NUMERICAL MODELING OF CO_2 SEQUESTRATION IN GEOLOGIC FORMATIONS - RECENT RESULTS AND OPEN CHALLENGES

KARSTEN PRUESS

Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, U.S.A.

1. INTRODUCTION

Rising atmospheric concentrations of CO_2, and their role in global warming, have prompted efforts to reduce emissions of CO_2 from burning of fossil fuels. An attractive mitigation option under consideration in many countries is the injection of CO_2 from stationary sources, such as fossil-fueled power plants, into deep, stable geologic formations, where it would be stored and kept out of the atmosphere for time periods of hundreds to thousands of years or more. Potential geologic storage reservoirs include depleted or depleting oil and gas reservoirs, unmineable coal seams, and saline formations. While oil and gas reservoirs may provide some attractive early targets for CO_2 storage, estimates for geographic regions worldwide have suggested that only saline formations would provide sufficient storage capacity to substantially impact atmospheric releases. This paper will focus on CO_2 storage in saline formations.

Injection of CO_2 into a saline aquifer will give rise to immiscible displacement of brine by the advancing CO_2. The lower viscosity of CO_2 relative to aqueous fluids provides a potential for hydrodynamic instabilities during the displacement process. At typical subsurface conditions of temperature and pressure, CO_2 is less dense than aqueous fluids and is subject to upward buoyancy force in environments where pressures are controlled by an ambient aqueous phase. Thus CO_2 would tend to rise towards the top of a permeable formation and accumulate beneath the caprock. Some CO_2 will also dissolve in the aqueous phase, while the CO_2-rich phase may dissolve some formation waters, which would tend to dry out the vicinity of the injection wells. CO_2 will make formation waters more acidic, and will induce chemical rections that may precipitate and dissolve mineral phases (Xu et al., 2004). As a consequence of CO_2 injection, significant pressurization of formation fluids would occur over large areas. These pressurization effects will change effective stresses, and may cause movement along faults with associated seismicity and increases in permeability that could lead to leakage from the storage reservoir (Rutqvist and Tsang, 2005).

Because of the complexity of coupled hydrodynamic, chemical, mechanical and thermal processes accompanying CO_2 storage and leakage, and because of the large range of space and time scales involved, numerical modeling is playing a key role in examining the feasibility and security of large-scale CO_2 injection. A recent code intercomparison study examined the ability of numerical simulators to model prototypical flow problems that arise in geologic storage of CO_2 (Pruess et al., 2004). Eight problems were specified that addressed saline formations as well as oil and gas reservoirs. The emphasis was on fluid flow, but chemically and mechanically coupled problems were included as well. Simulations submitted by ten groups from six countries demonstrated that currently available simulation codes are capable of modeling the complex phenomena accompanying geologic storage in a robust manner, and with quantitatively similar results. Applications of numerical simulation involve the design and monitoring of injection projects, and assessment of the long-term fate of CO_2 injected underground. Modeling of natural CO_2 reservoirs and natural CO_2 degassing, especially in volcanic areas, can provide important insights into the subsurface behavior of CO_2 on space and time scales relevant for man-made geologic storage systems (Todesco et al., 2004).

Issues to be addressed by numerical modeling include the following. What fraction of subsurface volume can be accessed by the CO_2? How is the utilization of subsurface space affected by viscous instability, gravity override and formation heterogeneities? What fraction of CO_2 is stored as free phase (mobile or trapped), dissolved in the aqueous phase, and sequestered in solid minerals? How do the relative proportions of CO_2 in these different storage modes change over time? What is the fate of leaking CO_2? Can CO_2 leaks self-seal or self-enhance? How does the evolution of CO_2 leaks depend on coupling of chemical, mechanical, and thermal effects? Is it possible for a CO_2 leak to self-enhance to the point of a high-energy, eruptive release? What is the role of relative permeability and capillary pressure effects in CO_2 containment and leakage? What is the role of different phase compositions (supercritical, liquid, gaseous CO_2; CO_2 dissolved in water) and phase changes in CO_2 leakage?

The critical point of CO_2 is at temperature and pressure conditions of (T, P) = (31.04 ˚C, 73.82 bar), meaning that at lower temperatures and pressures, CO_2 can exist either as a liquid or a gas, while at conditions above the critical point it forms a single "supercritical" phase. When dealing with two-phase mixtures of an aqueous and a single CO_2-rich phase, we usually refer to the latter simply as "gas." It is a fortuitous aspect of terrestrial geology that under normal crustal conditions of a geothermal gradient of 30 ˚C/km and hydrostatic pressures, at about 750 m depth both temperatures and pressures will be near the critical point of CO_2. There is a consensus in the technical community that aquifer storage of CO_2 would be made at greater depth and supercritical pressures. However, as will be seen below, for analyzing leakage behavior it may be necessary to consider near-critical conditions with their extreme non-linearities, as well as liquid-gas phase change and associated thermal effects.

2. LONG-TERM FATE OF STORED CO_2

In the early phase of an aquifer CO_2 storage project, most of the injected CO_2 forms a separate supercritical phase with gas-like viscosity and liquid-like density. Because of buoyancy forces, injected CO_2 is expected to rise to the top of the permeable formation; this was confirmed by time-lapse seismic surveys at the commercial-scale CO_2 storage project at Sleipner, Norwegian sector of the North Sea (Arts et al., 2004). CO_2 invasion is a drainage process, so that irreducible gas saturations are very small, and CO_2 is highly mobile. Containment of the advancing CO_2 must rely on capillary entry effects in a caprock of low permeability. A fraction of the CO_2 dissolves in the aqueous phase, increasing its density by a small amount of order 1 %. The associated (negative) buoyancy force can induce convective circulation that will carry dissolved CO_2 downward, while causing additional dissolution of CO_2 into upflowing waters that are low in CO_2. Given "sufficient" vertical permeability and time, much or most of the injected CO_2 may eventually (after thousands of years) end up dissolved in the aqueous phase. Useful insights into the convective instability associated with dissolution of CO_2, and the space and time scales relevant for this process, have been obtained through analytical stability analysis (Ennis-King and Paterson, 2003). Numerical simulation of this process is extremely difficult due to spatial and temporal structures on multiple scales. Obtaining grid-converged solutions for the convection process requires spatial resolution down to a few centimeters, which limits the achievable spatial coverage to a small fraction of the CO_2 plume size (Lindeberg and Bergmo, 2003). A realistic representation of the mixing due to density-driven convection in large-scale 3-D models of CO_2 storage systems remains an open challenge.

Another mechanism that is of great practical interest and significance for long-term storage security is the trapping of CO_2 at the trailing edge of the plume. After CO_2 injection is terminated, fluid pressures near the injection well will decline, and CO_2 will tend to rise, allowing water to invade regions previously swept by CO_2. This is an imbibition process that may cause substantial amounts of free-phase CO_2 to become trapped (Kumar et al., 2004). Indeed, experience with aquifer gas storage projects indicates that trapped gas saturations during imbibition may reach as high as 50 % or more (Katz and Lee, 1990). The hysteretic effects coming into play as different portions of the CO_2 plume change from drainage to imbibition involve strong non-linearities and make numerical simulations considerably more difficult.

CO_2 dissolved in the aqueous phase may react with rock minerals. A number of divalent cations, such as Ca++, Mg++, and Fe++, form carbonates of low solubility that can sequester CO_2 in solid form. Experimental work and theoretical studies indicate that mineralization of CO_2 is a slow process at ambient temperature conditions, that may take hundreds to thousands of years for significant CO_2 uptake to occur. Long-term reactive chemical transport modeling for the Sleipner project has shown that buoyancy-driven flow that crosses chemically heterogeneous sand-shale sequences can give rise to distinct dissolution-precipitation cycles (Audigane et al., 2006). Some workers have proposed to store CO_2 in geothermal reservoirs, where due to the higher temperatures mineral sequestration would be a much faster process.

3. LEAKAGE BEHAVIOR

The amounts of CO_2 that would need to be stored to make a significant impact on atmospheric emissions of CO_2 are very large. The U.S. currently emits about 8 billion tonnes of CO_2 per year, approximately one fourth of total anthropogenic emissions globally. A single large coal-fired power plant with 1000 MW electric capacity generates approximately 30,000 tonnes of CO_2 per day, 10 million tonnes per year (Hitchon, 1996). If stored underground, the CO_2 generated over the lifetime of such a plant, of order 30 years, may occupy a large area of order 100 km^2 or more. Given the large areal extent expected for CO_2 plumes, it appears likely that geologic imperfections such as fractures or faults will be encountered in the caprock that would allow some CO_2 to migrate away from the primary storage reservoir. Additional leakage risks arise from pre-existing wells that may be improperly abandoned, or whose cement plugs may corrode under the attack from carbonic acid. A general consensus appears to be building in the technical community that leakage rates of order 0.1 % of stored inventory per year or less are acceptable for achieving substantial reductions in atmospheric emissions. However, there are other potential adverse environmental impacts from CO_2 leakage, such as acidification of groundwaters, or asphyxiation hazard at the land surface, that depend not only on overall CO_2 leakage rates but on spatial localization, temporal structure, and near-surface dispersion processes (Oldenburg and Unger, 2003, 2004).

3.1 Fractures and Faults.

We present simulations of CO_2 leakage for a schematic model of a fault zone (Fig. 1), that were obtained with our TOUGH2 general-purpose simulator (Pruess, 2004). The fault initially contains water in a normal geothermal gradient of 30 ˚C/km with a land surface temperature of 15 ˚C, in hydrostatic equilibrium. CO_2 discharge is initiated by injecting CO_2 at an overpressure of approximately 10 bar in a portion of the fault at 710 m depth. The numerical simulation includes two- and three-phase flow of aqueous, liquid CO_2, and gaseous CO_2 phases in the fault. The wall rocks are assumed impermeable, but conductive heat exchange with the fluids in the fault zone is important and is modeled with the semi-analytical technique of Vinsome and Westerveld (1980). Simulations were performed for different fault zone thickness; results for a thickness of 1 m are presented in Figs. 2 and 3.

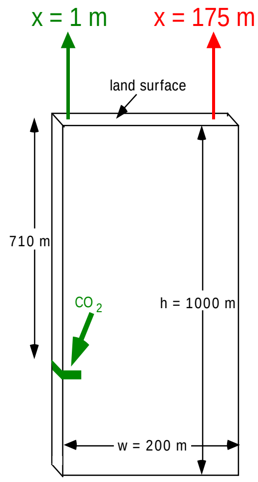

Figure 1. Schematic model of a fault zone (from Pruess, 2005b).

We find strong cooling due to the Joule-Thomson effect as rising CO_2 expands (Katz and Lee, 1990). Additional temperature decline occurs when liquid CO_2 boils into gas. Temperature and pressure conditions are drawn towards the critical point and along the saturation line (Fig. 2). The coupling between fluid flow and heat transfer gives rise to persistent cyclic behavior with increasing and decreasing leakage rates after a period of initial growth (Fig. 3). No non-monotonic behavior is observed when flow system temperatures are held constant at their initial values, indicating that heat transfer limitations are a key aspect of the non-monotonic discharge behavior. The portion of the fault volume in which fluids are in three-phase conditions (aqueous–liquid CO_2–gaseous CO_2) also goes through cyclic variations. The cycles are strongly correlated, with surface discharge reaching a maximum when three-phase volume has a minimum. This is explained by strong flow interference in three-phase regions, where effective permeabilities are low for all phases. The non-monotonic flow behavior is due to different time scales for multiphase flow in the fault, and heat transfer perpendicular to it. More information is available in (Pruess, 2005a, b).

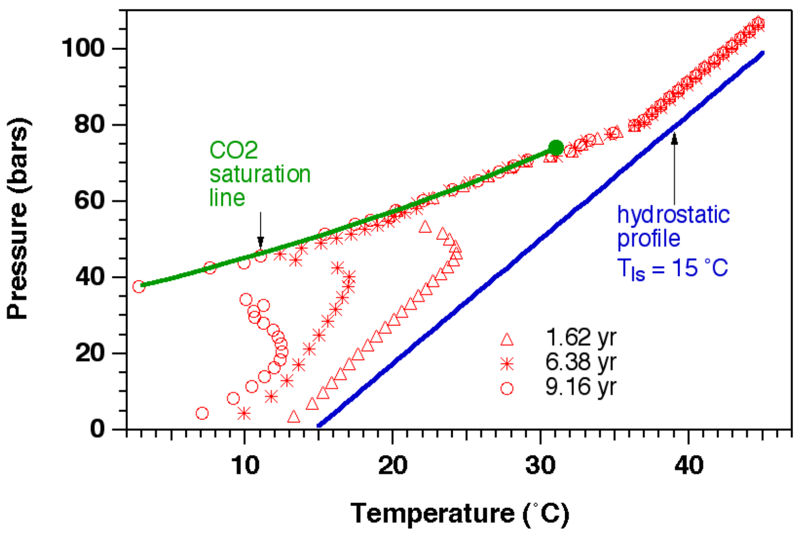

Figure 2. Pressure-temperature profiles in the left-most column of grid blocks at different times (from Pruess, 2005b).

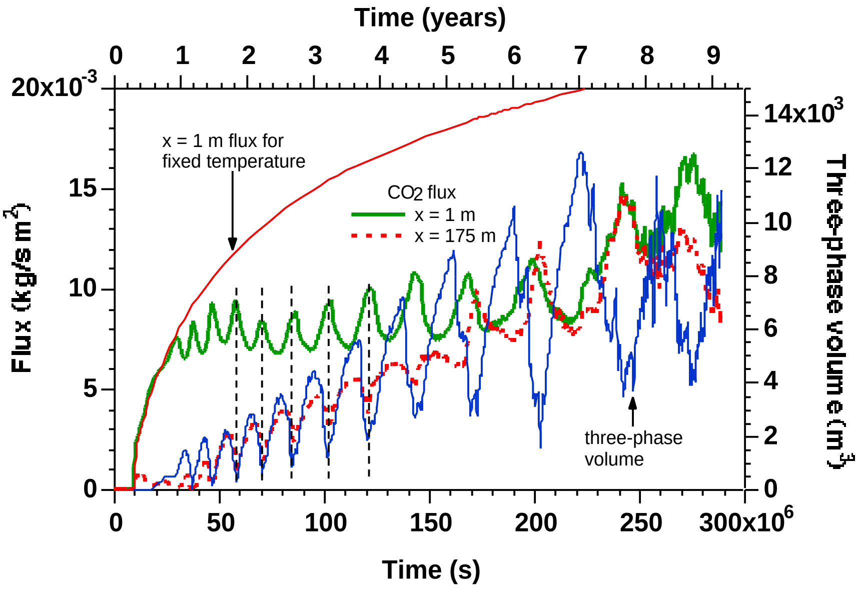

Figure 3. Temporal variation of CO_2 leakage fluxes at two different positions at the land surface. Total flow system volume with three-phase conditions is also shown. The vertical dashed lines are drawn to highlight the anticorrelation between leakage flux at x = 1 m on the one hand, and leakage flux at x = 175 m and three-phase volume on the other (from Pruess, 2005b).

3.2 Wellbores

Leakage along pre-existing wells that may be improperly plugged, or whose cements may corrode, constitutes perhaps the most likely scenario for loss of CO_2 from storage. Important work on quantifying leakage along wellbores has been performed by Celia and co-workers (Celia et al., 2004; Nordbotten et al., 2004). These authors used a stochastic approach to estimate leakage in an environment where the number of wells is too large, and their locations and flow properties too uncertain, to permit mechanistic modeling. A limitation of the approach of Celia et al. is that they conceptualize wellbore flow as Darcian. This will be satisfactory for wells that provide relatively "small" flow pathways, as e.g. cracks in cement plugs. However, flow behavior in open-hole sections, or along an open annulus, cannot be described by the Darcian model. There is concern that a few open-hole flow paths could contribute more to total CO_2 leakage than a multitude of slightly leaky wellbores, and approaches are needed to quantify and perhaps mitigate associated risks.

A more realistic description of wellbore flow can be achieved with the "drift flux" model (Zuber and Findlay, 1965). This model considers a two-phase liquid-gas mixture as a single effective fluid phase with volumetrically averaged properties, but accounts for slip between gas and liquid arising from non-uniform velocity profiles, as well as from buoyancy forces. We have incorporated this model into our TOUGH2 simulator, and present preliminary simulation results for the discharge of CO_2-laden water from a well (Fig. 4). A wellbore of 20 cm diameter extending to 250 m depth is held in a normal geothermal gradient of 30 ˚C/km and is subjected to inflow of water with 3.5 % CO_2 by weight, which is slightly below the CO_2 solubility limit for prevailing temperature and pressure conditions at 250 m depth. The well discharges to atmospheric conditions of (T, P) = (15 ˚C, 1.013 bar). Although the fluid feeding the well is just a single aqueous phase, two-phase conditions develop as rising fluid encounters lower pressures and CO_2 exsolves. Fig. 4 shows the simulated discharge behavior for a constant aqueous phase injection rate of 0.2 kg/s at the base of the well. Discharge rate is constant in the initial time period during which the pure water in the well is replaced by injected water with dissolved CO_2. Subsequent to this incubation period of approximately 22,000 s, the discharge goes through regular cyclic variations with a period of approximately 1,600 s, i.e., the well behaves as a geyser. The geysering is due to an interplay between different flow velocities for gas and liquid, and associated changes in the average density of the two-phase mixture as CO_2 gas exsolves. Discharge is enhanced by CO_2 gas coming out of solution, but the preferential upflow of CO_2 also depletes the fluid of gas. This produces alternating cycles of self-enhancement and self-limitation.

In natural systems CO_2 venting usually occurs in a diffuse manner, but there are "cold" geysers that produce quasi-periodic discharges of cold water-CO_2 mixtures. An example is the Crystal Geyser in Utah, whose discharges are considerably stronger, however, than in the simulation model presented here (Shipton et al., 2004). Field observations and numerical simulations demonstrate that geysering does not necessarily require thermal energy, but can be entirely powered by the energy released when high-pressure CO_2 expands.

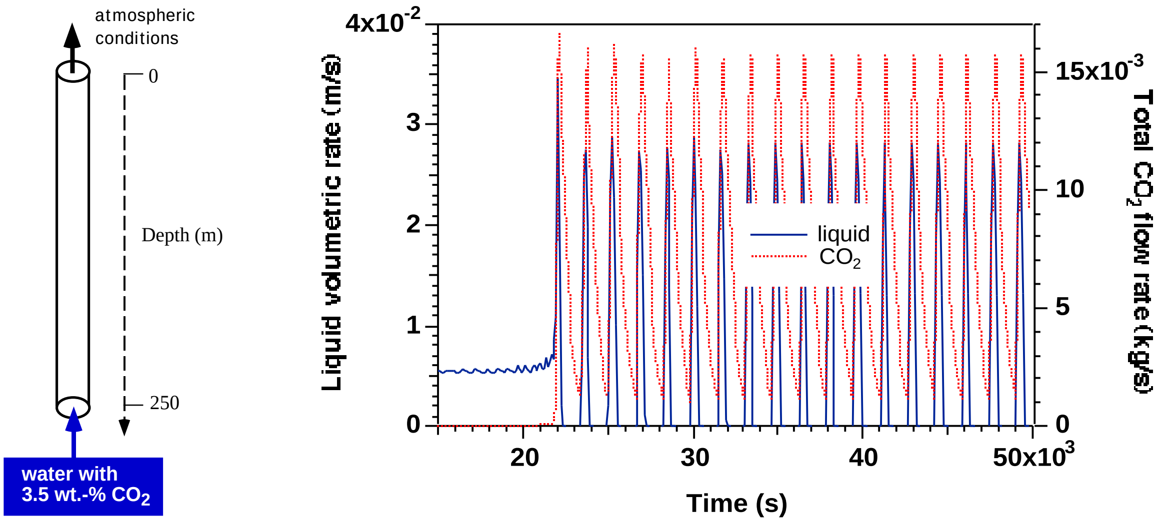

Figure 4. Discharge of a water-CO_2 mixture from a well. The wellbore model is shown on the left, while the right panel shows simulated discharge rates from the well.

4. CONCLUDING REMARKS

Geologic storage of CO_2 is a relatively new field of study that provides great needs and opportunities for numerical modeling. Much of the standard multi-phase flow simulation techniques developed for oil and gas reservoirs, and for vadose zone and near-surface processes are applicable, but new and subtle problems arise from (1) the great range of space and time scales that affect CO_2 behavior in the subsurface, (2) the importance of couplings between fluid flow and chemical and geomechanical processes, (3) coupling of processes at interfaces such as lithologic contacts and the ground surface, and (4) the complexities of near-critical behavior that becomes important when CO_2 leaks from the primary storage reservoir. The fate of CO_2 stored in saline formations is determined by an interplay between drainage and imbibition processes, gravity override, changes in effective stress with associated changes in the permeability of faults and fracture zones, CO_2 dissolution into the aqueous phase, buoyant convection of aqueous phase, and chemical interactions between aqueous CO_2 and host rock and caprock minerals. Thermal effects may also come into play. The long-term fate of stored CO_2 involves complex coupled processes on multiple scales, and current simulation approaches invariably entail fairly crude approximations, either with respect to spatial and temporal resolution, or with respect to coupled processes, or both.

At typical subsurface conditions of temperature and pressure, CO_2 has lower density and viscosity in comparison to aqueous fluids, which provides a potential for leakage to become self-enhancing. In the volcanological literature the possibility of a "pneumatic eruption" has been suggested, which presumably could be powered entirely by the mechanical energy of compressed gas, chiefly CO_2 (Giggenbach et al., 1991). However, we are not aware of any demonstration, through detailed process analysis or numerical simulation, that an eruption without substantial contribution from thermal energy is indeed possible. Our studies of leakage systems have demonstrated self-enhancement mechanisms, but have invariably revealed strong self-limiting features as well, that typically result in cyclic discharge behavior of CO_2. Self-limiting features include Joule-Thomson cooling during expansion of rising CO_2, and reduced fluid mobility due to interference between different phases (aqueous, liquid CO_2, gaseous CO_2). Whether or not a high-energy discharge of stored CO_2 is at all physically possible, and if so, under what conditions, is a practically important question that remains unanswered at the present time.

ACKNOWLEDGEMENT

Thanks are due to Curt Oldenburg and Christine Doughty for a careful review of the manuscript and the suggestions of improvements. This work was supported by the Zero Emission Research and Technology project (ZERT) under Contract No. DE-AC02-05CH11231 with the U.S. Department of Energy.

REFERENCES

- Arts, R., O. Eiken, A. Chadwick, P. Zweigel, B. van der Meer and G. Kirby. Seismic Monitoring at the Sleipner Underground CO2 Storage Site (North Sea), in: S.J. Baines and R.H. Worden (eds.), *Geological Storage of Carbon Dioxide*, Geological Society, London, Special Publications, Vol. 233, pp. 181–191, London, England, 2004.
- Audigane, P., I. Gaus, I. Czernichowski-Lauriol, K. Pruess and T. Xu. Two-Dimensional Reactive Transport Modeling of CO2 Injection in a Saline Aquifer at the Sleipner Site, submitted to *American Journal of Science*, 2006.
- Celia, M., S. Bachu, J.M. Nordbotten, S.E. Gasda and H.K. Dahle. Quantitative Estimation of CO2 Leakage from Geological Storage: Analytical Models, Numerical Models, and Data Needs, paper 228, presented at 7th International Conference on Greenhouse Gas Control Technologies. Vancouver, Canada. September 5-9, 2004.
- Ennis-King, J. and L. Paterson. Role of Convective Mixing in the Long-Term Storage of Carbon Dioxide in Deep Saline Formations, paper SPE-84344, presented at *Society of Petroleum Engineers Annual Fall Technical Conference and Exhibition,* Denver, CO, October 2003.
- Giggenbach, W.F., Y. Sano, and H.U. Schmincke. CO2-rich Gases from Lakes Nyos and Monoun, Cameroon; Lacher See, Germany; Dieng, Indonesia, and Mt. Gambier, Australia – Variations on a Common Theme, *J. Volcanol. Geotherm. Res.*, Vol. 45, pp. 311–323, 1991.
- Hitchon, B. (ed.). *Aquifer Disposal of Carbon Dioxide,* Geoscience Publishing, Ltd., Sherwood Park, Alberta, Canada, 1996.
- Katz, D.L. and R.L. Lee. *Natural Gas Engineering*, McGraw-Hill Publ. Comp., New York, NY 1990.
- Kumar, A., M. Noh, G.A. Pope, K. Sepehrnoori, S. Bryant and L.W. Lake. Reservoir Simulation of CO2 Storage in Deep Saline Aquifers, paper SPE-89343, presented at 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery, Tulsa, Oklahoma, U.S.A., 17–21 April 2004.
- Lindeberg, E. and P. Bergmo. The Long-Term Fate of CO2 Injected into an Aquifer, in: J. Gale and Y. Kaya (eds.), *Greenhouse Gas Control Technologies*, pp. 489–494, Elsevier Science, Ltd., Amsterdam, The Netherlands, 2003.

- Nordbotten, J.M., M.A. Celia and S. Bachu. Analytical Solutions for Leakage Rates through Abandoned Wells, *Water Resour. Res.*, Vol. 40, W04204, doi:10.1029/2003WR002997, 2004.
- Oldenburg, C.M. and A.J.A. Unger. On Leakage and Seepage from Geologic Carbon Sequestration Sites: Unsaturated Zone Attenuation, *Vadose Zone Journal*, Vol. 2, pp. 287–296, 2003.
- Oldenburg, C.M. and A.J.A. Unger. Coupled Vadose Zone and Atmospheric Surface-Layer Transport of CO2 from Geologic Carbon Sequestration Sites, *Vadose Zone Journal*, Vol. 3, pp. 848–857, 2004.
- Pruess, K. The TOUGH Codes—A Family of Simulation Tools for Multiphase Flow and Transport Processes in Permeable Media, *Vadose Zone J.*, Vol. 3, pp. 738–746, 2004.
- Pruess, K. Numerical Simulations Show Potential for Strong Non-isothermal Effects During Fluid Leakage from a Geologic Disposal Reservoir for CO_2, B. Faybishenko, P.A. Witherspoon and J. Gale (eds.), *Dynamics of Fluids and Transport in Fractured Rock,* Geophysical Monograph 162, pp. 81–89, American Geophysical Union, Washington, DC, 2005a.
- Pruess, K. Numerical Studies of Fluid Leakage from a Geologic Disposal Reservoir for CO2 Show Self-Limiting Feedback between Fluid Flow and Heat Transfer, *Geophys. Res. Lett.,* Vol. 32, No. 14, L14404, doi:10.1029/2005GL023250, July 2005b.
- Pruess, K., J. García, T. Kovscek, C. Oldenburg, J. Rutqvist, C. Steefel and T. Xu. Code Intercomparison Builds Confidence in Numerical Simulation Models for Geologic Disposal of CO2, *Energy*, Vol. 29, Issues 9-10, pp. 1431–1444, doi:10.1016/j.energy.2004.03.077, July-August 2004.
- Rutqvist, J. and C.F. Tsang. Coupled Hydromechanical Effects of CO2 Injection, in C.F. Tsang and J.A. Apps (editors), *Underground Injection Science and Technology*, Elsevier, pp. 649–679, 2005.
- Shipton, Z.K., J.P. Evans, D. Kirschner, P.T. Kolesar, A.P. Williams and J. Heath. Analysis of CO2 Leakage through 'Low-permeability' Faults from Natural Reservoirs in the Colorado Plateau, East-central Utah, in: S.J. Baines and R.H. Worden (eds.), *Geological Storage of Carbon Dioxide*, Geological Society, London, Special Publications, Vol. 233, pp. 43–58, London, England, 2004.
- Todesco, M., J. Rutqvist, G. Chiodini, K Pruess and C. Oldenburg. Modeling of Recent Volcanic Episodes at Phlegrean Fields (Italy): Geochemical Variations and Ground Deformation, *Geothermics*, Vol. 33, No. 4, pp. 531–547, August 2004.
- Vinsome, P.K.W. and J. Westerveld. A Simple Method for Predicting Cap and Base Rock Heat Losses in Thermal Reservoir Simulators, *J. Canadian Pet. Tech.*, 19 (3), 87–90, July-September 1980.
- Xu, T, J.A. Apps, and K. Pruess. Numerical Simulation of CO2 Disposal by Mineral Trapping in Deep Aquifers, *Applied Geochemistry,* Vol. 19, Issue 6, pp. 917–936, June 2004.
- Zuber, N. and J.A. Findlay. Average Volumetric Concentration in Two-Phase Flow Systems, *J. Heat Transfer, Trans. ASME,* Vol. 87, No. 4, pp. 453–468, 1965.