

# The effects of gas-fluid-rock interactions on CO<sub>2</sub> injection and storage: insights from reactive transport modeling

Yitian Xiao<sup>a\*</sup>, Tianfu Xu<sup>b</sup>, and Karsten Pruess<sup>b</sup>

<sup>a</sup>*ExxonMobil Upstream Research Company, Houston TX 77027, USA*

<sup>b</sup>*Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

---

## Abstract

Possible means of reducing atmospheric CO<sub>2</sub> emissions include injecting CO<sub>2</sub> in petroleum reservoirs for Enhanced Oil Recovery or storing CO<sub>2</sub> in deep saline aquifers. Large-scale injection of CO<sub>2</sub> into subsurface reservoirs would induce a complex interplay of multiphase flow, capillary trapping, dissolution, diffusion, convection, and chemical reactions that may have significant impacts on both short-term injection performance and long-term fate of CO<sub>2</sub> storage. Reactive Transport Modeling is a promising approach that can be used to predict the spatial and temporal evolution of injected CO<sub>2</sub> and associated gas-fluid-rock interactions. This presentation will summarize recent advances in reactive transport modeling of CO<sub>2</sub> storage and review key technical issues on (1) the short- and long-term behavior of injected CO<sub>2</sub> in geological formations; (2) the role of reservoir mineral heterogeneity on injection performance and storage security; (3) the effect of gas mixtures (e.g., H<sub>2</sub>S and SO<sub>2</sub>) on CO<sub>2</sub> storage; and (4) the physical and chemical processes during potential leakage of CO<sub>2</sub> from the primary storage reservoir. Simulation results suggest that CO<sub>2</sub> trapping capacity, rate, and impact on reservoir rocks depend on primary mineral composition and injecting gas mixtures. For example, models predict that the injection of CO<sub>2</sub> alone or co-injection with H<sub>2</sub>S in both sandstone and carbonate reservoirs lead to acidified zones and mineral dissolution adjacent to the injection well, and carbonate precipitation and mineral trapping away from the well. Co-injection of CO<sub>2</sub> with H<sub>2</sub>S and in particular with SO<sub>2</sub> causes greater formation alteration and complex sulfur mineral (alunite, anhydrite, and pyrite) trapping, sometimes at a much faster rate than previously thought. The results from Reactive Transport Modeling provide valuable insights for analyzing and assessing the dynamic behaviors of injected CO<sub>2</sub>, identifying and characterizing potential storage sites, and managing injection performance and reducing costs.

*Keywords:* CO<sub>2</sub> injection and storage, gas-fluid-rock interactions, reactive transport modeling, ccs.

---

## 1. Introduction

Possible means of reducing atmospheric CO<sub>2</sub> emissions include injecting CO<sub>2</sub> in petroleum reservoirs for EOR or storing CO<sub>2</sub> in deep saline aquifers. Sequestering raw CO<sub>2</sub> containing H<sub>2</sub>S and/or SO<sub>2</sub> requires less energy to separate from flue gas or a coal gasification process and therefore might be the preferred disposal option [1, 2]. Large-scale injection of CO<sub>2</sub> and other gases into subsurface reservoirs may induce a complex interplay of multiphase flow, dissolution, precipitation, diffusion, convection, and other chemical reactions [3, 4]. Compared to CO<sub>2</sub> residual and solubility trapping, mineral trapping of CO<sub>2</sub> is potentially attractive because it could immobilize CO<sub>2</sub> for long time scales and increase storage security. Depending on the spatial distribution and temporal evolution of the CO<sub>2</sub> injection and associated mineral dissolution and precipitation (artificial diagenesis), the gas-fluid-rock interactions could have a significant impact on injection performance and storage capacity and security. Alteration of the predominant host rock minerals is usually very slow and therefore is not experimentally accessible under deep reservoir or aquifer conditions. Reactive Transport Modeling (RTM) is a promising approach that can be used to predict the spatial and temporal evolution of injected CO<sub>2</sub>/H<sub>2</sub>S/SO<sub>2</sub> and associated formation alteration [1, 2]. The objective of this study was to conduct reactive transport simulations to investigate mineral alteration and sequestration of mixed CO<sub>2</sub>, H<sub>2</sub>S and SO<sub>2</sub> in a siliciclastic and a carbonate reservoir.

## 2. Reactive Transport Modeling Approach

A reactive transport model relies on a mathematical formulation to describe geochemical processes involving fluid-rock interactions. The general governing equation can be written as:

$$\frac{\partial}{\partial t}(\phi C_i) = \frac{\partial}{\partial x} \left( \phi D \frac{\partial C_i}{\partial x} \right) - \phi v \frac{\partial C_i}{\partial x} + \phi \sum_k \left( \frac{\partial C_i}{\partial t} \right)_k \quad (1)$$

Where  $C_i$  is the concentration of a specific species in the pore fluid,  $D$  is the combined diffusion and dispersion coefficient term,  $v$  is the linear fluid flow rate, and  $\phi$  is the porosity. The first two terms on the right hand side describe the transport process (diffusion, dispersion, and advection) while the last term describes the effect of geochemical reactions (Figure 1).

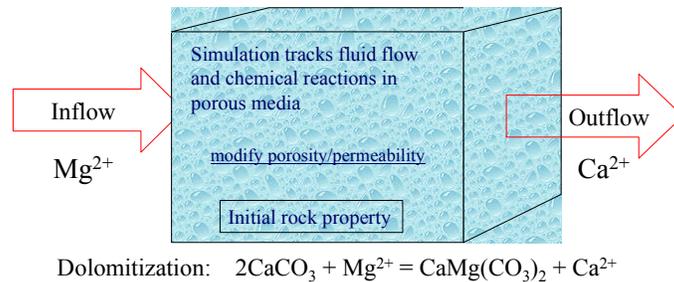


Figure 1. Schematic diagram showing the reactive transport process involving dolomitization.

For example, the reaction of dolomitization can be expressed as:

$$\frac{\partial C_{dolo}}{\partial t} = S A e^{-\frac{E_a}{RT}} \left( \frac{Q}{K_{eq}} - 1 \right)^{2.26} \quad (2)$$

Where S represents the reactive surface area, A is the rate constant,  $E_a$  is the activation energy,  $Q/K_{eq}$  is the saturation index, and 2.26 is the reaction order [5].

Due to complex boundary conditions and complicated coupling between the transport and reaction terms, it is impossible to provide analytical solutions to equation (1) for even the simplest geochemical system. Therefore numerical solutions have to be used. Fortunately, due to the exponential increase in computational power, realistic reactive transport models are beginning to provide new insights to CO<sub>2</sub> injection and storage at both injection and geological time scales. The simulations in this study were carried out using the non-isothermal reactive geochemical transport code TOUGHREACT [6]. The program treats multi-phase fluid and heat flow, advection and diffusion. It models geochemical reactions including aqueous complexation, mineral dissolution and precipitation, gas dissolution and exsolution, and ion exchange. Special modeling considerations include CO<sub>2</sub> solubility dependence on P, T, and salinity, changes in porosity and permeability due to mineral dissolution and precipitation, gas phase and gaseous species are active in flow, transport, and other reactions. Two previous studies [1, 2] applied reactive transport modeling to investigate mixed CO<sub>2</sub>/H<sub>2</sub>S/SO<sub>2</sub> injections in sandstone reservoirs, this study covered gas injection and storage in both siliciclastic and carbonate reservoirs.

### 3. Reactive Transport Modeling Design

The 1D radial reactive transport models represent CO<sub>2</sub> injection in a siliciclastic and carbonate reservoir at 2 km depth and 70 °C. CO<sub>2</sub> and other gases were injected in the reservoir at a rate of 1 million ton per year over a period of 100 years. The reactive transport models simulate the system from 0 to 10,000 years. There are three scenarios of mixed gas injected: CO<sub>2</sub> only, CO<sub>2</sub> + H<sub>2</sub>S, and CO<sub>2</sub> + SO<sub>2</sub>. [You need to say something about how the gases are introduced; I presume that both H<sub>2</sub>S and SO<sub>2</sub> are injected as aqueous solutes, because TOUGHREACT currently is not able to inject them directly as “free” gases.] The reservoirs are specified to have an initial porosity of 0.30 and initial permeability of 100 mD. The siliciclastic and carbonate reservoirs were defined by hypothetical mineral assemblages, representing an oligoclase/feldspar-rich sandstone reservoir and a limestone-rich reservoir, respectively (Table 1). Other primary and secondary minerals are listed in Table 1 as well.

Table 1. Initial mineral compositions of the siliciclastic and carbonate reservoirs and secondary minerals considered in the simulation (after Xu et al, [1]).

<i>Mineral</i>	<i>Chemical formula</i>	<i>Volume percent</i>	
		<i>Siliciclastic Reservoir</i>	<i>Carbonate Reservoir</i>
<b>Primary:</b>			
Quartz	SiO <sub>2</sub>	40.6	1.0
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	1.41	0.15
Calcite	CaCO <sub>3</sub>	1.35	63.0
Illite	K <sub>0.6</sub> Mg <sub>0.25</sub> Al <sub>1.8</sub> (Al <sub>0.5</sub> Si <sub>3.5</sub> O <sub>10</sub> )(OH) <sub>2</sub>	0.7	0.06
Oligoclase	Ca <sub>0.2</sub> Na <sub>0.8</sub> Al <sub>1.2</sub> Si <sub>2.8</sub> O <sub>8</sub>	13.86	0.05
K-feldspar	KAlSi <sub>3</sub> O <sub>8</sub>	5.74	0.12
Na-smectite	Na <sub>0.290</sub> Mg <sub>0.26</sub> Al <sub>1.77</sub> Si <sub>3.97</sub> O <sub>10</sub> (OH) <sub>2</sub>	4.8	0.06
Chlorite	Mg <sub>2.5</sub> Fe <sub>2.5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	3.19	0.39
Hematite	Fe <sub>2</sub> O <sub>3</sub>	0.35	0.00
Porosity		30	30
<b>Secondary:</b>			
Anhydrite	CaSO <sub>4</sub>		
Magnesite	MgCO <sub>3</sub>		
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>		
Low-albite	NaAlSi <sub>3</sub> O <sub>8</sub>		
Siderite	FeCO <sub>3</sub>		
Ankerite	CaMg <sub>0.3</sub> Fe <sub>0.7</sub> (CO <sub>3</sub> ) <sub>2</sub>		
Dawsonite	NaAlCO <sub>3</sub> (OH) <sub>2</sub>		
Ca-smectite	Na <sub>0.145</sub> Mg <sub>0.26</sub> Al <sub>1.77</sub> Si <sub>3.97</sub> O <sub>10</sub> (OH) <sub>2</sub>		
Alunite	KAl <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>		
Pyrite	FeS <sub>2</sub>		
Opal-A	SiO <sub>2</sub>		

## 4. Simulation Results: Sandstone Reservoir Injection

### 4.1 pH Evolution

The simulation results from the CO<sub>2</sub> only case are similar to those from CO<sub>2</sub> + H<sub>2</sub>S. The results from CO<sub>2</sub> + SO<sub>2</sub> case are however, significantly different (Figure 2). CO<sub>2</sub> and CO<sub>2</sub> + H<sub>2</sub>S injection leads to lower pH (~4) near the well bore, resulting from the dissolution of CO<sub>2</sub> and H<sub>2</sub>S in the formation water. Once the injection stops, the pH is quickly buffered by the reservoir minerals and goes back to a more neutral value (~6). Co-injection of SO<sub>2</sub> with CO<sub>2</sub> leads to very low pH (~0), presumably due to the dissolution of SO<sub>2</sub> and the formation of sulphuric acid zone close to the injection well. Corrosion and well abandonment are potential issues. After injection, the pH is buffered but still remains considerably low near the well bore.

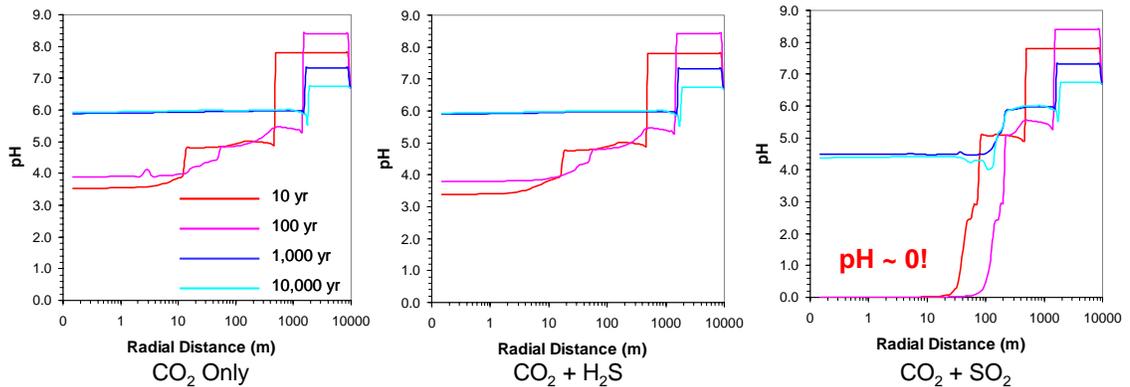


Figure 2. Simulated pH distribution as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a siliciclastic reservoir (after Xu et al, [1]).

#### 4.2 Mineral Dissolution/Precipitation

Simulation results reveal that both CO<sub>2</sub> and CO<sub>2</sub> + H<sub>2</sub>S injections would dissolve oligoclase and precipitate smectite, although at a relatively slow rate (~0.1%/yr) with a gradual reaction front extending 100 meters. The CO<sub>2</sub> + SO<sub>2</sub> injection however, dissolves both minerals at much faster rates (~1%/yr) with a sharp reaction front (Figure 3).

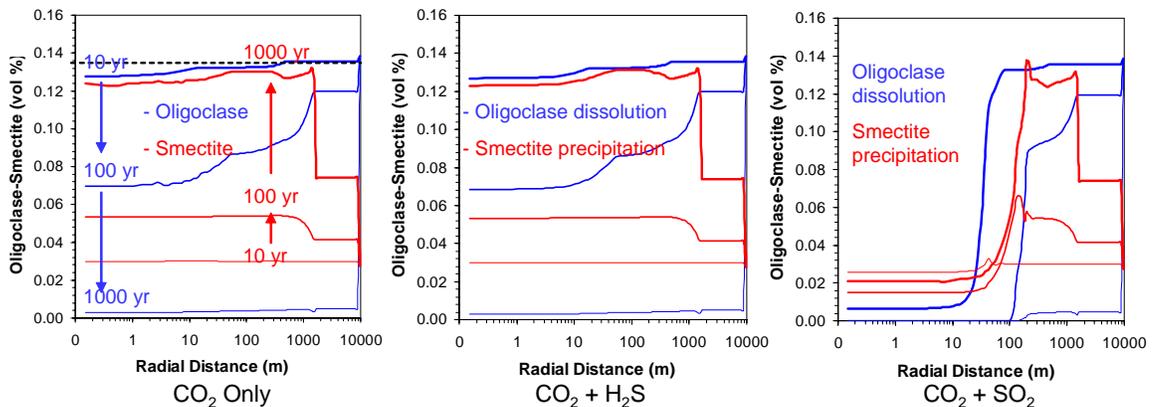


Figure 3. Simulated mineral (oligoclase and smectite) evolution as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a siliciclastic reservoir.

#### 4.3 CO<sub>2</sub> Sequestration Capacity

Simulation results indicate that most sequestered CO<sub>2</sub> is in the form of ankerite and dawsonite, and can reach 80 kg/m<sup>3</sup> or ~5% of bulk mineral weight over 10,000 years (Figure 4). The mineral trapping zones associated with CO<sub>2</sub> and CO<sub>2</sub> + H<sub>2</sub>S injection are broader while CO<sub>2</sub> + SO<sub>2</sub> injection leads to a narrower trapping zone farther away from the injection well. The RTM results are consistent with field observations [7, 8] and natural analogue studies [9].

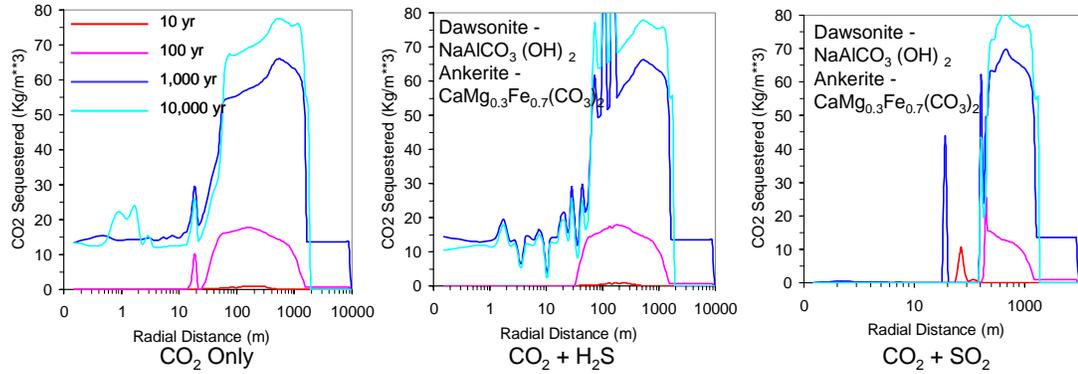


Figure 4. Simulated mineral trapping capacity (via dawsonite and ankerite) as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a siliciclastic reservoir (after Xu et al, [1]).

## 5. Simulation Results: Carbonate Reservoir Injection

### 5.1 pH Evolution

The simulation results from the CO<sub>2</sub> only case are similar to those from CO<sub>2</sub> + H<sub>2</sub>S. The results from CO<sub>2</sub> + SO<sub>2</sub> case are however, significantly different (Figure 5). CO<sub>2</sub> and CO<sub>2</sub> + H<sub>2</sub>S injection leads to lower pH (~4.5, less so comparing to siliciclastic reservoir) near the well bore, resulting from the dissolution of CO<sub>2</sub> and H<sub>2</sub>S in the formation water and quicker buffering reactions. Once the injection stops, the pH increases slightly (~5) but does not rebound to more neutral pH due to limited buffering capability. Co-injection of SO<sub>2</sub> with CO<sub>2</sub> leads to very low pH (~0), presumably due to the dissolution of SO<sub>2</sub> and the formation of a sulphuric acid zone close to the injection well. Corrosion and well abandonment can be potential issues. After the injection, the pH is buffered but still remains considerably low near the well bore.

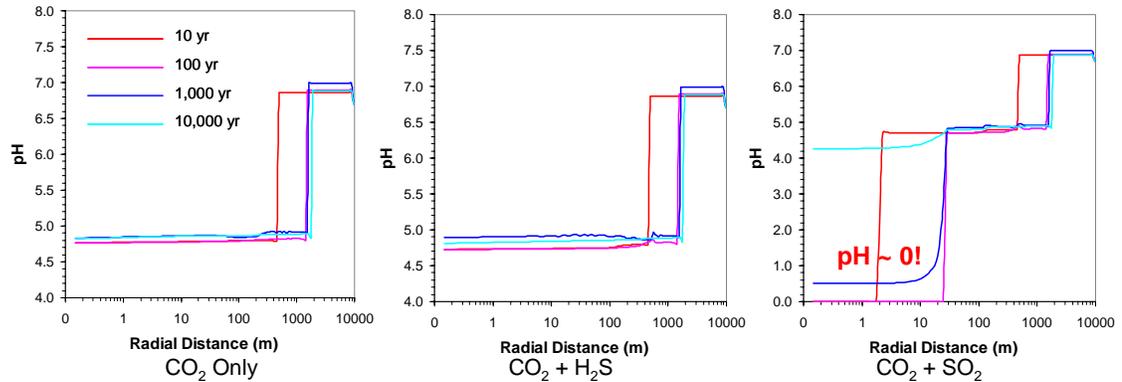


Figure 5. Simulated pH distribution as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a carbonate reservoir.

### 5.2 Mineral Dissolution/Precipitation

Simulation results reveal that calcite dissolution occurs in all cases at a much faster rate compared to the siliciclastic reservoir injection. Under mixed CO<sub>2</sub> + SO<sub>2</sub> injection, significant and rapid calcite dissolution and anhydrite precipitation occurs near the well bore with a sharp reaction front. The latter could lead to

significant loss of injection performance due to porosity reduction. The simulation results are comparable with field observations of acid gas injections in carbonate reservoirs [10].

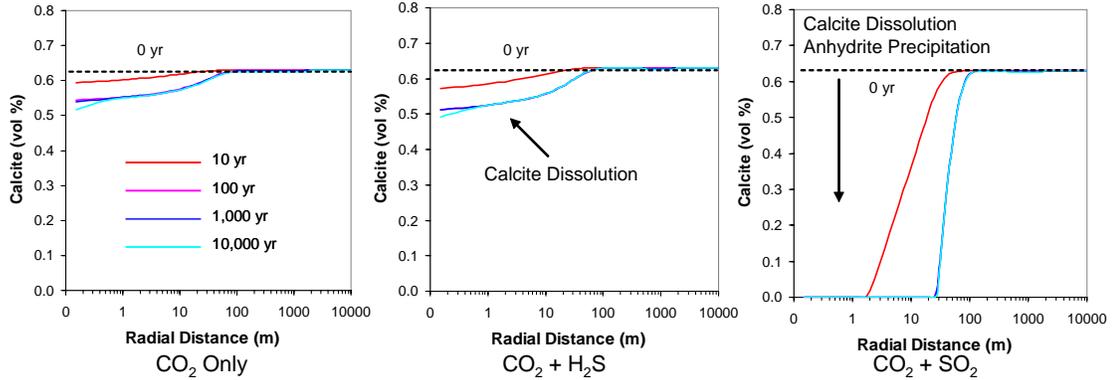


Figure 6. Simulated mineral (calcite) evolution as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a carbonate reservoir.

## 6. Porosity Evolution

**Siliciclastic Reservoir:** The gas injection leads to an increase in porosity close to the well due to net mineral dissolution, and a decrease at distances due to mineral trapping in all three cases (Figure 7). However, the porosity gains associated with  $\text{CO}_2$  and  $\text{CO}_2 + \text{H}_2\text{S}$  injection are much smaller (0.30 to 0.32) compared to the  $\text{CO}_2 + \text{SO}_2$  injection (0.30 to 0.50) at 100 years. The same trend is observed for mineral trapping.

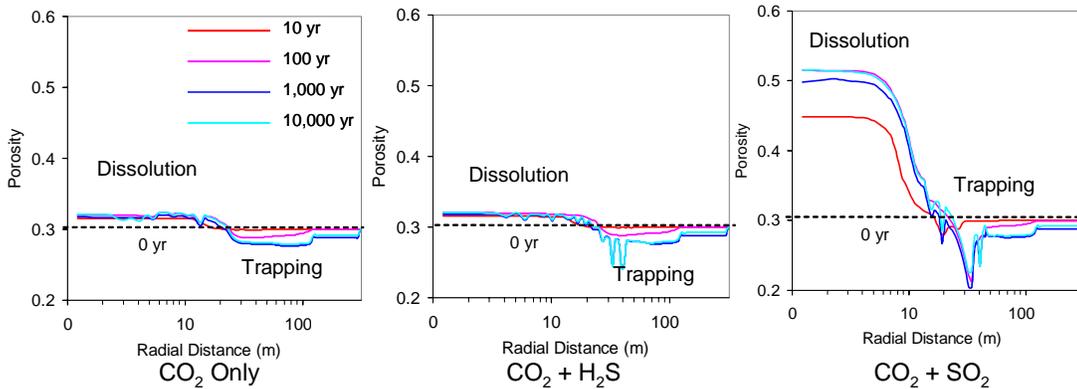


Figure 7. Simulated porosity evolution as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a siliciclastic reservoir (after Xu et al, [1]).

**Carbonate Reservoir:** Simulation results indicate that there are significant porosity increases (0.30 to 0.40 at 100 years) associated with  $\text{CO}_2$  and  $\text{CO}_2 + \text{H}_2\text{S}$  injection due to calcite dissolution near the well bore (Figure 8). However, there is significant porosity decrease (0.30 to 0.20) associated with  $\text{CO}_2 + \text{SO}_2$  injection due to anhydrite precipitation. There is little mineral trapping in all three mixed gas injection scenarios, suggesting limited  $\text{CO}_2$  sequestration capacity in a limestone dominated carbonate reservoir.

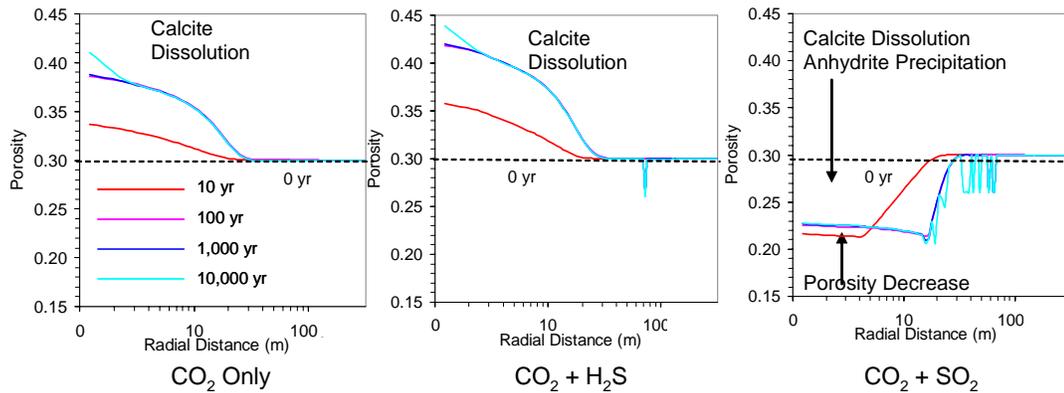


Figure 8. Simulated porosity evolution as a function of radial distance at 10, 100, 1,000, and 10,000 years for the three mixed gas injection scenarios in a carbonate reservoir.

## 7. Summary and Conclusions

- The behavior of CO<sub>2</sub> and acid gas injection and storage is controlled by gas mixtures, reservoir mineralogy, timing, and injection design.
- Co-injection of H<sub>2</sub>S yields similar behavior compared to CO<sub>2</sub> injection. Co-injection of SO<sub>2</sub> results in the formation of sulfuric acid close to the well. Corrosion of pipes and well abandonment are potential issues.
- Significantly more CO<sub>2</sub> is sequestered as ankerite and dawsonite in siliciclastic reservoirs than in carbonate reservoirs, with the mineral trapping capability reaching as much as 80 kg/m<sup>3</sup>.
- Most injection scenarios result in porosity increase close to the well and decrease at distances. However, co-injection of SO<sub>2</sub> in a carbonate reservoir leads to significant anhydrite precipitation and porosity reduction in the near-well region.
- The results from Reactive Transport Modeling provide valuable insights for describing, analyzing, interpreting, and assessing the physical properties and dynamic behaviours of injected CO<sub>2</sub> and facilitating the screening and evaluation of CO<sub>2</sub> storage strategy.

## 8. Acknowledgments

The paper benefited from fruitful discussions with ExxonMobil colleagues Will Maze, Gary Teletzke, John Wilkinson, Lee Esch, Bob Pottorf, and Mark Richardson. Careful reviews by Chris Reaves and Bill Clendenen improved the manuscript. Permission by ExxonMobil to release the paper is greatly appreciated. Drs. Tianfu Xu and Karsten Pruess were supported by the Zero Emission Research and Technology project (ZERT) of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 with Lawrence Berkeley National Laboratory.

## 9. References

1. Xu, T, J. A. Apps, K. Pruess, and H. Yamamoto, 2007. Numerical modeling of injection and mineral trapping of CO<sub>2</sub> with H<sub>2</sub>S and SO<sub>2</sub> in a sandstone formation. *Chemical Geology*, Volume 242, Issues 3-4, 15 August 2007, Pages 319-346
2. Knauss, K.G., Johnson, J.W., Steefel, C.I., 2005. Evaluation of the impact of CO<sub>2</sub>, co-contaminant gas, aqueous fluid, and reservoir rock interactions on the geologic sequestration of CO<sub>2</sub>. *Chem. Geol.* 217, 339-350.
3. Pruess, K., Xu, T., Apps, J., García, J., 2003. Numerical modeling of aquifer disposal of CO<sub>2</sub>. *SPE (Society of Petroleum Engineers) Journal*, p. 49-59, March (2003).
4. Johnson, J.W., Nitao, J.J., Steefel, C.I., Knaus, K.G., 2001. Reactive transport modeling of geologic CO<sub>2</sub> sequestration in saline aquifers: The influence of intra-aquifer shales and the relative effectiveness of structural, solubility, and mineral trapping during prograde and retrograde sequestration, In proceedings: First National Conference on Carbon Sequestration. Washington, DC.
5. Arvidson, R. S. and Mackenzie, F.T. 1999. The dolomite problem: control of precipitation kinetics by temperature and saturation state: *American Journal of Science*, v. 299, p. 257-288.
6. Xu, T., E.L. Sonnenthal, N. Spycher, and K. Pruess, 2006. TOURGHREACT: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media. *Computer & Geosciences* 32, 145-165.
7. Watson, M.N., Zwingmann, N., Lemon, N.M., 2004. The Ladbroke Grove–Katnook carbon dioxide natural laboratory: A recent CO<sub>2</sub> accumulation in a lithic sandstone reservoir. *Energy*, 29(9-10), 1457-1466.
8. Moore, J., Adams, M., Allis, R., Lutz, S., Rauzi, S., 2005. Mineralogical and geochemical consequences of the long-term presence of CO<sub>2</sub> in natural reservoirs: An example from the Springerville–St. Johns Field, Arizona, and New Mexico, U.S.A. *Chemical Geology*, 217, 365-385.
9. Worden R H (2006) Dawsonite cement in the Triassic Lam Formation, Shabwa Basin, Yemen: a natural analogue for a potential mineral product of subsurface CO<sub>2</sub> storage for greenhouse gas reduction. *Marine and Petroleum Geology*, 23, pp.61-67.
10. Huang, N S, G.E. Aho, B.H. Baker and P.A. Foglesong, T.R. Matthews, R.J. Pottorf, 2007. Integrated Reservoir Modeling to Maximize the Value of a Large Sour-Gas Field with High Concentrations of Inerts. *SPE paper # 11202*.