ORIGINAL ARTICLE

On CO₂ fluid flow and heat transfer behavior in the subsurface, following leakage from a geologic storage reservoir

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Abstract Geologic storage of CO_2 is expected to produce plumes of large areal extent, and some leakage may occur along fractures, fault zones, or improperly plugged pre-existing wellbores. A review of physical and chemical processes accompanying leakage suggests a potential for self-enhancement. The numerical simulations presented here confirm this expectation, but reveal self-limiting features as well. It seems unlikely that CO_2 leakage could trigger a high-energy run-away discharge, a so-called "pneumatic eruption," but present understanding is insufficient to rule out this possibility. The most promising avenue for increasing understanding of CO_2 leakage behavior is the study of natural analogues.

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 1,000 MWe coal-fired power plant emits ~30,000 tonnes of CO_2 per day, 10 Mtonnes 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 km² 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 km² (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.

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, which would reduce the efficiency of sequestration, and (4) damage from a high-energy, eruptive discharge (if such discharge is physically possible). For the purposes of this paper, we define "eruption" as a release or discharge of mass and energy that is localized in space and time; i.e., a flow event that occurs over a specific, generally brief period of time and in a specific location, as opposed to being spread out over a large area and a large time period.

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 concerns related to leakage from the primary storage reservoir 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

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demonstration that the risks are acceptably small or can be mitigated. General probabilistic and systems-analysis approaches based on identifying FEP-scenarios (features, events, and 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).

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, transport, and chemical 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. 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 Garcia 2002; Rutqvist and Tsang 2002, 2005; 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.

Limiting CO_2 injection pressure so as not to exceed the capillary entry threshold of the caprock may not be suffi-

cient to ensure containment. In some subsurface environments, microbially mediated conversion of CO_2 to methane may be possible (Hoth et al. 2005). 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 (Lemmon et al. 2005). 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 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. This paper presents numerical simulation of water-CO_2 discharges from a wellbore that use the "drift flux model" (Zuber and Findlay 1965) to properly represent the main physical mechanisms for two-phase flow in pipes.

CO_2 has a number of physical and chemical properties that suggest that a discharge, once initiated, may be subject to self-enhancement. CO_2 has lower density than water and would be subject to increasing buoyancy force when along a discharge path water is replaced by buoyant and more mobile CO_2. The lower viscosity of CO_2 as compared to water means that large increases in volumetric rates of fluid

flow can occur when CO_2 replaces water. 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 much 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, additional exsolution, and increased buoyancy force. 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 (Gherardi et al. 2005). 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 (Rutqvist and Tsang 2005).

As will be seen below, leakage of CO_2 toward the land surface is subject to significant self-limiting features as well.

Non-isothermal effects

Pressure decrease and associated volume expansion 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 changes 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).

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

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 CO_2 as 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) versus 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
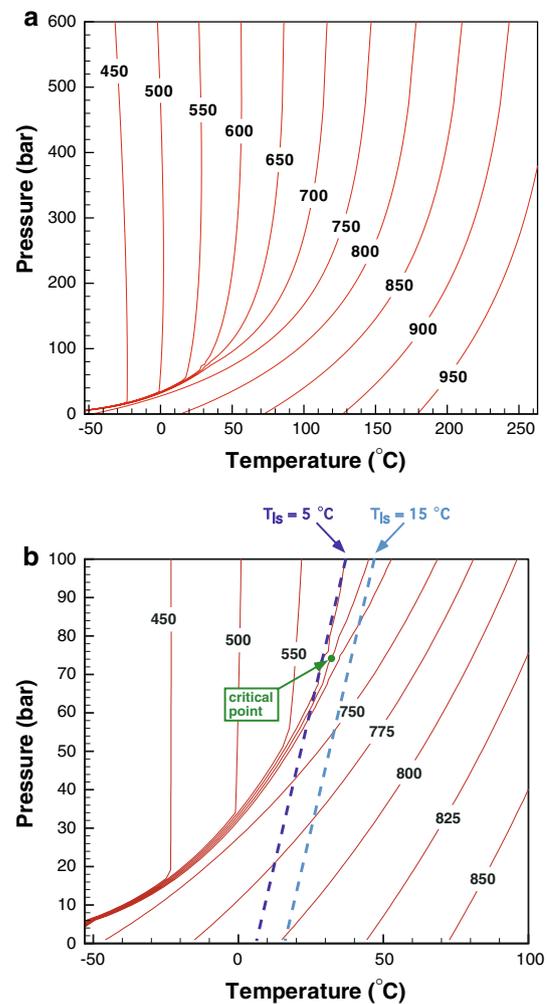

Fig. 1 Specific enthalpy of CO_2 in units of kJ/kg as function of temperature and pressure. The lower panel gives an enlarged view of the region $T < 100°C$, $P < 100$ bar, and includes two geothermal-hydrostatic profiles for normal continental crust. The critical point of CO_2 at $T = 31.04°C$, $P =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

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 $(T, P) \approx (24°C, 30 bar)$. Figure 1 shows that the CO_2 accumulating in these (T, P)-conditions has a specific enthalpy of ~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 –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 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 CO_2 (–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

The manner in which CO_2 would leak from a deep geologic disposal reservoir and migrate toward the land surface is determined by an interplay of physical and chemical properties of CO_2 with subsurface formations. Realistic modeling of CO_2 migration requires a detailed representation of the permeability and porosity structure of the pathways through which the leakage might occur. This section briefly summarizes numerical simulation studies

that were undertaken with a more limited objective, namely, to gain an understanding of the fluid flow and heat transfer processes that would accompany CO_2 migration away from the primary storage reservoir, toward shallow depths and ultimately to the land surface. All simulations were carried out with the general-purpose multiphase flow simulator TOUGH2, using specialized fluid property modules that accurately represent thermophysical properties of CO_2-brine mixtures (Pruess and Garcia 2002; Pruess 2004, 2005c).

CO_2 migration along a fault

CO_2 migration is simulated for a schematic model of a fault zone as shown in Fig. 2. 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. The migration pathway from the primary storage reservoir to the fault is not modeled; instead, CO_2 discharge is initiated simply by injecting CO_2 at a constant pressure of 80 bar (~10 bar above hydrostatic) in a portion of the fault at 710 m depth. The numerical simulation includes CO_2 dissolution into and exsolution from the aqueous phase,
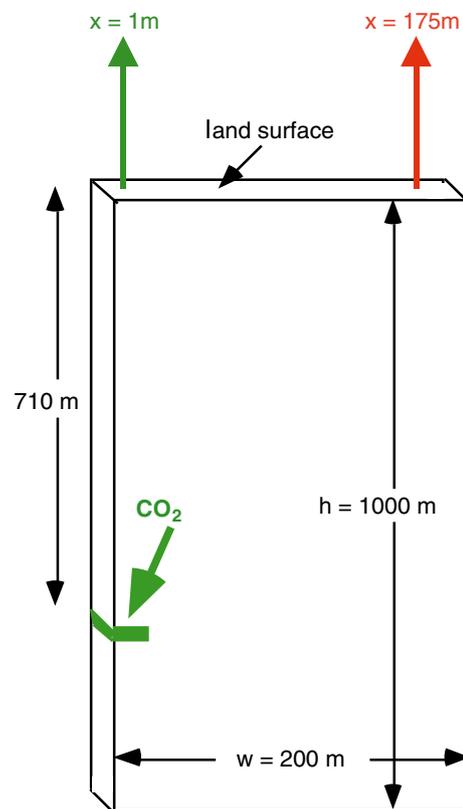
Fig. 2 Schematic of idealized vertical fault zone for modeling CO_2 leakage. Land surface points at 1 and 175 m distance from the left boundary are used to monitor leakage fluxes

transitions from super- to sub-critical conditions, phase change between liquid and gaseous CO_2, two- and three-phase flow of aqueous phase and liquid and gaseous CO_2 phases under viscous, gravity, and capillary forces, and conductive heat exchange with the wall rocks that are assumed impermeable (Pruess 2005a, b).

Strong cooling arises due to the Joule–Thomson effect (Katz and Lee 1990) as rising CO_2 expands (Pruess 2004), driving temperatures below the critical point. Additional temperature decline occurs when liquid CO_2 boils into gas. Temperatures reach a minimum above the injection point near the top of the three-phase zone, where boiling effects and associated heat losses are strongest (Fig. 3). Figure 4
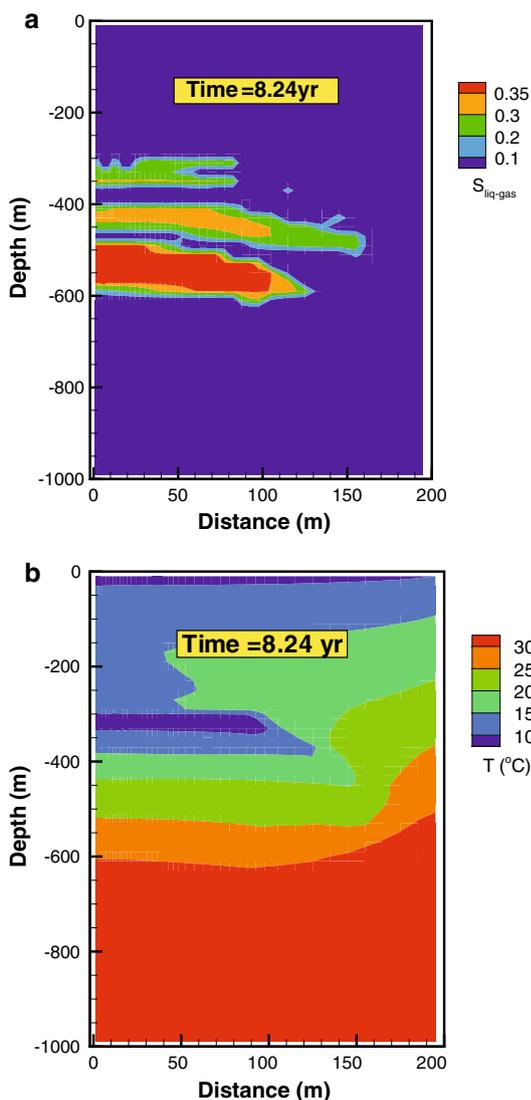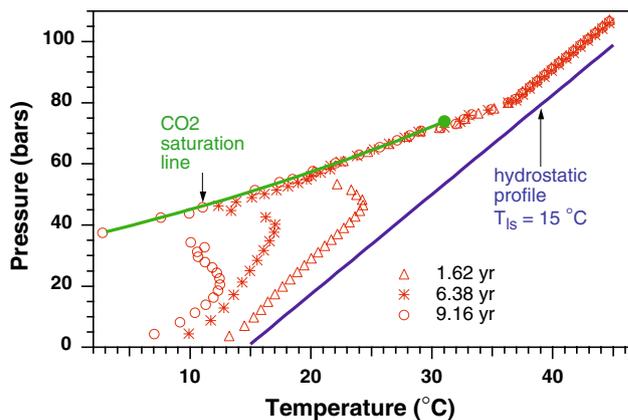

Fig. 4 Pressure–temperature profiles in the leftmost column of grid blocks at different times

shows that thermodynamic conditions get drawn toward the critical point and then along the CO_2 saturation line (Pruess 2005a). Over time, temperatures at the boiling front decline to low values (Fig. 4), and for the conditions specified in this simulation would eventually reach the freezing point of water, as well as conditions where CO_2-hydrates may form. The simulator used here currently has no provisions to deal with phase transitions to water ice and hydrates, so that the simulation must be stopped before such transitions would occur. It seems likely that evolution of solid (ice and/or hydrate) phases would tend to reduce or disperse leakage.

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. 5). 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
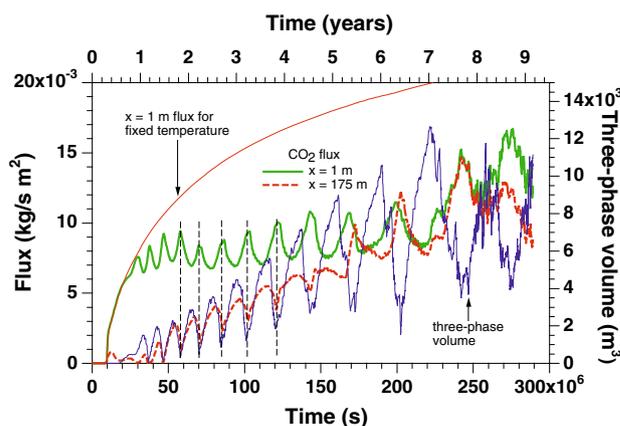

Fig. 3 Extent of three-phase conditions (**a**) and temperatures throughout the fault zone (**b**) after 8.24 years. The parameter $S_{liq\text{–}gas}$ (where saturation S is the volume fraction of a fluid phase) is defined as $\sqrt{S_{liq} \times S_{gas}}$, which is non-zero only for three-phase conditions

Fig. 5 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

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 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 (Pruess 2005b).

Discharge of a water/CO_2 mixture from a well

This section presents simulation results for the discharge of CO_2-laden water from a well (Fig. 6). 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 $(T, P) = (15°C, 1.013 \text{ bar})$.

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, the "drift flux" model (DFM) of Zuber and Findlay (1965) was incorporated into the 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. Following Shi et al. (2005), the average gas phase flow velocity in the DFM is written as

$$V_g = C_0 V_m + V_d, \tag{2}$$

where V_m is the volumetric flux of the two-phase mixture and C_0 is an empirical parameter typically of order 1.2. The volumetric flux V_m has units of $\text{m}^3/(\text{m}^2 \text{ s}) = \text{m/s}$, and is identical to the (average) velocity of the two-phase mixture. C_0 accounts for the fact that gas concentrations tend to be highest near the center of the pipe, where the mixture velocity is largest. V_d describes the drift of gas relative to the liquid due to buoyancy, and is written by Shi et al. (2005) as

$$V_d = \frac{(1 - C_0 S_g) C_0 V_c K_u}{C_0 S_g \sqrt{\rho_g / \rho_l} + 1 - C_0 S_g}. \tag{3}$$

In Eq. 3, the volumetric fraction of gas was denoted with the same symbol S_g as is commonly used for flows in
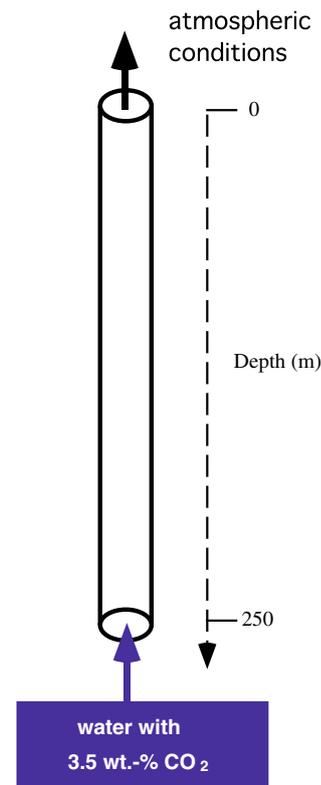

Fig. 6 Schematic of a wellbore that is discharging a CO_2-water mixture

porous media. V_c is the "characteristic velocity," a measure of the velocity of bubble rise in a liquid column, and is given by

$$V_c = \left[\frac{\sigma g (\rho_l - \rho_g)}{\rho_l^2} \right]^{1/4}, \tag{4}$$

where σ is the surface tension. ρ_g and ρ_l are gas and liquid densities, respectively, and K_u is the "critical Kutateladze number," which is a function of pipe diameter and density difference between liquid and gas (Shi et al. 2005). The volumetric flux of the gas–liquid mixture can be written as

$$V_m = S_g V_g + (1 - S_g) V_l, \tag{5}$$

where V_l is the average liquid velocity. Using Eq. 2 in (5), V_l can be written as

$$V_l = \left(\frac{1 - S_g C_0}{1 - S_g} \right) V_m - \left(\frac{S_g}{1 - S_g} \right) V_d. \tag{6}$$

Assuming a constant aqueous phase injection rate of 0.2 kg/s at the base of the well, we obtain the discharge behavior shown in Fig. 7. Discharge rate is constant in the initial time period during which the pure water in the well
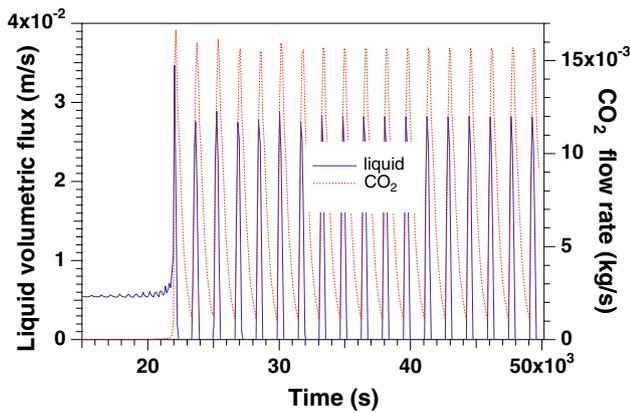
Fig. 7 Simulated discharge behavior of a well

is replaced by injected water with dissolved CO_2. Subsequent to this incubation period of ~22,000 s, the discharge goes through regular cyclic variations with a period of ~1,600 s, i.e., the well behaves as a geyser (Lu 2004). 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 up-flow 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).

In addition to the examples presented in this paper we have investigated a variety of leakage scenarios that would appear to have a potential for a self-enhancing, high-energy discharge. All of them have shown self-limiting features as well, and none has come close to generating an eruptive release. This seems to suggest that a CO_2 eruption is unlikely, but it 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, ~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 ~700 kg/m³), can be estimated as $N =$

$$dE/dt = PdV/dt \approx (P/\rho)dM/dt \approx \left(10^7 \text{ Pa}/700 \text{ kg m}^{-3}\right) \times 3 \times 10^7 \text{ kg day}^{-1}/\left(86,400 \text{ s day}^{-1}\right) \approx 5 \text{ MW.}$$ The total compressive energy stored during a typical anticipated operating life of a CO_2 disposal project of 30 years then amounts to ~4.74×10^{15} J, which is equivalent to the energy content of 1.1 Mtonnes of TNT (1 Mtonne of TNT corresponds to 4.184×10^{15} J; Wikipedia 2004). For another perspective on this number, consider a large prehistoric hydrothermal eruption at Rotokawa, New Zealand, which ejected ~10^7 m³ of material and generated a crater of more than 250 m diameter. The energy released in this eruption was estimated as 10^{14} J (Browne and Lawless 2001), equivalent to 23.9 ktonnes 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. This topic warrants further study because such release, if it were possible, 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. Eruptive discharges are 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. In the volcanological literature the possibility of "pneumatic eruptions" has been suggested (Giggenbach et al. 1991; Fischer et al. 1996; Browne and Lawless 2001; Benson et al. 2002). 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). Non-condensible gases, chiefly CO_2, are known to have played an ancillary role in many hydrothermal eruptions (Chivas et al. 1987; Browne and Lawless 2001), and it is rather obvious that the presence of CO_2 can contribute to and enhance a hydrothermal eruption process. 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. There appears to be no direct evidence, however, either from field observations or numerical simulation, that an eruptive release from a

subsurface storage reservoir can be powered solely by the mechanical energy stored in an accumulation of compressed gas, without substantial contributions from thermal energy.

An eruptive discharge event from a subsurface accumulation of CO_2 at ambient temperature may have extremely small probability, or may be altogether impossible. In risk analysis it is common to think of risk (R) as the product of probability of occurrence of an event (P) and its potential consequences (C), $R = P \times C$ (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. These experiences suggest that a thorough evaluation of the possibility of high-energy discharges of CO_2 from geologic storage reservoirs is important 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. Modeling studies presented here for schematic, idealized leakage scenarios have confirmed a potential for self-

enhancement of CO_2 discharges, but they have invariably shown self-limiting features as well. Due to the length of the flow pathway, and due to the large magnitude of adiabatic cooling when CO_2 depressurizes as it migrates upwards, leakage of CO_2 from a deep geologic reservoir as such does not appear capable of producing a concentrated high-energy discharge at the land surface. Accumulation of leaking CO_2 in a secondary "parasitic" storage reservoir closer to the land surface may be more conducive to creating conditions for a rapid, eruptive release.

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. However, studies of the physics and chemistry of CO_2 leakage behavior to date have been quite limited, and the possibility of a high-energy discharge has not been ruled out. 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 (Wassink 2005). 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, to identify favorable as well as unfavorable geologic conditions, and to gain assurance that a high-energy, eruptive discharge is not possible.

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