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Migration Mechanisms and Potential Impacts of CO₂ Leakage and Seepage

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ABSTRACT

Carbon dioxide injected into deep geological formations will generally be in the supercritical phase and tend to rise buoyantly through native brines subject to the limitations of the low permeability of geologic formations through which it flows. Assuming conductive pathways such as abandoned wells and permeable faults exist to allow injected CO₂ to migrate from the deep subsurface to shallower regions, leaking CO₂ may intrude into shallower aquifers containing potable water, accumulate in the vadose zone, seep into basements and buildings, pond in low-lying areas, and bubble into surface water. There are circumstances under which the health, safety, and environmental impacts of the migration of CO₂ into these regions are serious concerns. Nevertheless, it must be kept in mind that CO₂ is naturally abundant and relatively benign. Even in the unlikely event that significant leakage fluxes of CO₂ were to occur, natural or engineered dispersion and mixing processes can mitigate the potential health, safety, and environmental impacts associated with CO₂ leakage and seepage discussed here. Although any leakage and seepage may be considered unacceptable for a variety of reasons by a variety of people, a limited and small amount of CO₂ leakage and seepage appears to be acceptable from the perspective of health, safety, and environmental impact.

1. INTRODUCTION

The injection of carbon dioxide (CO₂) through wells into deep geologic formations creates driving forces that tend to cause CO₂ to migrate away from the injection point. During injection, these driving forces are dominated by the high pressure gradients associated with injection. At later times following injection, or at large distances from the injection well, the main driving force for CO₂ migration will be the upward buoyancy force that arises when CO₂ is injected into denser native brine. When upward flow is restricted by low-permeability formations, CO₂ will tend to accumulate and spread laterally on the underside of the sealing formations. Regardless of the driving force, the tendency for CO₂ to migrate laterally and upwards in the subsurface is a fundamental aspect of deep CO₂ injection.

Subsurface CO₂ flow will be limited and strongly controlled by the properties of the geologic formations, predominantly their effective permeability and structure. It is the presence of thick and laterally extensive low-permeability formations and large-scale geologic trapping structures that act as seals to upward migration that make geologic storage of CO₂ attractive. The understanding of the deep subsurface generated through more than 100 years of experience with groundwater and hydrocarbon (oil and gas) extraction and exploration suggests that CO₂ can be injected into deep subsurface geologic traps where it should remain indefinitely. Nevertheless, imperfect knowledge of the integrity of sealing formations and uncertainty regarding the presence and behavior of faults and abandoned wells that penetrate the formations into which CO₂ will be injected

motivate research into what could happen in the unlikely event that significant quantities of CO₂ were to leak away from the intended storage formation, migrate upwards to the near-surface environment, and eventually seep out of the ground. Questions raised by the possibility of leakage include (1) what are the potential impacts of CO₂ on water resources in aquifers, and (2) what are the potential impacts of CO₂ in the near-surface environment in both the subsurface and above-ground regions?

A sketch of some potential processes that could result from CO₂ leakage relevant to health, safety, and environmental (HSE) impacts is presented in Figure 1 as a function of depth with increasing expected impact from left to right. Starting in the deepest regions of the vulnerable environment, the figure indicates the potential for induced seismicity associated with injection in the storage formation. However, this process appears on the left-hand side of the figure because potential microearthquakes associated with induced seismicity are not expected to have a large HSE impact. Similarly, brine or other native fluids will be displaced at depth, but only insofar as brines contaminate aquifers will brine displacement have an HSE impact. The smallest HSE impact of those leakage-related processes presented (left-most in the figure) is the intrusion of CO₂ into hydrocarbon reservoirs, although it is important to point out that such intrusion could have very important economic impacts because the value of the hydrocarbon may be degraded by the intrusion of CO₂. Moving up in depth, the intrusion of CO₂ into potable aquifers, into the vadose zone, root zone, and above-ground regions may have considerable potential HSE impacts and therefore appear farther to the right-hand side in the figure. The event with the greatest HSE impact shown in the figure is a ground

plume, defined as a large dense cloud of nearly pure CO₂ traveling along the ground surface with little dispersion and engulfing people and animals in homes and fields. The purpose of this chapter is to review the mechanisms and potential HSE impacts of CO₂ leakage and seepage in regions spanning the upper parts of the vulnerable environment as outlined by the dashed box in Figure 1.

Before addressing the questions of potential impacts, it is appropriate to review the properties of CO₂ and relevant subsurface flow processes to gain an appreciation for expected CO₂ flow and transport mechanisms. In the first part of the chapter, we review the phase diagram and the changes in properties of CO₂ that would occur if CO₂ were to rise upward through the subsurface. The first part of the chapter sets the stage for the second part which is a discussion of potential impacts that may occur if CO₂ were to leak significantly from a storage formation to the near-surface environment and eventually seep out of the ground. We discuss flow and transport processes and impacts of CO₂ in aquifers, the vadose zone, surface water, and above the ground surface as shown in Figure 1. For clarity and precision throughout this chapter, it is useful to adopt the terminology that defines *leakage* as CO₂ migration away from an intended storage formation, and *seepage* as CO₂ transport across an interface such as the ground surface or the bottom or surface of a water body such as a lake. We further define the *near-surface environment* as the region within +/- 10 m of the ground surface.

Because geologic CO₂ storage has not yet been widely deployed, and there is no evidence that existing projects are leaking, direct experience with leakage and seepage is lacking.

There have also been very few field or laboratory experiments focused on the effects of deep CO₂ injections although many are currently being planned. As new knowledge becomes available, for example from field pilot studies currently underway, our understanding of flow mechanisms and impacts may have to be revised. Therefore, the second part of the chapter is qualitative relative to the first, and it is also speculative in that the serious impacts discussed are predicated on the unlikely occurrence of large-scale leakage of CO₂ upward across kilometers of vertical distance.

2. FLUID PROPERTIES RELEVANT TO GEOLOGIC STORAGE

2.1 Native Fluids

The properties of CO₂ presented in this section should be looked at in the context of how they relate to the native fluids into which CO₂ will be injected or through which CO₂ will migrate. The most common native fluid will be groundwater with varying amounts of dissolved solids (TDS), predominately sodium chloride (NaCl). Potable groundwater typically has less than 1000 mg/L TDS, whereas dense brine has more than 100,000 mg/L TDS, and seawater is approximately 35,000 mg/L TDS. Injected CO₂ may also encounter native hydrocarbons such as oil and natural gas, either at the injection point or after migrating into existing hydrocarbon traps.

The properties of fluids in the subsurface are controlled by pressure (P), temperature (T), and composition (x). Pressure and temperature vary in the subsurface in broadly predictable ways. In particular, pressure in the pore space of rock generally increases with depth following a hydrostatic pressure gradient, and temperature increases with

depth along what is called a geothermal gradient. The geothermal gradient can be high (e.g., 30 °C/km) in areas with active geothermal systems, or low (e.g., 15 °C/km) in areas of large-scale downward-flowing groundwater. As fluid migrates in the subsurface from one depth to another, it is said to follow a *PT path* because pressure and temperature will vary systematically as the fluid parcel migrates. As for composition, groundwater in the crust generally becomes more saline (higher TDS) with depth and the majority of potable groundwater is found at depths shallower than several hundred meters.

In terms of phase composition, water, brine, and oil will always be in liquid form in the subsurface (outside of permafrost regions) whereas natural gas (methane, CH₄) will be in gaseous form. Liquid densities are weak functions of pressure but vary with temperature and composition. The density of groundwater will vary from approximately 950 kg/m³ for warm fresh water to 1200 kg/m³ for dense brine. Oil density varies widely but is generally lower than local reservoir water as evidenced by its accumulation in traps. Natural gas density is a strong function of pressure and temperature, and is generally in the range of 130–300 kg/m³ in hydrostatic reservoirs at depths between 2–4 km.

Ambient air in the vadose zone and above ground has a density of approximately 1.2 kg/m³. The viscosity of groundwater is approximately 0.4–1 x 10⁻³ Pa s, while oil viscosity tends to be higher. The viscosity of methane and air is of order 10⁻⁵ Pa s and increases with increasing pressure. A summary of some native fluid densities and viscosities at representative conditions is presented in Table 1 along with CO₂ properties for comparison. With these properties as a point of reference, we proceed below to discuss the properties of CO₂ in the subsurface in more detail.

Table 1. Native fluid and CO₂ properties at nominal representative conditions.

Property (<i>P</i> (bar), <i>T</i> (°C))	Depth	Units	Water	Brine	CH ₄	Air	CO ₂
ρ (density) (201, 60 °C)	2 km	kg/m ³	992 ^a	1191 ^b	130 ^a	200 ^d	725 ^a
ρ (density) (1, 10 °C)	Ground surface	kg/m ³	1000 ^a	1205 ^b	0.68 ^a	1.2 ^d	1.9 ^a
μ (viscosity) (201, 60 °C)	2 km	10 ⁻⁶ Pa s	470 ^a	940 ^c	18 ^a	24 ^d	60 ^a
μ (viscosity) (1, 10 °C)	Ground surface	10 ⁻⁶ Pa s	1300 ^a	1800 ^c	11 ^a	18 ^d	14 ^a

^aLemmon et al. (2005) (NIST Webbook).

^bDuan et al. (1996) (Geofluids)

^cKansas Geological Survey, 2003 (extrapolated to 10 °C)

^dNIST14 Database (dry air)

2.2 Phase Diagram

Carbon dioxide in dilute and concentrated forms as gaseous and solid phases is common in everyday life, specifically as a component of the air we breathe, as a gas exsolving from carbonated beverages, and as a solid (dry ice) for keeping fish and other foods cold for long periods. In the subsurface of the earth, CO₂ can exist as a dissolved component in groundwater as well as in gaseous and liquid phases, and in the most common state that is somewhere inbetween gas and liquid known as the supercritical phase. The phase diagram for CO₂ at conditions relevant to the subsurface is shown in Figure 2, where the gas, liquid, and supercritical regions have been colored for clarity. Superimposed on the phase diagram are (1) the line showing a PT path in the earth for the case of geothermal gradient of 15 °C/km assuming a 10 °C surface temperature, (2) the line showing a PT path for a geothermal gradient of 30 °C/km, and (3) lines of constant density with density labels (modified from Roedder (1982) and Price et al. (2005)). This single figure shows the most important information relevant to CO₂ leakage driving forces in the subsurface.

Referring to Figure 2, starting at a depth of 4 km on the low-geothermal gradient line (15 °C/km), CO₂ is in supercritical conditions. As CO₂ rises along this PT path, it transitions to liquid conditions at a depth of 1465 m (146.5 bars) with no significant jump in density. With continued rise along the same geothermal gradient, CO₂ will pass over the phase boundary (saturation line) at a depth of 530 m (53 bars) and undergo a large expansion (decrease in density) from 800 kg/m³ to 150 kg/m³ as it transitions from the liquid to the gas phase. Although uncommon, in areas of low geothermal gradient, CO₂ liquid may be stable at depths between approximately 500-1500 m. A natural example is Mt. Gambier in Australia (Chivas et al., 1987), where it is thought that liquid CO₂ occurs at depth.

Next we consider the high-geothermal gradient PT path of Figure 2. As we ascend along this PT line from 4 km depth, we move through the supercritical region and pass very near the critical point (end of the heavy black saturation line in the figure) and enter immediately into the gas region. The density isopleths show a smooth but steep decrease in density as the CO₂ ascends through supercritical to gaseous conditions. This interesting behavior motivates a closer look at the density and viscosity changes of CO₂ as controlled by pressure and temperature in the subsurface.

2.3 Density and Viscosity

The expected density and viscosity of CO₂ in the subsurface as calculated by the NIST14 database (NIST, 1992) down to 4 km are shown in Figure 3 for the low and high geothermal gradients (15 °C/km, and 30 °C/km), with indication of phase stability (see

also Figure 2) given along the temperature profiles. As shown, density (ρ) in the low-geothermal gradient case jumps from to 800 kg/m^3 down to 150 kg/m^3 as CO_2 transitions from liquid to gas along the low-geothermal gradient PT path at a depth of 530 m. An analogous jump in viscosity (μ) occurs at the same transition, although it is important to note that the viscosity of liquid CO_2 ($\mu = 8 \times 10^{-5} \text{ Pa s}$) is more than 10 times smaller than the viscosity of liquid water ($\mu \sim 10^{-3} \text{ Pa s}$) at ambient surface conditions. For the high-geothermal gradient case, density decreases upon transitioning from supercritical to gas conditions, but the transition is smooth and the total change is smaller than in the low-geothermal gradient case, approximately 650 kg/m^3 to 200 kg/m^3 . Viscosity changes even less relative to the low-geothermal gradient case at this same transition, and the viscosity of supercritical CO_2 is approximately 20 times smaller than that of water, while the density is 65% that of water at these same conditions. Thus supercritical CO_2 is liquid-like in density, and gas-like in viscosity. Here in a nutshell is the fascinating behavior of the supercritical phase: it is at once gas-like and liquid-like. In deep water-saturated formations and oil reservoirs, CO_2 will tend to rise because it is less dense than native fluids and its low viscosity will make it mobile and subject to fingering into more viscous brine or oil phases it displaces. In gas reservoirs, CO_2 will tend to sink and displace native CH_4 stably (without fingering) because it is denser and more viscous than methane (e.g., Oldenburg et al., 2001). In the near-surface environment, CO_2 will tend to sink because it is denser than ambient air, but the form of CO_2 flow is highly dependent on how it enters the near-surface environment (see Sections 3.2 and 3.4).

2.4 Solubility

The description of properties so far assumes that CO₂ remains as a separate phase, i.e., is immiscible, relative to the native fluids. In fact, CO₂ has a finite solubility in the native fluids, and therefore will tend to partition into those fluids where they come into contact. The solubility of CO₂ is evident from carbonated beverages, and it is exploited in certain oil reservoirs where CO₂ dissolves into oil to decrease density and viscosity and thereby improve oil recovery, a process known as CO₂-EOR (enhanced oil recovery). In this section, we discuss the dissolution of CO₂ into native groundwater and brine.

In general, gas solubility in water decreases with increasing temperature, and CO₂ is no exception. The air bubbles that appear in a glass of water left on the counter overnight are testimony to this effect. As the water heats up to room temperature, air exsolves and forms bubbles on the sides of the glass. However, gas solubility in water is also higher at higher gas pressures, and therefore we expect some compensating effects of temperature and pressure along a typical PT path in the earth. Solubility is also a function of TDS (e.g., salinity), and the increasing TDS decreases the solubility of groundwater to gases such as CO₂.

In Figure 4 are plotted the predicted mole fractions of CO₂ in aqueous solutions ($x_{\text{liq}}^{\text{CO}_2}$) in equilibrium with CO₂ at the given PT conditions as a function of depth in the earth for two different geothermal gradients (PT paths) and three different salinities. These values are calculated using methods similar to those presented in Spycher et al. (2003) and

Spycher and Pruess (2004). As shown, salinity diminishes CO₂ solubility at all pressures and temperatures. The effects of geothermal gradient are more complicated. The stable phase region for each PT path is shown in the the plot of temperature vs. depth by the line color and label consistent with the phase diagram of Figure 2 (red is gaseous, green is liquid, and blue is supercritical). In the gaseous regions of the phase diagram, CO₂ solubility increases strongly as depth increases. Upon reaching the liquid or supercritical regions, however, changes in solubility become more subtle and sensitive to temperature and salinity. At depths greater than approximately 2 km, CO₂ solubility increases, slowly for the 15 °C/km geothermal gradient, and much faster for the 30 °C/km geothermal gradient. The implication of decreasing solubility as CO₂ rises into the near-surface environment is that ebullition is likely to occur making gas seepage likely.

2.5 Summary of CO₂ Properties

Relative to the native fluid phases groundwater, dense brine, and oil, CO₂ will always be buoyant and therefore tend to rise upward in the subsurface. If CO₂ is injected or migrates into natural gas reservoirs, however, it will tend to sink due to the higher density of CO₂ relative to CH₄. In the near-surface environment, CO₂ will be a gas with density ($\rho = 1.8 \text{ kg/m}^3$) much larger than that of air ($\rho = 1.2 \text{ kg/m}^3$) and therefore will tend to sink. Because of the geothermal gradient, CO₂ in the subsurface will most commonly be supercritical, with much lower viscosity than groundwater. The solubility of CO₂ in native water is a strong function of salinity. The solubility of CO₂ increases as a CO₂ plume rises until approximately 500-800 m depth, at which point solubility begins to decrease with further rise.

3. CO₂ FLOW PROCESSES AND POTENTIAL IMPACTS

3.1 Aquifers

Flow Processes

CO₂ injected deep into the subsurface will exist mostly as an immiscible phase within native fluids (e.g., saline groundwater) on a variety of length scales from microscopic bubbles to km-scale plumes. Buoyancy forces will tend to drive CO₂ upward on all length scales. At the pore scale, immiscible gas phases such as CO₂ can flow as discrete bubbles within the pores or fractures (e.g., Roosevelt and Corapcioglu, 1998), or as a connected phase called channel flow (Ji et al., 1993). Large regions of supercritical or gaseous CO₂ can be called plumes, whether they are in the subsurface or above ground. A sketch of these forms of CO₂ and the related flow processes is shown in Figure 5.

The main driving force for CO₂ following the injection period is buoyancy, while formation permeability and the viscosity of both the CO₂ and the native fluid resist flow. The low permeability of geologic formations containing thick sequences of sub-horizontal sedimentary rocks such as shale will strongly limit upward migration of buoyant CO₂ on the plume and bubble scales. While some studies have found that crustal permeability tends to be larger for larger-scale flows (e.g., Neuman, 1994), others have argued for a lack of scale dependence and emphasized that very low permeability is found in shales over a large range of length scales (Neuzil, 1994). The demonstrated capacity of thick shale units to trap hydrocarbons and seal reservoirs for millions of years suggests that such formations will be effective at preventing large-scale upward buoyant

flows of CO₂. The concern for CO₂ leakage through sealing formations is that flow paths such as abandoned or improperly sealed wells (e.g., Nordbotten et al., 2004; Scherer et al., 2005) or reactivated faults and fractures (Streit et al., 2004) may exist that could act as conduits for upward CO₂ to bypass low-permeability formations. Over very long time scales or short length scales, molecular diffusion of CO₂ in native liquids can be an important transport mechanism, but not for large-scale leakage that would bring CO₂ to the near-surface environment with significant potential impact. Molecular diffusion is much faster in the gas phase, and could be an important mechanism of CO₂ transport within gas reservoirs over shorter time scales (Patzek et al., 2003; Oldenburg et al., 2004).

Impacts

Despite the predominance in terms of volume of immiscible-phase CO₂ associated with any large-scale injection, it is important to remember that dissolution of CO₂ into native groundwater will occur both within pores containing residual water as well as at the leading edges of the large-scale plume. The solubility of CO₂ in brine at depth (see Figure 4) is on the order of a few percent by mass. As a dissolved component, CO₂ will slightly increase the density of groundwater and thereby eliminate the upward buoyancy driving force. In this case, leakage of CO₂ will occur only by groundwater migration caused by some other driving force. However, this does not mean that CO₂ leakage has a negligible impact on groundwater. On the contrary, for long-term and low-flux leakage with dissolution into groundwater, the geochemical effects of CO₂ on groundwater are of great concern. In particular, if CO₂ leaks into relatively shallow potable aquifers even at

low rates, it can have potentially detrimental effects on groundwater quality as discussed below.

Dissolution of CO₂ into groundwater will tend to increase slightly the acidity (decrease the pH) of the water, as controlled by buffering reactions involving matrix mineral grains. For small to moderate leakage dissolving into native groundwater, CO₂ should be dominantly present in the aqueous phase as dissolved inorganic carbon, DIC (CO₂(aq), H₂CO₂, HCO₃⁻, CO₃²⁻). Alkalinity (defined as the ability of water to accept protons (H⁺)) in potable groundwater is mostly due to the presence of HCO₃⁻ and CO₃²⁻, and therefore alkalinity can increase as CO₂ dissolution occurs. As the pH and alkalinity of groundwater change due to CO₂, the equilibrium between water and rock is altered and complex dissolution or precipitation reactions involving matrix minerals will tend to occur. Assuming the kinetics allow the reaction to occur, these reactions will further alter pH, DIC, isotopic composition, and the concentrations of major and minor cations in solution. For example, dissolution of carbonate minerals such as calcite (CaCO₃) by the reaction $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^-$ results in the doubling of DIC (i.e., one mole of CO₂ reacts to produce two moles of HCO₃⁻) and a release of Ca²⁺ to solution. Similar reactions are possible involving alteration of biotite, plagioclase and alkali feldspar, and other minerals (e.g., Xu et al., 2005). Trace elements in the minerals including heavy metals such as lead may also be released into groundwater as alteration reactions occur with associated degradation of groundwater quality (Schuett et al., 2005; Wang and Jaffe, 2004). Continued use of such water would have to be under close

monitoring and potentially with blending from other sources to ensure levels did not exceed recommended standards.

Microbiological effects are also expected as a result of CO₂ injection and leakage (Onstott, 2005). Although cell density declines by 3-6 orders of magnitude from the ground surface to 4 km depth, there are abundant microbes at the depths of potable groundwater that could be affected if CO₂ were to intrude into this region. The alteration of feldspars by slightly acidic water due to CO₂ leakage will release iron which can stimulate Fe(III)-reducing communities and result in methanogenesis. Further studies of the effects of CO₂ leakage on microbial communities and the coupling to geochemistry and groundwater quality are needed to improve our understanding of the implications of microbial impact.

In the case of high-flux leakage, for example focused CO₂ gas or supercritical fluid entering into an aquifer, detrimental hydraulic effects may occur that will affect groundwater production. For example, a large CO₂ plume could impinge upon a producing well and either cause mechanical problems due to corrosion or hydraulic problems as the pump tries to impel low-density CO₂ gas. Even if the CO₂ plume did not directly encounter a well, the plume could rapidly displace groundwater potentially suspending particles and causing turbidity that would impact groundwater quality at a nearby well.

3.2 Vadose Zone

Flow Processes

Carbon dioxide is a dense gas relative to air. As such, CO₂ can be expected to displace soil gas if the CO₂ migrates downward from above in the vadose zone, all other things being equal. However, the form of CO₂ flow in the vadose zone is strongly dependent on how it arrives there. Specifically, if CO₂ arrives at the ground surface from a spill of CO₂ liquid, e.g., from a truck or pipeline, the CO₂ will tend to seep into the ground and sink as it displaces native soil gas. The situation we are considering with leakage and seepage is quite different, in that CO₂ is leaking upward from below largely driven by buoyancy forces relative to saturated sediments. In this case, CO₂ arrives at the vadose zone at the water table as either a dissolved component in groundwater, as discrete bubbles, or as a plume with an overpressure (e.g., as a result of high-flux leakage through an abandoned well) relative to the ambient pressure at the water table. If CO₂ degasses from the groundwater or arrives as small bubbles, we can expect the density effects to dominate and CO₂ will tend to remain at the water table because of its greater density relative to ambient soil gas. However, if CO₂ arrives in the form of a plume with overpressure, the pressure-gradient may overwhelm the buoyancy effects and drive CO₂ upward to the ground surface where it will seep out of the ground. This type of flow has been studied by Oldenburg and Unger (2003; 2004), who found that CO₂ concentrations in the vadose zone will eventually reach nearly 100% even if the leakage flux is quite low. However, for very thick vadose zones in arid regions, it may take a long time for CO₂ leaking up from the saturated zone to fill up the vadose zone. Simply put, there are few attenuating mechanisms in the vadose zone, and even a small leakage flux will tend to displace soil

gas over time. Among the attenuating mechanisms are diffusion and barometric pumping. Oldenburg and Unger (2003) found that barometric pumping had little effect on seepage flux as averaged over a year for the scenario considered. Other work suggest that barometric pumping may be more significant at removing contaminant gases from the vadose zone, particularly in scenarios where the gas component is not actively leaking (e.g., Auer et al., 1996). In summary, if CO₂ arrives as a pressurized plume or through an abandoned well, the CO₂ will easily flow across the vadose zone and seep out of the ground (Oldenburg and Unger, 2003; 2004). If it arrives by smaller fluxes, it may resist seeping but still tend to fill up the vadose zone with attenuation due to molecular diffusion and barometric pumping. Once CO₂ is in the vadose zone, traditional vapor extraction methods appear to be viable for removing it (Zhang et al., 2004).

Impacts

The most obvious impacts of CO₂ in the vadose zone are vegetation kills observed in areas of natural CO₂ emissions. Probably the most well known example is the tree kill area at Mammoth Mountain, California, in which conifers have died over several areas where anomalous CO₂ emissions were recently recorded. The cause of death is thought to be due to soil-gas CO₂ at concentrations of more than 20-30% by volume interfering with respiration of the roots of the trees (Farrar et al., 1995; Qi et al., 1999). Another example is in Dixie Valley, Nevada, where there is a nearly 1 km² area referred to as the dead zone in which many plants are stressed and some dying due to changes in geothermal gas venting (Bergfeld et al., 2001). In this latter case, both high temperatures and CO₂ in the root zone probably cause plant mortality. Although not documented, in

all likelihood burrowing animals are also displaced or die upon intrusion of CO₂ at high concentrations in the vadose zone. More subtle effects of CO₂ in the vadose zone include geochemical effects such as those that occur at deeper locations due to CO₂ leakage (see Section 3.1), with the exception that much of the vadose zone is aerated and oxidizing as opposed to anaerobic. In general, the vadose zone and soils support a great variety of biota and the particular geochemical and soil gas characteristics that have developed over long time periods (e.g., Amundson and Davidson, 1990) will be altered by leaking CO₂. Overall, the detailed effects of leaking CO₂ on the vadose zone and root zone are not well understood, and additional research on the effects of leaking and seeping CO₂ including field experimentation with long-term monitoring is needed to understand better the long-term effects of CO₂ leakage.

3.3 Surface Water

Flow Processes

If CO₂ leaks to the near-surface environment and enters surface water, it may either be in a bubble form or as a dissolved component. Except in the deep oceans or very cold lakes, both of which are areas beyond the scope of this chapter, separate-phase CO₂ will be in gaseous form in surface water. Bubble and diffusive transport in surface water has been studied extensively mostly in the context of CH₄ efflux from either biogenic (Casper et al., 2000) or hydrocarbon reservoir sources (Hornafius et al., 1999; Leifer and Patro, 2002). The strong contrast in density between gas and surface water means that CO₂ bubbles will rise rapidly and discharge at the surface. A comprehensive summary of the flow and transport of CO₂ in surface water is given in Oldenburg and Lewicki (2005).

Impacts

The most important potential impact of CO₂ seepage into surface water occurs when the CO₂ does not bubble through but rather accumulates as a dissolved component at the bottom, resulting in potentially catastrophic episodic outbursts such as those that occur from stratified equatorial lakes (e.g., Giggenbach et al., 1991). Fortunately, the stratification possible in equatorial lakes is not common in other areas, and frequent mixing by currents or seasonal overturn in non-equatorial lakes, rivers, and wetlands will prevent the kind of buildup that leads to catastrophic releases. Impacts of CO₂ bubbling through surface water are small because the residence time is short. For example, benign CO₂ bubbles are observed in the Green River near the Crystal Geyser along the trace of a fault associated with CO₂ seepage (Shipton et al., 2005). In the common cases, bubbling and/or diffusive transport of CO₂ will be an effective means of transport and impacts to surface water will be limited to small pH changes and increased alkalinity. The effects of CO₂ discharge to the atmosphere above the surface water are analogous to those above the ground surface and are discussed below.

3.4 Surface Environment

Flow Processes

If leaking CO₂ reaches the vadose zone, it is very likely that it will seep out of the ground. The form of seepage will strongly control the behavior, with a range from small diffusive fluxes with no density-dependence to large-scale emissions with strong density-dependence (Oldenburg and Unger, 2005). Dense gas dispersion has received

considerable attention from the chemical processing and transportation industry (e.g., Britter, 1989; Hanna et al., 2002). In addition, natural CO₂ outbursts occur in many places on earth and the flow behavior and hazards of these plumes are well known (Giggenbach et al., 1991). The primary concern of dense gas emissions is that the high density will prevent dispersion and deliver the ground plume to vulnerable receptors such as humans or other animals. In the case that there is wind and seepage fluxes are not as large as might occur from an open well, turbulence in the atmosphere causes dispersion processes that are effective at dispersing CO₂ plumes (Oldenburg and Unger, 2004). In the case that an open well emits CO₂ at high flux, the energy of the emission itself can help disperse the CO₂ as it drives the plume upward in the atmospheric boundary layer and entrains ambient air. Stable atmospheric conditions such as occur at night and early mornings are not conducive to mixing and are the most dangerous for CO₂ seepage accumulation. Similarly, basements and buildings are known from studies of radon to offer closed space in which mixing and dispersion are limited and high concentrations of seeping gases can occur (Robinson and Sextro, 1995; Robinson et al., 1997).

Impacts

The impact of primary concern for CO₂ seepage above ground is asphyxiation of humans and animals (Benson et al, 2002). As a dense gas, CO₂ has the potential to either migrate along the ground surface as a dense ground plume, or to seep into basements or other buildings and resist mixing and dispersion. As a colorless and odorless gas, there is the potential for people to become engulfed or enter into CO₂-rich air-space unknowingly and succumb due to lack of oxygen in the air. This occurred at Mammoth Mountain,

California, when a ranger entered a building buried in snow and sensed a lack of oxygen but was able to exit safely (Farrar et al., 1999). In the outside environment, diffuse seepage under stable atmospheric conditions or large-scale leakage such as through open boreholes and other catastrophic failures can cause health effects in human and other animals. Probably the more common situation will be diffuse seepage or seepage from multiple locations at low fluxes, in which case no significant HSE risks are expected above ground, and seepage detection becomes the main challenge (Oldenburg et al., 2003). Although well studied for the case of spills and leaks from above-ground tanks and pipes in the chemical industry, additional research is needed to investigate the behavior of dense gases leaking from below the ground surface. Experimental approaches involving long-term subsurface release with careful monitoring are particularly needed to develop and calibrate models.

5. DISCUSSION AND CONCLUSIONS

This chapter has discussed the properties, flow processes, and potential impacts of CO₂ leakage and seepage in potable aquifers, the vadose zone, surface water, and the above-ground environment. Our understanding of CO₂ flow and transport is sufficient to know that there are circumstances under which CO₂ leakage and seepage may have detrimental effects on health, safety, and the environment as discussed above. However, these circumstances appear to be unlikely given the low permeability of the sealing formations that will be sought out as geologic CO₂ storage sites. In the case of faults or wells acting as unexpected conduits, CO₂ may migrate into potable aquifers and possibly higher in the geologic section.

From an HSE impact perspective, it must be kept in mind that CO₂ is naturally abundant and relatively benign. The HSE impact that leakage or seepage of CO₂ would have is strongly dependent on how much CO₂ enters a given region and over what time this occurs. Current understanding does not allow us to establish a hard limit, but we know that natural biological systems can produce CO₂ fluxes on the order of order 10⁻⁷ kg/(m² s) and some order-of-magnitude factor times this flux is likely to cause no significant impact in the near-surface environment. Regardless of the flux value, natural and engineered dispersion and mixing processes will tend to reduce high CO₂ concentrations that cause the hazards associated with leakage and seepage. Thus even in the cases where CO₂ leakage and seepage could create negative impacts, such occurrences do not appear to be insurmountable mitigation challenges insofar as HSE impacts are concerned. The implication for policy is that limited small leakage and seepage fluxes of CO₂ from geologic storage sites may be acceptable from an HSE perspective. Research needs to be continued to refine understanding of just how large leakage and seepage fluxes can be while maintaining acceptability from all of the various perspectives, e.g., HSE, energy, cost, and public perception.

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Figure Captions.

Figure 1. CO₂ storage impacts of increasing severity from left to right as a function of depth. Leakage and seepage processes discussed in this chapter are show within the box outlined by the dashed-lines.

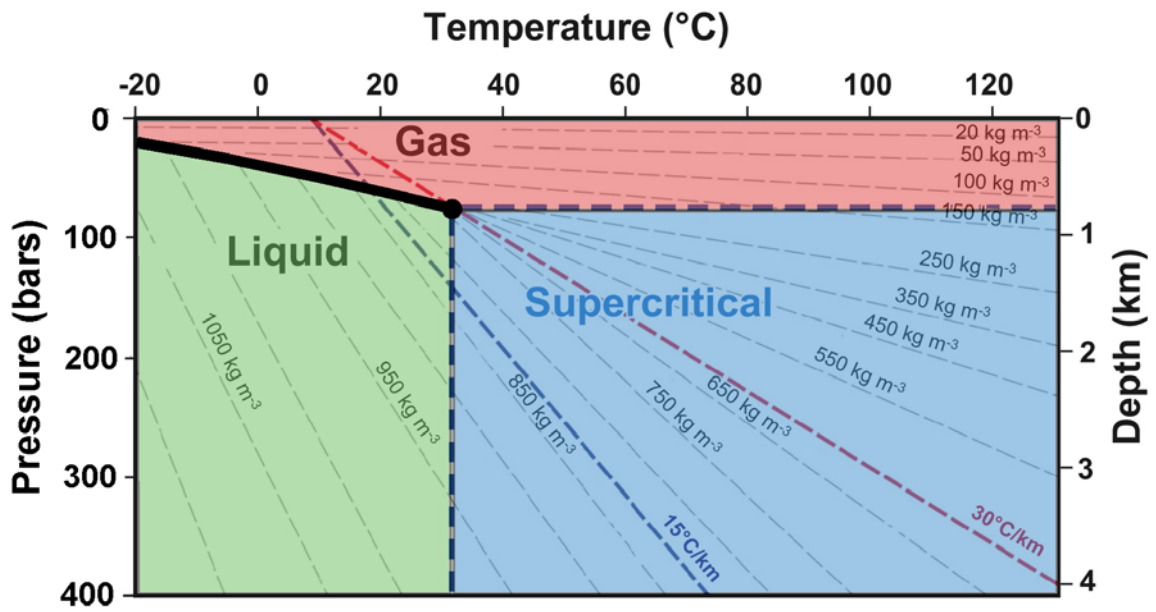
Figure 2. Phase diagram for CO₂ with gas, liquid, and supercritical regions colored and superimposed on isopleths of density and two PT paths (modified after Price et al. (2005) and Roedder (1982)).

Figure 3. Density and viscosity of CO₂ as a function of depth for two different PT paths. Phase stability of CO₂ is indicated on temperature profiles.

Figure 4. Mole fraction CO₂ in groundwaters for two different PT paths. Phase stability of CO₂ is indicated on temperature profiles.

Figure 5. Forms of CO₂ flow with increasing length scale. (a) bubbles, (b) channel flow, (c) subsurface plume, and (d) ground plume.

Figures



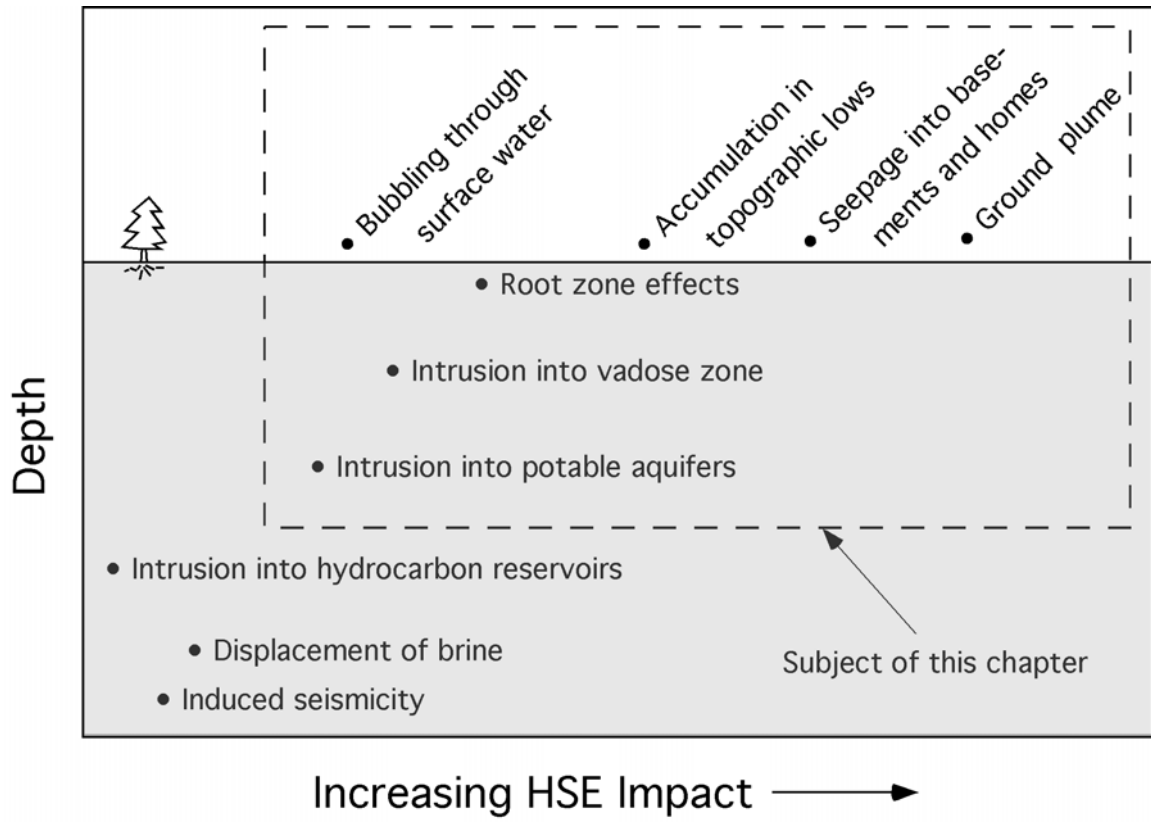


Figure 2.

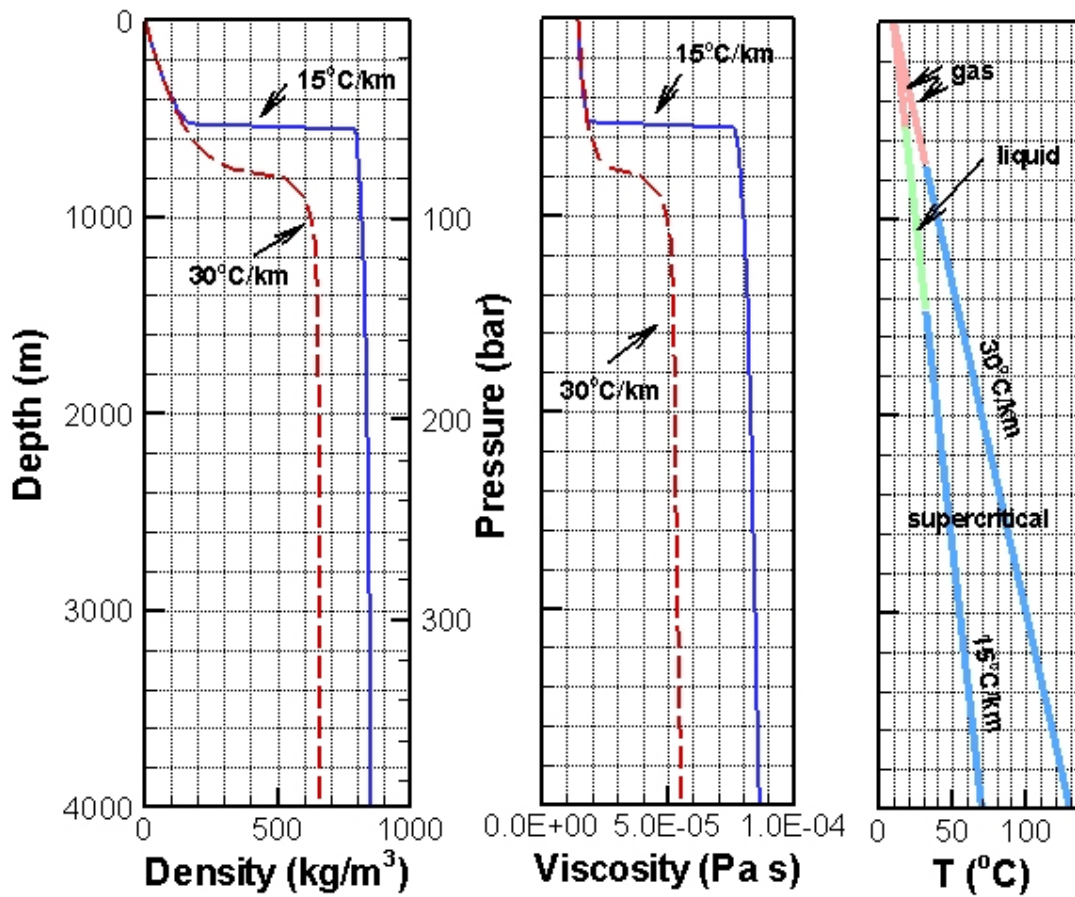


Figure 3.

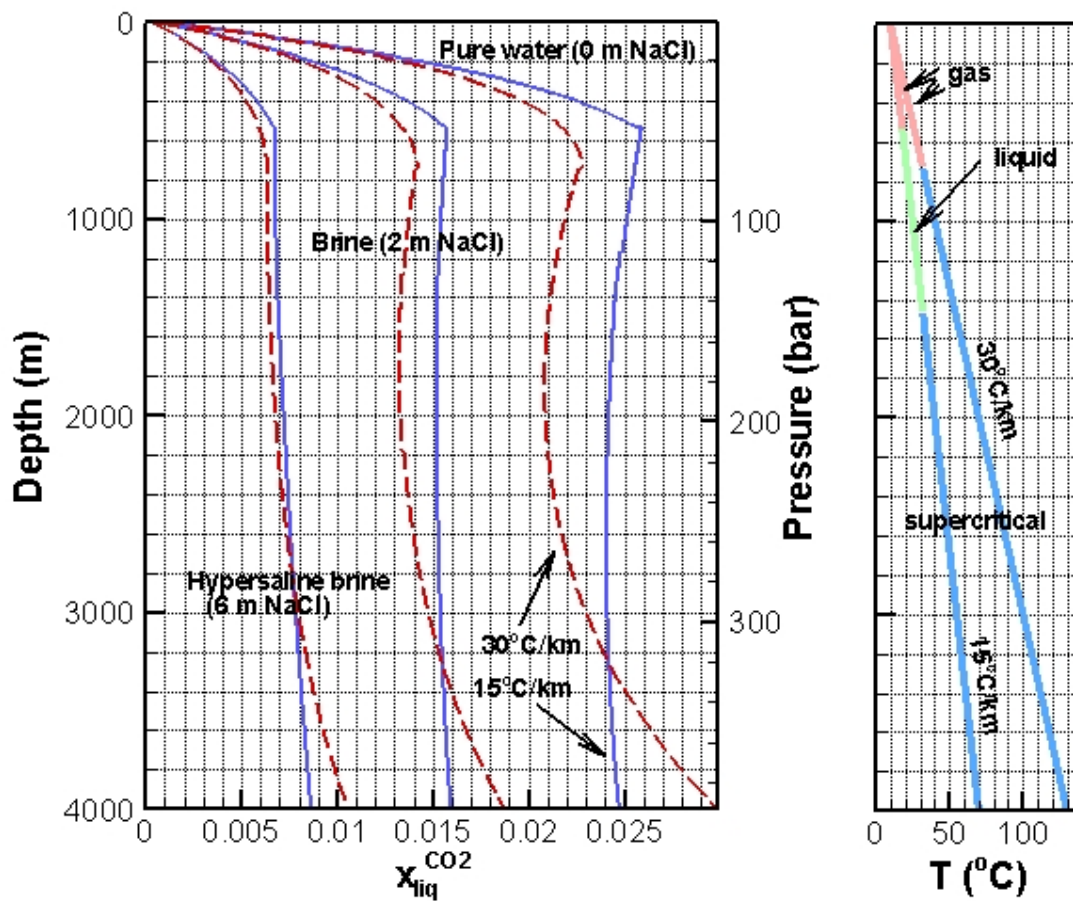


Figure 4.

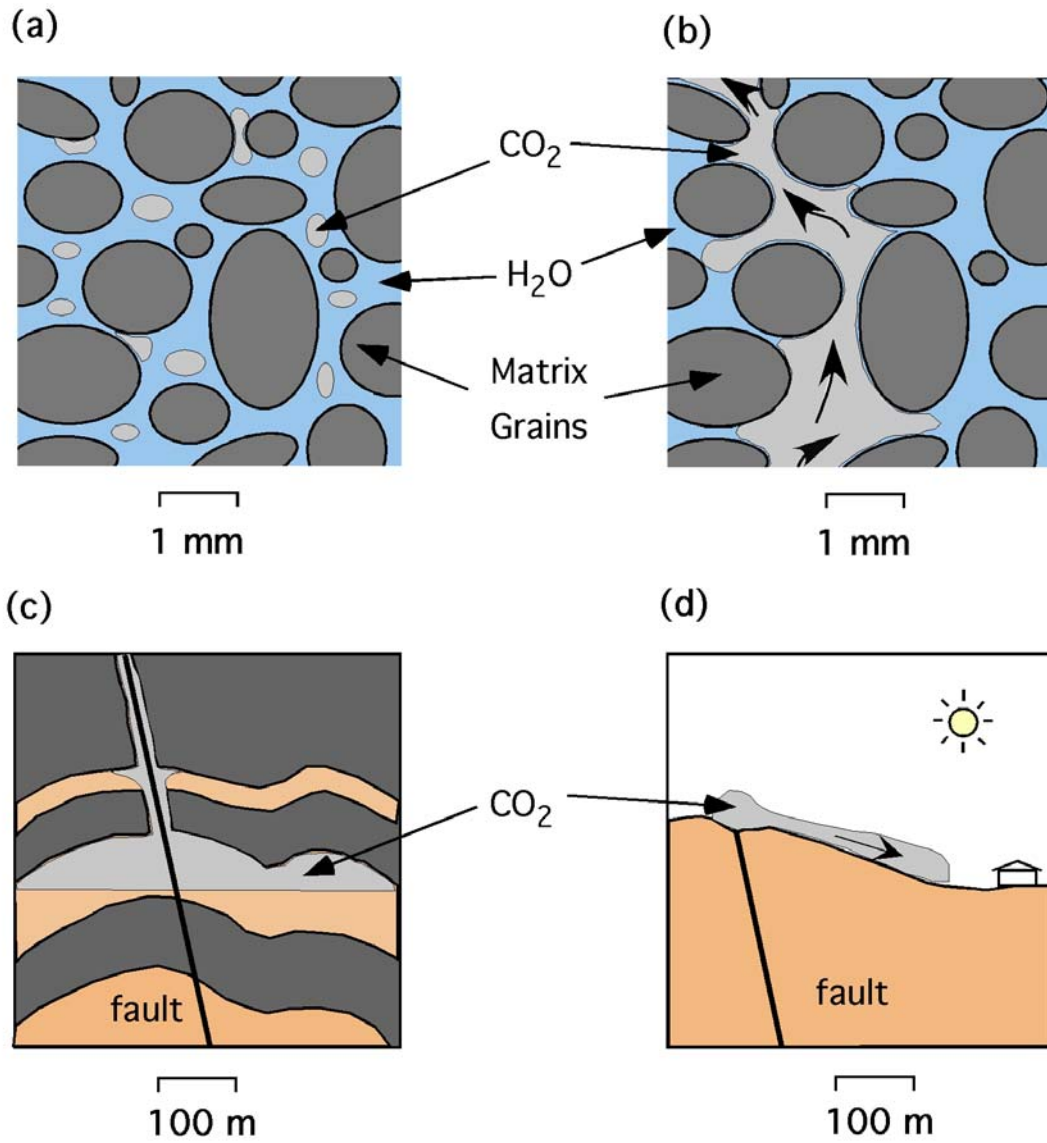


Figure 5.