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Perspective

Prospects for Subsurface CO_2 Sequestration

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Introduction

Natural gas, oil, and coal provide approximately 85% of humankind's primary energy sources.[1] Studies indicate that the high share of fossil fuels in primary energy production (the energy found in nature which has not been subjected to conversion and transformation processes) may remain constant over the next 20 years,[1] despite much interest and activities in the development of alternative energy sources. Alternatives to natural gas and oil are limited. Both technological and institutional problems preclude energy generation from alternative sources on a scale comparable to oil and gas utilization in the foreseeable future. The main reason for this heavy reliance on fossil fuels is growth in energy demand in developing countries, where the increase in the standard of living is tied to energy usage.

Burning of fossil fuels produces large quantities of CO_2. The annual release of CO_2 into the atmosphere is estimated to be around 28 Gigatons. For the last few centuries prior to the industrial revolution, the average atmospheric CO_2 concentration was about 280 ppm.[2] Since the onset of the industrial revolution, there has been an increase in the CO_2 concentration to the current level of around 390 ppm. The annual increase in the atmospheric CO_2 concentration is currently[2] at a high level of 1 to 2 ppm.[2] In the past 400,000 years, there have been four cycles of abrupt climate change. Various studies show that these abrupt changes are closely linked to the concentration of CO_2, and to a lesser degree to other greenhouse gases.[3] In a article published in 1895, the Swedish chemist Svante Arrhenius predicted that CO_2 concentration in the atmosphere would have a greenhouse effect resulting in global warming.[4] His concern was the use of too much coal in the future. Coal has a high carbon to hydrogen ratio while natural gas, the premium fuel of this century, has the lowest C/H ratio among fossil fuels. Arrhenius calculated that one should expect an increase of 5 to 6°C in the earth's average surface temperature with a doubling of CO_2 concentration from 280 ppm (at his time) to 560 ppm. Surprisingly, Arrhenius' calculation is consistent with current estimates of global warming. The fourth assessment report of the Intergovernmental Panel on Climate Change[5] warns that "warming of the climate system is unequivocal." According to some recent studies, we have already reached CO_2 levels that compromise the stability of the polar ice sheets.[6] Satellite data reveal that the mass loss of Greenland and Antarctic ice sheets is accelerating with time and more closely follows a quadratic trend than a linear one.[7] There are various indications that further increase in CO_2 concentration in the atmosphere will increase the Earth's temperature.[3] Another consequence of rising CO_2 concentration in the atmosphere is the increase in CO_2 solubility in the oceans and the consequent increase in ocean acidification, with currently unknown effects on the marine life. Anthropogenic climate change may give rise to physical, chemical, biological, economic, and political effects whose possible consequences defy imagination. A solution to this new and major challenge facing humankind will likely require a multifaceted and interdisciplinary approach. The chemical engineering profession can play a leading role in finding solutions to many aspects of this challenge.

Perhaps the most effective way to solve the issue of global warming is reduction of CO_2 emissions to the atmosphere from combustion of fossil fuels through capture from stationary sources. A single coal-fired power plant with 1,000 MWe capacity generates about 20,000 tons of CO_2 a day. Such a large amount can be stored in a nearby subsurface formation. Other options such as ocean storage in the form of small droplets of CO_2 or creation of large CO_2 lakes are being increasingly ruled out because of environmental, legal, and economic concerns.[8] Still other options, such as enhancing CO_2 uptake by plants and soil microorganisms are currently considered to be of limited potential, but can be effective as supplements.

In this Perspective, the focus will be on storage, and we will argue that subsurface storage is a natural choice, and that there is much storage potential in the subsurface geological formations. The most costly component is CO_2 capture, which will be briefly reviewed first.

Carbon Capture

Large-scale carbon dioxide removal from gases has been in use for several decades. Some of the natural gases obtained from the subsurface have large quantities of CO_2. The

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removed CO_2 has often been released to the atmosphere. In recent years, some projects have included removal of CO_2 from natural gases and subsurface storage, either in saline aquifers[9] or in depleted nearby gas reservoirs.[10] For CO_2 capture from large power plants, there is a need for more economical CO_2 separation technologies, where at least 70% of the total capture and storage costs may be involved.[11] Four methods of capture will be reviewed: (1) postcombustion capture, (2) precombustion capture, (3) oxy-fuel combustion, and (4) direct capture from the atmosphere. The last option is not necessarily connected with power plants.

The standard technique for postcombustion capture is use of a solvent to absorb CO_2 from the flue gas, similar to CO_2 removal from natural gases. Amines like monoethanolamine have been used as a solvent for a long time.[12] Both high CO_2 solubility and high mass-transfer rates may be achieved using a mixture of amino alcohols with amines.[13] Membrane techniques are being increasingly considered for removal in high CO_2-content natural gases and in capture from power plants. The action of the membranes may be facilitated with chemical agents that react selectively and reversibly with CO_2.[14] An advantage of postcombustion capture is that the necessary technological components can be readily added to existing host plants.

The relatively low CO_2 concentration in the flue gas, however, limits the efficiency of these capture methods. This deficiency is circumvented in precombustion capture, where fuel is converted to a clean synthesis gas (syngas) in a gasifier that can operate at a pressure of 65 bar or higher.[8] The highly concentrated CO_2 can be removed from the syngas before it reaches the combustion chamber. After CO_2 removal, the syngas is rich in hydrogen (H_2); the overall efficiency may be improved by using the H_2 to run fuel cells or to serve as a fuel in electricity-generating turbines.

Oxy-fuel combustion is carried out in an oxygen-rich mixture of recycled flue gas and high-purity oxygen supplied by a cryogenic air separation unit (ASU). As a result, the product is rich in CO_2 and water vapor. Carbon dioxide is separated by condensing the water vapor. This technology can also be retrofitted to existing plants, and unlike in postcombustion capture, no solvents are required. The need for an ASU and recycling of flue gas, however, significantly increases the cost. A more inexpensive alternative may be to use metal oxides to serve as oxygen carriers during combustion.[8]

Perhaps the most ambitious and least developed method is capture from ambient air to reduce atmospheric CO_2 concentration directly. Because of rapid mixing processes in the atmosphere, air capture plants can be effective even when built in remote areas.[15] This allows flexibility to build them near remote sequestration sites or in areas where construction and operation costs may be low. Funding in air capture research has been limited mainly due to concerns about economic viability, although a true assessment of the costs will be possible only when a pilot-scale development is completed.[16] Even with the limited funding currently available, some success has been reported with both solid sorbents (e.g., amines on a mesoporous silica substrate), and liquid sorbents (alkaline solutions).[16]

CO_2 Storage in the Subsurface

There is plenty of CO_2 in subsurface formations. In a large number of oil and gas reservoirs, CO_2 content is very high. In some oil reservoirs, the CO_2 content is as high as 70–80 mol %.[17] In gas reservoirs, CO_2 content can be higher than 90 mol %.[17] Most of the CO_2 used for improved oil recovery is drawn from the naturally occurring sources in the subsurface. There is a large amount of CO_2 dissolved in some aquifers below the oil and gas formations. Concentration of CO_2 in some aquifers is around 5 weight %. The size of the aquifers can sometimes be orders of magnitude larger than the aforementioned oil and gas formations.

Carbon dioxide and water are the main volatile species in Earth's upper mantle and crust. CO_2 is generated by rapid reaction of calcite and quartz at high-temperature and pressure in the upper mantle.[18] The source of CO_2 in some oil and gas reservoirs is likely the upper mantle and crust.

CO_2 can be stored in the subsurface in different types of formations. Two forms of CO_2 placement help with oil and methane production and may have immediate economic benefits.

CO_2 for Improved Oil Recovery

CO_2 has been injected in subsurface hydrocarbon reservoirs for the purpose of improved oil recovery in the last four decades. Current CO_2 injection for improved oil recovery is around 70,000 tons per day worldwide.[19] This modest amount is about the same as the CO_2 generated from a 3,500 MWe coal-fired power plant. The improved oil production from CO_2 injection is about 300,000 barrels of oil per day worldwide.[19] The main mechanism for CO_2 improved recovery is solubilization of CO_2 in the oil, which can result in compositions as rich as 70–80 mol % CO_2. The solubility of CO_2 can drastically decrease viscosity (one- or two-orders of magnitude for some oils) and can result in oil swelling by as much as 50–60%.[20] Swelling gives rise to the increase in oil recovery, and viscosity reduction improves the mobility ratio of the phases and results in increased well productivity.[20,21]

CO_2 injection for the purpose of improved recovery has been mainly limited to the USA and Canada, due to the proximity to natural CO_2 reservoirs. The potential for CO_2 injection worldwide is much higher. Current oil production from CO_2-improved recovery is less than 0.4% of total oil production worldwide. We believe when CO_2 becomes available economically from capture, its injection for improved oil recovery can potentially increase by one or two-orders of magnitude. Very large-scale fluid injection in oil reservoirs, when beneficial, can be carried out successfully. In the Cantarell oil field complex in Mexico, nitrogen extracted from the air is being injected at the level of 55,000 tons per day,[22] which is of the same order as the amount of CO_2 injection for improved recovery in the world. We would like to point out that current numerical models require much advancement to reliably predict CO_2 injection in both complex hydrocarbon reservoirs, as well as in saline aquifer formations. The deficiency in the current algorithms is that not all of the important physics of CO_2 injection is taken into account properly.[20,23]

CO_2 Storage in Depleted Oil and Gas Reservoirs

A large number of oil and gas reservoirs in different parts of the world have been depleted. Some of these reservoirs can be used to store CO_2. The resulting pressure increase can be allowed as long as the integrity of the cap rock (the seal at the top of formation) is maintained. Much information from the hydrocarbon production stage is available which can help with the design of such projects.

Injection of CO_2 in depleted oil and gas reservoirs is particularly attractive when large volumes of CO_2 are being produced from separation of CO_2 in oil and gas production operations. An example is the CO_2CRC Otway project, in Australia. In this project CO_2 is captured from a nearby gas field that contains approximately 80% CO_2 and 20% methane (by weight), and is injected in a depleted gas reservoir.[10] Our own estimate for CO_2 storage in depleted oil and gas reservoirs is of the order of 50 Gigatons worldwide.

CO_2 Storage in Coal Seams

In coal seams, part of the methane is adsorbed onto the rock substrate. Production of methane from coal seams leave substantial amounts of this gas adsorbed onto the rock in the formation. Injection of CO_2 can help release the methane and result in adsorption[24] of CO_2. Estimates of CO_2 storage in coal seams[25] are of the order 100 Gigatons. However, the low permeability of the rock toward CO_2, and its swelling from CO_2 adsorption remain considerable challenges that must be overcome.

CO_2 Storage in Saline Aquifers

Saline aquifers are not thought of as a source of water for either drinking or agriculture, and, therefore, can be considered for CO_2 storage. In the following discussion, CO_2 possesses unusual density characteristics, both in the pure state and when dissolved in some liquids. CO_2 is also unusual in having a low viscosity across a range of conditions in which the density can change by an order of magnitude. The low viscosity allows injection of large quantities of CO_2 in the subsurface at high-flow rates in a single well. We will briefly discuss density aspects.

Density of CO_2, CO_2-Water, and CO_2-brine

The density of CO_2 depends sensitively on pressure and temperature at the conditions existing in saline aquifers, and can vary between 200 and 1,000 kg/m^3. CO_2 density can be higher than water density at sufficiently high pressure. High CO_2 density gives rise to high-storage capacity.

The density of water often decreases with dissolution of gases other than carbon dioxide.[26] The dissolution of CO_2 in water or in brine increases the density by 1 to 2%.[27] The increase of density from CO_2 dissolution is also observed in hydrocarbon liquids under appropriate temperatures.[21,28] CO_2 when dissolved in normal decane, for example, increases the mass density by 15% at 5°C. The density increase becomes less pronounced as the temperature increases to 100°C.[28] As we will see, the density increase may have a significant effect on mixing of CO_2-water, and CO_2-brine systems in open space (cavity without porous media), and in porous media. Many aspects of mixing and the numerical simulation of the process require further research.[29]

Distribution of Deep Saline Aquifers Around the World

Unlike coal, oil and gas, which are not uniformly distributed, saline aquifers are evenly distributed in various parts of the world. On the other hand, unlike hydrocarbon reservoirs, basic parameters such as permeability and pore volume are not generally available or accurately known for saline aquifers.

Aquifers suitable for storage are plentiful in the USA and in many other parts of the world (Figure 1). Basins are often multiply-layered, with one aquifer formation lying on top of another within the same area. The aquifers studied by the US Dept. of Energy (USDOE) for its Carbon Sequestration Atlas of the USA and Canada (Atlas II),[25] encompass an area of approximately 9×10^6 km^2 (equal to more than 90% of total US area).

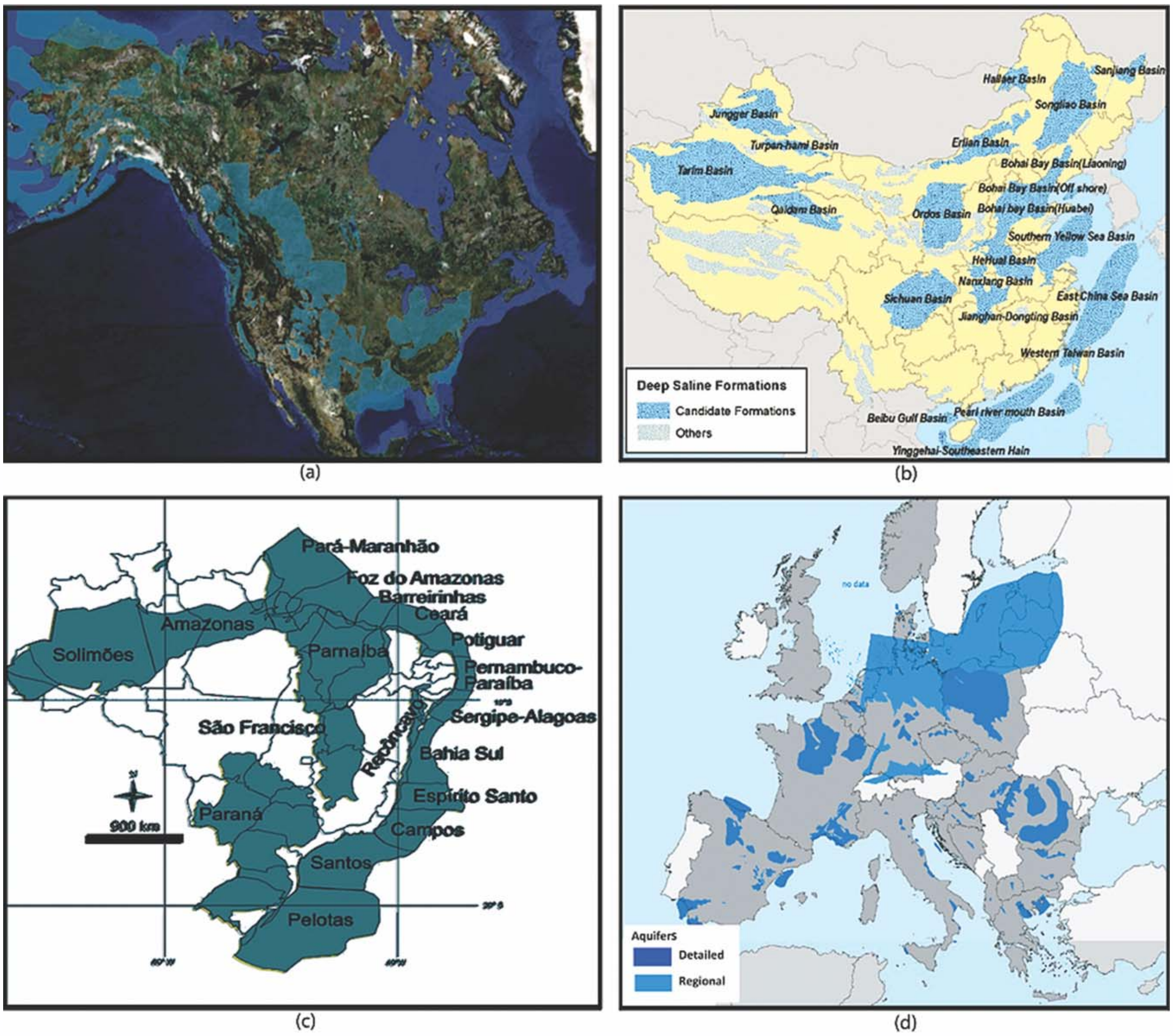
Aquifers in other parts of the world are similarly distributed. In China, a sizeable fraction (10 out of 27 total basins) of the suitable aquifers ("candidate formations") exist offshore. Aquifer basins in Brazil cover approximately 4.8×10^6 km^2 (equal to more than half of the total area), and are especially prevalent in the southeast, where most of the CO_2 stationary sources are located. Although not shown in Figure 1d, large aquifer basins exist in the North Sea; in the Sleipner project in the North Sea, CO_2 has been injected at an annual rate of about 1 Megaton since 1996.

Size of Deep Saline Aquifers Around the World

Knowledge of the pore volume and permeability of aquifer formations are central to storage capacity estimates. Total pore volumes are presented in Table 1 for selected regions of the world. It is important to note the caveats associated with each value. When possible, we cite total pore volume data directly from the literature. In the case of Brazil, we present the pore volume of one large aquifer system which sets the lower limit. However, in most cases, the pore volume is not readily available and is instead calculated based on a published storage capacity value. Storage capacity calculations in the literature have generally been based on one of two methodologies. The one developed by the USDOE[25] assumes that CO_2 injected into an aquifer displaces the water in the entire formation, whereas the one developed by the Carbon Sequestration Leadership Forum (CSLF) proposes that injected CO_2 displaces the water located only in stratigraphic traps.[24,36] The calculated value for the total pore volume depends on whether or not the entire formation is considered. In both methods it is assumed that CO_2 does not dissolve in water. Our estimate of the total pore volume of oil reservoirs in the world is of the order of 10×10^{12} m^3, which is orders of magnitude less than the pore volume of the saline aquifers.

Key Aspects of CO_2 Storage Capacity in Aquifers

For the purpose of illustration we consider a cavity of constant volume and constant temperature filled with permeable media and saturated with water. The pressure of water in the cavity will change when there is charge. As a result of CO_2 addition, pressure will increase due to the positive partial molar volume of CO_2 and nearly constant partial molar



(a) (b)

(c) (d)

Figure 1. Aquifer distribution in selected regions of the world.

(a) USA and Canada (adapted from NETL[25]). Focus is on aquifers (turquoise) in the USA and certain parts of western Canada, Gulf of Mexico, and the Bering Sea, (b) China (adapted from Dahowski et al.[30]). More suitable formations are in deep blue, while less suitable ones are in light gray, (c) Brazil (adapted from Ketzer et al.[31]). Basins (teal blue) cover more than half of total area. Basins along the southeastern coast include extensive off-shore sites, and (d) the EU (adapted from Anthonsen et al.[32]). Data were compiled from publicly available information (detailed mapping), and/or from regional studies by participating countries (dark gray) of the EU GeoCapacity project.[33]

volume of water. The increase in pressure is a key factor for assessing how much CO_2 can be stored in the cavity. The pressure increase is a function of water compressibility, pore compressibility, the degree of CO_2 dissolution in water, and chemical reaction of CO_2 with the permeable media. We will not consider the reaction of CO_2 with mineral species in the permeable media. The reaction can occur with a limited suite of rock-forming chemical components. The amount of CO_2 stored as a result of the reaction of host rock can be comparable to other processes mentioned previously, but the rate is very slow to reach equilibrium.

The compressibility of water is around 2.5 to 7 $\times$ 10^{-5} bar^{-1} across a wide range of pressure and temperature conditions (from 313 to 413 K, and from atmospheric pressure to 700 bar). For a pressure increase of about 70 bar (say, from initial pressure of 230 to 300 bar), the decrease in water volume is around 0.35% for a compressibility of 5×10^{-5} bar^{-1}.

The pore volume of the permeable media can vary over a much larger range than water volume changes associated with the same pressure increase. For rocks such as Boise, Bandera, and Berea sandstones,[37] the pore compressibility varies in the range of 3–25 $\times$ 10^{-5} bar^{-1}. The variation in pore compressibility is mainly due to differences in pore structure. For reservoir rocks, a pore compressibility of 25 $\times$ 10^{-5} bar^{-1} is not uncommon. The change in gravitational potential from the sun and the moon can be used to measure the pore compressibility in the subsurface.[38] Production data from hydrocarbon reservoirs confirm the accuracy of compressibility determination

Table 1. Estimated Total Pore Volume of Saline Aquifers in Selected Regions of the World

Country/Region	Total Pore Volume (m^3)	Notes
United States and Canada[25]	3.3×10^{14}–1.6×10^{15}	Considered the entire formation (not only stratigraphic traps)
China[30]	1.1×10^{14}	Calculated from a theoretical CO_2 storage capacity
Brazil[34]	$>5.7 \times 10^{13}$	Size of Mercosul aquifer system that spans the entire Paraná Basin cited as a lower limit
European Union[33]	2.4×10^{12}–1.2×10^{13}	Very conservative estimate. Some countries considered traps only
Australia[35]	7×10^{12}	Directly cited from source. Total pore volume of 65 potential sites

from the gravitational potential change. For a pore compressibility of 25×10^{-5} bar^{-1}, the pore volume change for a pressure increase of 70 bar is 1.75%. For abnormally-pressured formations in which the pore pressure is above the hydrostatic head of a column of water, the pore compressibility can be even higher than the gas compressibility. Despite its significance, the effect of formation compressibility has been often overlooked in CO_2 sequestration studies in saline aquifers.

The third important effect on storage relates to the dissolution of CO_2 in water. This effect, due to its importance for storage and for a major reduction of CO_2 leakage, will be discussed in more detail.

Let us consider the sketch shown in Figure 2a, and pressure evolution in Figure 2b. In Figure 2a, CO_2 is placed on top of water in permeable media.[39] Comparison of the measured pressure drop with that computed from Fickian diffusion reveals a large difference. The mixing of CO_2 and water is much faster than the diffusion prediction. Due to a small density increase from CO_2 solubility ($\Delta\rho = 5$ kg/m^3), the density at the top of the liquid column is higher than water density. As a result, natural convection develops. Figure 3 shows the early process of mixing, with CO_2 placed on top of a column of normal decane in open space.[29] For accurate modeling of natural convection in open space (1) the swelling of the liquid, as a result of CO_2 dissolution, and (2) the moving boundary between the CO_2-rich and liquid-rich phases, and the rotational nature of flow, as well as slip boundary conditions should be considered.[29,40] Due to solubility, the column of water could rise as much as 7%.

There is much theoretical work in the literature on buoyancy-driven flow in CO_2-liquid systems. A restrictive assumption in most cases is the fixed interface between the CO_2-rich and water-rich phases. Because of the large swelling of the water, a fixed boundary may not be a good assumption.

CO_2 Storage Capacity

First we assume that CO_2 forms a separate phase, immiscible with water. CO_2 only displaces the water to raise the pressure. Let us assume a pore volume capacity of 1,000 m^3. The initial pressure is 230 bar and the temperature is 100°C. The pore volume created by a pressure increase of 70 bar is around 0.3% based on a value of water compressibility of 4.5×10^{-5} bar^{-1}. For a CO_2 density of 625 kg/m^3, the stored CO_2 from water compressibility is two tons. The pressure increase may create an even higher pore volume as a result of pore compressibility. Let us assume a pore compressibility of 2×10^{-4} bar^{-1}. For the same pressure increase, the pore volume created is 1.4% of the initial pore space. The CO_2 storage, is, therefore, about eight tons. The combined storage capacity is of order of 10 tons of CO_2, which is equivalent to 1% of the weight of water. If we assume a pore compressibility of 10^{-4} bar^{-1}, the pore volume increase will be 0.7%.

Now let us assume that all the CO_2 will dissolve in water at a pressure of 300 bar. When 0.9 mol % of CO_2 is dissolved in water, there is a volume increase of about 1.8%, which is

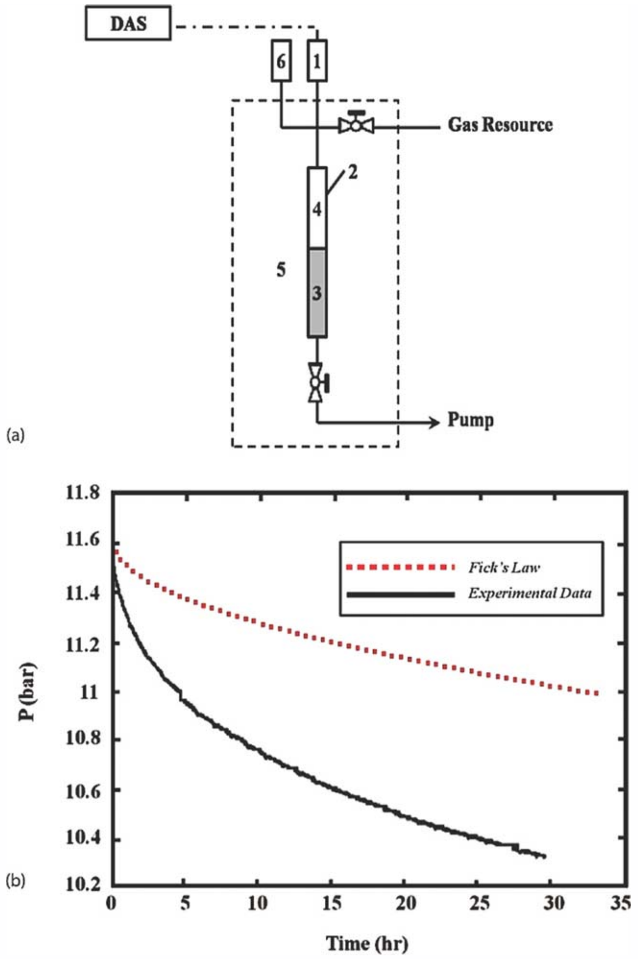


Figure 2. **Schematic of the apparatus (a) used to measure the rate of dissolution of CO_2 in porous media saturated with water at room-temperature.**

Plot of pressure evolution vs. time showing measured data and computed results using only Fickian diffusion (b). In the top plot numbers represent: (1) the pressure transducer, (2) the cell, (3) the liquid phase, (4) the CO_2 phase, (5) the bath, and (6) the pressure safety valve. DAS represents the data acquisition system (adapted from Farajzadeh et al.[39]).

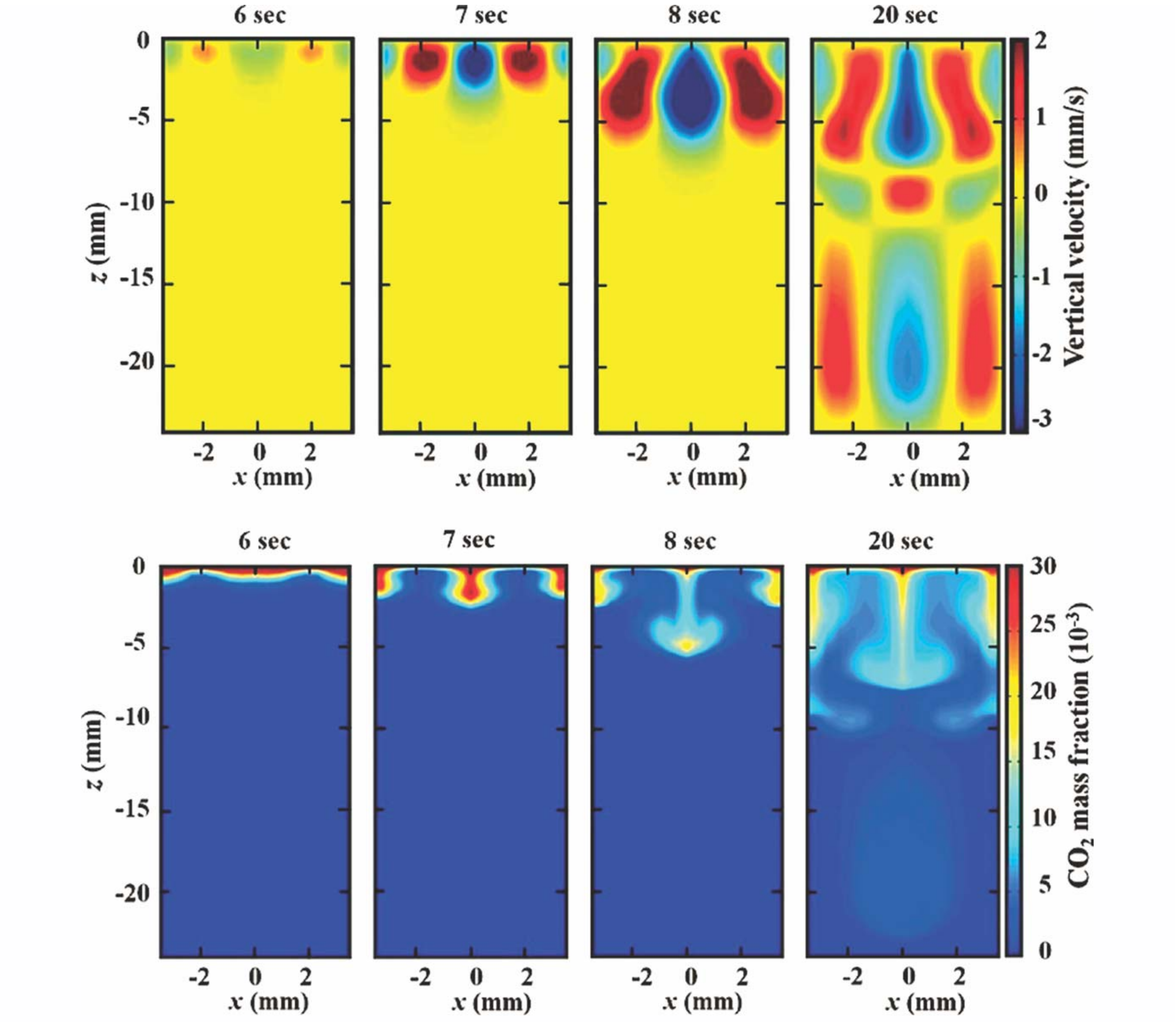


Figure 3. Velocity (top), and concentration(bottom) profiles at early times for a small cavity when CO_2 is placed on top of a liquid column of normal decane at an initial pressure of 12 bar and temperature of 25°C.

Depth zero indicates the free-liquid surface where there is movement due to swelling from CO_2 dissolution in the liquid phase. As a result of density increase from CO_2 dissolution, natural convention accelerates the mixing (adapted from Haugen and Firoozabadi[29]).

equivalent to the volume created from the combined water and pore compressibility from a pressure increase of 70 bar based on a high-pore compressibility. The dissolution will allow storage of about 20 tons of CO_2, about twice the storage calculated assuming that the CO_2 does not dissolve. Because of a density increase of 10 kg/m^3, CO_2 is expected to dissolve in water rapidly in highly permeable media. For a pore compressibility of 10^{-4} bar^{-1}, the CO_2 dissolution may be around 10 tons.

The size of saline aquifers in the United States and Canada is estimated to be of the order of 10^{15} m^3; 1 to 2 wt % CO_2 can be stored in such aquifers. The storage capacity, therefore, is of the order of 1 to 2 $\times$ 10^{13} tons; or 1 to 2 $\times$ 10^4 Gigatons. The annual CO_2 production in the USA and Canada is around 6 Gigatons (ca. 20% of world production). Our simple computations provide evidence that there is adequate storage capacity in saline aquifers for all of the produced CO_2. The key to success is selection of aquifers on the basis of full solubility of CO_2 in water to minimize CO_2 leakage to the atmosphere in case the cap rock integrity is lost. When CO_2 is dissolved in water there will be only a rise in water level, without release of CO_2.We would like to emphasize that in order to benefit from rapid dissolution of CO_2 in water or in brine, only high-permeability aquifers should be selected for storage. This important aspect is being neglected in current studies. There is very little information for the permeability of saline aquifers. This information will be required for assessing the rate of dissolution of CO_2, with proper numerical models.

Our storage capacity calculation based on the assumption of dissolution can be compared with that calculated by the USDOE,[25] which assumes that injected CO_2 displaces water in the entire aquifer. The formations are assumed to be open systems unconfined laterally by impermeable layers.[36] The storage capacity is calculated as the product of the total pore volume with a representative CO_2 density and a storage efficiency factor E. This efficiency factor is expressed as a product of several correction parameters. It takes into account technical and physical limitations such as the fraction of the aquifer that is suitable for storage. Each parameter is assigned a likely range. Monte Carlo simulations are performed to obtain low- and high-end E estimates of 0.01 and 0.04, respectively. The storage capacity for the aquifers in the study is calculated to be between 3.30×10^3 and 1.26×10^4 Gigatons. Remarkably, our simple calculation approach gives estimates of the same order as those by USDOE.

Discussion and Concluding Remarks

Despite the gravity of the challenges from global warming, there are viable options for reducing CO_2 emissions to the atmosphere and mitigating the problem. Storage of CO_2 produced from combustion of fossil flues in subsurface formations may be a natural choice. There is already some CO_2 in the subsurface; it is not foreign to the Earth's crust and to the subsurface.

Perhaps one of the most important issues of CO_2 sequestration in saline aquifers relates to the dissolution rate of CO_2 in the aqueous phase. The dissolution increases the storage capacity by a factor of two or more, depending on the temperature and pressure conditions. A more important aspect relates to leakage in case the cap rock integrity is lost due to pressure increase. When CO_2 is dissolved in water, and there is a leak, water will move upward with the dissolved CO_2. Because of high pressure, CO_2 will remain in solution until a new hydrostatic equilibrium is reached. The pressure from the column of the rock is about twice as much as the hydrostatic column of water; therefore, water movement will stop after some displacement. However, if CO_2 does not dissolve in water, the upward movement and decrease in density may lead to leakage into the atmosphere. The rate of dissolution of CO_2 in water and in brine, both in porous media and in open space, is of fundamental importance. In porous media, the permeability has an important effect on natural convection arising from the density increase. With better understanding and modeling, a more intelligent selection of saline aquifers can be made.

In the last few years, we have evaluated the benefits of CO_2-improved oil recovery in a number of very large hydrocarbon reservoirs in different parts of the world. One specific example is given in Hoteit and Firoozabadi.[23] There appear to be great benefits in increased recovery in some cases. Once CO_2 becomes available from capture in power plants, it could significantly assist improved oil recovery.

In our simple computations related to CO_2 storage capacity, instead of using the properties of brines, we use water properties. In brines, the solubility of CO_2 is less than in water. However, the results do not change appreciably for the dissolution range in our computations. Whether with water or with brines, saline aquifers provide adequate capacity for storage of CO_2.

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Literature Cited

1. National Petroleum Council. Facing the Hard Truths about Energy: A Comprehensive View to 2030 of Global Oil and Natural Gas. US Dept of Energy; 2007.
2. Doney SC, Fabry VJ, Feely RA, Kleypas JA. Ocean acidification: The other CO_2 problem. *Annu Rev Mar Sci*. 2009;1:169.
3. Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola JM, Basile I, Bender M, Chappellaz J, Davis M, Delaygue G, Delmotte M, Kotlyakov VM, Legrand M, Lipenkov VY, Lorius C, Pépin L, Ritz C, Saltzman E, Stievenard M. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature*. 1999;399:429.
4. Arrhenius S. On the influence of carbonic acid in the air upon the temperature of the ground. *Philos Mag*. 1896;41:237.
5. Intergovernmental Panel on Climate Change (IPCC). Fourth Assessment Report: Climate Change 2007. Cambridge University Press; 2007.
6. Hansen J, Sato M, Kharecha P, Beerling D, Berner R, Masson-Delmotte V, Pagani M, Raymo M, Royer DL, Zachos JC. Target atmospheric CO_2: Where should humanity aim?. *Open Atmos Sci J*. 2008;2:217.
7. Velicogna I. Increasing rates of ice mass loss from the Greenland and Antarctic ice sheets revealed by GRACE. *Geophys Res Lett*. 2009;36:L19503.
8. Plasynski SI, Litynski JT, McIlvried HG, Srivastava RD. Progress and new developments in carbon capture and storage. *Crit Rev Plant Sci*. 2009;28:123.
9. Torp TA, Gale J. Demonstrating storage of CO_2 in geological reservoirs: The Sleipner and SACS projects. *Energy*. 2004;29:1361.
10. Bouquet S, Gendrin A, Labregere D, Le Nir I, Dance T, Xu J, Cinar Y. CO_2CRC Otway Project, Australia: Parameters Influencing Dynamic Modeling of CO_2 Injection into a Depleted Gas Reservoir. SPE Offshore Europe Oil & Gas Conference & Exhibition: Aberdeen, U.K.; 2009.
11. Haszeldine RS. Carbon capture and storage: How green can black be? *Science*. 2009;325:1647.
12. Rochelle GT. Amine scrubbing for CO_2 capture. *Science*. 2009;325:1652.
13. Maneeintr K, Idem RO, Tontiwachwuthikul P, Wee AGH. Comparative mass transfer performance studies of CO_2 absorption into aqueous solutions of DEAB and MEA. *Ind Eng Chem Res*. 2010;49:2857.
14. Francisco GJ, Chakma A, Feng X. Membranes comprising of alkanolamines incorporated into poly (vinyl alcohol) matrix for CO_2/N_2 separation. *J Membr Sci*. 2007;303:54.
15. Lackner KS. A guide to CO_2 sequestration. *Science*. 2003;300:1677.
16. Keith, DW. Why capture CO_2 from the atmosphere? *Science*. 2009;325:1654.

17. Badessich MF, Gait M, Carbone C, Dzelalija F, Giampaoli P. Integrated Reservoir Characterization for the Redevelopment of a Highly Complex Field. SPE Europec/EAGE Annual Conference: Madrid, Spain; 2005.
18. Rumble D, Ferry JM. Hoering TC, Boucot AJ. Fluid flow during metamorphism at the Beaver Brook fossil locality, New Hampshire. *Am J Sci*. 1982;282:886.
19. Koottungal L, ed. Worldwide EOR Survey. *Oil Gas J*. 2008;106:47.
20. Moortgat J, Sun S, Firoozabadi A. Compositional modeling of three-phase flow with gravity using higher-order finite element methods and applications to CO_2 injection. *Adv Water Res*. submitted 2010.
21. Nasrabadi H, Firoozabadi A. Complex flow and composition path in CO_2 injection schemes from density effects in 2 and 3D. *SPE Reserv Eval Eng*. submitted, 2010.
22. Sánchez JL, Astudillo A, Rodríguez F, Morales J, Rodríguez A. Nitrogen Injection in the Cantarell Complex: Results after Four Years of Operation. SPE Latin American and Caribbean Petroleum Engineering Conference: Rio de Janeiro, Brazil; 2005.
23. Hoteit, H., Firoozabadi A. Numerical modeling of diffusion in fractured media for gas injection and recycling schemes. *SPE J*. 2009;14:323.
24. Bachu S, Bonijoly D, Bradshaw J, Burruss R, Holloway S, Christensen NP, Mathiassen OM. CO_2 Storage capacity estimation: methodology and gaps. *Int J Greenhouse Gas Control*. 2007;1:430.
25. Carbon Sequestration Atlas of the United States and Canada II. National Energy Technology Laboratory (NETL); 2008, US Dept of Energy. Available at http://www.netl.doe.gov/technologies/carbon_seq/refshelf/refshelf.html.
26. Ashcroft SJ, Isa MB. Effect of dissolved gases on the densities of hydrocarbons. *J Chem Eng Data*. 1997;42:1244.
27. Li Z, Firoozabadi A. Cubic-plus-association CPA equation of state for water-containing mixtures: Is cross association necessary? *AIChE J*. 2009;55:1803.
28. Reamer HH, Sage BH. Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of the *n*-decane-CO_2 system. *J Chem Eng Data*. 1963;8:508.
29. Haugen K, Firoozabadi A. Momentum balance at the interface between two fluid phases. submitted 2010.
30. Dahowski RT, Li X, Davidson CL, Wei N, Dooley JJ. Regional Opportunities for Carbon Dioxide Capture and Storage in China: A Comprehensive CO_2 Storage Cost Curve and Analysis of the Potential for Large Scale Carbon Dioxide Capture and Storage in the People's Republic of China. US Dept of Energy; 2009. Contract DE-AC05-76RL01830.
31. Ketzer JM, Villwock JA, Caporale G, da Rocha LH, Rockett G, Braum H, Giraffa L. Opportunities for CO_2 capture and geological storage in Brazil: The CARBMAP Project. Sixth Annual Conference on Carbon Capture and Sequestration; Pittsburgh, PA, 2007.
32. Anthonsen KL, Vangkilde-Pedersen T, Vangkilde-Pedersen LH. Estimates of CO_2 storage capacity in Europe. *IOP Conf Ser Earth Environ Sci*. 2009;6:172006.
33. EU GeoCapacity Project. Assessing European Capacity for Geological Storage of Carbon Dioxide. Sixth Framework Programme of the European Community for Research, D16 WP2 Report Storage Capacity; 2009.
34. Araújo LM, França AB, Potter PE. Hydrogeology of the Mercosul aquifer system in the Paraná and Chaco-Paraná basins, South America, and comparison with the Navajo-Nugget aquifer system, USA. *Hydrogeol J*. 1999;7:317.
35. Bradshaw J, Allinson G, Bradshaw BE, Nguyen V, Rigg AJ, Spencer L, Wilson P. Australia's CO_2 geological storage potential and matching of emission sources to potential sinks. *Energy*. 2004;29:9.
36. Cooperative Research Centre for Greenhouse Gas Technologies (CO_2CRC). Aquifer storage - development issues. International Energy Agency Greenhouse Gas R&D Programme (IEAGHG). Report No. 2008/12; 2008.
37. Zimmerman RW. Compressibility of Sandstones. Elsevier; 1991.
38. Chang E, Firoozabadi A. Gravitational potential variations of the sun and moon for the estimation of reservoir compressibility. *SPE J*. 2000;5:456.
39. Farajzadeh R, Salimi H, Zitha PLJ, Bruining J. Numerical simulation of density-driven natural convection in porous media with application for CO_2 injection projects. *Int J Heat Mass Transfer*. 2008;50:5054.
40. Haugen K, Firoozabadi A. Composition at the interface between multicomponent non-equilibrium phases. *J Chem Phys*, 2009;130:064707.