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Introduction

The amounts of CO_2 that would need to be injected into geologic storage reservoirs to achieve a significant reduction of atmospheric emissions are very large. A 1000 MWe coal-fired power plant emits approximately 30,000 tonnes of CO_2 per day, 10 Mt per year (Hitchon, 1996). When injected underground over a typical lifetime of 30 years of such a plant, the CO_2 plume may occupy a large area of order 100 km^2 or more, and fluid pressure increase in excess of 1 bar (corresponding to 10 m water head) may extend over an area of more than 2,500 km^2 (Pruess et al., 2003). The large areal extent expected for CO_2 plumes makes it likely that caprock imperfections will be encountered, such as fault zones or fractures, which may allow some CO_2 to escape from the primary storage reservoir. Under most subsurface conditions of temperature and pressure, CO_2 is buoyant relative to groundwaters. If (sub-)vertical pathways are available, CO_2 will tend to flow upward and, depending on geologic conditions, may eventually reach potable groundwater aquifers or even the land surface. Leakage of CO_2 could also occur along wellbores, including pre-existing and improperly abandoned wells, or wells drilled in connection with the CO_2 storage operations. The pressure increases accompanying CO_2 injection will give rise to changes in effective stress that could cause movement along faults, increasing permeability and potential for leakage.

Escape of CO_2 from a primary geologic storage reservoir and potential hazards associated with its discharge at the land surface raise a number of concerns, including (1) acidification of groundwater resources, (2) asphyxiation hazard when leaking CO_2 is discharged at the land surface, (3) increase in atmospheric concentrations of CO_2, and (4) damage from a high-energy, eruptive discharge (if such discharge is physically possible). In order to gain public acceptance for geologic storage as a viable technology for reducing atmospheric emissions of CO_2, it is necessary to address these issues and demonstrate that CO_2 can be injected and stored safely in geologic formations. This requires an understanding of the risks and hazards associated with geologic storage, and a demonstration that the risks are acceptably small or can be mitigated. Much work is currently underway to develop comprehensive approaches towards risk assessment from a systems analysis perspective, which in general requires a simplified description of physical and chemical processes (Maul et al., 2004, Espie, 2004; Wildenborg et al., 2004; Walton et al., 2004). This type of approach is very important, but needs to be complemented with development of an understanding of the physical and chemical processes associated with CO_2 storage and leakage (Evans et al., 2004).

Mechanisms and Issues for Loss of CO_2 from Storage

The nature of CO_2 leakage behavior will depend on properties of the geologic formations, primarily their permeability structure, and on the thermodynamic and transport properties of CO_2 as well as other fluids with which it may interact in the subsurface. At typical temperature and pressure conditions in the shallow crust (depth < 5 km), CO_2 is less dense than water, and therefore is buoyant in most subsurface environments. Smaller viscosity of CO_2 as compared to water implies higher flow rate for a given pressure gradient. In geologic formations that are suitable for CO_2 storage, CO_2 would normally be contained beneath a caprock of low absolute permeability with "significant" gas entry pressure. Upward migration of CO_2 will occur whenever appropriate (sub-) vertical permeability is available, and/or when the capillary entry pressure of the caprock is exceeded (Krooss et al., 2004; Zweigel et al., 2004; Gibson-Poole et al., 2004; Moreno et al., 2004). Three main potential pathways for CO_2 release have been recognized (Zweigel et al., 2004; Espie, 2004), (1) leakage through the caprock (Lindeberg and Bergmo, 2003; Krooss et al., 2004), (2) migration along sub-vertical faults or fracture zones (Pruess and García, 2002; Rutqvist and Tsang, 2002; Streit and Hillis, 2003, 2004), and (3) escape through boreholes (Celia et al., 2004; Bachu et al., 2004; Duguid et al., 2004).

It is obvious that leakage from geologic storage reservoirs for CO_2 must not exceed a "small" fraction of total inventory, in order not to defeat the main objective of geologic sequestration, namely, to keep greenhouse gases out of the atmosphere (Lindeberg, 2003; Hawkins, 2004). A general consensus appears to be building in the technical community that storage losses should not exceed 0.1 % of inventory per year in order to be acceptable (Pacala, 2003; Hepple and Benson, 2003; Ha-Duong and Keith, 2003). Additional concerns arise from environmental impacts of leaking CO_2 and the associated potential for adverse effects to health and safety. General probabilistic and systems-analysis approaches based on identifying FEP-scenarios (features, events, processes) are being used to evaluate risks associated with geologic storage of CO_2 (Maul et al., 2004, Espie, 2004; Wildenborg et al., 2004). This approach is similar to what has been used for nuclear waste repositories. In order to be useful and credible, such high-level risk analysis with FEP-based modeling approaches must rely on sound models for the underlying physical, chemical, and biological processes (Walton et al., 2004; Evans et al., 2004).

Limiting CO_2 injection pressure so as not to exceed the capillary entry threshold of the caprock may not be sufficient to ensure containment. In some subsurface environments, microbially-mediated conversion of CO_2 to methane may be possible. Such conversion may occur on an equimolar basis (generating one mole of methane for each mole of CO_2 consumed), and therefore would be accompanied by large pressure and/or volume increase. This is because the real gas compressibility factor Z is approximately twice as large for methane as for CO_2 at typical temperature and pressure conditions of interest for geologic storage of CO_2. A complete conversion of CO_2 to CH_4 would therefore be accompanied by a doubling of the pressure*volume product. The possibility of microbially-mediated pressure-volume increases in a storage reservoir of CO_2 appears not to have been previously recognized as an issue for storage integrity.

Sedimentary basins with previous oil and gas exploration and production are well characterized geologically, have considerable infrastructure in place, and constitute perhaps the most natural early targets for CO_2 storage. Such basins may have a large number of wells; e.g. there are more than 350,000 wells in the Alberta Basin, many of which are in poor or unknown conditions of cementing and abandonment (Celia et al., 2004). Leakage along pre-existing wells that may be improperly plugged, or whose cements may corrode (Duguid et al., 2004), 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. A few open-hole flow paths may 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.

After a discharge of CO_2 is initiated it may be subject to "self-enhancement," when along the discharge path water is replaced by buoyant and more mobile CO_2. As CO_2 migrates upwards and displaces aqueous phase along a sub-vertical flow path, fluid pressures may increase at shallower horizons because the weight of a column of CO_2 is less than the weight of a column of water that it replaces. CO_2 has larger compressibility than water, so that modest pressure reductions can cause a large volumetric expansion. Similarly, exsolution of CO_2 from an aqueous phase will be accompanied by volume expansion and reduction in average fluid density, with a potential for pressure decline and additional exsolution. Upflow of CO_2 will be impeded by phase interference between CO_2 and the aqueous phase. As CO_2 migrates upward, water saturations and phase interference will be reduced over time, increasing CO_2 flow rates, because water will be removed by (immiscible) displacement, as well as by vaporization into the flowing CO_2 stream.

Self-enhancement may also occur from geochemically and/or geomechanically coupled processes. Aqueous fluids contacted by migrating CO_2 would have low pH of typically 4-5, would be capable of dissolving a variety of caprock minerals, and thereby enhance the permeability of the CO_2 pathway. Pressure increases associated with CO_2 storage and leakage will reduce effective normal stress and may thereby induce movement of faults, leading to induced seismicity in addition to permeability enhancement.

Non-isothermal effects

Pressure decrease when CO_2 migrates upward may give rise to strong temperature effects. Fluid flow that involves significant decompression, while being fast enough to make heat exchange with bodies surrounding the fluid negligibly small, can be approximated as isenthalpic; i.e., during the process of fluid migration and expansion the specific enthalpy remains constant. The isenthalpic approximation is often applied to flows of gases or liquid-gas mixtures in wellbores (Katz and Lee, 1990). It is a very convenient tool, because it permits estimation of temperature drops in an extremely simple manner. The temperature change arising in decompression without heat transfer is known as the Joule-Thomson effect, and is quantified by the Joule-Thomson coefficient μ (Katz and Lee, 1990).

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = -\frac{\left(\partial h/\partial P\right)_T}{\left(\partial h/\partial T\right)_P} \tag{1}$$

where the subscripts h, T and P indicate that the various derivatives are taken at, respectively, constant specific enthalpy, constant temperature, and constant pressure. For ideal gases the Joule-Thomson coefficient is identically zero (no temperature effect upon expansion). For most real gases the coefficient is positive, so that isenthalpic expansion ($\Delta P < 0$) will give rise to cooling ($\Delta T < 0$).

A plot of isenthalps (lines of constant specific enthalpy) vs. temperature and pressure provides a convenient means for evaluating temperature effects during isenthalpic expansion. The slope of the isenthalps is just the inverse of the Joule-Thomson coefficient, and is positive for the temperature and pressure conditions of interest to geologic storage of CO_2 (Fig. 1). The lower panel of Fig. 1 also includes geothermal-hydrostatic profiles of temperature and pressure, corresponding to land surface temperatures of 5 and 15 ˚C, respectively, and a geothermal gradient of 30 ˚C per km that is typical for continental crust.

Suppose CO_2 is leaking from a geologic storage reservoir and accumulates in a secondary trap at about 300 m depth, where temperature and pressure conditions for 15 ˚C land surface temperature are approximately (T, P) ≈ (24 ˚C, 30 bar). Fig. 1 shows that the CO_2 accumulating in these (T, P)-conditions has a specific enthalpy of approximately 775 kJ/kg. Substantial cooling would take place if this CO_2 could rise to the land surface through an open wellbore, or through a highly permeable fracture zone. In fact, if this CO_2 would expand to atmospheric pressure with no heat transfer from the surroundings, its temperature would drop to approximately -15 ˚C! Of course, were such a discharge to happen the CO_2 flow would not in fact be entirely isenthalpic, as the expanding and cooling CO_2 would pick up heat from the surroundings of the pathway through which it would be migrating. However, the rate of such heat supply is rather limited, because geologic media generally have low thermal conductivity, and furthermore, the rate of heat transfer to the rising CO_2 would rapidly decrease with time as the surrounding media are cooled from the CO_2. A sustained outflow of CO_2 would quickly approximate the idealization of an isenthalpic expansion. If the CO_2 would be accumulating near 540 m depth, corresponding to (T, P) ≈ (31 ˚C, 54 bar), its specific enthalpy

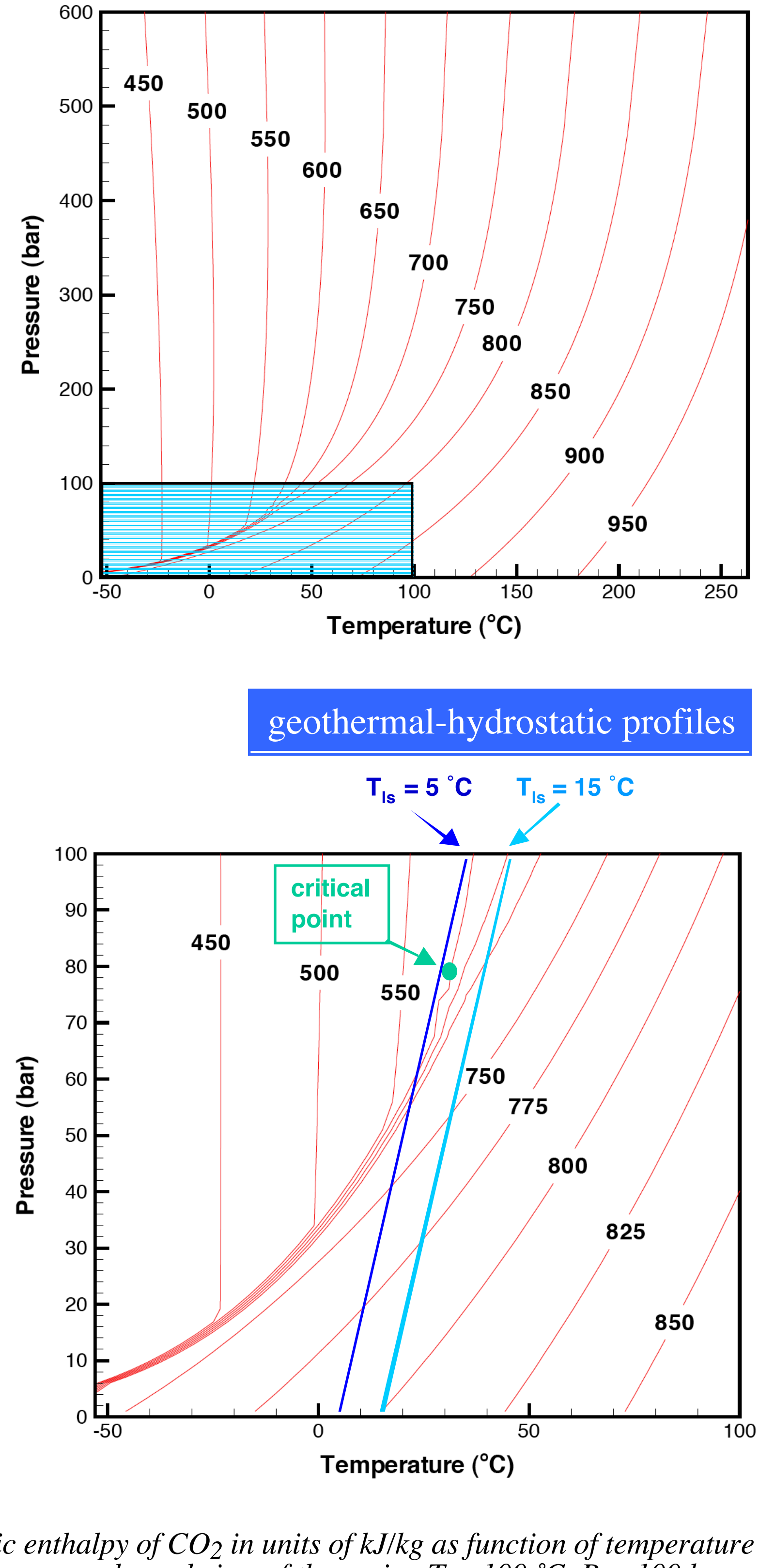

Figure 1. Specific enthalpy of CO_2 in units of kJ/kg as function of temperature and pressure. The lower panel gives an enlarged view of the region $T < 100$ °C, $P < 100$ bar, and includes two geothermal-hydrostatic profiles for normal continental crust. The critical point of CO_2 at $T = 31.04$ °C, $P = 73.82$ bar, is also shown.

would be 750 kJ/kg, and isenthalpic expansion to atmospheric pressure would cause temperatures to drop to approximately - 47 ˚C (lower panel of Fig. 1). Cooling effects would be even stronger if land surface temperature were lower. These concepts are confirmed by observations of CO_2 breakthrough at production wells in CO_2 flooding projects for enhanced oil recovery. Substantial CO_2 release events have been reported, in which flowing wellhead temperatures declined to near the triple point of CO2 (-56.35 ˚C, 5.11 bar), so that CO_2 was ejected as solid particles ("dry ice;" Skinner, 2003).

The strong cooling effects expected for rising CO_2 provide self-limiting feedback to the discharge: as the density of CO_2 increases when temperatures decline, the buoyancy force pushing the CO_2 upward is reduced.

Numerical Simulations

Here we briefly summarize results of numerical simulation studies for a variety of leakage and discharge scenarios that have demonstrated self-enhancement. However, all discharge scenarios we have investigated so far have shown self-limiting features as well. One strong self-limiting feature is provided by the temperature decline that occurs when high-pressure CO_2 is decompressed.

CO_2 Migration along a Fault

Fig. 2 shows a schematic model of a fault zone, along with simulation results for CO_2 discharge through this fault. 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, as well as conductive heat transfer with the wall rocks that are assumed impermeable (Pruess, 2005a, b).

We find strong cooling due to the Joule-Thomson effect (Katz and Lee, 1990) as rising CO_2 expands (Pruess, 2004). Additional temperature decline occurs when liquid CO_2 boils into gas. 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. 2). 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; surface discharge reaches 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. There is an interplay between self-enhancing and self-limiting features. The non-monotonic flow behavior is due to different time scales for multiphase flow in the fault, and heat transfer perpendicular to it.

Discharge of a Water/CO_2 Mixture from a Well

We present preliminary simulation results for the discharge of CO_2-laden water from a well (Fig. 3). A wellbore of 20 cm diameter extending to 250 m depth 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. In order to model two-phase flow in the wellbore, we incorporated the "drift flux" model of Zuber and Findlay (1965) into our TOUGH2 simulator. This model considers the 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. Fig. 3 shows the simulated

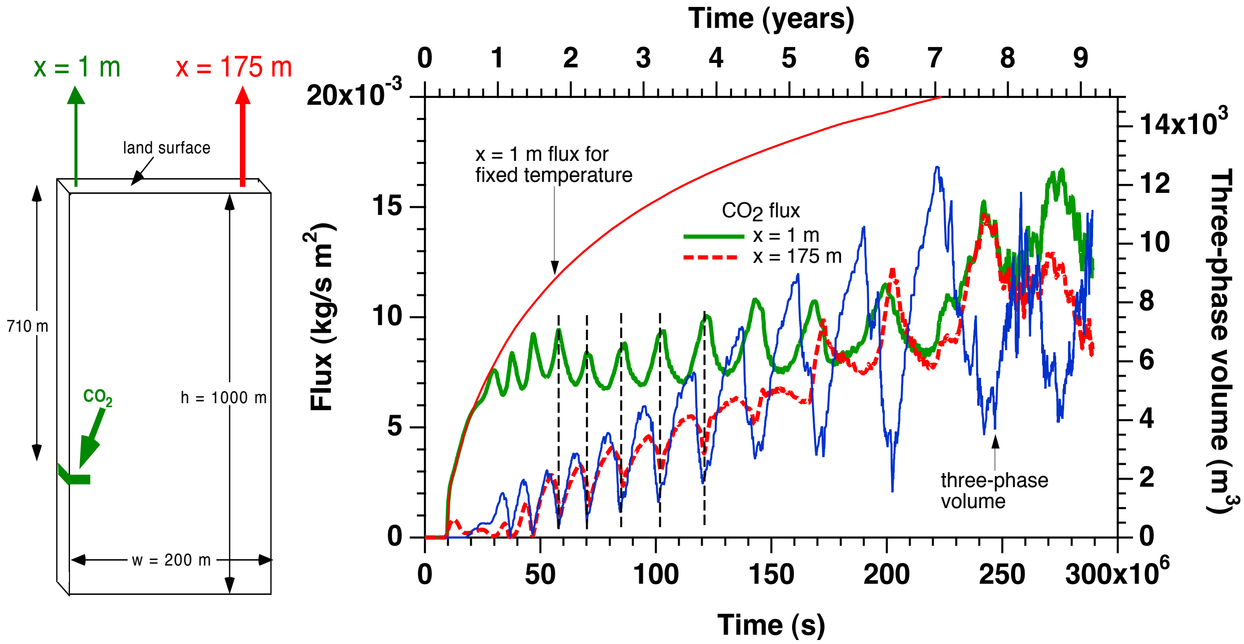

Figure 2. CO_2 leakage along a fault zone (Pruess, 2005b). A schematic model of a fault zone is shown on the left. The right panel gives temporal variation of CO_2 leakage fluxes at two different positions at the land surface. Total flow system volume with three-phase conditions is also shown. The vertical 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.

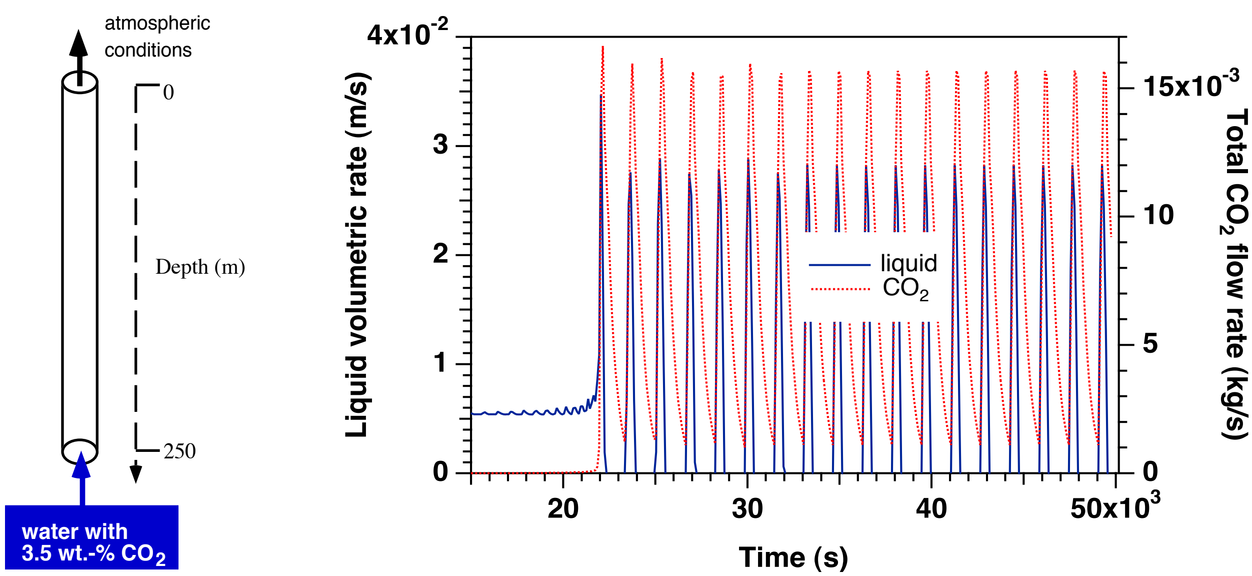

Figure 3. Discharge of a water-CO_2 mixture from a well. The wellbore model is shown on the left, while the right panel shows simulated discharge rates from the well.

discharge behavior for a constant aqueous phase injection rate of 0.2 kg/s applied 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, reducing and eventually removing the driving force for enhanced discharge. 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 are entirely powered by the energy released when high-pressure CO_2 expands. An example is the Crystal Geyser in Utah, whose discharges are considerably stronger than in the simulation model presented here (Shipton et al., 2004).

The current status of our leakage studies is that different scenarios have been investigated that would appear to have a potential for a self-enhancing, high-energy discharge; yet none of them has come close to generating an eruptive release. This seems to suggest that a CO_2 eruption is unlikely, but it certainly does not prove that an eruption is not possible.

"Pneumatic" Eruption?

The mechanical energy of compression accumulated in a CO_2 storage reservoir is very large. A coal fired plant of 1,000 MW electric power capacity generates on the order of 30,000 tonnes of CO_2 per day, approximately 10 million tonnes per year (Hitchon, 1996). The compression power (energy per second) required to store this CO_2 at representative *in situ* conditions at 1,000 m depth ($P \approx 100$ bar, $T \approx 36$ ˚C, with *in situ* density of approximately 700 kg/m^3), can be estimated as $N = dE/dt = PdV/dt \approx (P/\rho)dM/dt \approx (10^7 \text{ Pa}/700 \text{ kg m}^{-3})*3*10^7 \text{ kg day}^{-1}/(86400 \text{ s day}^{-1}) \approx 5$ MW. The total compressive energy stored during a typical anticipated operating life of a CO_2 disposal project of 30 years then amounts to approximately 4.74×10^{15} J, which is equivalent to the energy content of 1.1 megatonnes of TNT (1 megatonne of TNT corresponds to 4.184×10^{15} J; Wikipedia, 2004). For another perspective on this number, we note that a large prehistoric hydrothermal eruption at Rotokawa, New Zealand, which ejected approximately 10^7 m^3 of material and generated a crater of more than 250 m diameter, has been estimated as having released an energy of 10^{14} J (Browne and Lawless, 2001), equivalent to 23.9 kilotonnes of TNT, similar to the atomic bomb that was dropped on Hiroshima. It is not known whether or not it would be physically possible for a significant fraction of the compressive energy stored in a CO_2 plume to be released in localized fashion over a short period of time. However, if such release were possible it could generate very serious consequences.

There is an extensive body of work on degassing of CO_2 in volcanic areas, which can help to define conceptual models for CO_2 leakage systems (Barnes et al., 1978; Sorey et al., 1998; Benson et al., 2002; Chiodini et al., 2004; Streit and Watson, 2004; Evans et al., 2002). The ultimate source of these discharges is deep-seated magma that contains dissolved non-condensible gases and volatiles. Discharges are usually primarily powered by thermal energy, which makes them of limited relevance in connection with potential leakage from man-made geologic storage reservoirs of CO_2. However, in the volcanological literature the possibility of "pneumatic eruptions" has been suggested (Giggenbach, 1991). Whereas hydrothermal (or "phreatic") eruptions are powered by the thermal energy of hot liquid water that is flashing into steam, pneumatic eruptions are presumed to be primarily driven by the mechanical energy contained in accumulations of compressed gas, chiefly CO_2. Gas-powered eruptions have been proposed as being instrumental in maar formation (Chivas et al., 1987), as well as having caused the 1979 catastrophic gas release at the Dieng Volcanic Complex, Indonesia, that caused 149 fatalities (Giggenbach et al., 1991). It is rather obvious that the presence of CO_2 can contribute to and enhance a hydrothermal eruption process (Chivas et al., 1987). Indeed, when CO_2 is present less pressure reduction is needed for a gas phase to evolve, and large volume expansion and gas saturations with increased fluid mobility can be more easily attained. However, although there are numerous references to pneumatic eruptions in the volcanological literature (Fischer et al., 1996; Browne and Lawless, 2001; Benson et al., 2002), we are not aware of a definitive proof or demonstration, either through field evidence or numerical simulation, that an eruptive release can be powered solely by the mechanical energy stored in an accumulation of non-condensible gas, without substantial contributions from thermal energy.

An eruptive discharge event from a subsurface accumulation of CO_2 at ambient temperature may have extremeley small probability, or may be altogether impossible. In risk analysis it is common to think of risk as the product of probability of occurrence of an event and its potential consequences (Bowden and Rigg, 2004). Eruptive discharge of CO_2 from geologic storage, if it is at all possible, may be a "low probability–large consequence" type of event. Although such events may not qualify as "high risk" in formal risk analysis, experience has shown that the public is extremely reluctant to accept technologies that have a potential for accidents with large consequences, even if the probability of such accidents may be exceedingly low. Examples of this are provided by nuclear power installations and proposed geologic repositories of nuclear waste. For these reasons we believe that a thorough evaluation of the possibility of high-energy discharges of CO_2 from geologic storage reservoirs is essential for demonstrating technical feasibility and achieving public acceptance of the technology.

Field observations of CO_2 discharges combined with numerical simulation can help clarify flow mechanisms. It would seem especially fruitful to investigate more thoroughly alleged pneumatic eruption events in volcanic areas.

Concluding Remarks

CO_2 leakage from man-made storage reservoirs is possible through a variety of mechanisms. A credible analysis of associated risks must be based on a sound understanding of the underlying physical and chemical processes, and on an adequate characterization of potential leakage pathways. Naturally leaky CO_2 reservoirs provide ideal settings for studying the behavior of CO_2 in the subsurface over the large space and time scales required for CO_2 storage. Studies of natural CO_2 discharges in the Colorado Plateau region have documented extensive mineral deposition, yet many CO_2 vents and springs do not self-seal, and persist for thousands of years (Evans et al., 2004). These observations are consistent with recent findings from reactive chemical transport modeling (Gherardi et al., 2005).

Although leakage from CO_2 storage reservoirs would most likely occur in diffuse manner at small rates, an important issue is whether or not it may be possible for CO_2 to discharge in the form of a "pneumatic" eruption. Current evidence suggests that it is not possible to generate a high-energy discharge that would be powered solely by the mechanical energy of compressed gas, without a substantial contribution from thermal energy, but nothing approaching a proof is available. Studies of the physics and chemistry of CO_2 leakage behavior to date have been quite limited. Popular news media have made reference to the lethal CO_2 bursts at Lakes Monoun (Sigurdsson et al., 1987) and Nyos (Tazieff, 1991) to suggest that geologic storage of CO_2 may be dangerous. The mechanisms that released major CO_2 accumulations at these lakes cannot be replicated in subsurface storage reservoirs; yet concerns raised by these eruptions may seriously impede public acceptance of geologic storage of CO_2. Focused research efforts are needed to provide a rational basis for assessing risks associated with geologic storage of CO_2, and to gain assurance that a high-energy, eruptive discharge is not possible.

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