Mineral Trapping of CO_2 with H_2S and SO_2 in a Sandstone-Shale Formation

Tianfu Xu[1], John A. Apps[1], Karsten Pruess[1], and Hajime Yamamoto[2]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA 94720

[2]Civil Engineering Research Institute, Taisei Corporation, Japan

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OVERVIEW

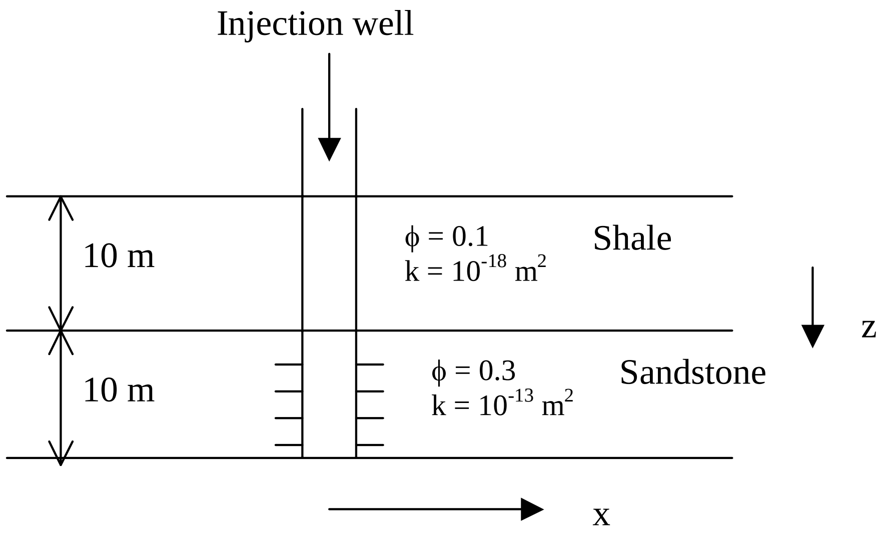
- Introduction
- Problem Setup
  - Geometric and flow conditions
  - Geochemical system
- Numerical Simulator
- Results
- Comparison with field data
- Summary and conclusions

INTRODUCTION

- One possible means of reducing atmospheric CO_2 emissions is to dispose of CO_2 in deep saline aquifers.
- Mineral trapping is potentially attractive because it could immobilize CO_2 for long time scales.
- Sequestering less-pure flue gas (CO_2) containing H_2S and/or SO_2 requires less energy to separate.
- Numerical modeling is a necessary tool for investigating long-term acid gas disposal.
- Here we present simulation results on mineral alteration, and consequent sequestration of CO_2, H_2S and SO_2 in a Gulf Coast Frio formation.

GEOMETROC AND FLOW CONDITIONS

- Before conducting site-specific investigations, it is necessary to explore features in a generic manner.
- Hydrological parameters were chosen to be representative of conditions that may be encountered in Texas Gulf Coast sediments at 2 km depth.
- Aquifer is infinite-acting and homogeneous with a 10 m thickness, 1 M NaCl, and 75°C.
- A 1-D model is used with grid spacing gradually increasing away from the well field.
- Assume gas injection over a period of 100 years. Reactive chemical transport simulated for 10,000 years.



Xu, Apps, and Pruess, *JGR* , 2003; *Appl. Geochem,* 2004; *Chem. Geology,* 2005 (in press)

GEOCALMICAL SYSTEM

Mineral phases (kinetics)

Mineral	Chemical composition	Vol.% of medium	
		Sand	Shale
***Primary*:**			
quartz		40.6	17.3
kaolinite		1.41	3.95
calcite	$CaCO_3$	1.35	9.81
illite		0.7	25.33
kerogen-OS		0.0	1.8
oligoclase		13.86	4.75
K-feldspar		5.74	4.27
Na-smectite		2.8	20.7
chlorite		3.19	2.12
hematite		0.35	0.0
porosity		30	10
***Secondary*:**			
anhydrite	$CaSO_4$		
magnesite	$MgCO_3$		
low-albite			
dolomite	$CaMg(CO_3)_2$		
siderite	$FeCO_3$		
Ca-smectite			
pyrite			
ankerite	$CaMg_{0.3}Fe_{0.7}(CO_3)_2$		
dawsonite	$NaAlCO_3(OH)_2$		
alunite	$KAl_3(OH)_6(SO_4)_2$		

Aqueous species

H_2O	$FeCO_3(aq)$
H^+	$FeCl_4^{-2}$
Ca^{+2}	$NaHCO_3(aq)$
Mg^{+2}	$CaHCO_3^+$
Na^+	$MgHCO_3^+$
K^+	$CO_2(aq)$
Fe^{+2}	$CO3^{-2}$
$SiO_2(aq)$	CaCO3(aq)
HCO_3^-	KCl(aq)
SO_4^{-2}	$MgCl^+$
AlO_2^-	$MgSO_4(aq)$
Cl^-	$NaSO_4^-$
O2(aq)	KSO_4^-
OH^-	$NaHSiO_3(aq)$
Al^{+3}	$CaOH^+$
$HAlO_2(aq)$	NaOH(aq)
$NaAlO_2(aq)$	$NaCO_3^-$
$AlOH^{+2}$	$H_3SiO_4^-$
$Al(OH)_2^+$	Fe^{+3}
$Al(OH)_3(aq)$	HS^-
$CaCl^+$	$H_2S(aq)$
$CaCl_2(aq)$	$CH_4(aq)$
$CaSO_4(aq)$	$H_2(aq)$
NaCl(aq)	acetic~acid(aq)
$FeCl^+$	$SO_2(aq)$
$FeHCO_3^+$	HSO_3

INJECTION SCENARIOS

Injection rates (kg/s, over 5 m thickness sandstone)

Case	*CO_2*	*Water*	*H_2S*	*SO_2*
CO_2 only	0.5	0.25		
CO_2 + H_2S	0.5	0.245	0.005	
CO_2 + SO_2	0.5	0.245		0.005
CO_2 + H_2S + SO_2	0.5	0.245	0.0025	0.0025

SIMULATOR: TOUGHREACT

Processes:

- Multiphase fluid and heat flow: TOUGH2 V2 (Pruess, et al., 1999)
- Transport: advection and diffusion in both liquid and gas phases
- Chemical reactions:
  - Aqueous complexation
  - Acid-base
  - Redox
  - Mineral dissol./precip. (equilibrium and/or kinetics)
  - Gas dissol./exsol.
  - Cation exchange
  - Surface complexation
  - Linear Kd adsorption
  - Decay

Special Features:

- Changes in porosity and permeability, and unsaturated zone properties due to mineral dissolution and precipitation
- Gas phase and gaseous species are active in flow, transport, and reaction
- Pitzer and Debye-Hückel activity coefficient models
- General: Porous and fractured media; 5 ϕ-k models; rate laws; any number of chemical species
- Two types of thermodynamic database including EQ3/6 (Wolery, 2004)
- Wide range of conditions
- Publicly available (DOE Software Center)
- http:/esd.lbl.gov/TOUGHREACT/

LBNL-55460

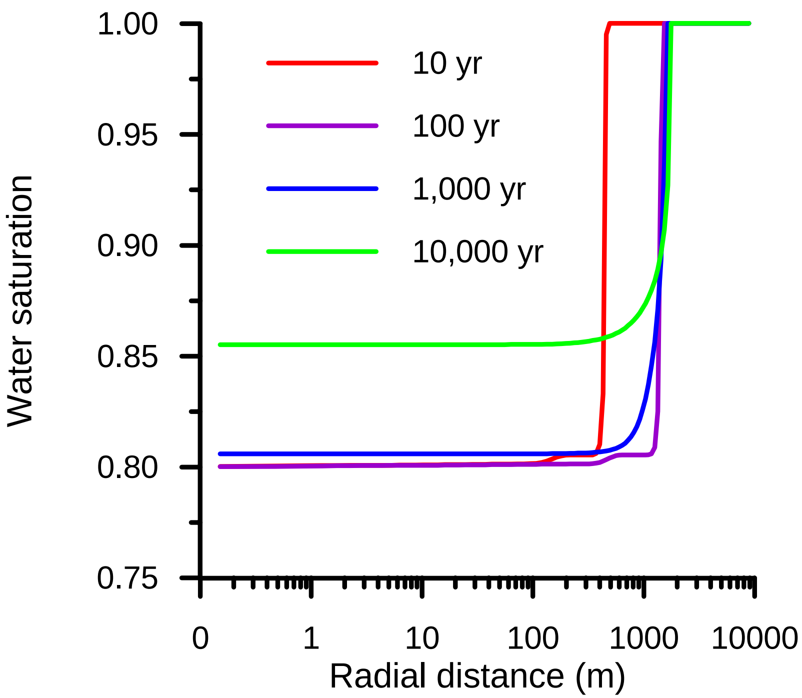
TOUGHREACT User's Guide: A Simulation Program for Non-isothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media

Tianfu Xu, Eric Sonnenthal, Nicolas Spycher and Karsten Pruess

August 2004

RESULTS (1)

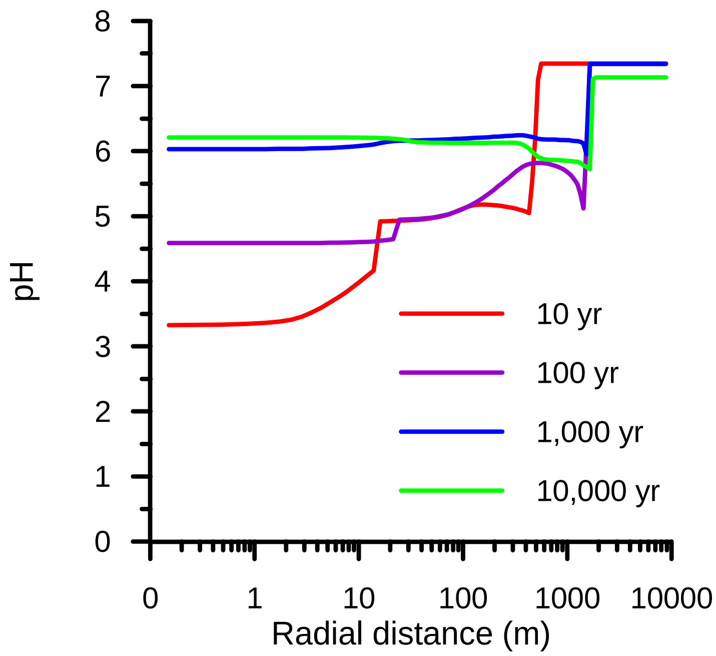
- The fluid flow pattern is very similar for the four cases.



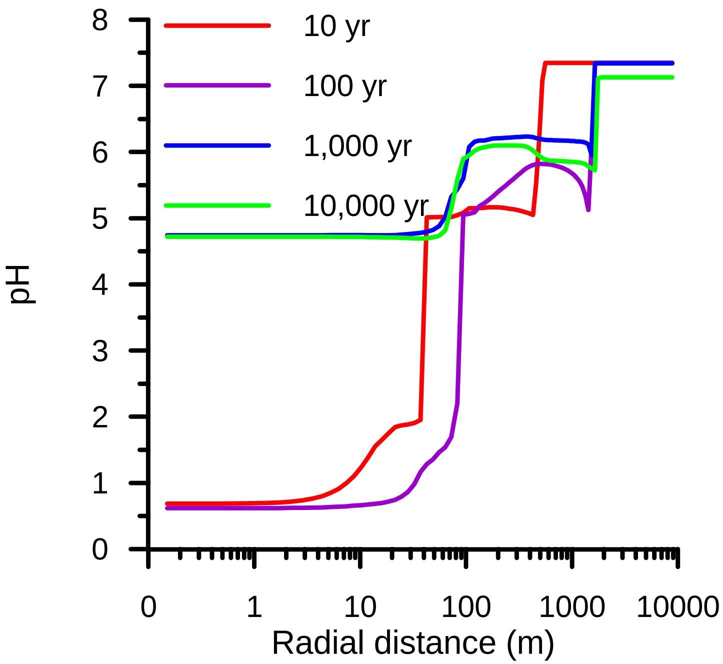
- The reactive chemical modeling results obtained from the CO_2 only case are similar to those from CO_2 + H_2S.
- The results from CO_2 + SO_2 case are similar to those from CO_2 + SO_2 + H_2S.
- Results from CO_2 only and CO_2 + SO_2 cases will be presented here.

RESULTS (2)

- Co-injection of SO_2 → stronger acidic zone close to the well. Corrosion and well abandonment are issues.



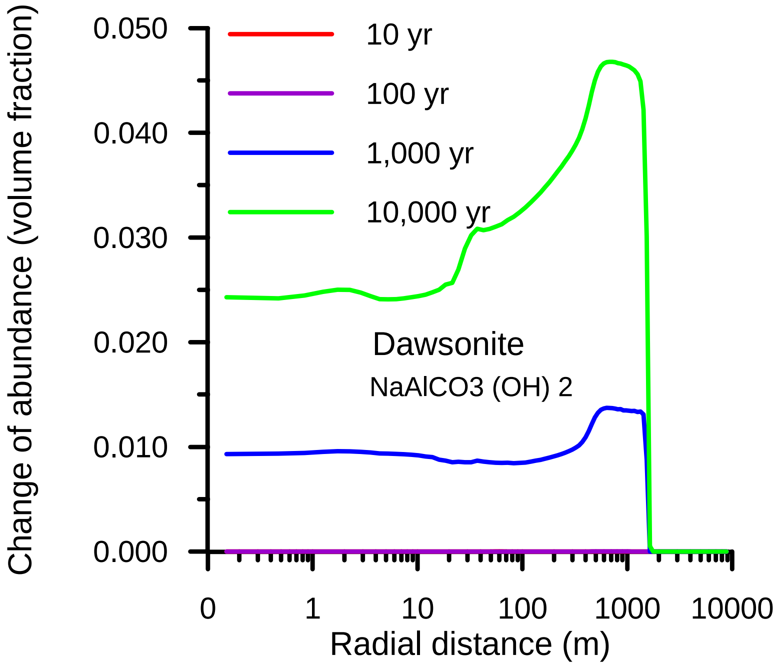
(a) CO_2 only



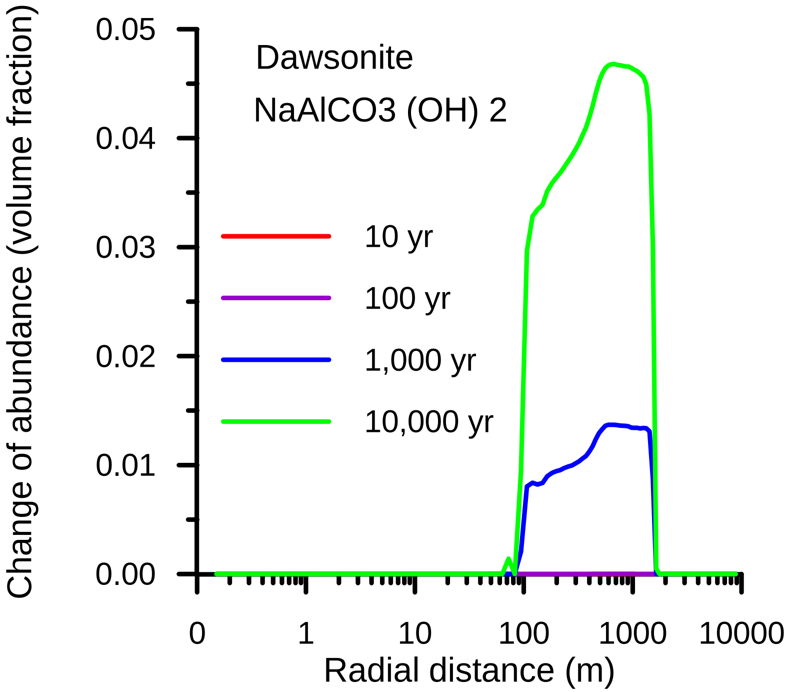
(b) CO_2+ SO_2

RESULTS (3)

- CO_2 is sequestered in ankerite and dawsonite, and some in siderite.



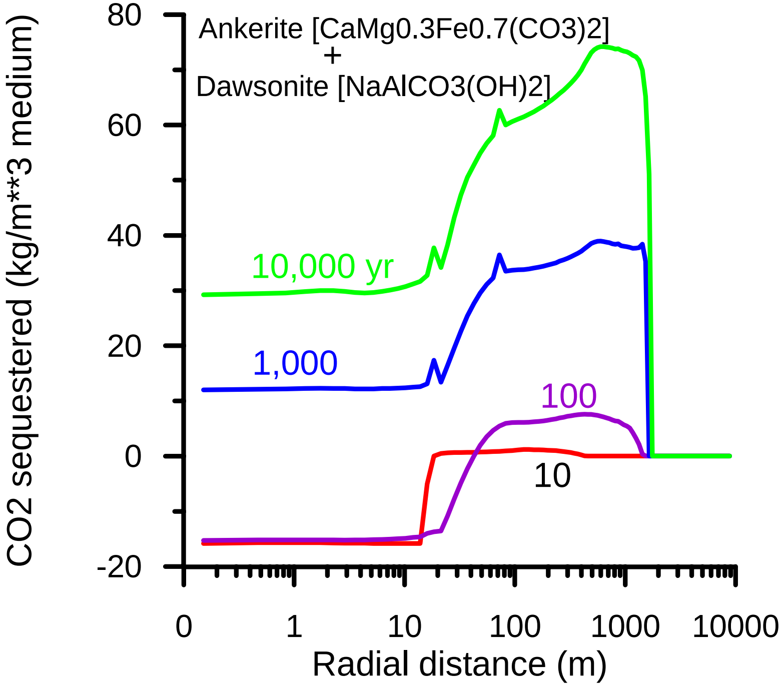
(a) CO_2 only



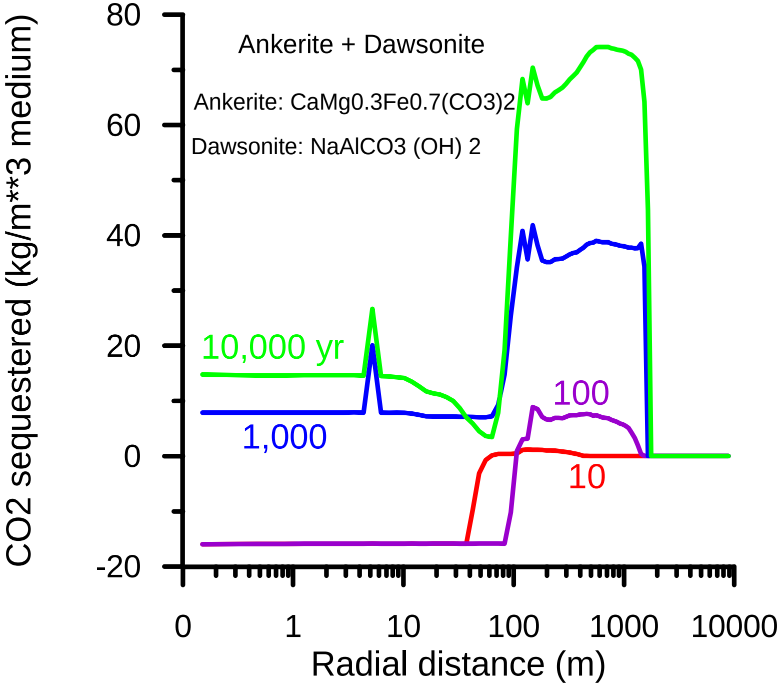
(b) CO_2+ SO_2

RESULTS (4)

- The CO_2 mineral trapping capability can reach 80 kg/m[3] medium.



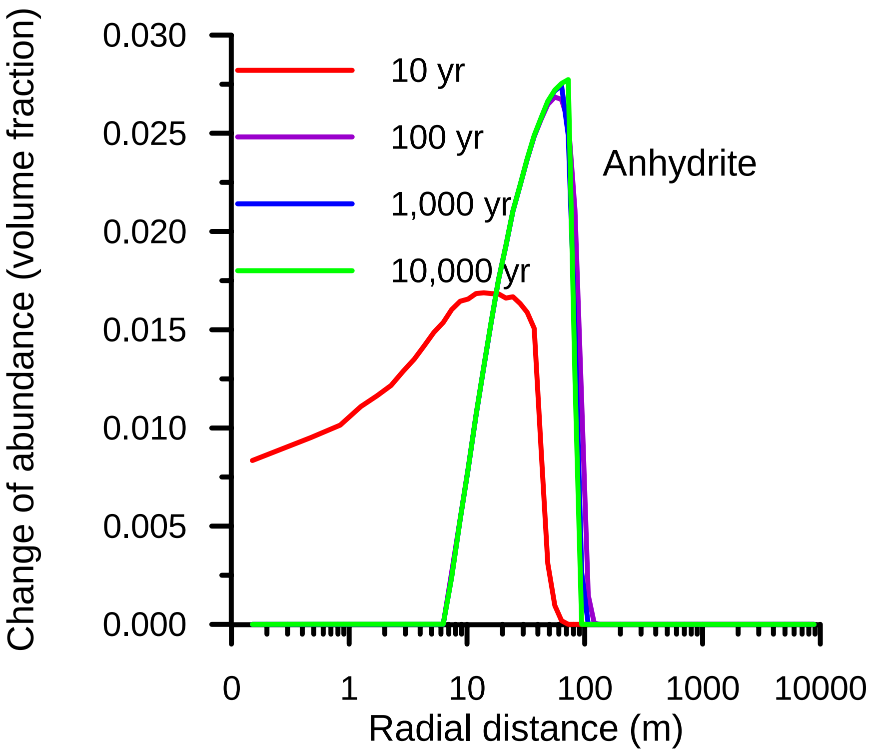
(a) CO_2 only

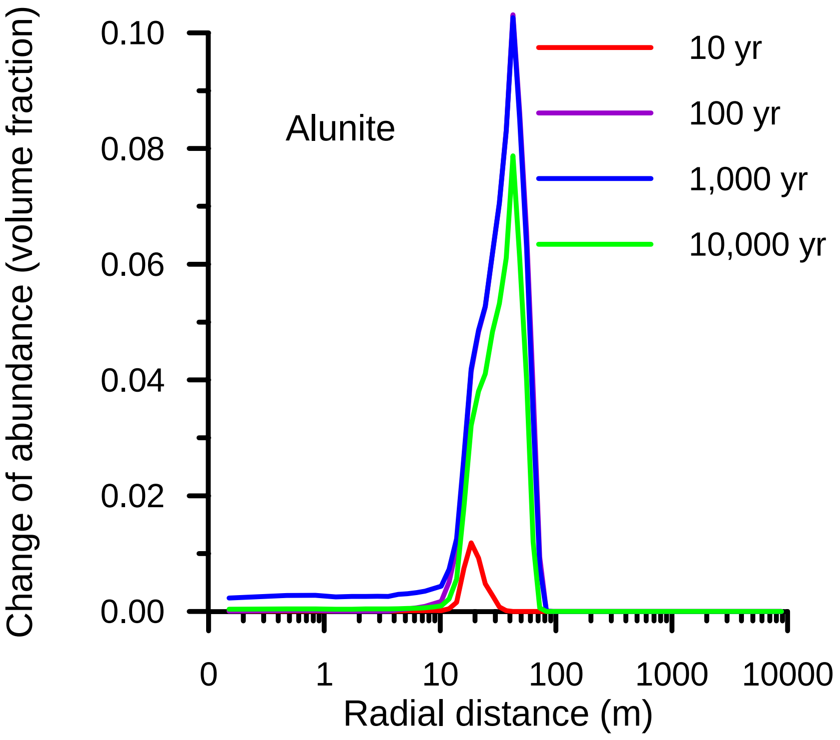


(b) CO_2+ SO_2

RESULTS (5)

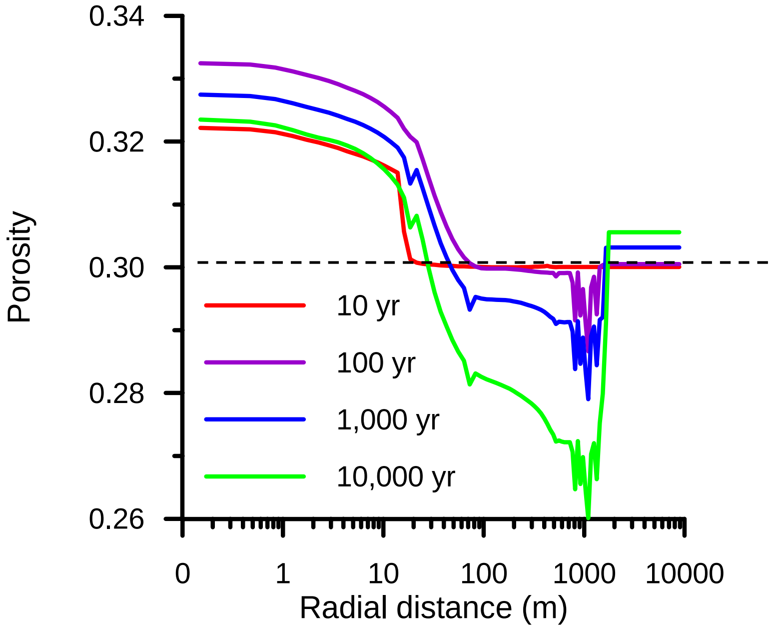
- **Sulfur trapping minerals for CO_2+SO_2 case**



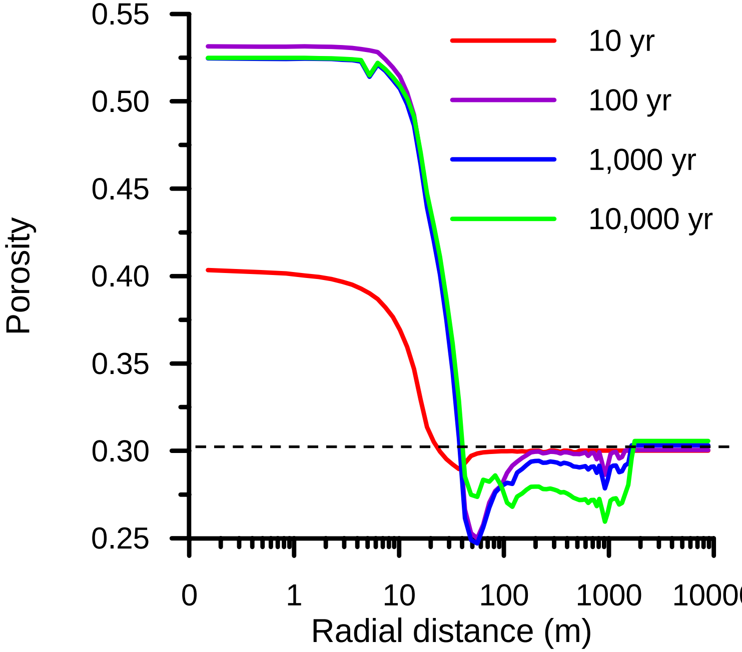


RESULTS (6)

- Increase in porosity close to the well
- Decrease at distances.



(a) CO_2 only



(b) CO_2+ SO_2

COMPARISON WITH FIELD DATA (1)

- Recently, mineralogical changes have been described in a lithic sandstone formation invaded by magmatic CO_2 (Watson et al., 2002).
- The similarities include the destruction of chlorite, net corrosion of the feldspars, a reduction in the concentration of calcite, an increase of siderite, a significant increase of ankerite, and a substantial increase in secondary kaolinite.
- No evidence of dawsonite formation has been reported even though an evaluation of the recovered groundwater indicates that it should have been supersaturated with respect to dawsonite.
- The simulation differs in that the CO_2 pressure is higher (260 vs. approximately 150 bar) and the Cl^- and Na^+ concentrations are somewhat higher.

COMPARISON WITH FIELD (2)

- Moore et al. (2003) describe the formation of dawsonite and kaolinite in siltstones of the Permian Supai Formation of the Springerville-St. John CO2 field on the border between Arizona and New Mexico. They observed dawsonite spatially associated with corroded plagioclase and potassium feldspar, which is consistent with our simulations.
- Other field evidence supports that magmatic CO_2 can also lead to the formation of dawsonite in arenaceous sedimentary formations, notably in the Bowen, Gunnedah and Sydney Basins of New South Wales (Baker et al., 1995), and the Denison Trough of east-central Queensland (Baker, 1991; Baker and Caritat, 1992).
- Dawsonite and kaolinite in these sedimentary accumulations appear to have been produced at the expense of detrital feldspars (Loughnan and Goldbery, 1972).

SUMMARY AND CONCLUSIONS

- Co-injection of SO_2 results in a larger and stronger acidic zone close to the well.
- Precipitation of CO_2 trapping minerals occurs in the higher pH ranges beyond acidic zones.
- Sulfur trapping minerals are stable in the low pH ranges (below 5) in the front of acidic zone.
- Corrosion and well abandonment caused by co-injection of SO_2 may be a significant issue.
- Significant CO_2 is sequestered in ankerite and dawsonite, and some in siderite. The CO_2 mineral trapping capability can reach 80 kg/m^3 medium.
- Increase in porosity close to the well, but decrease at a distance.

ACKNOWLEDGEMENTS

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