Utilization of CO_2 as Cushion Gas for Porous Media Compressed Air Energy Storage

Curtis M. Oldenburg[1] and Lehua Pan

Earth Sciences Division 90-1116

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

[1]Corresponding Author cmoldenburg@lbl.gov

Abstract

Porous media compressed air energy storage (PM-CAES) and geologic carbon sequestration (GCS) can potentially be combined when CO_2 is used as the cushion gas. The large increase in density of CO_2 around its critical pressure at near-critical temperature means that a PM-CAES reservoir operated around the CO_2 critical pressure could potentially store more air (energy) for a given pressure rise in the reservoir. One-dimensional (1D) radial TOUGH2 simulations of PM-CAES with CO_2 as the cushion gas have been carried out to investigate pressurization and gas-gas mixing effects. We find that pervasive pressure gradients in PM-CAES make it desirable to position the air-CO_2 interface close to the well, but cushion gas at such locations is subject to strong and undesirable air-CO_2 mixing and subsequent production of CO_2 up the well. To avoid this negative effect, CO_2 cushion gas should be located at the far outer margins of storage reservoirs where mixing will be very slow. In such a configuration, the super-compressibility of CO_2 will not be exploited, but CO_2 can be stored in the GCS context potentially earning significant value for the PM-CAES project depending on the price of carbon.

Introduction

Compressed air energy storage (CAES) as carried out today is the process by which air is compressed using inexpensive electricity during periods of excess supply (e.g., during late night and very early morning periods) and injected through wells into subsurface caverns where it is stored. During periods of high demand (after mid-day) the high-pressure air (working gas) is produced and fed into a gas turbine with natural gas to generate electricity. In CAES, a large portion of the stored air is never produced; this air is referred to as the cushion gas because it provides pressure support to the air that is produced (working gas). CAES systems can be built in caverns or in porous media systems such as aquifers or depleted hydrocarbon reservoirs.

CAES in porous media systems such as aquifers and depleted hydrocarbon reservoirs (PM-CAES) is a promising approach for electrical energy storage for large-scale deployment of intermittent solar and wind energy systems[1, 2]. At the same time, carbon dioxide capture and storage (CCS) is a critical component of the multiple approaches needed to reduce net CO_2 emissions from the use of fossil fuels[3]. Given that the large majority of air in a PM-CAES reservoir is cushion (or base) gas, that is, air that is never produced but is instead only for pressure support, the question arises as to whether CO_2 could be used as the cushion gas for PM-CAES reservoirs.

There are several potential benefits to using CO_2 as a cushion gas for CAES. First, assuming there is someday a price on carbon, a CAES operator could earn money by taking a fixed mass of CO_2 over a period of time from an emitter such as a fossil-fuel power plant or refinery and storing (sequestering) it in a reservoir for use as cushion gas for CAES. Second, CO_2 has a large compressibility under certain pressure-temperature (*P*-*T*) conditions, and can therefore possibly be exploited to allow more air injection (greater energy storage) than would be possible in the

same reservoir using air as the cushion gas. These same potential benefits of CO_2 utilization and storage were described 10 years ago in the context of the suggestion to use CO_2 as a cushion gas for natural gas storage[4].

In this paper, we use numerical simulation of an idealized one-dimensional (1D) radial system to model PM-CAES with and without CO_2 as a cushion gas. We focus on two main questions: (1) can the super-compressibility of CO_2 be feasibly exploited? and, (2) what are the characteristics of mixing between the air (working gas) and the CO_2 (cushion gas)? Our simulation results and analysis of these two questions, along with reference to our previous findings on standard PM-CAES[5], are used in the discussion section to assess the challenges and opportunities of using CO_2 as a cushion gas for PM-CAES.

Background

Although there are no current examples of PM-CAES systems in operation, there are two cavern CAES systems (Huntorf, Germany; and McIntosh, Alabama) that have been operating continuously for decades[6,7]). Despite there being only two CAES plants worldwide, CAES is second only to pumped-storage hydroelectricity (PSH, pumping water from low-elevation reservoirs up into higher-elevation reservoirs) in the amount of worldwide grid-scale energy storage it provides.[8] In fact, 99% of worldwide grid-scale energy storage is carried out by either PSH or by CAES, with CAES a distant second to PSH[8]. The current cavern CAES plants work by using excess electricity (purchased at low cost) to compress air, which is then injected into subsurface caverns that are sealed to prevent leakage. When demand increases and electricity cost goes up during times of high demand typically around mid-day, the pressurized air is produced and fed into a gas turbine along with natural gas to generate electricity. PM-CAES

shares many similarities with cavern CAES, but also important differences. The main difference is that whereas a cavern becomes uniformly pressurized upon air injection, a PM-CAES reservoir has large pressure gradients radiating away from the well during injection and production of working gas. These pressure gradients are an intrinsic part of PM-CAES and are caused by the resistance to flow in the porous rock, i.e., caused by formation permeability[5].

In both cavern and PM-CAES, most of the air in the reservoir is neither injected nor produced during reservoir cycling, but rather provides the compressibility to accommodate injection and aid production of the working gas (the mass of air that is injected and produced). This gas that is neither injected nor produced is called the cushion (or base) gas.

With fossil fuels currently providing over 80% of primary energy supply worldwide, and scientific consensus that CO_2 concentrations in the atmosphere are causing climate change, there is an urgent need for implementation of multiple mitigation approaches, among which is carbon dioxide capture and storage (CCS)[9]. In geologic carbon sequestration (GCS), CO_2 is injected deep underground into saline aquifers or depleted hydrocarbon reservoirs where it is expected to stay sequestered for millennia[3]. The same properties of cap rocks that seal effective GCS storage sites are needed for PM-CAES, as is permeability and connectivity of the reservoir itself for sufficient injectivity and storage capacity to match the storage requirements. With this intersection of common properties between PM-CAES and GCS sites, the obvious question arises as to whether CO_2 can be used beneficially as a cushion gas for PM-CAES.

Prior Work

While no one to date has investigated the performance of CO_2 as a cushion gas for PM-CAES, prior work has been done in the area of aquifer natural gas storage on the use of alternate cushion

gases such as nitrogen[10,11] and CO_2[4]. The motivation for using an inert cushion gas for aquifer natural gas storage is to avoid the large cost of the CH_4 used for the cushion gas, a cost which generally cannot be recouped even after decommissioning of the storage site due to residual gas trapping. Rather than using an expensive commodity such as CH_4 as the cushion gas, it may be advantageous for the operator to use a cheap inert gas such as nitrogen, or better, a gas such as CO_2 that may have value for the operator through trading of carbon emission credits. For PM-CAES, the motivation for using CO_2 as the cushion gas would be the potential value of emission credits, and the favorable compressibility of CO_2.

Oldenburg (2003)[4] pointed out that there may be an advantage to using CO_2 because of its unique properties, specifically its super-compressibility through the critical pressure at temperatures just above the critical temperature. This feature is shown in Fig. 1 for CO_2-air mixtures by plotting density vs. pressure at a temperature T = 35 °C which is just above the critical temperature of CO_2 (T_{crit} = 31 °C). These densities are calculated using WebGasEOS[12] assuming air is 80% N_2 and 20% O_2 by volume. As shown, for high-concentration CO_2 gas, the compressibility is very large around the critical pressure of CO_2 (P_{crit} = 7.1 MPa), a feature which would allow storage of more air for a given pressure rise in the reservoir, assuming the cushion could be subject to this pressure swing during cycling.

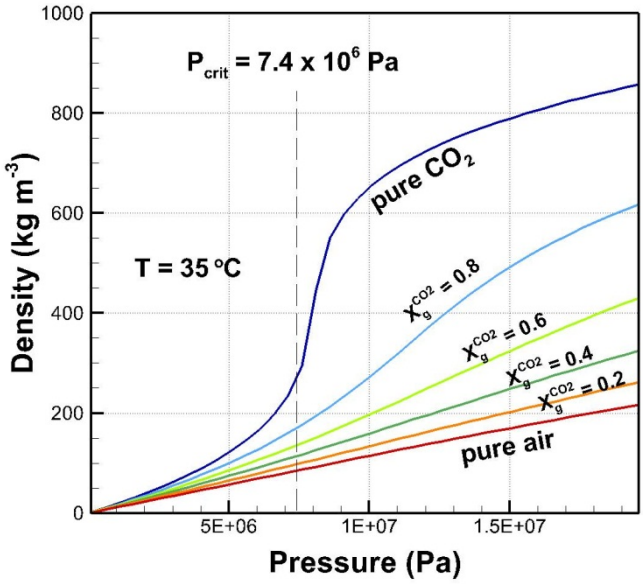


Figure 1. Density vs. pressure for various compositions of CO_2-air mixtures at 35 °C showing the super-compressibility effect for gas mixtures with high CO_2 concentration near $P = 7.4 \times 10^6$ Pa, and nearly linear (approximately ideal gas) behavior for air-dominated mixtures at all pressures.

A first-order challenge in the use of any contrasting working gas-cushion gas combination is controlling mixing between the working and cushion gases. The question of mixing between an inert cushion gas and natural gas was addressed by Gardner et al. (1962)[13] who determined that mixing would not be a problem for decades in a natural gas storage reservoir as long as the contact area between the cushion and the working gas was small, such as would occur if cushion gas were positioned laterally adjacent to the working gas over a small thickness of reservoir. A particularly bad configuration was determined to be the case where the cushion gas is located below the working gas along a large horizontal contact area[13].

A more recent study by Kilinç and Gümra (2000)[14] used numerical simulation of a particular reservoir to evaluate the degree of mixing that would occur in a natural gas reservoir with nitrogen as the cushion gas. They determined that mixing would not lead to the production of nitrogen at the production wells for the configuration of interest, namely a system with cushion gas injected in the distant margins of the structure, and gas storage occurring in a set of wells near the center of the structure. This configuration assured that the natural gas-nitrogen contact would not encroach on the produced gas during many years of storage and recovery cycles.

Gas-gas mixing has also been studied in the context of the use of CO_2 for enhanced natural gas recovery[15,16]. Because mixing in porous media occurs by both diffusive and advective processes, often referred to as hydrodynamic dispersion, the more flow there is in the reservoir, the more mixing will occur. The non-mixing of cushion and working gases is favored in natural gas storage reservoirs because there is usually only a single annual (seasonal) cycle between storage and production. In contrast, PM-CAES reservoirs may have to be operated to respond to daily or weekly variations in electricity supply as controlled by the effects of weather on wind and cloud cover (number of sunny days) which controls the output of wind and solar energy systems. The number of cycles that occur in 30 years in a natural gas storage reservoir might occur in one month in a PM-CAES reservoir. This difference in cycling frequency may play a large role in the feasibility of PM-CAES reservoirs to use CO_2 as a cushion gas.

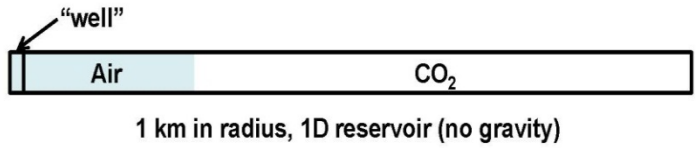
Methods

To address the key issues of mixing and whether or not the super-compressibility of CO_2 can be exploited in a PM-CAES reservoir with CO_2 as cushion gas, we make use of a research module of the numerical simulator TOUGH2[17] that extends EOS7C[18] to model the components H_2O,

CO_2, CH_4, and air. Partitioning of the components between the gas and aqueous phases is modeled using effective Henry coefficients so that effects of dissolution of the gas components into the immobile aqueous phase are accounted for. Note that in the cases studied here, we set the CH_4 mass fraction to be zero. For the analysis, we use a simple 1D radial system to avoid complexities of vertical flow in the reservoir and coupled wellbore-reservoir flow that we have simulated in previous work[5]. We start the simulation with varying amounts of CO_2 cushion gas with the air-CO_2 interface positioned at different distances from the injection well, and we simulate 30 days of daily non-isothermal CAES cycling. Although not simulated here, we envision emplacement of the CO_2 cushion to be analogous to a GCS project in which CO_2 is injected through a well into the reservoir, followed by air injection to create a working gas bubble that displaces the cushion to the distance desired. Mixing during the storage reservoir development phase is not considered in this study.

The domain and discretization are shown in Fig. 2. There are 323 grid blocks which vary in size as shown in Fig. 2b. The grid-block sizes are highly graded from very fine near the well to much coarser far from the well. There is also a grid block of radius 0.53 m attached on the left-hand side that plays the role of the well in which air is injected and produced depending on the cycle. Properties of the 1D reservoir conceived to be at a depth of approximately 750 m are shown in Table 1. By use of this simple model system, we will demonstrate clearly pressurization and mixing effects of PM-CAES with CO_2 as cushion gas. A round of preliminary simulations (not shown here) allowed us to define this system thickness and *P-T* conditions that can accommodate one-half (single cavern) of the two-cavern Huntorf air injection and production schedule (see Table 2) while producing pressurization in the range that we wanted to straddle the critical pressure of CO_2 (7.4 MPa).

(a)



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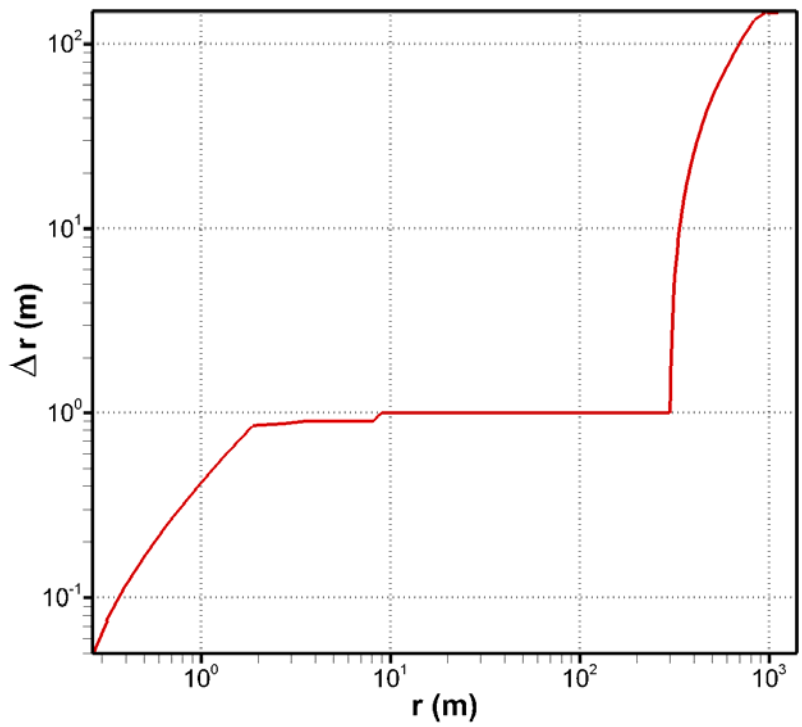

Figure 2. (a) Sketch of 1D radial domain and (b) grid spacing as a function of radius (*r*) in the 1D domain.

Table 1. Properties of the prototypical PM-CAES system.

Reservoir Properties	
Reservoir thickness	25 m
Radius	1000 m
Porosity (ϕ)	0.20
Permeability (k)	1.0×10^{-12} m^2
Density of grains in reservoir formation	2600 kg/m^3
Compressibility of reservoir	1×10^{-10} Pa^{-1}
Thermal conductivity of reservoir	2.51 W/(m K)
Heat capacity (C_P) of saturated reservoir	920 J/(kg K)
Capillary pressure (P_{cap}) and relative permeability (k_r) *Terminology:* m_{vG} = 1-1/n = parameter related to pore-size distribution S_{ar} = aqueous-phase residual saturation S_{gr}= gas-phase residual saturation P_{c0} = capillary pressure strength between aqueous and gas phases P_{cmax} = maximum possible value of P_{cap}	van Genuchten[1] P_c and k_r with Corey[2] relative permeability for gas m_{vG} = 0.20 S_{ar} = 0.25 for P_{cap}, 0.27 for k_r S_{gr} = 0.01 P_{c0} = 1189 Pa P_{cmax} = 1×10^5 Pa
Initial pressure	7.5×10^6 Pa (75 bar)
Initial temperature	35 °C
Initial gas saturation	0.80

[1]van Genuchten (1980)[19]
[2]Corey (1954)[20]

Table 2. Operational parameters of the idealized 1D PM-CAES system.

Operational Parameters	
Injection rates	Air 53.992 kg/s; H_2O 0.008 kg/s; enthalpy 3.1983×10^5 J/kg
Production rate	208.5 kg/s
Daily schedule	12 hr recharge 4.5 hr shut in 3 hr production 4.5 hr shut in

Results

Pressure Change

The pressure evolution as a function of time at the well is shown in Fig. 3 for the four cases studied (no-CO_2 cushion; CO_2 cushion positioned at 20 m, at 50 m, and at 100 m). We note first that the change in pressure is larger during production than during injection due to the smaller mass flow rate (54.0 kg/s) during the recharge period than that (208.5 kg/s) during the production period. We note second that regardless of whether all 30 cycles or just five cycles are shown, the differences in pressure at the well between the four cases are not very large. With the CO_2 cushion, the expectation is that the large compressibility of CO_2 will lead to less pressure increase during injection and therefore greater storage capacity of the reservoir. What this first result demonstrates is that the effect is present, but that it is quite small. We also note that these simulations are non-isothermal, and that the temperature variations (not shown) followed the

same patterns of rise and fall associated with injection and production, respectively, as presented in Oldenburg and Pan (2013)[5].

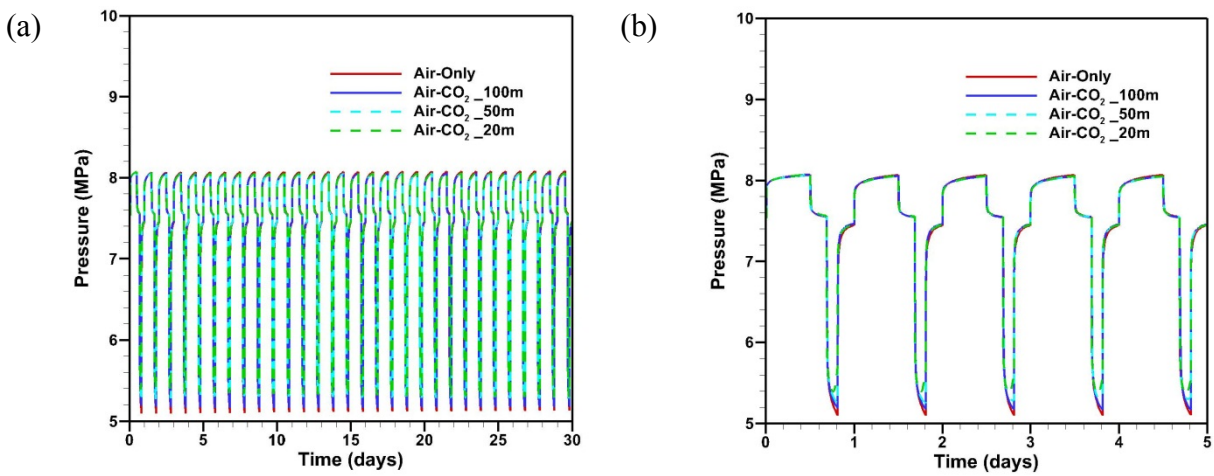

Figure 3. Pressure vs. time at the well for (a) all 30 cycles of the PM-CAES reservoir, and (b) the first five cycles for four different cushion gas scenarios: (1) no CO_2 cushion, (2) CO_2 cushion starting at r = 100 m, (3) CO_2 cushion starting at r = 50 m, and (4) CO_2 cushion starting at r = 20 m. Very little difference in pressure response can be discerned at this scale.

By expanding the scale of the pressure (vertical) axis of the figure, we can more clearly see the benefit of using the CO_2 cushion as shown in Fig. 4. The largest and smallest pressures during the injection and production periods, respectively, occur for the no-CO_2 cushion cases as we would expect, and the pressures are the most attenuated for the case where the CO_2 cushion is the largest (air-CO_2 = 20 m). But the overall beneficial impact of the CO_2 cushion is modest.

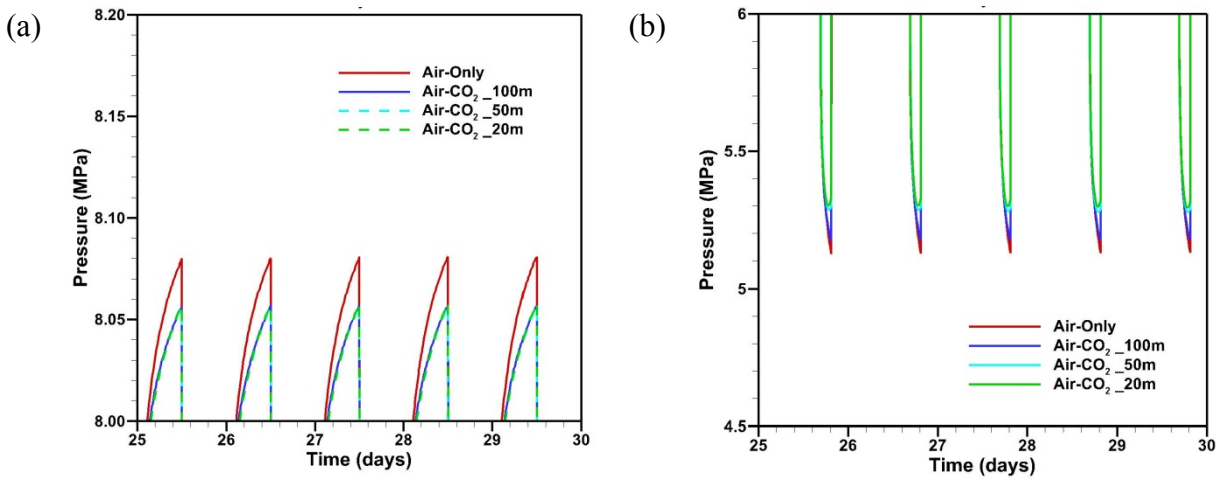

Figure 4. Pressure vs. time at the well for four scenarios of the last five cycles shown at a scale that enhances the differences in (a) maximum pressure (during injection) and (b) minimum pressure during production.

Looking into the reason that the effect of the CO_2 cushion is modest, we plot in Fig. 5 the pressure variations during injection and production cycles for all time as a function of radius with the mass fractions of CO_2 shown as solid black lines. First, we observe again by the maximum and minimum radius reached by various pressures (color-contoured background) that CO_2 cushion gas moderates pressure change as expected. We also observe that the production-induced pressure changes extend farther into the reservoir than the injection-induced changes because the change in pressure at the well is larger during production than injection due to the larger flow (air production) rate. This kind of behavior would not be observed in a cavern because pressure is effectively uniform (quickly equilibrated) throughout a cavern whereas in a PM-CAES system, permeability limits the rate of pressure equilibration throughout the reservoir resulting in pressure gradients.

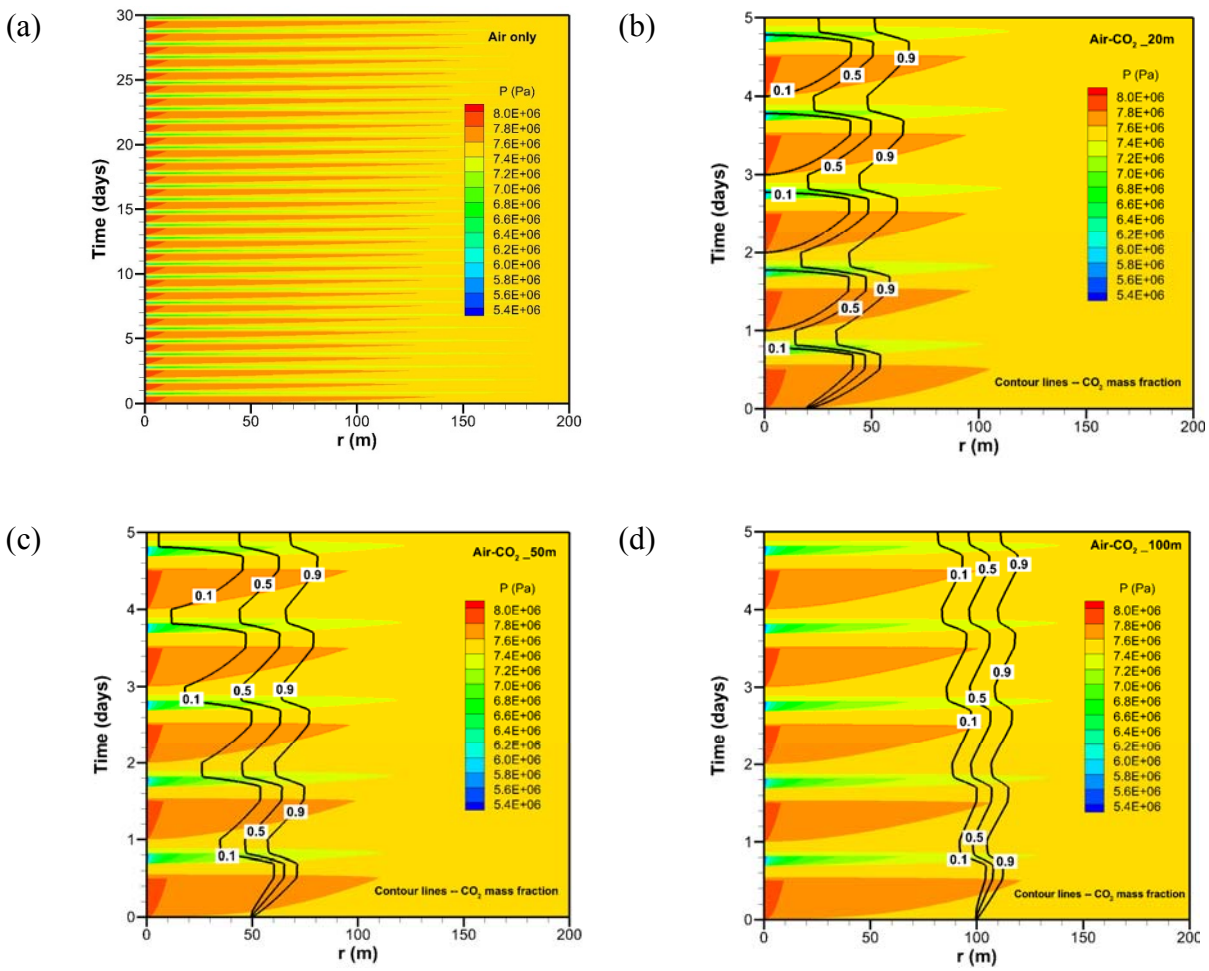

Figure 5. Pressure (color contours) and mass fraction of CO_2 in the gas phase (solid lines) as a function of radius (horizontal axis) and time (vertical axis). (a) No-CO_2 cushion, all 30 cycles, pressurization on first cycle (deep orange color) extends to ~130 m; (b) first five cycles for the case of CO_2 cushion starting at r = 20 m, pressurization extends to ~95 m; (c) r = 50 m, pressurization extends to ~90 m; and (d) r = 100 m, pressurization extends to ~100 m.

Looking only at the middle solid line of CO_2 mass fraction in Figs. 5b-d, which represents the effective transition from mostly air to mostly CO_2, we observe that the pressure variations do not penetrate very far into the region that contains mostly CO_2. And when the pressure variations do

penetrate into the region with CO_2 cushion (e.g., Fig. 5b), there tends also to be non-zero CO_2 mass fraction at the well, i.e., CO_2 will be produced out the well. This is the conundrum at the heart of exploiting CO_2 properties to benefit PM-CAES. Specifically, porous media systems are dominated by pressure gradients, which means in order to get a swing above and below P_{crit} deep within the cushion, the well-bottom pressure would have to undergo a much large pressure swing, typically larger than would be practical given limitations imposed by fracturing of the reservoir rock. If the CO_2 cushion is placed very near the well, the pressure swings will occur in the CO_2 cushion, but you also get the likelihood of producing the cushion gas out the well as discussed next.

Mixing

Here we consider the mixing between air and the CO_2 cushion. As shown in Fig. 5b-d the distance between the 0.1 and 0.9 CO_2 mass fraction curves increases with time indicating a smearing of the interface between working (air) and cushion (CO_2) gases. With zero gas- and liquid-phase diffusion assumed in our model, this smearing effect is caused solely by numerical dispersion. At r = 10 m, the typical pore velocities in the 1D radial here are on the order of 10^{-2} and 10^{-3} m/s during production and injection, respectively, while at r = 100 m these velocities are of order 10^{-3} and 10^{-4} m/s during production and injection, respectively. With grid spacing Δr = 1 m, the numerical dispersivity is $\Delta r/2$ = 0.5 m, making the dispersion coefficient ($D_{num} = \Delta r/2 * U_{Darcy}$) in the simulations on the order of 10^{-3} m^2/s at around 10 m from the well, and dropping off quickly with distance from the well. Although numerical dispersion is strictly an artifact of our integrated finite difference method, actual hydrodynamic dispersion would occur in any porous media system. It turns out that the numerical dispersivity in this 1D model (0.5 m) is roughly equivalent to measurements from multiple studies of hydrodynamic longitudinal

dispersivity, which ranges from 0.5 to 5 m when applied to mixing over 10 to 100 m length scales[21]. Therefore, the numerical dispersion in our model is analogous and likely within an order of magnitude or two of the hydrodynamic dispersion that would occur in an actual reservoir.

Although we cannot be precise about the magnitude of hydrodynamic dispersion in general, we know that flow back and forth in any reservoir will lead to dispersion of the air-CO_2 interface over time. And we can say that the faster the flow velocity is, the more mixing there will be. This aspect of dispersion is revealed in our simulations as shown by the size of the mixing zone (δ_{mix}) represented by the distance between the 0.1 and 0.9 isopleths. As shown in Fig. 5 and 6, the mixed zone increases in size with time, and this spacing increases more rapidly when the air-CO_2 interface is closer to the injection well. In fact, when the air-CO_2 interface is initially at 20 and 50 m, the dispersion is sufficient to lead to a mixed zone that intersects the well, leading to the production of CO_2 out of the well. This is clearly not something that would be desirable operationally from either the gas-turbine energy recovery or GCS perspectives.

The mass fraction in the well as a function of time is shown in Fig. 6d. One interesting feature shown in Fig. 6 is the reversal in production of CO_2 for the case of the air-CO_2 interface at 50 m. It seems that when CO_2 cushion gas is produced early in the cycling and replaced by air in subsequent injections, it shifts the average air-CO_2 interface to a larger radius, making the production of CO_2 less and less of a problem at later time. Nevertheless, in so doing, it makes the pressurization advantage of the CO_2 cushion less because the bulk of the CO_2 tends to reside at larger radius locations where the pressure swing is smaller. For an air-CO_2 interface position at 100 m or larger, only very small amounts of CO_2 end up at the well.

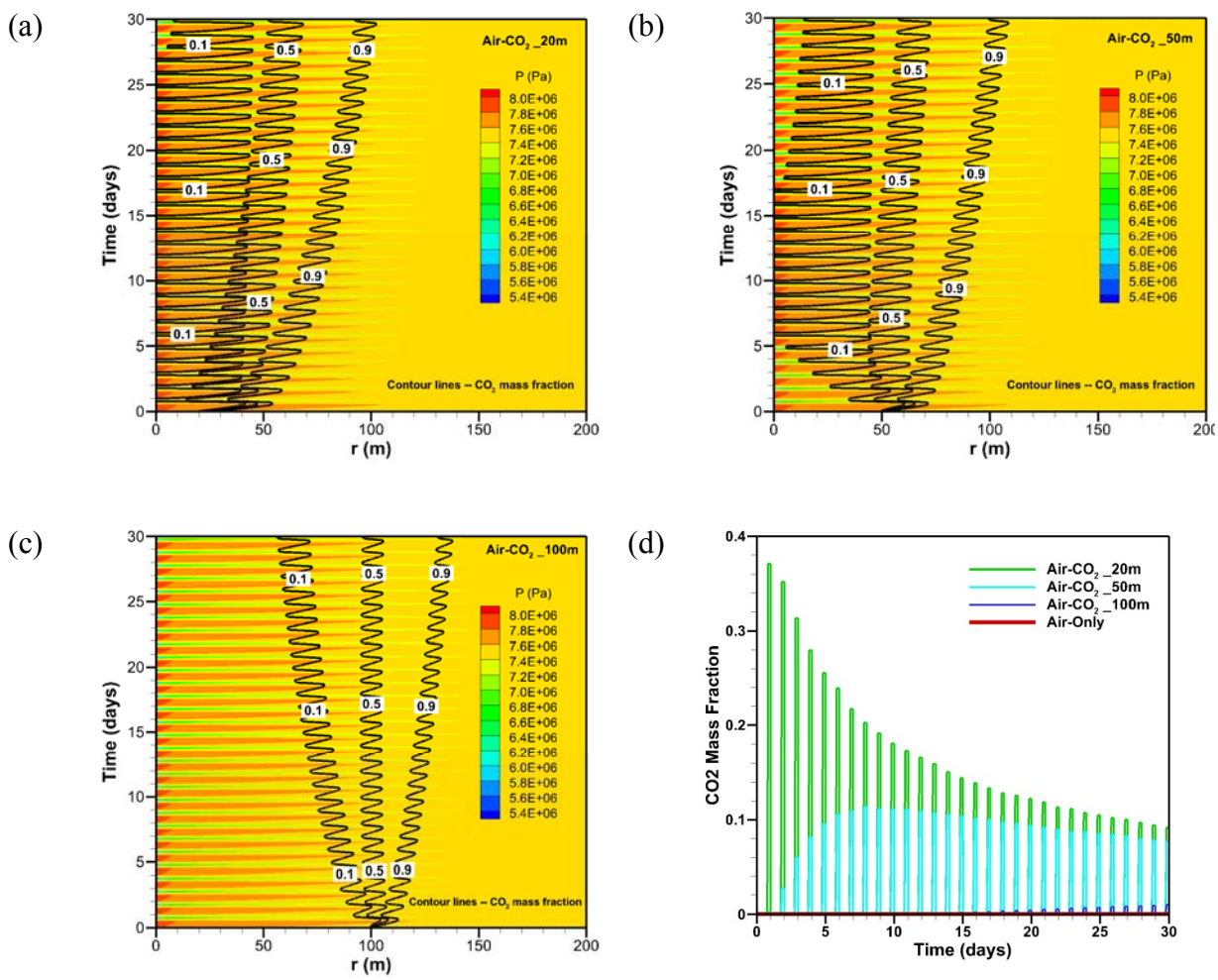

Figure 6. Pressure (color contours) and mass fraction of CO_2 in the gas phase (solid lines) as a function of radius (horizontal axis) and time (vertical axis). (a) CO_2 cushion starting at r = 20 m; (b) starting at r = 50 m; (c) starting at r = 100 m; (d) CO_2 mass fraction in the well as a function of time for the four scenarios. As shown, significant amounts of the cushion gas are produced for the air-CO_2 interface at 20 and 50 m, while negligible CO_2 is produced for the case of cushion gas starting at 100 m.

The size of the mixed zone after 30 cycles is shown explicitly in Fig. 7 as a function of the distance of the initial interface between the working gas (air) and the cushion gas (CO_2). In general, the mixing zone is much smaller for interfaces at greater distances from the well. The reason for this is that the velocities of the gases during production and injection are much smaller away from the well due to the radial geometry of the system. With an air-CO_2 interface greater than 500 m, advective velocities are so small that mixing would be primarily by molecular diffusion. A typical time scale for gas-phase molecular diffusion to act over 100 m would be at least 30 years ($(100\ \mathrm{m})^2/(10^{-6}\ \mathrm{m}^2/\mathrm{s}) = 10^{10}\ \mathrm{s} \approx 30$ yrs) assuming a conservative value of CO_2-N_2 diffusivity of $10^{-6}\ \mathrm{m}^2/\mathrm{s}$, which is about twice the high values reported by Li et al. (2011)[22] after adjustments are made for the actual pressure and temperature of the reservoir (6.5 MPa, 35 °C) following Vargaftik (1975)[23] as described by Pruess et al. (1999)[17].

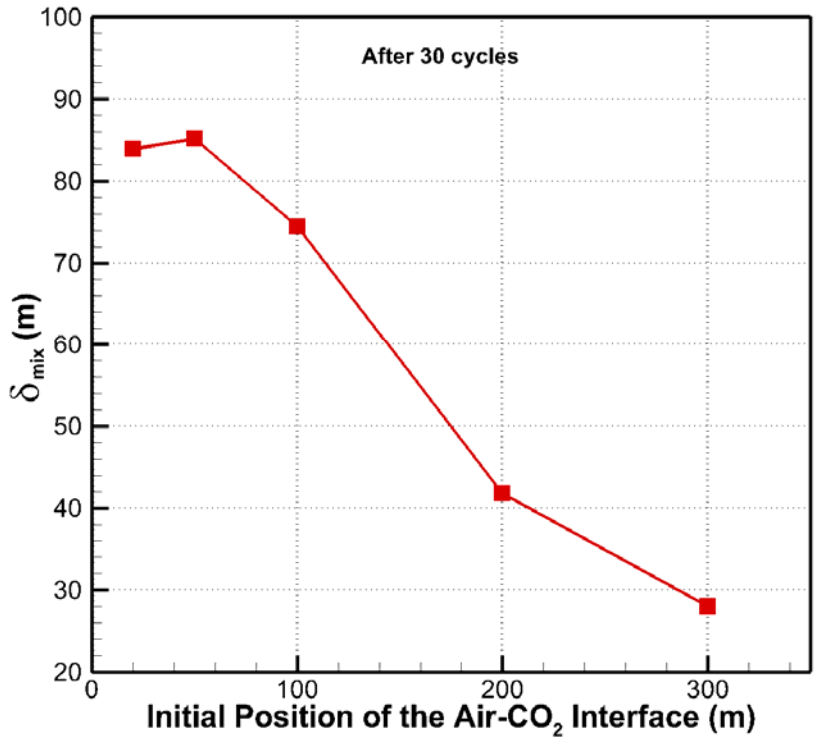

Figure 7. Thickness of the mixed zone ($0.1 < X_g^{CO_2} < 0.9$) after 30 cycles as a function of the initial position of the air-CO_2 interface. As shown, as long as the cushion gas is far from the well, mixing is slow due to slower gas velocities during reservoir cycling.

In order to investigate long-term mixing effects, we simulated a case with the air-CO_2 interface at 700 m and ran the daily cycling schedule out to 10 years with gas molecular diffusion set at 10^{-6} m^2 s^{-1}. We discretized the domain as before near the well, but restricted the maximum Δr of the grid blocks to 1 m in order to minimize numerical dispersion throughout the domain. We also changed the injection and production schedule so that total injected mass each day (2,332,800 kg) is equal to total produced mass each day (i.e., no make-up injection). The results are shown

in Fig. 8 as 10-day excerpts shown at two-year intervals of the pressure field (contours) and gas-phase CO_2 mass fraction (X_g^{CO2}) isopleths equal to 0.1, 0.5, and 0.9. The pressure field shows the effects of daily cycling, while X_g^{CO2} show the growing mixing zone over the decade. Mixing in this case is occurring by molecular diffusion and a small amount of numerical dispersion due to very small non-zero back-and-forth velocities in the vicinity of 700 m. The results in Fig. 8 show that the pressure changes upon injection and production increase with time. This occurs because the CO_2 cushion is becoming less effective over time as it mixes with air (see Fig. 1). The other primary observation is that the size of the air-CO_2 mixed zone increases with time up to about 100 m in size after 10 years of daily cycling. Another interesting effect is that the $X_g^{CO2} = 0.9$ isopleth remains fixed in space over time while the 0.1 and 0.5 isopleths migrate toward the well. We believe this effect arises from the increasing velocity with decreasing distance to the well due purely to the radial geometry, along with the larger velocity (in alternating directions) that occurs during cycling due to the larger pressure gradient arising from reduced overall density of the air-CO_2 gas combination as it mixes in the reservoir. Despite the dispersive mixing effects, the mixed zone is still only approximately 10% the radius of the reservoir, and this 1D PM-CAES system could go on operating for decades more before CO_2 would be produced at the well.

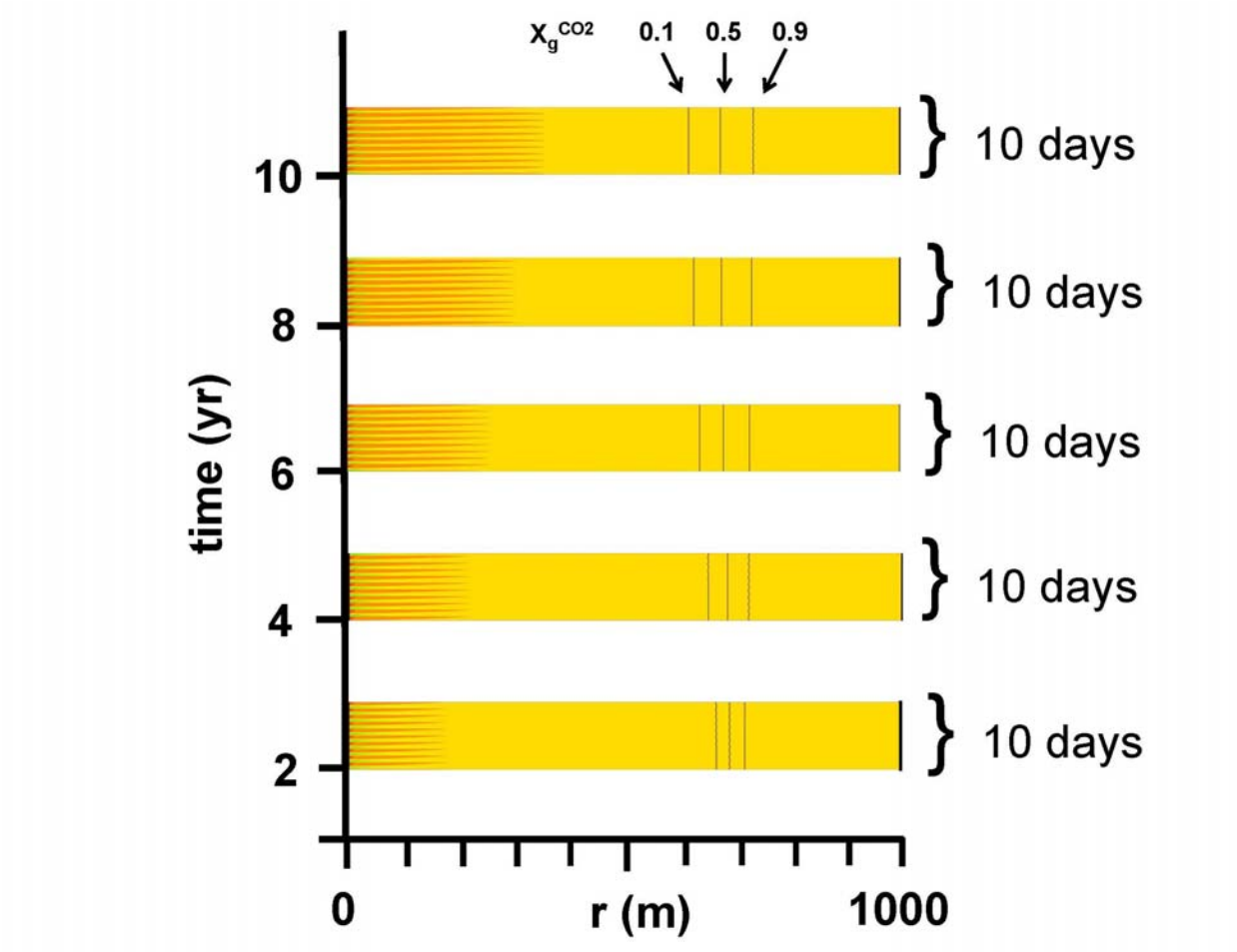

Figure 8. Evolution over 10 years of the pressure variation and thickness of mixed zone between air and the CO_2 cushion shown by extracted 10-day cycles. Note that the maximum pressure in the reservoir increases over time as the CO_2 cushion loses effectiveness due to mixing with air. The $X_g^{CO2} = 0.9$ isopleth does not move while the 0.5 and 0.1 isopleths migrate to the left.

Discussion

As shown from our simulations of an idealized 1D radial system, there is a trade-off between gaining an advantage in terms of pressurization by using CO_2 cushion gas close to the well, and producing CO_2 out of the well. In other words, in order to get the advantage of CO_2 as cushion gas, the CO_2 cushion region needs to feel the large pressure swings that are relatively close to the

well. On the other hand, gases close to the well are subject to more dispersive mixing because of higher velocities, and greater likelihood of eventually being produced out the well. In PM-CAES, the cycling frequency may be daily or weekly, which means there is a lot of flow in the PM-CAES reservoir relative to seasonal cycling carried out in a natural gas storage reservoir. Whereas natural gas storage may be able to exploit CO_2 as a cushion gas without significant mixing, PM-CAES may have problems with mixing because of the high cycling frequency. Furthermore, CO_2 is denser than air and will tend to underplate the air working gas. This configuration was noted by Gardner et al. (1962)[13] to promote mixing.

But this negative result insofar as mixing and exploiting CO_2 properties is concerned should not be taken as meaning that using CO_2 as cushion gas cannot be advantageous for PM-CAES in certain situations. On the contrary, CO_2 is in fact as good or better a cushion gas than air even if it is located in the far reaches of the reservoir where it is safe from being produced. In the 1D system presented here, an air-CO_2 cushion interface located at some radius greater than 500 m from the well would avoid any substantial CO_2-air mixing provided the air-CO_2 interface remained approximately vertical as assumed in our 1D model. In an actual reservoir, downward migration of CO_2 and override of air could occur which would enhance mixing. Further studies of particular reservoir geometries and properties are needed to understand better these vertical flow-related mixing effects.

The storage capacity for CO_2 in the far reaches of a PM-CAES reservoir could be significant for the PM-CAES project. For example, in the 1D radial system studied here, the fraction of the total reservoir volume contained within the region from r_1 = 500 m to r_2 = 1 km (where the CO_2 cushion could be positioned) is approximately 75% of the total reservoir volume ($V_{cush}/V_{total} = (r_2^2 - r_1^2)/r_2^2 = ((10^3\ \mathrm{m})^2 - (500\ \mathrm{m})^2)/(10^3\ \mathrm{m})^2 = 0.75$). In a very conservative case such as the

one we investigated to study long-term mixing effects in which the air-CO_2 interface is positioned at approximately r = 700 m, the CO_2 cushion would comprise 50% of the volume of the reservoir. The total pore volume potentially available for CO_2 storage is approximately ($V_{cush} = \phi S_g \pi (r_2^2 - r_1^2) h = 0.20 * 0.80 * \pi ((10^3 \text{ m})^2 - (700 \text{ m})^2) * 25 \text{ m} = 6\times10^6 \text{ m}^3$. Assuming a CO_2 density of 190 kg m^{-3} at 6.5 MPa (approximate average pressure in the reservoir) and 35 °C, the reservoir could hold over 1.2 million tonnes of CO_2 as cushion gas. While this mass of CO_2 pales in comparison to the emissions from a 1000 MW coal-fired power plant which may be over six times as much annually (~8 MtCO2/yr), its use as cushion gas could generate CO_2 storage revenue under a carbon tax or cap and trade policy that could make a difference in the startup economics of the PM-CAES plant. Our simulations suggest that after 10 years of operation, the zone of mixed working and cushion gas would likely be on the order of 100 m.

To consider a non-radial example, we have the Kilinç and Gümra (2000)[14] reservoir for which we calculate that 12.5 million tonnes of CO_2 could be emplaced to occupy the same volume as the nitrogen they assumed could be injected into the reservoir at 14.7 MPa and 65 °C with negligible cushion gas production effects for natural gas storage (1.09×10^{10} ft^3 N_2 * $(0.3048 \text{ m})^3$ ft^{-3} * 1.185 kg N_2 m^{-3} / 14.47 kg N_2 m^{-3} * 496 kg CO_2 m^{-3} = 1.25×10^{10} kg CO_2). With an assumed price on CO_2 of $50/tonne and 80% of this cost going for capture and transportation, the storage of CO_2 could still be worth $120 million to the operator.

Granted the Kilinç and Gümra (2000)[14] example mixes aquifer and depleted gas reservoir storage paradigms, but it makes the point along with the 1D radial volume results that large amounts of CO_2 can be emplaced in subsurface reservoirs for potential use as cushion gas. And this use of CO_2 would allow the benefit of earning storage credits with no intent to take advantage of CO_2 super-compressibility. Furthermore, the CO_2 stored as cushion gas would be implicitly

monitored as part of the normal PM-CAES plant operations, allaying some of the concerns expressed about limited time periods of monitoring at future GCS sites, and accounting for the uncertainty in the extent of mixing that could occur in the reservoir. In short, when and if there is a significant price on carbon, the injection of CO_2 for storage over the course of several years of building the cushion could lead to substantial cash streams to subsidize the startup of the rest of the CAES system.

Conclusions

Simple 1D radial simulations of PM-CAES with and without CO_2 as a cushion gas show that pressure rise during air injection is modestly less in the reservoir when CO_2 is used as a cushion gas. The effect of CO_2 cushion on pressure is larger during the production period than during the recharge period in the case study because the production rate is about four times the injection rate, making pressure drop much larger during production than pressure rise is during injection. For the air-CO_2 cushion boundary placed 50 m from the well, CO_2 gradually enters the well at an increasing rate until the gas mass fraction in the well reaches about 0.1 and then it slowly decreases. In the case of 20 m air-CO_2 interface, significant amounts of CO_2 cushion are produced (lost) out of the well from the first production cycle. For the air-CO_2 interface at 100 m, CO_2 at the well occurs much later and in smaller concentrations.

The pressure gradients that are inherent in PM-CAES and absent in cavern CAES create a conundrum for exploiting CO_2 as a cushion gas. In other words, there is trade-off between exploiting the super-compressibility of CO_2 around its critical pressure and avoiding the production of the cushion gas itself at the well. Specifically, the super-compressibility is best exploited when the air-CO_2 interface is near the well, but at these locations the CO_2 cushion will

mix strongly with air due to large velocities which create large dispersive fluxes, and the cushion gas will tend to be produced with the working gas eventually. Because of this trade-off, we conclude that the best way to use CO_2 as a cushion gas is in the far reaches of the storage reservoir, where mixing will be very slow. Quantities of CO_2 significant for the economics of the CAES plant could be utilized in this manner, depending on the future price of carbon.

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