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Chemical and Hydrodynamic Mechanisms for Long-Term Geological Carbon Storage

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ABSTRACT: Geological storage of CO_2 (GCS), also referred to as carbon sequestration, is a critical component for decreasing anthropogenic CO_2 atmospheric emissions. Stored CO_2 will exist as a supercritical phase, most likely in deep, saline, sedimentary reservoirs. Research at the Center for Frontiers of Subsurface Energy Security (CFSES), a Department of Energy, Energy Frontier Research Center, provides insights into the storage process. The integration of pore-scale experiments, molecular dynamics simulations, and study of natural analogue sites has enabled understanding of the efficacy of capillary, solubility, and dissolution trapping of CO_2 for GCS. Molecular dynamics simulations provide insight on relative wetting of supercritical CO_2 and brine hydrophilic and hydrophobic basal surfaces of kaolinite. Column experiments of successive supercritical CO_2/brine flooding with high-resolution X-ray computed tomography imaging show a greater than 10% difference of residual trapping of CO_2 in hydrophobic media compared to hydrophilic media that trapped only 2% of the CO_2. Simulation results suggest that injecting a slug of nanoparticle dispersion into the storage reservoir before starting CO_2 injection could increase the overall efficiency of large-scale storage. We estimate that approximately 22% ± 17% of the initial CO_2 emplaced into the Bravo Dome field site of New Mexico has dissolved into the underlying brine. The rate of CO_2 dissolution may be considered limited over geological timescales. Field observations at the Little Grand Wash fault in Utah suggest that calcite precipitation results in shifts in preferential flow paths of the upward migrating CO_2-saturated-brine. Results of hybrid pore-scale and pore network modeling based on Little Grand Wash fault observations demonstrate that inclusion of realistic pore configurations, flow and transport physics, and geochemistry are needed to enhance our fundamental mechanistic explanations of how calcite precipitation alters flow paths by pore plugging to match the Little Grand Wash fault observations.
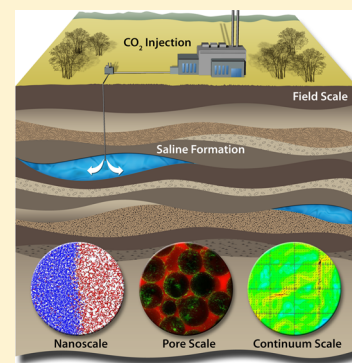
■ INTRODUCTION

Reversing the trend of increasing anthropogenic CO_2 emissions to the atmosphere requires multiple strategies.[1] One critical strategy is the capture and geological storage of CO_2, where CO_2 emitted from sources such as fossil-fueled power plants is separated from other combustion products on site, compressed, and then injected underground. To make the process more economical, injection of captured CO_2 can also be used for enhanced oil recovery. While the role of physical chemistry in the capture process is clear, its significant impact on the storage process is less widely appreciated. The impact arises from two factors: the nature of the storage reservoirs and the need to ensure that stored CO_2 remains in reservoirs after injection. Here

we describe insights into the storage process derived from research at the Center for Frontiers of Subsurface Energy Security (CFSES). CFSES is one of the Energy Frontier Research Centers established by the Office of Science, Basic Energy Sciences program in the U.S. Department of Energy in 2009.

Nature of Geological CO_2 Storage Reservoirs. To provide meaningful mitigation of the current global emission rate of approximately 35 gigatonnes (Gt) CO_2 per year from

fossil fuel consumption, the overall storage rate must be large, on the order of gigatonnes CO_2 per year (for context, global oil produces about 4 Gt of the CO_2-equivalent per year). On the basis of experience with two commercial scale projects, each injecting approximately 0.001 Gt CO_2/y, achieving this overall rate will require developing thousands to tens of thousands of individual storage reservoirs. Current consensus is that the number of potential storage reservoirs is more than sufficient to meet this demand; however, the response of these reservoirs to the introduction of CO_2 must now be evaluated.

The largest set of likely injection targets are deep layers of porous rock in sedimentary formations (greater than 1000 m below ground surface), composed of largely silicate, aluminosilicate, and carbonate mineral grains. At these depths, pressures and temperatures typically range from 10 to 30 MPa and 310 to 380 K. Under such conditions, stored CO_2 will exist as a supercritical phase (the critical point is a temperature of $T_c \sim$ 304 K and a pressure of $P_c \sim 7.4$ MPa depending on salinity of the formation water). The pores between the grains are filled with brines that vary in composition and ionic strength from seawater-like to almost saturated with respect to NaCl and other salts. The pH and dissolved carbonate concentrations of these brines are typically very far from the composition that would exist in equilibrium with a bulk supercritical CO_2 phase.

Geological CO_2 storage is thus, from a chemical perspective, a large-scale perturbation in a "reactor" with very heterogeneous degrees of mixing at multiple timescales. The composition of native brine will eventually equilibrate with the injected bulk CO_2 phase. The change in aqueous composition will drive not only mineral dissolution and precipitation reactions but also adsorption and desorption reactions on mineral surfaces. Of special note is a recently recognized class of interactions with minerals with a bulk CO_2 phase containing dissolved water[2,3] and acid gases.[4] These interactions are a new frontier for physical chemistry as well as for the geological storage community.

Security of Geological CO_2 Storage. At typical storage conditions encountered in saline reservoirs and oil/gas reservoirs, the supercritical CO_2 phase density is about 500 to 700 kg/m³. Ensuring that the positive buoyancy of the supercritical CO_2 phase relative to formation waters does not drive the stored supercritical CO_2 to the earth surface is therefore a central concern for storage security. Physical and chemical mechanisms for trapping CO_2 have been widely investigated, and several of them (i.e., residual trapping, solubility trapping, and mineral trapping) (Figure 1)[5] depend on the chemical interactions described above. Residual trapping refers to the disconnection of volumes of CO_2 from a bulk CO_2 phase as a consequence of capillarity-driven events at the scale of individual pores in the rock (from $\sim 10^{-6}$ to 10^{-4} m). The energetics of CO_2/mineral, brine/mineral, and CO_2/brine interfaces are thus fundamental to this mode of trapping, and the physical chemistry of initial (before injection) and perturbed (during and after injection) states is consequently important. Solubility trapping refers to the transfer of CO_2 by dissolution from a bulk free phase into a brine phase. Dissolving CO_2 into brine slightly increases its density, a desirable consequence for storage security because negative buoyancy will generate flow of stored CO_2 away from the earth's surface. The kinetics and thermodynamics of interphase mass transfer and the properties of the equilibrated phases are therefore of concern. While dissolution of CO_2 increases storage security, dissolved CO_2 can still escape through subsequent brine transport through faults, as observed near Green River, Utah[6] or through breached caprock. Mineral
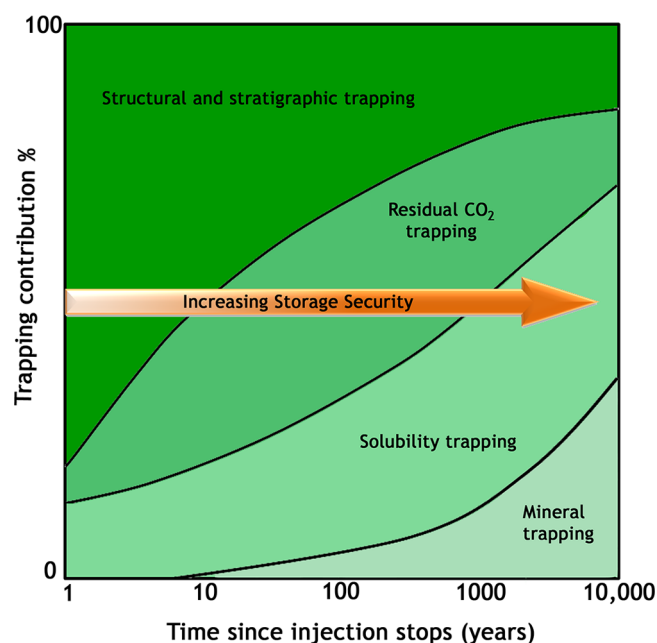

Figure 1. Relationship between the relative amount of CO_2 trapped by the different physical and chemical processes of trapping and time (modified after Benson et al.).[5] Note that the timescale is speculative.

trapping refers to the precipitation of carbonate minerals such as calcite ($CaCO_3$). The density and immobility of mineral phases makes them a desirable mode of storage, and the physical chemistry at the surfaces of minerals with CO_2 or CO_2-saturated brine is therefore vital.

Research Needs. Understanding the nature and security of geologic CO_2 storage lead to the following broad classes of research needs concerning physical chemistry: characterization of interfaces in the CO_2/brine/solid system wherein the solid includes an array of minerals common in the crustal rocks associated with carbon storage, characterization of chemical interactions and reactions at fluid/mineral interfaces, and understanding coupling between the above chemical processes and the movement or displacement of fluid(s) at several length and timescales.

The third class, chemical processes coupled with fluid displacement, has great practical importance: first, during injection as the CO_2 phase displaces native brine, and second, after injection as fluid phases migrate under the influence of buoyancy. Displacement and migration can bring fluids into contact with fresh minerals and brine, possibly creating self-limiting or self-reinforcing emergent behavior.

Within this context of research needs related to geological carbon storage (GCS), we discuss a number of specific questions. Small-scale experimental and modeling studies have been performed to measure residual trapping, to understand CO_2 wettability on different relevant surfaces, and to understand carbonate mineral precipitation and its impact on flow and transport. Results of computational simulations have been compared to observations at the Little Grand Wash fault, a site of CO_2 leakage from a subsurface reservoir, in Utah. Finally, Bravo Dome, a natural analogue for geological CO_2 storage in northeastern New Mexico is being used to estimate rates of solubility trapping.

To better understand residual trapping, the wettability of reservoir and caprock materials needs to be examined. Wettability and capillary forces dictate how injected supercritical

CO_2 moves within the pore spaces and how it may eventually become residually trapped. The relative wetting of pore surfaces in the rock matrix by CO_2 and brine, characterized macroscopically by CO_2−brine−mineral contact angles, controls the capillary pressure of fluids in pores and strongly influences the transport and ultimate distribution of CO_2 in the reservoir.[7,8] Previous experimental studies have examined the wettability of caprock and reservoir materials in CO_2−brine systems,[9−14] but reported wetting trends with respect to temperature, pressure, and brine composition are not always consistent.[15,16]

Residual Trapping. Residual trapping is generally thought to be most important after the injection period when the CO_2 buoyantly rises to the top of the formation. The residually trapped CO_2 remains important until it is dissolved or precipitated. Though, its relative importance compared to the other trapping mechanisms declines once the injected CO_2 plume ceases motion. Residual trapping is examined through in situ imaging using X-ray computed tomography and optical microscopy to measure contact angles and fraction of supercritical CO_2 trapped in pore spaces. Molecular dynamics simulations provide insight into the molecular control of wetting behavior of CO_2 at atomistic scales on mineral surfaces and mineral coatings at pore spaces. The combination of the experiments and molecular dynamics simulation studies can be used to improve capillary flow and capillary trapping models to better assess the fate of injected CO_2 in reservoirs. Finally, computational and theoretical studies assess and predict snap-off of CO_2 plumes into isolated bubbles.

Solubility Trapping. The dissolution of CO_2 in formation fluids (i.e., brine) is generally viewed as the most effective mechanism for trapping on the 10- to 100-year timescale.[4,18] Thus, within human timescales and typical injection scenarios, the most likely extensive mechanism for long-term trapping that may be monitored is solubility trapping. As mentioned above, the Bravo Dome site is a natural analogue for geological CO_2 storage via solubility trapping. Data from the field site allow for constraints on the magnitude and rate of solubility trapping. Bravo Dome is being studied to provide a direct test for long-term security of geological CO_2 storage. One objective of the Bravo Dome study is to determine the mass of CO_2 dissolved from time of emplacement of CO_2, by likely subsurface igneous activity, in order to constrain the magnitude of solubility trapping over geological time. The second objective is to determine CO_2 emplacement age to estimate an average rate of CO_2 dissolution in geological media. Currently, no such constraints based on field data exist, but they are crucial for testing the ability of numerical models to predict the long-term fate and storage security of geological CO_2 storage.

Mineral Trapping. With mineral trapping, dissolved CO_2 is precipitated as a carbonate mineral, such as calcite ($CaCO_3$), siderite ($FeCO_3$), or magnesite ($MgCO_3$), representing the most stable sink of carbon over geological time. Because reaction kinetics of carbonate precipitation are significantly slower than dissolution of supercritical CO_2 into brine, mineral trapping is generally considered less significant for carbon sequestration than solution trapping on human timescales.[4,18] However, effervescence and carbonate precipitation are expected during upward flow of CO_2-saturated brine,[17] a condition likely to be met if CO_2-charged brine leaks along faults and fractures bisecting caprock layers. Thus, mineral trapping may be a significant mechanism for self-sealing of leakage pathways for CO_2.

To assess mineral trapping and conduit sealing, we examine both reactive transport pore-scale and single-phase pore-network models. A hybrid pore-scale model, combining a lattice Boltzmann method for water flow with finite volume numerical methods for reactive transport, provides fundamental mechanistic explanations of the evolution of permeability, reactive surface area, and porosity in response to geochemical reactions during geological CO_2 storage. Moreover, pore-network modeling represents the first steps toward a predictive understanding of CO_2 leakage scenarios. Results of both hybrid pore-scale and pore-network models are compared to observations along the Little Grand Wash fault, a natural analogue for fault-controlled CO_2 leakage.[18] In the vicinity of the fault, CO_2 seeps reveal complex permeability alterations caused by precipitation-induced pore-blocking.

■ METHODS

Residual Trapping. Molecular dynamics calculations were combined with optical visual measurement of contact angles, high-resolution X-ray computed tomography (HRXCT),[19] and column experiments with X-ray CT to examine supercritical CO_2 wettability and residual trapping at increasing length and timescales.

Molecular dynamics simulations were used to investigate interfacial behavior and evaluate contact angles for CO_2−brine−mineral systems.[20,21] Accurate interatomic potentials[22,23] were used to evaluate the energy and forces associated with hundreds of thousands of atoms for various fluid droplet configurations on the basal surfaces of kaolinite, a common clay mineral. Kaolinite [$Al_2Si_2O_5(OH)_4$] is a 1:1 layer clay having an AlO_6 octahedral sheet and SiO_4 tetrahedral sheet comprising each layer. The basal surface of the octahedral sheet with surface hydroxyl groups is referred to as the gibbsite surface; the basal surface for the tetrahedral sheet is referred to as the siloxane surface. The siloxane surface is relatively hydrophobic, while the gibbsite surface is considerably hydrophilic and capable of significant hydrogen bonding.

The orthogonal simulation cell contains a three-layer slab of kaolinite (approximately 2 nm thick) with fluid located adjacent to the gibbsite surface. Periodic boundary conditions result in an infinitely long droplet or filament of the fluid phase. Multiple simulations were completed to investigate wetting phase chemistries (pure water, NaCl, and $CaCl_2$ brines), for CO_2 droplets in an aqueous phase and an aqueous droplet in CO_2, for both gibbsite and siloxane surfaces. Further details regarding the methods and parameters used for simulation and analysis can be found in Tenney and Cygan.[24]

Under an optical microscope, contact angles for supercritical CO_2 in a three phase system (supercritical CO_2, liquid water/brine, and mineral surfaces) were measured at 333 K and 13.7 MPa, conditions similar to CO_2 storage in shallow saline formation reservoirs. Advancing, receding, and static contact angles were measured on muscovite mica ($KAl_2(Si_3Al)$-$O_{10}(OH)_2$, an analogue for aluminosilicate clay minerals) and silica glass surfaces with deionized water (DI) and calcium chloride (brine). Postprocessing image analysis, for example, grayscale conversion, thresholding, and contrast along with a spline-based fitting algorithm,[25] were used to calculate contact angles from images.

Two-phase flow experiments were conducted under reservoir conditions (~12.4 MPa and ~333 K) for the HRXCT experiments. The voxel size of the images was 15 μm on a side; the viewing window was 1 cm. Polyether ether ketone
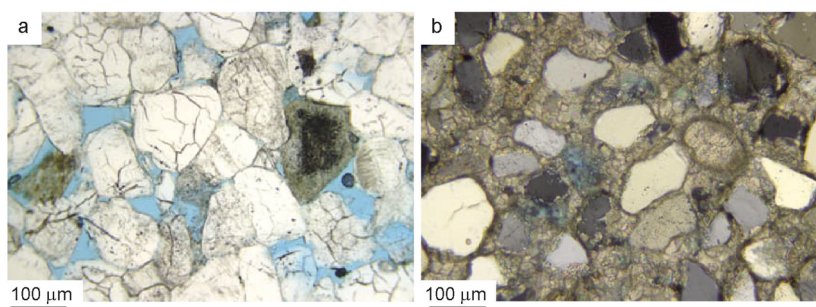
Figure 2. Photomicrographs of (a) unaltered and (b) altered sandstone in the vicinity of a natural CO_2 seepage conduit. Primary porosity, filled by blue epoxy in (a), has been completely occluded in altered sandstone [shown in (b)] by carbonate pore cement that precipitated from upward migrating CO_2-charged brine. Some secondary porosity resulted from grain dissolution. Little Grand Wash fault, Utah. (a) Plane-polarized light and (b) cross-polarized light. Reprinted from Mehmani et al.[41] with permission from Springer Science and Business Media.

(PEEK) columns with an inner diameter of 7.5 mm were filled with either glass beads (0.7–0.9 mm diameter), angular crushed glass, or Teflon beads (0.8 mm diameter). The borosilicate glass represented a hydrophilic surface, while the Teflon represented a hydrophobic CO_2-wetting surface. Because PEEK is naturally CO_2-wetting, a glass sleeve was inserted inside the PEEK column when the hydrophilic beads were used to obtain a fully hydrophilic system. The columns were initially saturated with 1% (by weight) NaBr-brine, approximating unperturbed natural reservoir conditions. The initial saturation was followed by a supercritical CO_2 flood and then another brine flood. Conditions mimicked an unperturbed natural reservoir, followed by a CO_2 injection, and finally natural brine replacement of supercritical CO_2. Brine replacement of CO_2 ultimately leads to capillary trapping, whereby capillary forces prevent CO_2 from passing through pore constrictions and immobilizing the CO_2. Image analysis, carried out using the commercial Avizo-Fire software (Visualization Sciences Group) and the code Blob3D,[26] involved several steps for noise removal, filtering, and thresholding.

Theoretical studies of the snap-off of CO_2 focused on extending previous theoretical criterion for the quasi-static snap-off of nonwetting fluids into isolated bubbles.[27] This was achieved by adding the local capillary pressure imbalance between the pore body and the pore throat for both circular and noncircular pores for a nonwetting fluid plume that extends across more than one pore.[28] The extended criterion was used to analyze results from computational fluid dynamics (CFD) simulations of multiphase flow with supercritical CO_2 as the nonwetting fluid and water as the wetting fluid. The CFD model directly solves the Navier–Stokes equations coupled with the volume-of-fluid approach for fluid interface tracking. The CFD simulations directly modeled the snap-off process, when it occurred, for various pore geometries. Simulation results were then compared to predictions using the extended theoretical criterion for snap-off occurrence.

The possibility of engineered controls to better ensure storage efficiency of injected CO_2 was explored. To examine the impact of engineered nanoparticles on the displacement front of brine being displaced by brine-saturated liquid CO_2, flow column experiments were conducted in a modified medical X-ray CT scanner. Experiments were conducted in a cylindrical core (length 30 cm, diameter 7.5 cm) of heterogeneous Boise sandstone (porosity approximately 27%, permeability approximately 1×10^{-12} m^2) with a low porosity region near the outlet of the core. The wetting phase was either 2 wt % NaBr brine (control case) or 2 wt % NaBr brine with 5 wt % suspended nanoparticles (nanoparticle case). To create an immiscible

displacement, the brine (or nanoparticle dispersion) was pre-equilibrated with CO_2 by injecting 100 mL of CO_2 per liter of brine into the brine accumulator over 5 h and letting the wetting fluid equilibrate with CO_2 for 48 h. Silica nanoparticles with a nominal diameter of 5 nm were used. The nanoparticles were surface-modified with polyethylene-glycol (PEG) ligand and received as a 19.265 wt % dispersion in deionized water. The nanoparticle dispersion was diluted to 5 wt % with NaBr aqueous phase, for a total salinity of 2 wt %. More details on the experimental design can be found in Aminzadeh et al.[29]

The core was placed horizontally in a modified medical CT scanner to capture in situ saturation in real time. The whole core was scanned at 0.5 cm intervals to measure the local density of the materials occupying each voxel. Since CO_2 is less dense than the brine or nanoparticle suspension, the measured density was converted to saturation by a linear interpolation between CT values of the core saturated with the brine (or nanoparticle suspension) and CO_2.

Solubility Trapping. The total mass lost from the entire Bravo Dome field (2200 km^2) since emplacement was estimated by subtracting the total final mass of CO_2 in the field in 1981 (just before production for enhanced oil recovery began) from the total initial mass of CO_2 in the field. The final mass of CO_2 is constrained directly from reservoir geometry and known reservoir pressures at the beginning of production, using data from approximately 700 wells. The total initial mass of gas present at Bravo Dome, however, cannot be determined directly.

At Bravo Dome, 99.8% of the gas is CO_2, a very soluble gas, and at 20 wells across the field, an abundance of ^{3}He, a very insoluble noble gas, has been determined. Combining compositional data with a range of geophysical and petrophysical data into a geological model constrains the distribution of gas within the field. Combining local estimates of dissolution based on Rayleigh fractionation with the estimate of the gas mass permits an estimate of the total change in the mass of the gas.[30,31]

An average rate of CO_2 dissolution at Bravo Dome can be determined based on an estimate of the emplacement age of the CO_2. On the basis of geochemical characteristics, the age of the Bravo Dome field was estimated, suggesting that it is of volcanic origin. Literature estimates give two dates for the age of Bravo Dome, a younger date of 8000 years and an older date of 1.2 million years, based on the ages of two local volcanic fields. Given the large difference in these ages, the potential dissolution rates of CO_2 are very uncertain. Previous studies in the literature have generally preferred the younger age of 8000 years.[32]

In an attempt to constrain the age of the CO_2 emplacement, a preliminary thermochronological study was conducted to

approximate the time of the reheating of the Bravo Dome reservoir due to the emplacement of hot volcanic CO_2. In general, such reheating is expected to be localized in the western part of the field, where CO_2 likely would have entered the reservoir based on gradients in noble gas abundances and current pressure gradients.

Mineral Trapping. A pore-scale model was used to mimic changes in dissolved CO_2 flow paths due to pore plugging from precipitates as observed in carbonate-cemented sandstone at the Little Grand Wash fault field site (Figure 2), a natural example of carbonate precipitation associated with CO_2 migration.[33,34] Yoon et al.[35] developed a hybrid pore-scale reactive transport model of coupled fluid flow, reactive transport, and calcium carbonate precipitation and dissolution. The model consists of a fluid flow module, a multicomponent reactive transport module, and a reaction module to account for heterogeneous reactions at the fluid−mineral interface. To solve fluid velocities in the pore space, the lattice−Boltzmann method (LBM) is used.[36] For reactive transport, a finite volume method is used, assuming instantaneous homogeneous (aqueous) reactions and kinetically controlled heterogeneous reactions at the mineral−water interface.[37] Heterogeneous reactions are solved using the boundary condition on the reactive surface. Recent studies offer detailed descriptions of model applications for different chemical conditions.[38−40] The hybrid pore-scale reactive transport model was rigorously validated against well-controlled experimental results to improve quantitative prediction capability.

A pore-network model was developed with an aim to capture emergent behavior resulting from coupling of convection and reaction at the pore-scale and to understand whether such coupling would suffice in explaining the redirection of escape pathways of upwardly migrating CO_2. A detailed discussion of methods used in the modeling can be found in Mehmani et al.[41]

Pore networks are composed of an assembly of interconnected pores (nodes) and throats (bonds). In pore-network modeling, pores are typically assigned single pressure and concentration values tied to the pressure and concentration values of neighboring pores via balance equations written at each node. Mass and species balances at the pores give rise to flow and transport systems, respectively. For a Newtonian and incompressible fluid, the pore pressures are obtained by solving the linear flow equations. Solutions for the pore-water concentrations (with nonlinear reactions) are solved using nonlinear transport equations. More details about how reactive flow and transport accompanied by mineral precipitation are modeled in pore networks is presented in Mehmani et al.[41]

An $8 \times 8 \times 1$ array of 64 pore networks (299129 pores total) with a permeability variation of more than 2 orders of magnitude was created and assembled. The assemblage was arranged so as to create two high-conductance pathways leading from the inlet toward the outlet of the domain. Interface Point Partitioning (IPP) mortar spaces[42] were used to seamlessly couple the pore networks together by establishing physically realistic boundary conditions at the interfaces between the subdomains. Details on the mathematical and numerical aspects of mortars have been presented by a number of researchers,[43−45] but the basic principle is that they "glue" subdomains together by ensuring continuity of material flux at the shared interfaces. Flow and transport equations over the subdomain were solved and coupled across interfaces using mortars, while the pore space was allowed to change as a result of calcite precipitation. The simulations were performed over a wide range of Damkohler numbers (Da) and

relative rates of carbonate forming reactions until complete disconnection of the inlet from the outlet (due to cementation) was observed.

RESULTS

Residual Trapping. Computational and experimental efforts were combined to better understand mechanisms for residual trapping of supercritical CO_2 during GCS. Equilibrated molecular dynamics simulations of both water and brine droplets on the gibbsite surface of kaolinite in the presence of CO_2 resulted in essentially complete wetting of the surface by the aqueous phase (Figure 3). The wetting behavior of supercritical
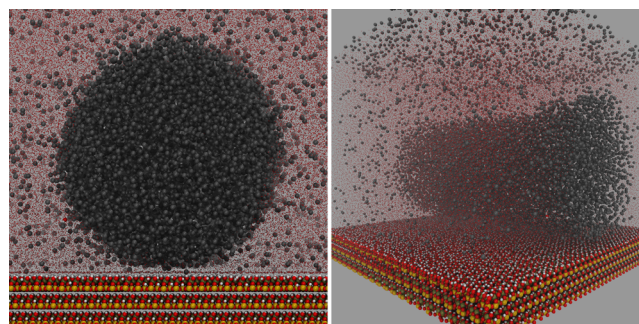

Figure 3. Snapshot of an infinitely long CO_2 "droplet" on the gibbsite surface of kaolinite in the presence of water containing dissolved CO_2 after 10 ns at 330 K and 20 MPa. The system contains 15000 CO_2 molecules and 130000 H_2O molecules. Aluminum, silicon, oxygen, and hydrogen atoms within the kaolinite slab are represented as brown, yellow, red, and white spheres, respectively. Above the kaolinite slab, black spheres are CO_2 carbon atoms and red dots are H_2O oxygen atoms. Atoms represented as spheres are rendered at 60% of their van der Waals radius. Adapted with permission from ref 24. Copyright 2014 American Chemical Society.

CO_2 on the hydrophilic gibbsite surface of kaolinite was strongly affected by intervening water at the mineral surface. This situation occurs when a CO_2 droplet is separated from the mineral surface by a thin, dense water layer. Replacing pure water with a brine reduces CO_2 wetting of the gibbsite surface; CO_2 droplets detach completely from the mineral surface. Significant adsorption of water, cations, and anions at the mineral surface were observed in our simulations. Outer-sphere adsorption of the divalent cation Ca^{2+} occurred with the cation preserving its complete water coordination at the surface, rather than adsorbing directly to the surface as an inner-sphere complex as observed for Na^+.

Strong wetting of a supercritical CO_2 droplet on the siloxane surface of kaolinite in the presence of water or brine was observed for the equilibrated simulations. In contrast to the results for the gibbsite surface, water was completely excluded at the siloxane surface. Beyond the edge of the wetting CO_2 droplet, CO_2 and H_2O both interact directly with the siloxane surface. A distinct CO_2 layer that interacted directly with the entire siloxane surface of the simulation cell was observed when any aqueous droplet was modeled in the presence of supercritical CO_2. Both H_2O (or brine) and CO_2 interacted directly with the siloxane surface when an aqueous phase was present above the surface. Unlike the behavior of brines over the gibbsite surface of kaolinite, there was no preferential ordering of ions relative to the siloxane surface. Instead, ions were distributed uniformly throughout the aqueous droplet. Also, unlike the interactions with the gibbsite surface, wetting behavior on the siloxane surface was not affected in
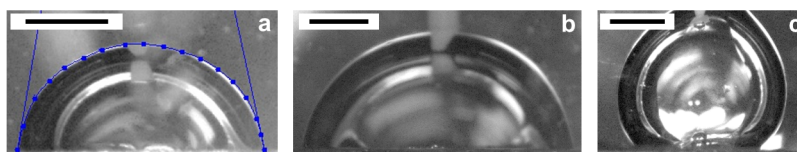
Figure 4. Contact angle measurement of supercritical CO_2 on mineral substrates in aqueous solutions at 333 K and 13.7 MPa (scale bar a–c ~ 1 mm). The images are shown upside down (supercritical CO_2 is buoyant relative to water at these conditions). (a) Supercritical CO_2 on silica glass in deionized water. The blue lines show results of applying a fitting algorithm calculating a contact angle of ~80°. (b) Similar measurement of supercritical CO_2 in deionized water on a muscovite (mica) substrate with a contact angle of ~75°. (c) Supercritical CO_2 contact angle in 6.33% $CaCl_2$ aqueous solution on a muscovite substrate showing a 135° contact angle.

simulations involving NaCl or $CaCl_2$ brines rather than pure water.

Contact angles are a macroscopic measurement of the relative wetting of pore surfaces within the rock matrix. Direct comparison of experimental and simulation contact angles on basal surfaces of kaolinite is difficult as kaolinite exists in GCS target saline formations in largely micrometer-size grains (i.e., clay-sized) lining pores of larger matrix clasts. Recent experimental measurements of contact angles for CO_2 on kaolinite in the presence of water or brine suggest that kaolinite is water-wetting.[46] Probably the closest analogue to kaolinite and other clay mineral surfaces would involve mica minerals with large surfaces with properties similar to those of clay minerals. Muscovite is a phyllosilicate mineral that provides centimeter-sized crystals that are easily cleaved to provide large uniform basal surfaces for practical wetting measurements. Using the optical microscopy technique, equilibrium contact angles on freshly cleaved muscovite mica and silica glass in deionized water are 75° and 80°, respectively (CO_2 wetting), while in a 6% $CaCl_2$ brine, contact angles increase to 135° (non CO_2-wetting) (Figure 4). These results are consistent with contact angle measurements in the existing literature for low salinity water[10] and higher salinity brine[47] but contrast with the molecular dynamics simulation results.

Unlike idealized kaolinite surfaces used in the molecular simulations, experimental contact angle measurements involving macroscopic surfaces cannot capture wetting at one specific surface of natural clay phases. Instead, experimental results correspond to contact angles measured over many mineral surfaces and topography composed of a likely random distribution of micro- and nanoscale grains, which present a distribution of hydrophobic and hydrophilic faces or edges to the fluid phase. The optical microscopy measurements show that supercritical CO_2 wettability will decrease with increasing ionic strength at conditions relevant to GCS, and perhaps, that supercritical CO_2 is slightly less wetting on muscovite (here a proxy for clay mineral surfaces) than on silica.

A logical progression for understanding the influence of wettability on residual trapping requires a shift from contact angle measurements to measurements involving pore scale textures with a variety of mineral surface analogues. Through HRXCT imaging, in the presence of supercritical CO_2 at 12.4 MPa and 333 K, 1 wt % NaBr brine makes a contact angle of 27° with the glass surface, a contact angle of 120° with the PEEK surface, and a contact angle of 125° with the Teflon surface, which is consistent with another recent study.[11]

Successive supercritical CO_2/brine flooding column experiments under reservoir conditions showed that hydrophilic beads trapped 15% of injected supercritical CO_2 both as individual bubbles and as larger clusters, whereas hydrophobic beads trapped only 2% of the injected supercritical CO_2 as minute

pockets in pore constrictions. Figure 5 presents a three-dimensional rendering of the HRXCT scans showing the difference in residual trapping of supercritical CO_2 in hydrophilic and hydrophobic bead matrices.
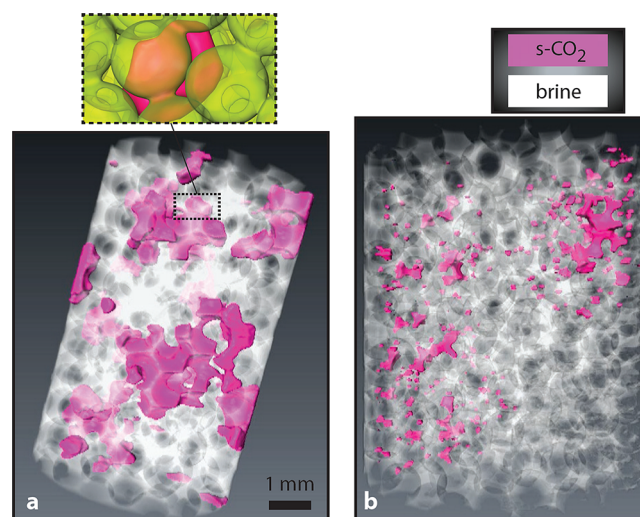

Figure 5. HRXCT images of residually trapped supercritical CO_2 in (a) hydrophilic glass and (b) hydrophobic Teflon beads. The solid beads are not rendered (but shown as transparent yellow in the inset figure), supercritical CO_2 is purple, and brine is white. Images taken after the secondary brine flood in a sequential brine–supercritical CO_2–brine flooding experiments. (Modified after Chaudhary et al.).[19]

In the snap-off studies, CFD simulations displayed snap-off when it would not have been predicted by the commonly used Roof criterion.[28] The classic Roof snap-off criterion does not consider the possibility of continuous multipore ganglia as observed by Chaudhary et al.[19] Theoretical calculations with the extended snap-off theoretical criterion, however, correctly predicted the CFD-modeled snap-off. Thus, the new criterion indicates a potentially greater extent of residual trapping of CO_2 because of the addition of the previously unrecognized snap-off mechanism.

The Roof-type snap-off phenomenon occurs in individual pore throats at the displacement front as injected CO_2 pushes native brine through the storage reservoir. Under ordinary circumstances, the snapped-off droplets of CO_2 coalesce and rejoin the advancing bulk phase. If, however, the brine contains a dispersion of suitably surface-treated nanoparticles, the nanoparticles can attach to the droplet surfaces before they coalesce. This attachment suggests a possible method for controlling CO_2 wettability and improving storage efficiency. The attachment occurs because the surface chemistry of the nanoparticle makes the interface between bulk CO_2 and bulk brine a low-energy

state, thus preventing subsequent coalescence and changing the nature of the displacement (Figure 6).[48] The change is beneficial
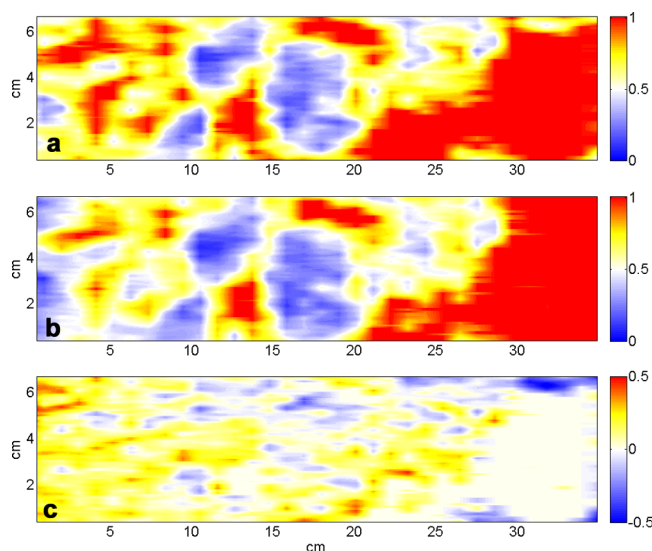

Figure 6. (a) Side view of the brine saturation distribution after injecting 0.25 pore volumes of CO_2 into a brine-saturated Boise sandstone core (control case). Nonuniform saturation distribution and gravity segregation (high water saturation in the bottom) are evident. (b) Side view of brine saturation distribution after injecting 0.25 pore volumes of CO_2 into a brine (containing 5 wt % nanoparticles)-saturated Boise sandstone (nanoparticle case). The presence of nanoparticles in the in situ brine increases the saturation behind the front and decreases gravity segregation. Point-by-point CO_2 saturation difference of the (a) control case and (b) nanoparticle case after 0.25 pore volumes of CO_2 injection in to the (c) Boise sandstone core. Higher CO_2 saturation in the control case is illustrated by cold color and higher CO_2 saturation in the nanoparticle case is red. (Modified after Aminzadeh et al.).[29]

for the purposes of storage because it enables the CO_2 to push its way into a broader portion of the rock, slowing down the rate of advance and increasing the volumetric storage efficiency. This result suggests that injecting a slug of nanoparticle dispersion into the storage reservoir before starting CO_2 injection could increase the overall efficiency of large-scale storage.

Solubility Trapping. CFSES study of solubility trapping includes both investigations of the kinetics of CO_2 dissolution into brine and how this may manifest in natural CO_2 reservoirs. What happened at Bravo Dome serves as an analogue for what might occur in GCS reservoirs over long timescales (post-

injection). The total mass of CO_2 in the Bravo Dome field in 1981 was estimated to be 1.2 ± 0.3 Gt CO_2. On the basis of the variations of the mass of CO_2 per unit area and the local fraction of dissolved gas, an estimate for the total change in mass of CO_2 across the field is approximately 230 Mt CO_2. While large, this amount of CO_2 corresponds to only $22\% \pm 17\%$ of the initial CO_2 emplaced into Bravo Dome. This is the first estimate of the total mass of CO_2 dissolved from a natural CO_2 reservoir over millennial timescales.[30,31]

Thermochonological (U−Th)/He dating of a reservoir sample from Bravo Dome indicates a thermal event occurred approximately 1.2 million years ago. This event was likely related to the emplacement of hot volcanic gas into the reservoir and falls within the time frame of volcanic activity in the area. This age dating provides preliminary evidence that the emplacement of CO_2 into Bravo Dome began more than one million years ago rather than 10000 years ago, previously assumed. The greater residence time of the CO_2 at Bravo Dome implies that the average rate of CO_2 dissolution at Bravo Dome is very slow, so there is only a finite amount of dissolved CO_2 that will be stored.

Mineral Trapping. CFSES research on mineral trapping has centered on observations of leakage from natural CO_2 reservoirs. Field observations of active and inactive CO_2 seeps along the Little Grand Wash fault, and radiometric dating of natural carbonate (travertine) deposits[33] suggest that calcite precipitation is both the result and cause of spatial and temporal shifts in preferential flow paths of upward migrating CO_2-saturated-brine. The hybrid pore-scale reactive transport model was used to understand whether alteration of flow paths by $CaCO_3$ precipitation could predict the observed patterns at the Little Grand Wash fault. In addition, the pore-network model was used to determine whether tight coupling of convection and reactions at the pore scale would suffice to cause such macroscopic "emergence".

The hybrid pore-scale reactive transport model was used as a basis for understanding how $CaCO_3$ precipitation alters flow paths by pore plugging under different geochemical compositions and pore configurations. Pore blocking was observed to be faster in a fracture near the main fault and propagated further away from the main fault, which qualitatively reflects the observed pattern at the Little Grand Wash fault. This demonstrates that inclusion of more realistic pore configurations and geochemical composition may enhance our fundamental mechanistic explanations of how leakage-induced calcite precipitation alters flow paths by pore plugging.

Contrary to observations at the Little Grand Wash fault, however, the pore-network model predictions suggest a
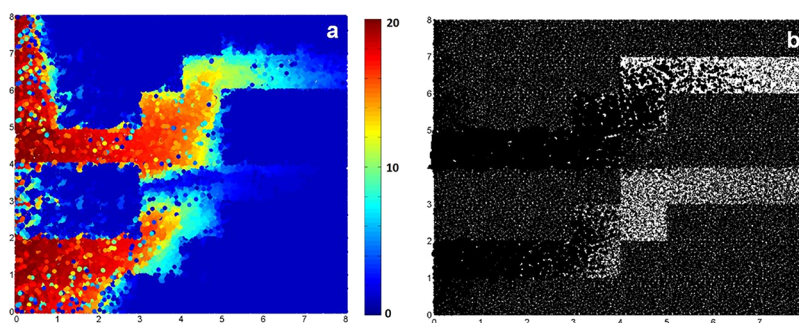

Figure 7. Normalized (a) concentration and (b) cementation fields of the 8×8-pore-network domain with two high-conductance pathways at 0.5 pore-volume throughput ($Da = 0.73$, $\alpha = 100$). White indicates no cementation, whereas black indicates more cementation. (Modified after Mehmani et al.[41] with permission from Springer Science and Business Media.)

persistence of pre-existing preferential flow paths throughout the cementation process (Figure 7). Therefore, despite the eventual occlusion of preferential flow paths due to cementation, the model does not predict a redirection of their trajectory under any transport/precipitation regime. Redirection of flow was not captured because as the overall permeability of the domain was decreasing, the relative dominance of the two high-flow-rate channels remained the same. This suggests either that the model did not contain sufficient flow/transport physics (e.g., complex reactions, dissolution, etc.) or that the presence of another important mechanism was excluded (e.g., geomechanical effects involving fault-related flow). A third possibility may be an inaccurate capture of the initial conditions; the model assumes that all pores are initially seeded with calcite.

■ DISCUSSION

The integration of molecular dynamics simulations, pore-scale experiments, pore-scale simulations, and the study of natural analog sites has provided useful insight in the efficacy of capillary, solubility, dissolution, and mineral trapping for geological CO_2 storage. These results also suggest potentially fruitful topics for further investigation.

Molecular dynamics simulations provide insight on the wetting behavior of water, brines, and supercritical CO_2 on the hydrophilic gibbsite and hydrophobic siloxane surfaces of kaolinite. This work predicts that the nanoscale distribution of wetting and nonwetting phases can differ significantly for different mineral surfaces, in spite of somewhat similar macroscopic contact angles. Because nucleation and precipitation of carbonate minerals depend strongly on the local distribution of CO_2, H_2O, and dissolved ion species, nanoscale surface interactions should also influence long-term mineralization of injected carbon. HRXCT imaging indicates that strongly hydrophilic media offer significant potential for supercritical CO_2 residual capillary trapping. Improvements in snap-off theory suggest more capillary trapping than previously predicted. Flow experiments show that nanoparticles, with appropriate surface chemistry, can prevent the coalescence of snapped off CO_2 droplets at CO_2/brine injection fronts, enabling a greater CO_2 storage efficiency. The possibility of designing surface chemistry to maximize storage efficiency with this effect is an interesting subject for further research.

Estimates on dissolution trapping using data from Bravo Dome showed that $22\% \pm 17\%$ of the CO_2 was trapped over long spans of geologic time. However, evidence suggests that dissolution rates are significantly slower than expected. Most potential storage formations have permeabilities similar to Bravo Dome, which implies slow solubility trapping and the persistence of buoyant CO_2 in the subsurface for millennia. The amount of storage capacity providing safe, long-term CO_2 storage through rapid solubility trapping may, therefore, be much smaller than currently assumed.

For mineral trapping, hybrid pore-scale and pore-network reactive transport modeling have demonstrated the importance of including realistic pore configurations, flow and transport physics, and geochemistry to predict how carbonate mineral precipitation alters flow paths by pore plugging. The mortar methods used are valuable in investigating how pore scale physics can be upscaled to reveal "emergent" behavior at CO_2 reservoir scales. Battiato and Tartakovsky[49] and Boso and Battiato[50] demonstrated that macroscopic equations for reactive transport break down for regimes dominated by heterogeneous reactions resulting in incomplete mixing at the pore scale. "Emergent"

phenomena typically result from strong coupling of different mechanisms at the micro (or pore)scale. Although macroscopic models are applicable to many such scenarios, there are cases where a macroscopic description alone cannot produce meaningful results.[49] In such cases, a dynamic exchange of information between the micro- and the macroscales becomes imperative. The mortar methods developed as part of CFSES provide one way of establishing this communication. These methods are independent of the specific pore-scale model used, as long as they apply to the case of single phase transport (in the method's current form).

Future work will extend the results presented here by developing engineered physicochemical strategies for improving subsurface storage of CO_2. The contact angle measurements by optical microscopy are being extended to study rate-dependent contact angle hysteresis and the changes in contact angle that occur as a result of supercritical CO_2-induced alteration on mineral substrates. The extended molecular dynamics work, including wetting on the basal surface of muscovite, will permit more direct comparison with the HRXCT and optical microscopy experiments. Such comparisons are valuable not only for validation of simulation results but also for identifying why simulation results using idealized (physically and chemically homogeneous) mineral surface models differ from experimental results using imperfect natural mineral samples. By extension, such understanding may also explain the disagreement between different experimental results.

A key challenge for applying pore-scale multiphysics to GCS efforts is upscaling of the results without loss of fidelity. Key relationships such as permeability−porosity, porosity−reactive surface area, and porosity−tortuosity can be constructed from pore-scale simulations which account for a range of reaction regimes characterized by the Damkohler and Peclet numbers.[51,52] Newly developed relationships (e.g., power law functions) from pore-scale simulations will then be used in a continuum-scale model that may account for large-scale phenomena mimicking lateral migration of surface CO_2 seeps. Comparison of field observations and simulations results will provide mechanistic explanations of the lateral migration and enhance our understanding of subsurface processes associated with CO_2 leakage and mineral and solubility trapping.

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Randall T. Cygan received his B.S. in chemistry from University of Illinois−Chicago in 1977, and his M.S. and Ph.D. in geochemistry and mineralogy from the Pennsylvania State University in 1980 and 1983, respectively. He then joined Sandia National Laboratories in Albuquerque, New Mexico, where he is now a Senior Scientist in the Geoscience Research and Applications Group. Cygan was also an Assistant Professor in the Geology Department at the University of Illinois for a short time. His research interests include chemical diffusion, mineral dissolution, adsorption phenomena, spectroscopy, and molecular simulation. He is a Centennial Fellow of Pennsylvania State University and a Fellow of the Mineralogical Society of America.

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Thomas Dewers has research interests and experience that include theoretical coupled thermal-mechanical-hydrological-chemical modeling, high temperature−high pressure and rock mechanics experimental methods, field investigations for geomicrobiology and hydrogeology, induced seismicity, and digital geologic mapping. Following graduation from Indiana University with a Ph.D. in 1991, where he worked in the Department of Chemistry, he was a postdoc in the Center for Tectonophysics at Texas A&M. Following this, he was a tenure-track and tenured professor at the University of Oklahoma School of Geology and Geophysics for 13 years. He is currently a Distinguished Member of the Technical Staff at Sandia National Laboratories where he has worked since 2007. Current research examines elasto-plasticity of pressure sensitive materials, acoustic tomography, aspects of subsurface carbon storage, multiphase flow, laser microscopy, coupled thermal-mechanical-hydrological-chemical model code development, and all things mudstone.

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Hongkyu Yoon obtained a Ph.D. in Environmental Engineering in Civil Engineering from the University of Illinois at Urbana–Champaign in 2005. He is an expert in hydrogeology, reactive transport experiments and modeling, and characterization of pore topology and surface properties of geomaterials using multiscale imaging techniques. As a technical staff at Sandia National Laboratories, he is developing models for multicomponent reactive transport and multiphase flow in porous and fractured media and applying them for reactive solute transport and water-rock interaction relevant to geologic carbon storage and geo-resources characterization.

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