Assessment of Key Physical and Chemical Research Findings for the Use of CO₂ as a Heat Exchanging Fluid for Geothermal Energy Production

Susan Carroll¹ and Greg Stillman²

¹Lawrence Livermore National Laboratory, Livermore, CA 94550
carroll6@llnl.gov

²Geothermal Technologies Office, U.S. DOE, 1000 Independence Ave. SW, Washington, DC 20585
greg.stillman@ee.doe.gov

Keywords: Supercritical Carbon Dioxide, Enhanced Geothermal Systems, Geochemistry

ABSTRACT

The geothermal community has produced a significant body of research exploring the use of CO₂ as a heat exchanging fluid for high temperature fractured hard rock systems and low temperature porous sedimentary systems. In this paper, we review the literature to evaluate the state of readiness of this novel technology for the production of geothermal energy. Specifically we discuss key findings related to:

1. Relative performance of CO₂ and H₂O Enhanced Geothermal Systems (EGS) in both high-temperature fractured and low-temperature porous media, key processes that have been shown in computational simulations to impact system behavior and performance;
2. Augmentation of the performance and cost of subsurface CO₂ storage through combination with CO₂-based geothermal systems;
3. Advancement in understanding of the geochemical reactivity of the reservoir and the wellbore environment, and how this augments system performance and;
4. Research topics that remain poorly understood and logical next steps for future research activities.

1. INTRODUCTION

Production of geothermal energy from CO₂ enhanced geothermal systems (CO₂-EGS) has the potential to stem the increase in atmospheric CO₂ and prevent associated impacts on global climate change by using CO₂ captured from fossil fuel energy power plants as a heat exchange fluid for high-temperature fractured and low-temperature porous systems. Properties of CO₂ as a heat exchange fluid provide additional motivation including (Pruess, 2006):

- A net buoyancy force caused by large density differences between cold and hot CO₂ that can reduce power consumption for driving fluid circulation
- A lower viscosity that creates larger flow velocities for a given pressure gradient
- As a polar molecule, CO₂ is much less effective as a solvent for rock mineral

The state of readiness of CO₂-EGS has been examined mostly through numerical simulation, with a limited number of experiments. A wave of such simulations and research activities, funded by the Department of Energy through the Recovery Act of 2009, has recently concluded. This has resulted in significant advances towards understanding the relationships between unique properties of CO₂, fluid flow, heat exchange, geochemical reactivity, energy production and cost since Brown (2000) first suggested using supercritical CO₂ as a heat exchanging fluid in hot, dry, and fractured geothermal reservoirs. In this paper we summarize literature results around two major themes:

1. Numerical simulations of heat extraction and system behavior
2. The role of geochemistry in changing permeability, heat transfer, storage integrity, and fluid flow

Research around these themes can generally be divided into detailed studies that focus on assessing the role that physical and chemical transport of supercritical CO₂ in hot fractured igneous or metamorphic geologies (150 to 400°C) and in lower temperature porous sedimentary geologies (100 to 150°C). Initial finding from economic assessments studies are summarized. Finally, potentially fruitful areas of additional research are presented.

2. RESERVOIR SIMULATIONS

Numerous reservoir simulation studies have been conducted on CO₂ based geothermal system since the idea was first introduced and disseminated by Brown (2000). Figure 1 maps simulation studies against their assumed resource temperature and depth. The literature
contains a mix of scoping studies and more detailed simulations. As a cursory assessment of how well the research community’s simulation assumptions match anticipated actual geothermal resource characteristics, thermal gradients composed from 80 to 100 mW/m² heat flows with a rock thermal conductivity of 2.0 w/m°C are added to Figure 1. These are combined with average permeability at various depths for carbonates and siliciclastic geologies (Kirby, 2012). These heat fluxes and permeability measurements represent some of the top candidate porous media hosted resources within and neighboring the Basin and Range (Allis et al., 2013). As can be seen from Figure 1, the simulations in porous media match well with characteristics from the Basin and Range. However, fractured media simulations tend to assume more aggressive thermal gradients than 50 °C/km. Generally, most simulation favor the use of 50 mD permeability, which are a fair assumption given measured values of ~30 mD. As can be seen from the orange color shading, those simulations conducted in deeper and hotter reservoir tend to show dominance of water as a heat exchange fluid. It should be noted that these heat fluxes and permeability represent the top candidates for geothermal systems hosted in hot stratigraphic reservoirs and not saline aquifers for carbon storage, which will likely have weaker heat flows.

The numerical simulations presented in Figure 1, the majority being scoping studies, have been instrumental in establishing the legitimacy and need to further research and develop of CO₂ based geothermal systems. From the body of studies completed to date, the following processes are of considerable importance to the effective deployment of CO₂-EGS:

- Real world host geologies will be heterogeneous, this heterogeneity will decrease CO₂ heat sweep efficiency from idealized estimates derived from homogenous models For igneous hosted systems, fracture geometries and characteristics are still not well constrained but will likely differ significantly from idealized parallel plate models. Acoustic emission derived estimates for reservoir volume greatly exceeds tracer-swept volume (Grant and Garg, 2012).
- Viscosity induced CO₂ channeling may create thermal short circuits (Pritchett, 2009).
- Nucleation and dissolution behavior of a gas that is highly soluble in a liquid phase may change the character of two phase flow, resulting in an increase of relative permeability of the gas over standard models (Stacey et al., 2010).
- The assumption that the host geology will completely dry out is unrealistic especially for porous media (Spycher and Pruess, 2010).
- Halite formation in flow paths and the rock matrix, as dry CO₂ displaces formation brine, significantly weakens heat extraction performance (Borgia et al., 2012).
- Geochemical processes will alter permeability, heat transfer area, and mechanical characteristics of the reservoir (Chandra et al., 2012)
- Flow of CO₂ within injection and production wells is not an isentropic process (Freifeld et al., 2013) Lateral heat transfer and changes in gravitational potential energy are non-trivial considerations during wellbore CO₂ flow (Freifeld 2013). High fidelity integrated wellbore-reservoir simulators can be used to understand these considerations (Pan and Oldenburg, 2012).

It is difficult to make a concise assessment of the superiority of one heat mining fluid over another for a given geothermal resource from the literature collection. While numerous studies, (Pruess, 2006; Prichett, 2009; Atrens et al., 2010; Randolph et al., 2011; Borgia et al, 2012) and others, have performed simulations to compare the performance of CO₂ and H₂O based geothermal systems, differing assumptions and modeling approaches make a quantiative inter-study comparison difficult. Additionally, it may not be completely necessary to determine superiority, as the focus should be on how best to exploit a given geothermal resource given a set of predetermined criterion. Two such criterions could be: reducing anthropogenic CO₂ emissions and maximizing the utilization of geothermal energy.
Figure 1 Plot of simulation studies performed on CO2-based geothermal systems. Field permeability measurements at various depths from the Basin and Range region of the Western U.S. are added for comparison against model assumed permeability listen below. Solid triangles represent simulation performed for porous media and open squares are fractured media models. Purple shading indicates CO2 performed more favorable for heat extraction than H2O in the given study, and orange shading indicates the reverse. 1Randolph and Saar, 2011, 50 mD; 2Randolph and Saar, 2011, 50/25 mD; 3Buscheck et al., 2012, 100 mD; 4Freiffeld et al., 2013, 1-350 mD (heterogeneous); 5Buscheck et al., 2012, 100 mD; 6Randolph and Saar, 2011, 50/25 mD; 7Borgia et al., 2012, 50 mD; 8Buscheck et al., 2012, 100 mD; 9Pan et al., 2012, 100 mD; 10Pritchett, 2009, 50 mD; 11Pruess 2006, 50 mD; 12Chandra et al., 2012, mD range; 13Atren et al., 2010, N/A; 14Buscheck et al., 2012, 100 mD; 15Agrawal et al., 2010, 60 mD
2.1 Reduce CO₂ Emissions with Carbon Capture and Storage - Geothermal’s Enabling Role

If the primary objective is to reduce CO₂ emissions from fossil fuel sources, combining geothermal energy production with carbon capture and storage (CCS) may have advantages over standalone CCS systems. There are three motivations for combining geothermal and carbon sequestration technologies, geothermal power production offsets CO₂ capture and injection requirements (primarily a cost benefit), producing fluids from the storage formation reduces over-pressurization and formation integrity risks, and co-produced fluids can have beneficial uses at the surface after desalination. The geothermal resource base, for such a combined system, has been narrowed to the subset of porous geologies where CO₂ storage potential is greater compared to igneous/fractured host geologies (NETL 2012). There is little competition for this segment of the resource from water-based geothermal developments as these carbon storage reservoirs are not likely to be hot enough for economically competitive water-based system. Tillner et al. (2013) shows the feasible synergetic use of a saline aquifer in the Northeast German Basin for carbon storage and geothermal energy production. Analysis has shown that geothermal electricity can make up for parasitic costs of carbon capture for capture rates of 30-90% of total fossil power plant CO₂ emissions (Frank et al., 2012). Randolph and Saar (2011) estimates that formation overpressure can be reduced by 10% through co-production of storage formation brine. Buscheck et al., (2013) presents scenarios where overpressure measured across a sealing, low-permeability, unit can be reduced by up to 4 MPa. Desalination of produced brine can be aided by using the thermal energy present in the fluid (Koroneos and Roumbas, 2012). Desalinated brine could offset carbon capture water consumption requirements which are estimated to increase fossil power plant water consumption by 37-95% depending on plant and capture technology (NETL 2007). For a subset of scenarios presented in Buscheck et al., (2013), 4,000-17,000 acre-feet of beneficial water is derived from co-produced storage formation brine per year. During fluid circulation, CO₂ formation leak-off or loss from the standpoint of fluid availability for heating shown is simulated to be between 5% (Buscheck et al., 2012) and 7% (Randolph and Saar, 2011) should not be viewed as sequestration potential however, as all CO₂ injected in these scenarios is destined for long-term subsurface storage. Frank et al.’s (2012) calculations show that the amount of energy generated by CO₂-EGS has the potential to fully offset the parasitic energy costs associated with capturing carbon from a conventional coal plant using standard amine technology and reduce the total carbon emissions from the coal plant by more than 80% (Figure 2).

Chandra et al. (2012) presents a study of an Integrated Gasification Combined Cycles (IGCC) plant coupled to an EGS reservoir that is operated with the CO₂ from the fossil plant. Their first-order conservative economic assessment (no value for CO₂ storage) gives an eight-year payback period for the combined system and a return on investment of 91%. Randolph and Saar (2011) calculate the net value of one ton of CO₂ sequestered and used for geothermal power generation to be $4.40. Levelized cost of electricity estimates (Atrens et al., 2011) are not competitive (> $0.10/kWh) and are most sensitive to wellbore construction costs. Life cycle analysis of an IGCC plant with and without CO₂-EGS found levelized cost of electricity to be slightly greater for IGCC-CO₂-EGS ($0.14/kWh) than for IGCC with carbon storage in a saline aquifer ($0.12/kWh) (Mohan et al., 2013). Without a carbon regulatory and market framework to support widespread carbon capture and storage, CO₂-based geothermal systems are unlikely to reach competitive costs.

2.2 Maximizing Geothermal Energy Adoption and Use

If the primary objective is to increase the adoption of geothermal energy, using CO₂ as the heat mining fluid expands the geothermal resource base that could be economically competitive for development into cooler thermal regimes (Randolph and Saar, 2011). Simulation studies show that heat extraction performance of CO₂ over water decreases with increasing resource temperature (Pruzess 2006), which suggest low to moderate temperature resources are candidates for CO₂ based systems. Additionally, rising CO₂ will cool due to wellbore frictional losses and Joule-Thompson expansion; these phenomena suggest that shallow wells preferentially benefit CO₂ systems over water-based systems (Atrens et al., 2010). Reservoir geometry influences energy extraction behavior, where greater flow paths (surface area) per rock volume equates to greater heat extraction efficiencies because the media can accommodate greater fluid flow and heat diffusion lengths are smaller. Under certain flow and geometry conditions, a spherical reservoir model has superior heat extraction/thermal draw down behavior compared to a parallel fracture model (Elsworth 1990). These factors combine to suggest that shallow, low to moderate temperature (< ~150 °C), porous media are attractive near-term targets for CO₂ based geothermal systems. Domestic resource potentials have been estimated to be ~7 GW for sedimentary systems >125 °C, shallower than 4.5 km, and no greater than 100 miles from a CO₂ source (Freifeld, 2013). This resource estimate is being updated based on additional available field data. Enhanced oil recovery (EOR) operations have considerable experience with subsurface injection and fluid handling of CO₂ and are
near-term opportunity targets for field tests (Freifeld et al., 2013).

Although current deployment of EGS is limited by economic performance, future deployment could be limited by the availability of water for heat mining. This is especially true when considering the best resources for EGS are in the Western U.S. where competition for water is the most intense (Clark et al., 2013). Using CO$_2$ would alleviate this possible adoption constraint. Here, leak-off should be considered as CO$_2$ sequestration potential as renewable electricity generation is the primary objective of these systems.

3. GEOCHEMISTRY

The presence of even small amounts of water with scCO$_2$ will perturb chemical equilibrium and react with the reservoir rock. In this section we summarize the current understanding of rock-water-scCO$_2$ interactions and their potential impact on reservoir integrity for both high-temperature fractured and low-temperature porous reservoirs. Our review is based on a small but growing number of experimental studies that have looked at mineral and whole rock reactivity in CO$_2$-water mixtures (Figure 3) as well as numerical studies that identify key processes within the reservoirs.

Figure 3 Experimental studies that have looked at the mineral and whole rock reactivity in CO$_2$ – water mixtures (Carroll and Knauss, 2005; Giammar et al., 2005; Bearat et al., 2006; Hanchen et al, 2006, 2008; Daval et al., 2009, 2011; Prigiobbe et al., 2009; Carroll et al., 2011; Lu et al., 2011; Sugama et al., 2011; Gysi and Stefannsson 2012; Re et al. 2012; Remoroz et al, 2012; Black and Haese, 2013; Carroll et al., 2013a,b; Galeczka et al, 2013; Smith et al., 2013a,b,c; Stockman et al., 2013; Wang and Giammar 2013).

3.1 High-Temperature Fractured Reservoirs

Spycher and Pruess (2010) simulations suggest that some water is present in the shear zone over much of the reservoir lifetime. The system evolves from one dominated by mixed fluids of water and CO$_2$ during the first 4 years to one dominated by a single CO$_2$ fluid with decreasing mole percent of water from 7 years (scCO$_2$ with 6 % H$_2$O) to 36 years (scCO$_2$ with 0.1 % H$_2$O). The length scale is important, because fossil fuel and geothermal power plants generally have a 30 to 50 year life-time and because CO$_2$ reactivity depends on the presence of water in the system. CO$_2$ dissolution in water creates slightly acidic solutions that tend to enhance mineral reaction rates and solubility, and wet scCO$_2$ has been shown to very reactive. In the discussions that follow we refer to Phase 1 CO$_2$-EGS to the period in which the shear zone is dominated by mixture of H$_2$O and scCO$_2$ fluids and Phase 2 as the period in which most of the water has been removed and a wet scCO$_2$ occupies the shear zone.

Geochemical reactions during Phase 1 have the potential to enhance shear zone permeability as was shown in a fractured core flood experiment. Smith et al (2013b) measured a marked increase in fracture permeability for a greywacke core that was reacted with CO$_2$-rich brine at 200°C and pCO$_2$ = 5.5 MPa. Tomography and modeling analysis revealed that the increase in permeability could be attributed to significant dissolution chlorite, feldspars and calcite both along the fracture and in the matrix adjacent to the fracture (Figure 4). These observations were supported by geochemical models of Ohaaki-Broadlands geothermal site in the Taupo Volcanic Zone, New Zealand, which serves as a natural analog site for CO$_2$-EGS. The hottest fluids at this site carry high levels of CO$_2$ from fractures in the deep greywacke basement rock into the overlying reservoir formations. Geochemical calculations from 100 to 300°C and up to 1 M dissolved CO$_2$ indicated that the greywacke mineral assemblage is not thermodynamically stable. Geochemical reactions are also thought to increase permeability for other volcanic mineralogy. Xu et al 2010a modeled the impact of geochemical reactions using the shear zone mineralogy and geothermal conditions at the H$_2$O-EGS field in Desert Peak, Nevada, and found that co-injection of CO$_2$ and H$_2$O enhanced shear zone porosity by 10 to 20% over a 10 day period near the injection well. The porosity increase was caused by dissolution of carbonate minerals. Silicate minerals also dissolved, but at a much slower rate the carbonate minerals. We infer that increased porosity translates to an increase in permeability.
Dissolution of primary silicates was also observed in experiments designed to mimic granite, sandstone, and basaltic glass reservoirs. Re et al (2012) measured the alteration of synthetic granite (mixture of quartz and feldspars) for 42 days at 250°C in batch experiments with mixtures of scCO$_2$ and water. The granite material generated secondary illite and smectite phases. Lu et al (2011) measured the alteration of sandstone for up to 63 days at 200°C in batch experiments with mixtures of scCO$_2$ and water. Enhanced dissolution of the feldspar generated the same secondary clay minerals (illite and smectite) as the synthetic granite experiment, along with some calcite. Gysi and Stefansson (2012) measured the alteration of basaltic glass for up to 125 days at 75, 150 and 250°C in batch experiments with mixtures of scCO$_2$ and water. Basaltic glass is arguably the most reactive rock type with the highest potential to store CO$_2$ as carbonate minerals owing to its mafic composition and amorphous structure. Alteration products were found to depend on temperature where faster glass dissolution rates at 150 and 250°C yielded high amounts of dissolved Mg, Fe, Si that promoted smectite precipitation over Mg and Fe carbonates; some CO$_2$ was stored as calcite.

Reservoir geology is likely to be reactive beyond the first few years of the CO$_2$-EGS system where the fluid is dominated by a wet scCO$_2$ fluid. There are two experimental studies that address the second phase of a CO$_2$-EGS reservoir where water has been largely displaced and a single scCO$_2$ fluid containing some fraction of water. Sugama et al (2011) reacted granite with vapor-saturated scCO$_2$ at 200 (42 days) and 250°C (4 days). They found that feldspar and biotite were very reactive and formed amorphous silica, amorphous clay, amorphous Na and K – carbonates, and crystalline Fe and Mg carbonates. In their experiments, precipitation of low soluble Fe and Mg carbonates tended to form a protective layer at the granite surface and inhibit further mineral alteration, and precipitation of high soluble Na and K carbonates allowed for permeable pathways and continued alteration of the rock. Remoroza et al (2012) reacted granitic rock at 200 and 250°C in nominally dry, CO$_2$ and developed a novel method of extracting elements dissolved in the CO$_2$. Although the authors claim that no significant rock-scCO$_2$ reactions occurred, the dissolved Si concentrations increase toward a plateau representative of steady state or equilibrium control. These authors made an effort to remove water from the initial granite rock, however the reported mineral alteration suggests that it very difficult to fully remove water in the lab, and most likely in the EGS reservoir as well. We document these experiments, because reactive transport simulations typically address the reactivity during Phase I only, assuming no reactivity during the second phases within the fracture zone (Wan et al., 2011; Xu et al., 2012).

3.2 Low Temperature Porous Reservoirs

An important attribute for low temperature systems (100 to 150°C) is that the working fluid is likely to be a reactive mixture of H$_2$O and scCO$_2$ and will not evolve towards a single scCO$_2$ fluid over the lifetime of the geothermal energy plant (30 years). The long-term presence of mixed H$_2$O-scCO$_2$ fluids is based on simulation results that strive to optimize both CO$_2$ storage and geothermal energy production by implementing multiple rings of alternating injection and extraction wells to contain the CO$_2$ storage footprint by imposing a hydraulic barrier by reinjection of produced brine (Elliot et al., 2012; Buscheck et al., 2013). We draw on the carbon storage literature to assess the impact of rock-water-CO$_2$ reactions on low temperature porous reservoirs because the same type of reservoirs are used in both technologies. One distinction between CO$_2$ storage reservoirs and low temperature CO$_2$ geothermal systems is that mixed water - CO$_2$ fluids will circulate between the geothermal injection and production wells. The circulation of mixed fluids experience shifts in temperature and continually exposes the rock matrix and well and turbine materials to slightly acid fluids that will promote reaction. In the storage only scenario, reactions are thought to be more limited because the fluids are not as well mixed, achieve chemical equilibrium at the reservoir conditions and are not exposed to production well or turbine materials.

Figure 4 New porosity that developed along the fracture (white to grey) in a greywacke sample (Ohaaki-Broadlands geothermal site, New Zealand) after reaction with CO$_2$-rich brine at 200°C. The increase in porosity was a consequence of mineral dissolution and was consistent with continued increase in permeability over the experiment (Smith et al., 2013b). Arrow indicates direction of flow path.
Experimental observations designed to probe the response of carbonate and sandstone CO$_2$ storage reservoirs to mixed H$_2$O-scCO$_2$ fluids are applicable to low-temperature CO$_2$ geothermal systems. Carbonate minerals are by far the most reactive mineral phases and their dissolution can alter porosity and permeability within the reservoir. This is especially true for carbonate formations where pore size is highly heterogeneous and can range by multiple orders of magnitude. Fast reaction kinetics and heterogeneity result in the development of preferential flow paths that may short circuit fluids and limit heat exchange (Figure 5). Optimization of geothermal energy from carbonate CO$_2$ storage reservoirs will likely require an understanding of chemically induced flow paths. Laboratory experiments can be used calibrate or constrain the key parameters used in reactive transport simulations, where the two most important factors are the conversion of porosity change to permeability change and estimation of the accessible reactive surface area (Carroll et al., 2013b; Hao et al., 2013).

Second to carbonate minerals, the dissolution of iron clay minerals are important because they provides source for secondary mineral precipitation in sandstone formations under CO$_2$ storage conditions (Palandri et al., 2005; Kharaka et al., 2006, 2009; Xu et al., 2010b; Carroll et al., 2011; Lu et al., 2012; Carroll et al., 2013b). The importance of the reactivity of iron clays is illustrated in detailed imaging of sandstone from the Cranfield storage unit. Figure 6 shows mineral and pore distribution in a sandstone sample where a substantive amount of chlorite (the iron clay shown in turquoise-blue) is associated with the connected pore space (shown in white). The proximity of the chlorite with connected pore space assures its contact with CO$_2$ rich brines and its reaction. Iron clays are the potential source of long-term mineral trapping of CO$_2$ as Fe-carbonates and the precipitation of secondary clays and hydroxides. In
carbon storage environments, dissolution of iron clay minerals appears to have no impact on the overall integrity of the sandstone storage reservoir or the caprock primarily because reaction rates are very slow. Slow dissolution kinetics also limit the amount of CO₂ stored as carbonate minerals.

3.3 Well Integrity

Here we draw on the carbon storage literature to frame role of geochemistry and mechanics on well integrity in CO₂-EGS environments. For carbon storage, there is concern that chemical alteration of the cements can create pathways for gas and brine leakage to shallow water resources and back to the atmosphere. This concern exists despite the utilization of CO₂ for enhanced oil recovery. Portland cements commonly used in primary cementing operations produce a series of reaction fronts that divide the cement into distinctive zones (Figure 7). These zones consist of the unreacted cement, portlandite-depleted (CH-depleted), calcium-carbonate enriched, and an outer amorphous zeolite in direct contact with the carbonated brine (Carey et al., 2007; Kutchko et al., 2007, 2008; Rimmel et al., 2008, 2009; Mason et al., 2013).

![Figure 7: Reaction fronts produced by flowing carbonated brine along the cement-caprock interface in a core-flood sample (Walsh et al., 2014).](image)

Permeability along fractures pathways within the cement and at the casing and rock boundaries appears to be controlled by concurrent chemical and mechanical alteration of the cement. One of the most interesting findings common to many of these experiments is an observed decrease in permeability despite measured increases porosity, especially in the outer amorphous silicate layer near the flow path (Carey et al., 2007, 2009; Duguid et al., 2005; Huerta et al., 2012; Kutchko et al., 2007, 2008, 2009; Mason et al., 2013; Scherer et al., 2011; Walsh et al., 2013a). Walsh et al (2014b) explain the observed decreases in permeability as compression of chemically weakened asperities that cause the fracture to close in response to the pressure placed on the sample. These processes are likely to occur within CO₂-EGS systems, however models will need to be calibrated to the higher temperatures of CO₂ EGS systems (100 to 400°C). The models, especially the mechanical components, are empirically based and more work is required to predict the impact for EGS.

3.2 Implications of Rock-Water-scCO₂ Reactions Reservoir Performance

3.2.1 Fractured Rock Reservoirs

Geochemical reactions are likely to persist over the lifetime of the CO₂-EGS reservoir because some amount of water is likely to be present. Here we discuss three potential impacts, all of which require future research.

The impact of enhanced permeability observed in experiment and simulations on heat extraction has not been fully evaluated. Geochemically induced permeability in igneous and metamorphic shear zones has the potential to sustain fluid transport within the shear zone by increasing the connection between flow paths exposing the fluid to a larger cross-section of the rock or by developing fast pathways that cut off smaller aperture fluid paths. Geochemical reactions also have potential to diminish shear zone permeability through asperity dissolution and clogging of pore throats with secondary clays or carbonates. We do not how these different mechanisms might impact heat extraction.

The precipitation of salts and carbonates originally dissolved in the reservoir brines may clog off fluid pathways, as wet scCO₂ becomes the dominant fluid (years 4 to 36) in geothermal shear zones. Simulations by Borgia et al (2012) found reduced energy production because matrix water, transported by capillary forces to shear zone, dissolved into the scCO₂ caused any salts in the water to precipitate and clog fracture permeability. In their simulations well lifetime was reduced to 6 years where most of the precipitation occurs near the injection well. There is some experimental evidence, discussed above, to suggest that carbonate minerals formed both by the dehydration process resulting from the solubility of water in scCO₂ and by reaction of the wet-scCO₂ with rock minerals could also limit reservoir lifetime (Sugama et al., 2011).

A third and important aspect of geochemical reactions within fractured CO₂-EGS systems is carbon storage. Most simulation studies approximate CO₂ storage with reported estimates of water loss in conventional geothermal systems (5 to 10%). Xu et al (2012) further estimated the amount of CO₂ that would be eventually stored as carbonate minerals in the matrix pore space adjacent to main fracture
flow path. They found that optimal temperatures for carbonate mineral formation are between 160 to 190°C and as one would expect, rocks with more of iron, magnesium, and calcium silicates lead more carbonate mineralization. Dissolution of iron, magnesium, and calcium silicates provide the cations needed to form common carbonate minerals.

![Figure 8. Example of CO2 mineral trapping (kg CO2 per m3 medium) from 30 to 240°C obtained with siliceous rhyolite Desert Peak tuff after 10 years. (Xu et al., 2012)](image)

### 3.2.2 Porous Sedimentary Reservoirs

Despite the presence of mixed H2O – CO2 fluids in porous sedimentary reservoirs, geochemical reactions are not likely to negatively impact geothermal energy production more than they do in conventional geothermal. This statement reflects the general observations that geochemical reactions do not appear to limit successful CO2 storage or enhanced oil recovery. As with enhanced oil recovery, optimization will be required to ensure that enhanced permeability in carbonate reservoirs maximizes the fluid sweep and does not lead to fast preferential flow paths that limit heat exchange with the rock. Presumably any corrosion, mineral or organic polymer scaling resulting from geochemical reactions can be addressed with the same solutions that are used for conventional geothermal energy production and for CO2-enhanced oil recovery which have similar water-CO2 fluid management issues.

Carbonate storage in porous sedimentary reservoirs should be comparable to that estimated for deep saline reservoirs (NETL 2012). Storage will largely be trapped as supercritical CO2, because silicate reaction kinetics are too slow to achieve a significant amount of carbonate precipitation.

### 3.2.3 Modeling Needs

Ideally one would want to model a CO2-EGS system over time and space to assess the impact of chemical reactions on EGS-CO2 reservoir integrity and on energy production. For mixed H2O – scCO2 fluids, adequate thermodynamic solubility and aqueous speciation databases are available, but mineral kinetic databases are lacking. We anticipate that silicate dissolution kinetics can generally be modeled with pH-dependent rate laws, because CO2 solubility tends to lower pH with minimal direct impact on mineral dissolution (Brady and Carroll, 1998; Carroll and Knauss, 2005; Smith et al., 2013a; Black and Haese, 2013). In the absence of high temperature kinetic rate parameters, models use rate laws extrapolated from lower temperatures such as those found in Palandri and Kharaka (2004) or arbitrarily fix rates of similar minerals, and treat precipitation rates as the inverse of dissolution rates (transition state theory). The Geothermal Technology Office at the Department of Energy is currently addressing the kinetic data gap for minerals present in EGS shear zones.

Modeling the transition from mixtures of scCO2 and water to a single phase of wet-CO2 is much more difficult and circumstantial, because thermodynamic properties of the solutions become largely non-ideal and require thermodynamic databases that account for concentrated brines and water-dissolved in CO2 (Apps and Pruess, 2011).

### 4. CONCLUDING REMARKS

We have reviewed recent research on CO2-EGS in both high-temperature fractured and low-temperature porous media, paying particular attention to the nature and reactivity of the heat exchanging fluids in these environments. In this final section of the paper we return to the notion that the primary motivation for CO2-EGS at this particular time should be to reducing anthropogenic CO2 emissions. If CO2-EGS is to be employed for carbon storage purposes, then the development of low – temperature sedimentary reservoirs should be a priority over fractured geological environments, because costs will be cheaper and storage volumes will be greater. Sedimentary reservoirs can produce power efficiently with CO2, and pressure reduction and treatment of produced water are viable options.

Geochemical reactions are not likely to negatively impact geothermal energy production in sedimentary reservoirs any more than they do CO2-enhanced oil recovery. Development of sedimentary reservoirs does not require extensive engineering, unlike the proposed stimulation of shear zones in high-temperature fractured media. The geothermal community is currently developing and assessing water-based EGS in hot fractured geologies with several field demonstrations. These demonstrations will evaluate the heat exchange requirements, such as flow rates, heat exchange surface area per unit volume, and geochemical impacts, that can then be optimized for CO2-EGS if appropriate.

Perhaps the most pressing unknown for CO2-based geothermal systems going forward is what the effective heat transfer area is for a given host geology and how this evolves over time. For reasons discussed in this assessment, the heat transfer area in contact with CO2
Carroll and Stillman

will be far less than the homogenous and non-reactive estimate. As the reservoir cools, rock masses will thermally contract and dynamically alter surrounding stress-states, altering flow paths and fracture geometries in addition to and coupled with dynamical geochemical alterations. Incorporating these processes into simulations constrained by field observations represents the next logical progression for study. Model validation through experiment and field tests will greatly advance the state of technology readiness.

ACKNOWLEDGEMENTS
We acknowledge support through the U.S. Department of Energy, Geothermal Technologies Office. Special thanks to Elisabet Metcalfe for her contributions and rendering of Figure 1. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27334.

REFERENCES


Carroll, S., McNab, W. Dai, Z.; Torres, S.: Reactivity of Mt. Simon sandstone and the Eau Claire shale under CO2 storage conditions, Environmental Science and Technology, 2012 dx.doi.org/10.1021/es3012269


