move in spite of experiencing an upward buoyancy force, and would no longer raise concerns about potential leakage (Kumar et al., 2004; Juanes et al., 2006; Doughty, 2007). Doughty (2007) demonstrated the potential significance of hysteretic trapping effects by

numerically simulating CO_2 injection into a hypothetical aquifer with no caprock whatsoever. Figure 5 shows CO_2 plumes at different times resulting from injection of 900,000 tonnes of CO_2 over a thirty-day period into the bottom 100 m of a 2-D cylindrically symmetric model with uniform permeability of 100 mD. Results are compared for three different assumptions about non-wetting phase relative permeabilities, (a) non-hysteretic with $S_{nw,ir} = 0$ ("slippery" plume), (b) non-hysteretic with $S_{nw,ir} = 25$ % ("sticky" plume), and (c) hysteretic, with $S_{nw,ir}$ varying dynamically from 0 for CO_2 invasion to 25 % for water invasion. It is seen that the "slippery" plume advances rapidly towards the land surface, and almost all the injected CO_2 leaks out eventually. In contrast, the "sticky" plume never reaches the land surface and remains trapped indefinitely. The hysteretic model predicts fairly rapid upward advancement of the plume at early times, but plume migration slows down when increasing amounts of CO_2 become trapped at depth as water reinvades pore space previously occupied by CO_2. Small amounts of CO_2 eventually reach the land surface, but leakage fluxes are much reduced and delayed relative to the "slippery" plume scenario.

CO_2 may also dissolve in resident aqueous phase, giving rise to a small increase in density so that aqueous phase with dissolved CO_2 actually has negative buoyancy (Weir et al., 1995; Lindeberg and Bergmo, 2003). As CO_2 dissolves into underlying aqueous phase, it is transported away from the phase boundary by molecular diffusion. This is a slow process, but dissolution can be greatly accelerated by convective currents that may form due to the gravitational instability of denser (CO_2-rich) aqueous phase above less dense aqueous phase. Accelerating CO_2 dissolution is very desirable from the standpoint of storage security, and the process of dissolution-diffusion-convection (DDC) has been studied by many investigators.

Mathematical models have focussed on the onset of convective instability, the growth of convective fingers, and the long-term rate of CO_2 dissolution (Ennis-King and Paterson, 2003a, b, 2005; Ennis-King et al., 2005; Hesse et al., 2006; Riaz et al., 2006; Xu et al., 2006; Rapaka et al., 2008). Convection induced by CO_2 dissolution has similarities to thermally-buoyant convection, as driven by geothermal temperature gradients, and the extensive literature in that field (e.g. Garg and Kassoy, 1981) has helped understanding of convection induced by CO_2 dissolution. There are important differences as well, the principal one being the prevalence of a constant (geothermal) temperature gradient as initial condition for thermal convection. This contrasts with the CO_2 dissolution problem, in which there is no significant pre-existing gradient of dissolved aqueous CO_2, making the system unconditionally unstable with respect to buoyant convection.

In numerical simulations of CO_2 storage, the need to discretize continuous space and time variables makes it very challenging to properly account for the DDC process with its multi-scale nature in both space and time (Zhang et al., 2007). Depending on formation parameters, onset times for convection may range from a fraction of a year to tens of years or more (Ennis-King and Paterson, 2005). The initial spatial scale of the convective instability is determined by the thickness $L = \sqrt{Dt}$ of the diffusive boundary layer, where D is diffusivity and t time. Molecular diffusivity of dissolved aqueous CO_2 is of order 10^{-9} m^2/s (Tewes and Boury, 2005), so that the length scale corresponding to estimated convective onset times ranges from a few centimeters to a few meters. Numerical simulations of field-scale CO_2 storage typically cannot properly resolve these small spatial scales; lack of spatial resolution results in delaying the onset of DDC and

reducing its efficiency, thus underestimating the rates and overestimating the time scales for CO_2 dissolution (Lindeberg and Bergmo, 2003; Audigane et al., 2007).

Alternative approaches that are not subject to limitations arising from space and time discretization are being pursued for modeling the long-term large-scale behavior of injected CO_2. An example is the similarity solution technique used by Nordbotten and collaborators to model the long-term behavior of CO_2 injected from a single vertical well into a homogeneous confined aquifer of constant thickness (Nordbotten and Celia, 2006). In addition to idealizing flow geometry and formation properties, these authors invoke approximations such as vertical pressure equilibrium, and assume that CO_2 invades as a sharp front across which there is a step change in saturation. The "payoff" from these simplifications is that the partial differential equations for two-phase flow of CO_2 and water can be transformed into an ordinary differential equation (ODE), that describes the dependence of vertical CO_2 plume thickness h on radial distance R and time t as a function of the "similarity variable" $\zeta = R^2/t$. The ODE is non-linear and must be solved numerically, but due to the similarity property a single solution of the ODE is sufficient to describe the plume behavior for all times and distances. Using similar assumptions of vertical equilibrium and a sharp interface between CO_2 and brine, Hesse et al. (2008) considered the migration of a CO_2 plume in linear flow geometry for horizontal as well as sloping aquifers. For horizontal aquifers, similarity solutions can be obtained, while sloping aquifers lead to a Riemann (hyperbolic) problem. Approximations to the equations governing two-phase flow of CO_2 and brine that will yield self-similar behavior are very valuable, because similarity solutions are inherently "multi-scale," and are thus ideally suited to describe processes extending over a broad range of time and space scales.

Dissolved CO_2 may chemically interact with formation minerals, leading to both dissolution and precipitation phenomena (Gunter et al., 1997; Johnson et al., 2001; Xu et al., 2005, 2007; Audigane et al., 2007; Gherardi et al., 2007; André et al., 2007; Gaus et al., 2008). Formation of solid carbonates is the most permanenent and desirable form of CO_2 storage, but is a slow process at ambient temperature conditions. There is considerable uncertainty about rock-fluid reaction rates applicable to field-scale systems, but it is likely that hundreds of years or more would be required for significant reaction process (Audigane et al., 2007).

3.3 Leakage along faults, fracture zones, and wellbores

Storage reservoirs and operations for CO_2 will be selected and designed in such a way that intact caprock overlying a CO_2 storage reservoir will adequately contain CO_2, due to sufficiently large entry pressure for non-wetting phase and/or sufficiently small permeability (Krooss et al., 2004; Chiquet et al., 2007; Bachu and Bennion, 2007). Concerns about long-term storage integrity arise from potential caprock imperfections that may provide preferential pathways for upward gas migration, such as fracture zones and faults, or improperly abandoned wells.

Geologic storage of CO_2 from large fossil-fueled power plants will generate plumes with linear dimensions of order 10 km or more over the lifetime of a power plant (Pruess et al., 2003). On such a scale it seems likely that in most geologic settings some fracture zones and faults will be encountered by the stored CO_2. Assessing the feasibility and long-term safety of CO_2 storage requires the evaluation of plausible leakage scenarios, to develop an understanding of controlling

mechanisms and parameters. From experience with natural CO_2 discharges, it is expected that the most likely manner in which CO_2 may migrate upwards is "diffuse degassing," in which low fluxes of CO_2 may be discharged over large areas (Barnes et al., 1978; Sorey et al., 1998; Chiodini et al., 2004). Physical and chemical properties of CO_2 suggest a potential for feedback processes that could either self-enhance or self-limit the rates of CO_2 migration. CO_2 is less viscous and less dense than water, so that large increases in volumetric flux and in fluid pressures at shallow horizons are possible when CO_2 replaces water in a leakage pathway. CO_2 has large compressibility, so that a small pressure reduction can cause large volume expansion. Exsolution of dissolved CO_2 also can cause large volume expansion. Depending on geochemical conditions, CO_2 may induce dissolution as well as precipitation of minerals, which may serve to enhance or reduce permeabilities along a flow path (Johnson et al., 2004; LeNindre and Gaus, 2004; Watson et al., 2004; Gherardi et al., 2007). Pressure increases associated with CO_2 storage and leakage can induce movement along faults, with a potential for increasing permeability (Streit and Hillis, 2004; Streit and Siggins, 2004; Chiaramonte et al., 2008; Rutqvist et al., 2008). Geomechanical and chemical effects may provide feedbacks that conceivably could enhance CO_2 leakage beyond what could occur from either mechanism in isolation; however, mathematical modeling is only beginning to address such couplings.

When CO_2 escapes from the primary storage reservoir and migrates to shallower depths, pressures may drop below the critical point (P_{crit} = 73.82 bar), and phase transitions between liquid and gaseous CO_2 may occur that will be accompanied by significant latent heat effects. Non-isothermal effects will also arise from decompression of gaseous CO_2, the so-called Joule-Thomson effect (Katz and Lee, 1990). Extremely strong cooling effects have been observed on a

few occasions where CO_2 used for enhanced oil recovery has broken through and discharged from oil production wells (Skinner, 2003). Numerical simulation studies have shown self-enhancing as well as self-limiting feedbacks between fluid flow and heat transfer, with three-phase flow of aqueous phase and liquid and gaseous CO_2 playing an important role in limiting overall fluid mobility, due to the generally small relative permeabilities in three-phase conditions (Stone, 1970; Pruess, 2005, 2008a, b). Figure 6 shows a leakage scenario in which CO_2 migrates upward from the deep storage aquifer along a blind fault, and accumulates in a secondary or "parasitic" reservoir at shallower depth (Pruess, 2008b). Discharge from the secondary accumulation is initiated when CO_2 reaches a spill point at which a second fault provides a permeable pathway towards the land surface. The particular geometric arrangement shown in Figure 6 was intentionally designed to facilitate strong CO_2 leakage, by first enabling a substantial accumulation of CO_2, and then allowing for self-enhancement of CO_2 flow due to depressurization and large volume expansion of CO_2 once a discharge gets underway. Simulated CO_2 outflow rates at the land surface show only weak self-enhancing feedbacks, as the maximum in CO_2 outflow rates increases somewhat super-linearly with applied CO_2 injection rate at depth (Figure 7). A profile of fluid saturations as the time of maximum discharge is approaching shows the upper fault being fed with a three-phase mixture of aqueous phase, and liquid and gaseous CO_2 (Figure 8). The strong interference between different fluid phases in three-phase flow reduces effective permeabilities for all phases, and limits discharge rates. Figure 8 also shows a temperature profile, indicating attainment of very low temperatures in the region where liquid CO_2 boils into gas.

In many parts of the world, sedimentary basins have been intensely explored and developed for oil and gas production. As an example, the Alberta Basin, Canada, has over 400,000 wells (Celia et al., 2004). Sedimentary basins also are the prime potential sites for geologic storage of CO_2, as they often host many sources of anthropogenic CO_2, such as fossil-fueled power plants, and have deep saline aquifers, and oil and gas reservoirs, with large capacity for CO_2 storage (Bradshaw and Dance, 2004; Bachu, 2008). Improperly abandoned wells may pose a threat to the integrity of CO_2 storage projects in sedimentary basins, and many studies have been performed to address this problem. A group at Princeton and Bergen universities has developed models for CO_2 leakage through wells penetrating formations that are conceptualized as a layer cake of alternating aquifers and aquitards (Figure 9; Celia et al., 2004, 2008; Nordbotten et al., 2004, 2005). Degradation of well cements due to corrosive action of injected CO_2 has also been modeled (Duguid et al., 2004). Fully deterministic models are impractical when dealing with very large numbers of potentially leaky wells, and the Princeton/Bergen group used a stochastic approach to model and aggregate the leakage behavior of individual well segments (Figure 10). One limitation of their approach is that flow in leaky well segments is modeled by Darcy's law. This will be appropriate for wells that provide relatively "small" flow pathways, as e.g. through small cracks in cement plugs. However, there is concern that leakage from a CO_2 storage reservoir could be dominated not by a multitude of slightly leaky wellbores, but by a small number of wells with open-hole sections. Flow behavior in open hole sections, or along an open annulus, cannot be described by Darcy's law, but requires modeling of velocity-dependent friction and acceleration effects (Zuber and Findlay, 1965; Brill and Mukherjee, 1999; Lu, 2004; Paterson et al., 2008).

In the volcanology literature the possibility of a "pneumatic eruption" has been suggested, so-called because it supposedly would be driven not by thermal energy, but by the mechanical energy stored in a volume of highly compressed gas (Giggenbach et al., 1991; Fischer et al., 1996; Browne and Lawless, 2001). We are not aware of any attempt, either in the volcanology or CO_2 storage communities, to mathematically model pneumatic eruptions, and the possibility of such eruptions remains hypothetical (Pruess, 2008a). A quantitative analysis of this problem would require significant advances in capabilities for modeling two- and three-phase flows of water-brine mixtures at high speeds and including non-isothermal effects.

4. Concluding remarks

CO_2 injection into subsurface formations for enhanced oil recovery (EOR) has been practiced for over 30 years, and currently about 50 Mt of CO_2 per year is injected underground in the U.S. (http://fossil.energy.gov/programs/reserves/npr/CO2_EOR_Fact_Sheet.pdf) for this purpose. Clearly, the technology to safely inject CO_2 underground exists, but CO_2 storage as a climate change mitigation strategy raises new issues, due to the very large amounts that would need to be injected, and the very large space and time scales that come into play. Excellent opportunities for learning about CO_2 behavior underground on relevant scales are provided by naturally occurring CO_2 discharges in volcanic or tectonically active regions (IEA, 2006; Annunziatellis et al., 2008). Mathematical modeling of the behavior and fate of CO_2 injected underground is a key tool for designing and safely operating large-scale CO_2 injection projects. Modeling capabilities developed in the context of oil and gas production and storage, geothermal energy extraction, and geologic disposal of industrial wastes have been adapted to the CO_2 problem, but further advances are needed to more accurately represent the complex multi-scale

processes of fluid flow, chemical and mechanical interactions, and heat transfer, that are induced by geologic storage of CO_2.

Acknowledgement

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Figures

Footprint Area of
Elevated Pressure

Footprint Area
of CO_2 Plume

Possible Brine
Leakage into
Shallow Units

Abandoned
Well

CO_2
Injection

Storage Formation
May Extend Updip to
Freshwater Resource

Brine Leakage into
Upper Strata

CO_2 Plume

Pressure Perturbation and
Brine Displacement

ESD08-020
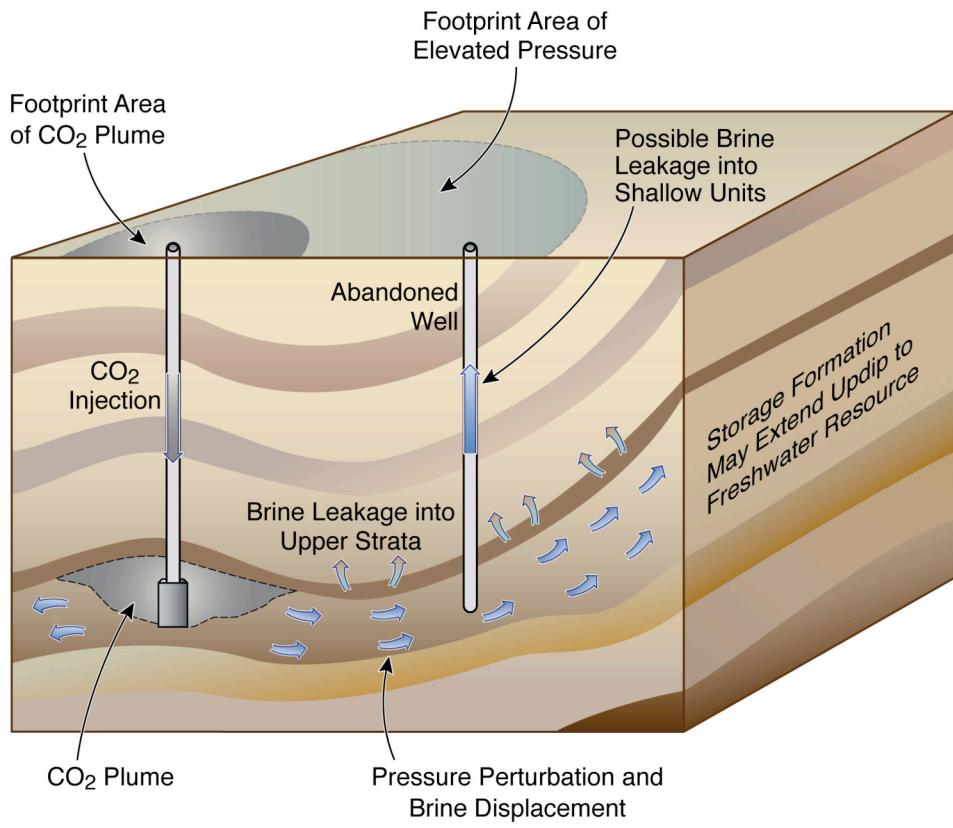
Figure 1.   Schematic showing different regions of influence related to CO_2 storage (from
   Birkholzer et al., 2008a; not to scale)
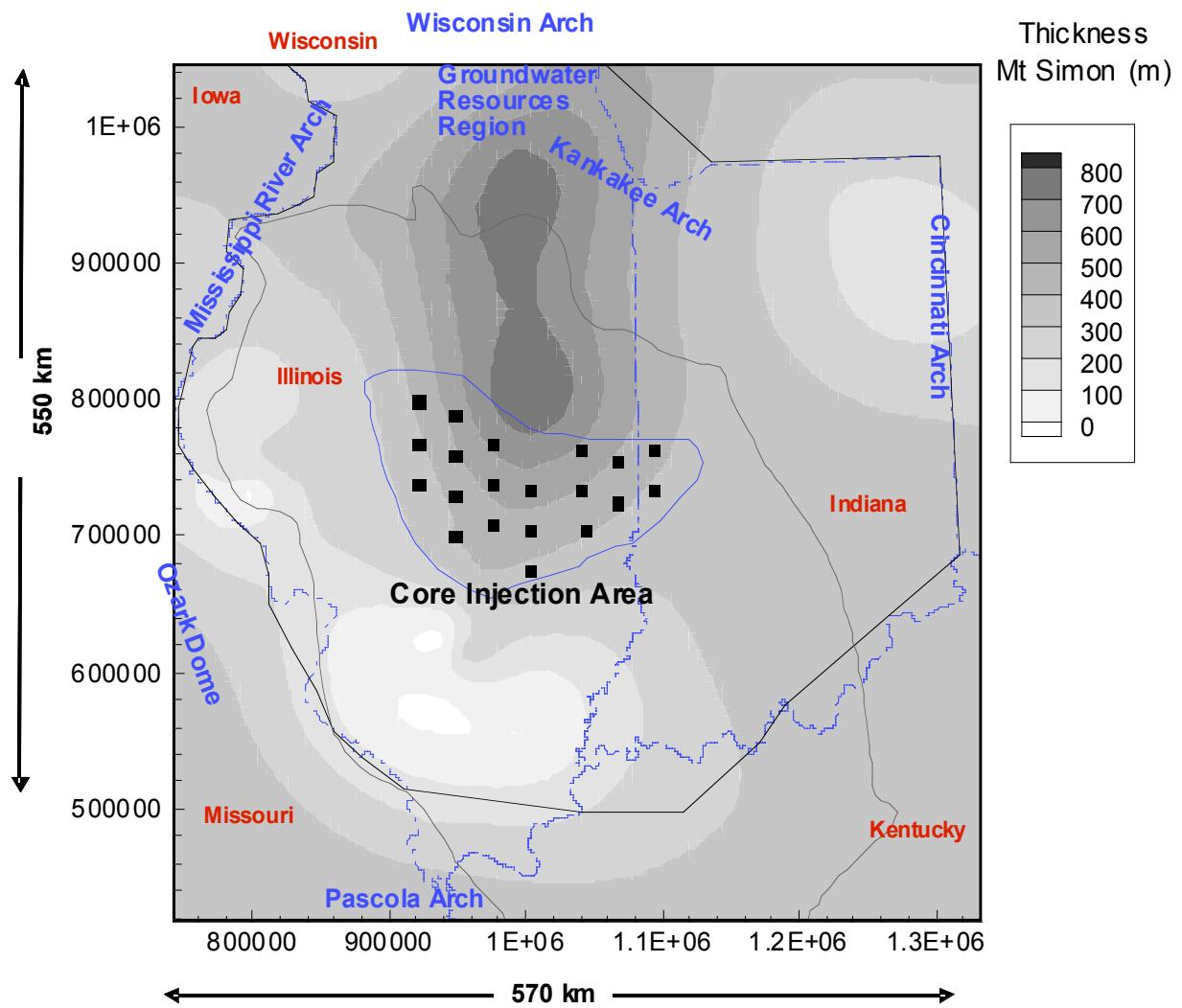
Figure 2. Boundary of the model domain (solid black line) and thickness of the Mount Simon (in m). Also shown are the core-injection area that hosts 20 hypothetical injection sites (squares), and the Illinois Basin boundary (in gray). Easting and northing coordinates are given in m.
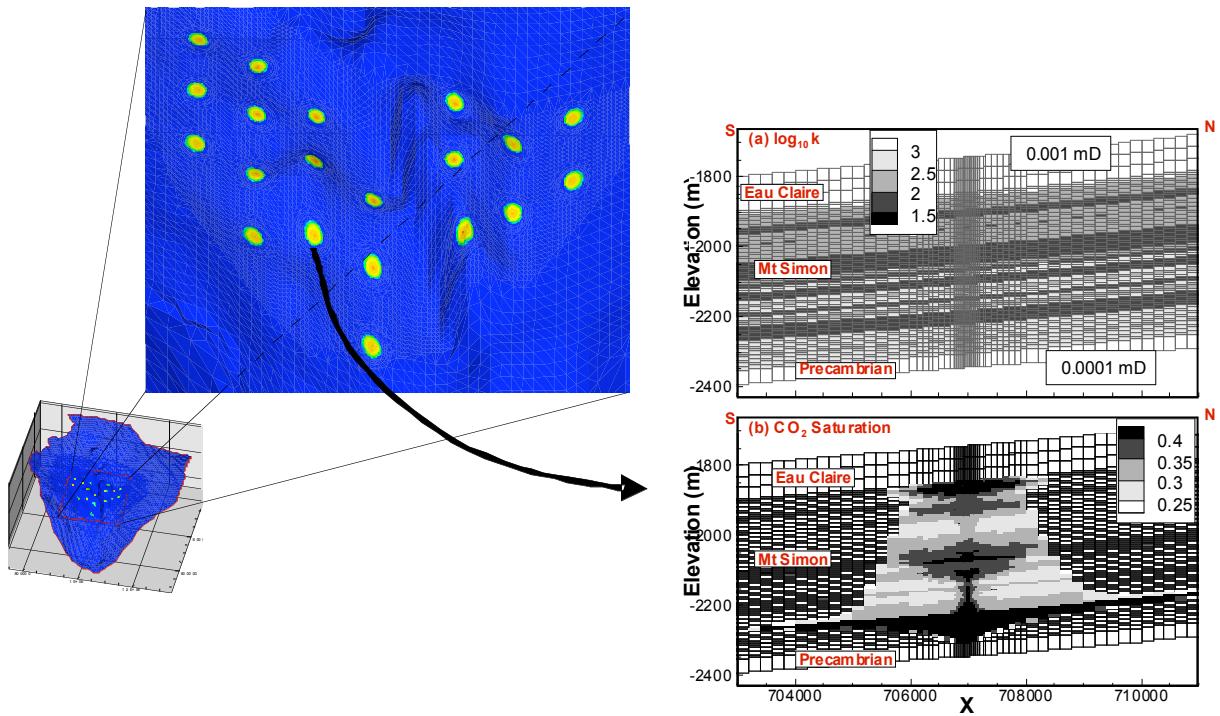
Figure 3. Graph on left shows contours of CO_2 saturation after 50 years of injection at elevation of maximum plume extent. Graphs on right show (a) vertical permeability (in millidarcy), and (b) CO_2 saturation in a south-north cross section for a selected injection site.
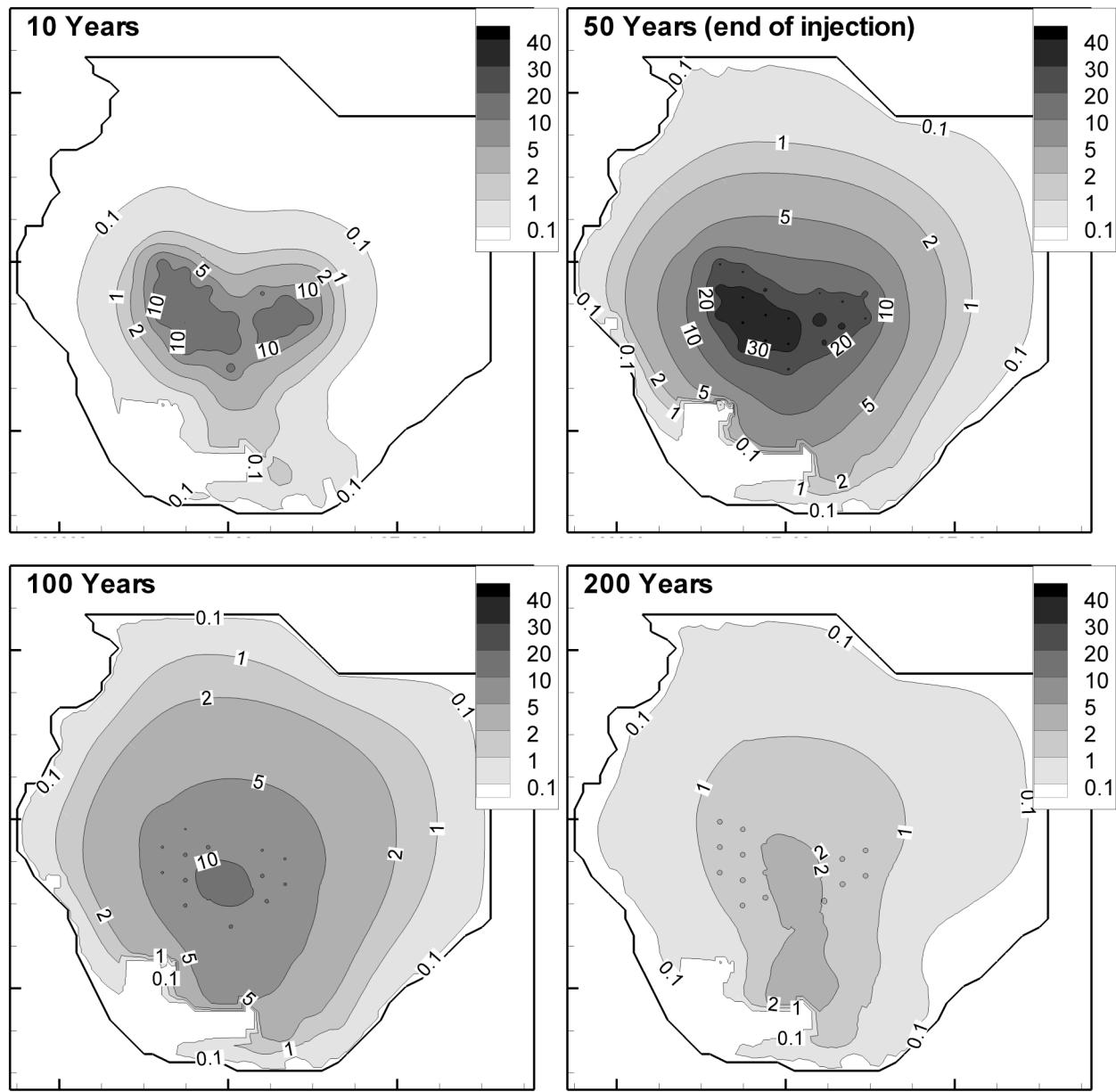
Figure 4. Contours of pressure increase (in bar) at the top of the Mount Simon Sandstone at 10, 50, 100, and 200 years after start of injection, assuming a 50-year injection period.
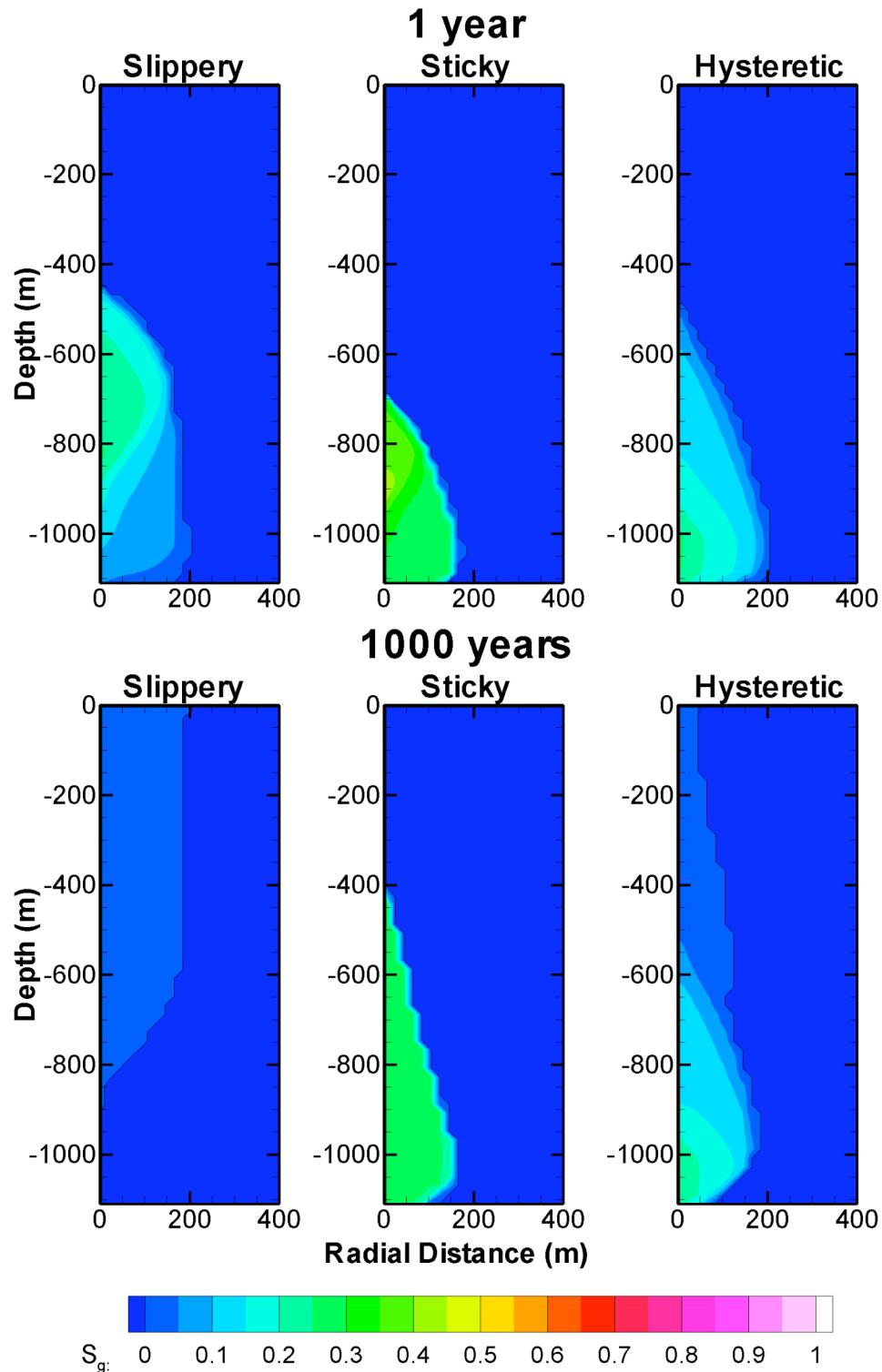
Figure 5. Simulated CO_2 plumes after 1 (top) and 1000 years (bottom). The different panels are for a "slippery" plume (left), a "sticky" plume (middle), and for a hysteretic model (right); see text. From Doughty (2007).
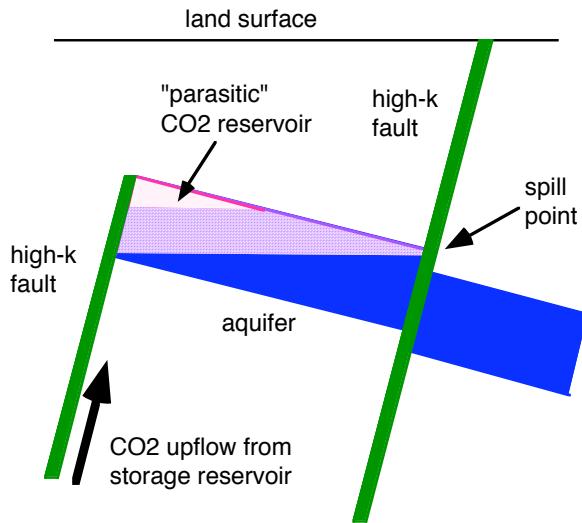
Figure 6. Conceptual leakage scenario that involves CO_2 migrating up a fault to accumulate in a secondary "parasitic" reservoir at shallower depth. Discharge of CO_2 at the land surface occurs after the accumulation reaches a spill point where it can enter another fault (from Pruess, 2008b).
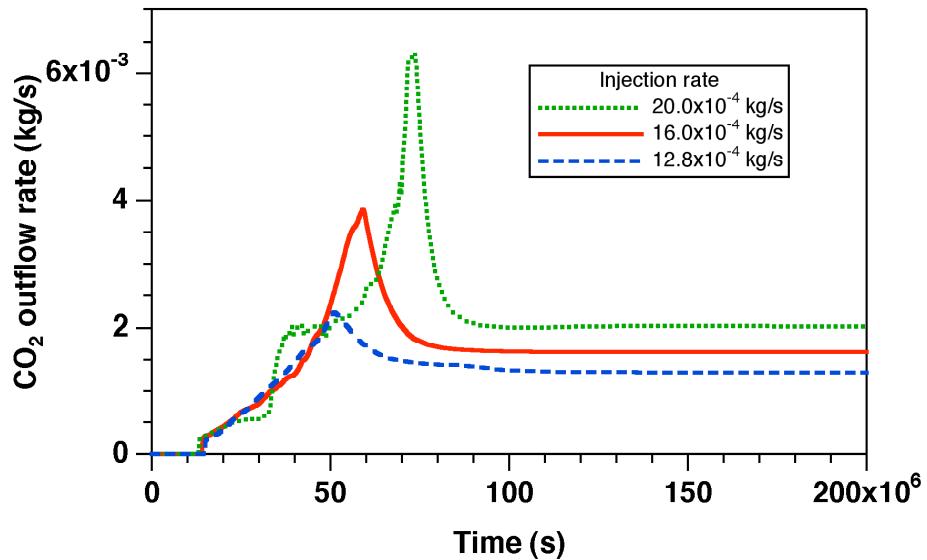
Figure 7. Dependence of CO_2 outflow behavior on injection rate (from Pruess, 2008b). Flow rates are for a vertical section of 1 m thickness.
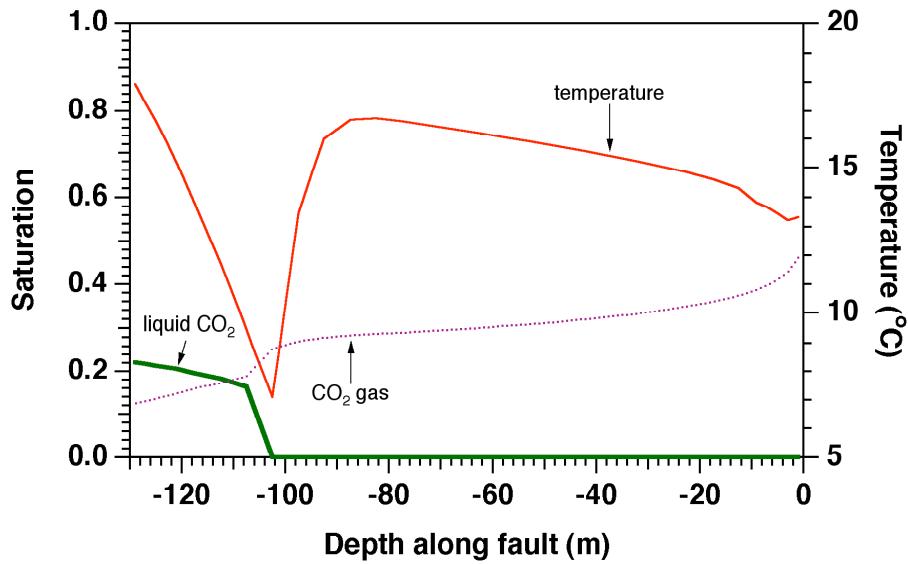
Figure 8. Profile of temperature and CO_2 saturations in upper fault at t = 1.50 yr (from Pruess, 2008b).
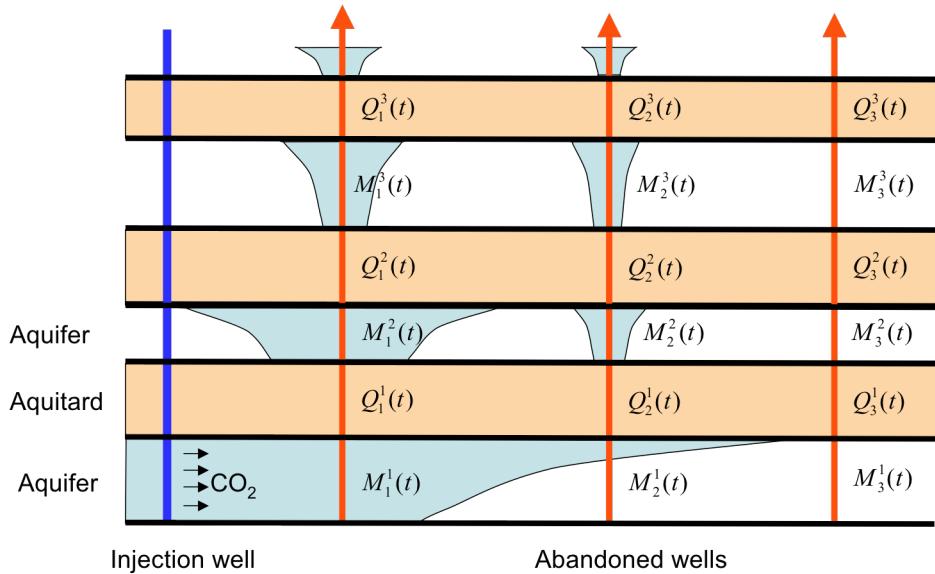

Figure 9. Conceptual model for leakage through wellbores in a sedimentary basin with layer cake stratigraphy (from Celia et al., 2008).
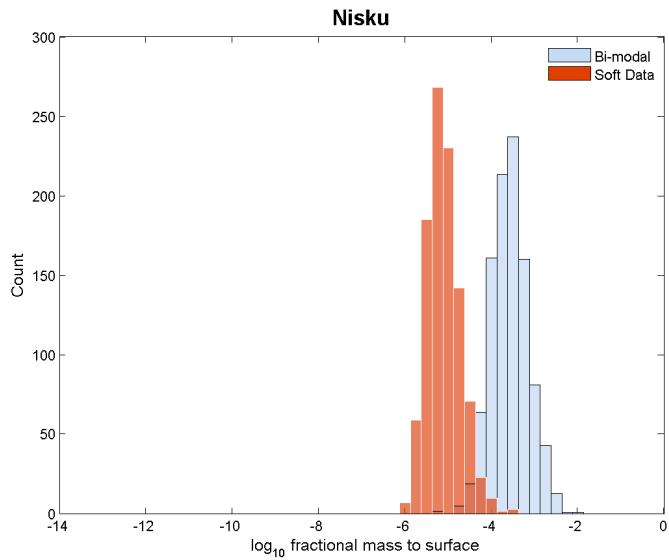
Figure 10. Histogram of the fraction of CO_2 leaked to the surface during injection over a 50 yr period into the Nisku formation, Alberta Basin, Canada. Model results are shown for two different stochastic distributions for the permeability of well segments, and using 1,000 realizations for each case (from Celia et al., 2008).