Numerical and Observational Studies of Cement Carbonation at Well 49-6, SACROC Unit, West Texas

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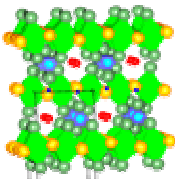

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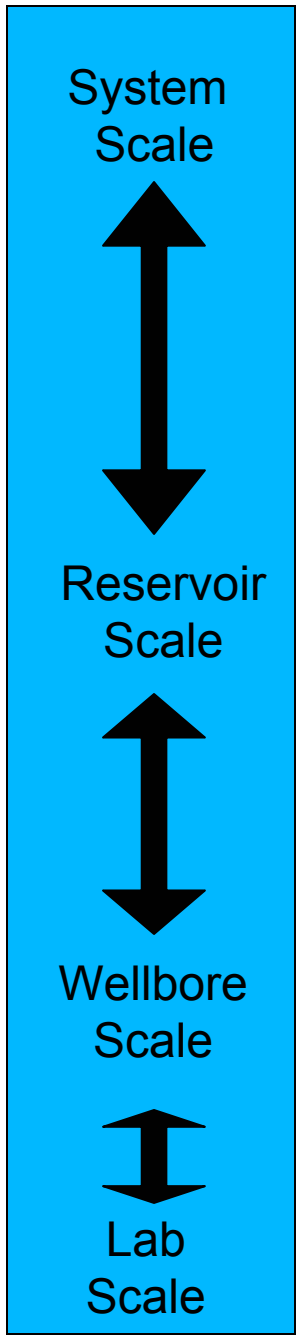
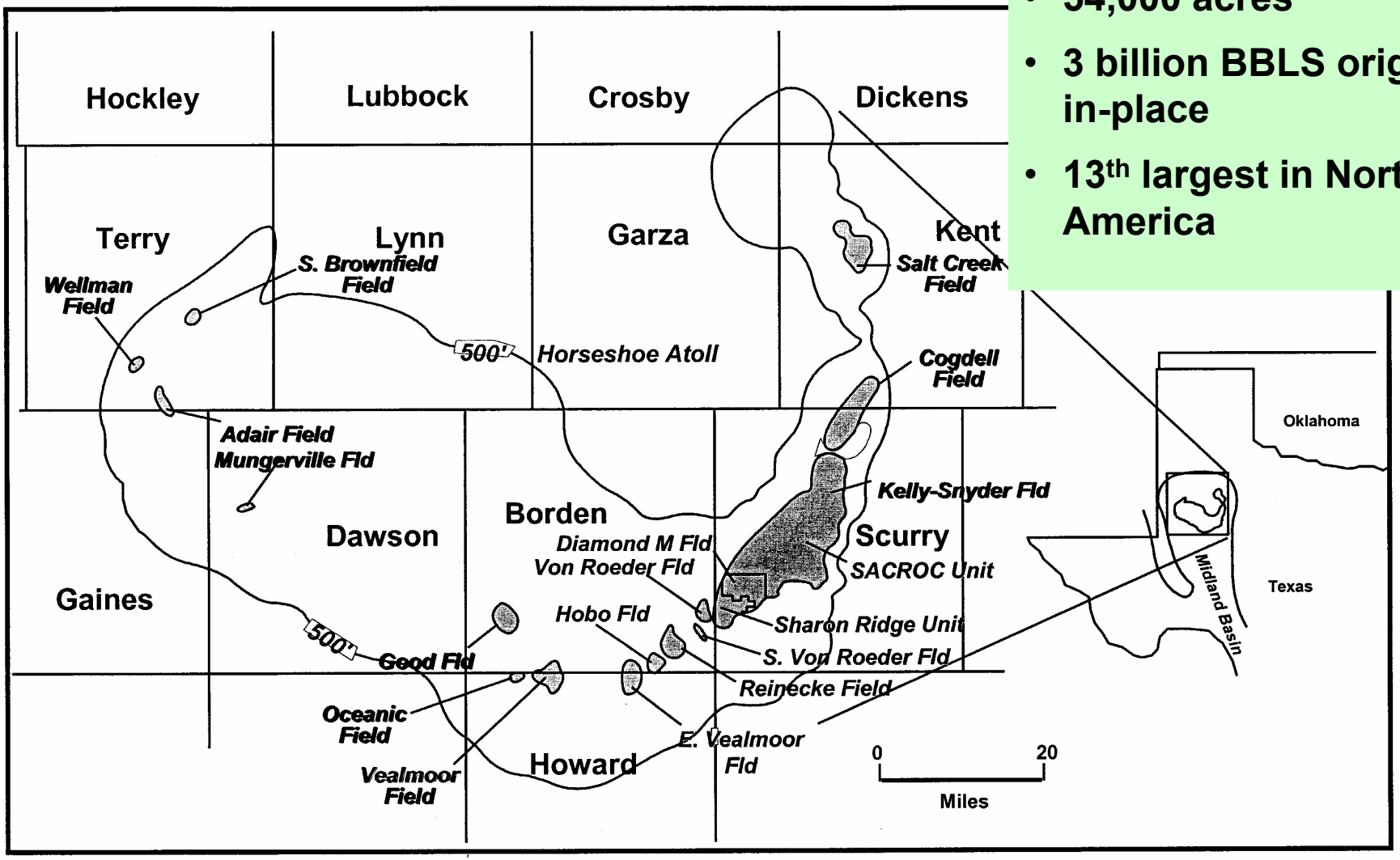
Motivation

- Wellbore integrity a key issue in permanent sequestration of CO_2
- Portland cement is chemically reactive in CO_2-saturated fluids
- Fate of cement likely depends on the particulars of the wellbore environment
- Use field observations to constrain environment and reactivity
- Use laboratory data to obtain fundamental parameters
- Integrate observations and experiments in reactive transport code
- Goal: develop predictive capability for the fate of Portland cement and any resulting transport of CO_2 along the wellbore



Field Studies: SACROC

- Pennsylvanian age reef system
- Discovered 1948
- 54,000 acres
- 3 billion BBLS original oil in-place
- 13th largest in North America



SACROC (Scurry Area Capital Reef Operations Committee)

- 81 mi^2, 1800 wells, 600 operational
- Productive zone at 7000' and is as thick as 800'
- Field temperature 50 ºC; Initial pressure 3200 psi (now 2600 psi)
- CO_2 flooding initiated 1972 (only one field in the world is older)
- CO_2 now obtained primarily from McElmo Dome, CO
- 62% of all CO_2 injected is effectively sequestered)
  - 68 million tonnes CO_2
  - 30 million tonnes obtained by separation from natural gas at Val Verde
- Drilling and production from zones above and below the Cisco/Canyon Reef complex have been free of CO_2

Observed Carbonation at SACROC

Phase	Gray Zone
Amorphous	Major
Portlandite	15-58%
Calcite	0-28%
Katoite	22-26%
Brucite	3-9%
Ettringite	3-4%
Friedel's Salt	2-4%
Halite	9-32%

Phase	Orange Zone
Calcite	44%
Aragonite	8%
Vaterite	33%
Halite	13%

- 30 years exposure to CO_2
- Gray, relatively unaltered cement
- Orange intensely carbonated cement
- "Shale-fragment-zone" interface
- CO_2-saturated brine diffuses along porous cement-shale interface zone

Numerical Analysis of Cement Degradation: FLOTRAN

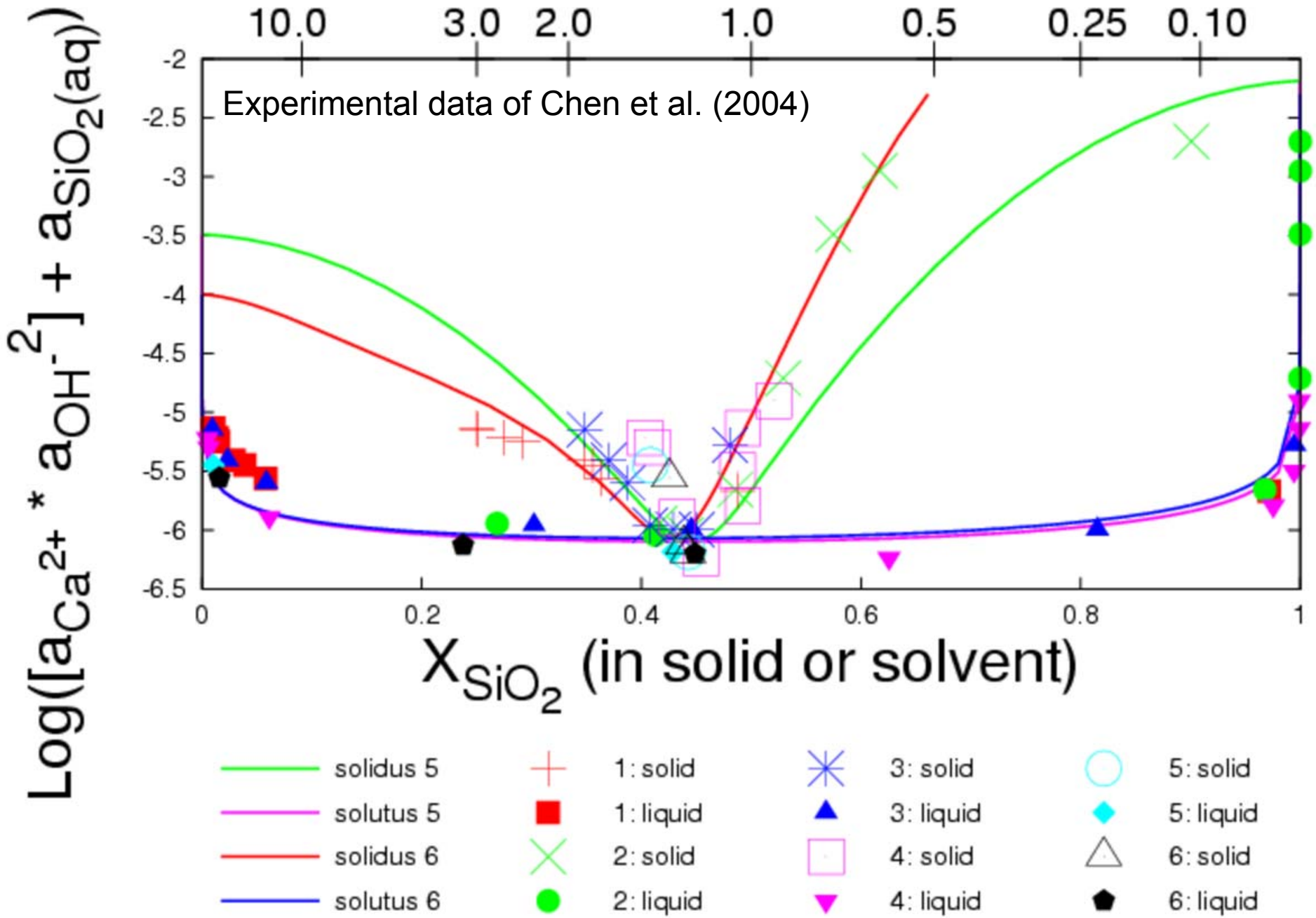
- Two-phase multicomponent reactive flow and transport
  - Mass & energy conservation
  - Single and dual continuum formulations
  - Darcy's law for two-phase liquid-air system
  - Aqueous speciation (Debye-Hückel and Pitzer)
  - Kinetic formulation of solid reactions
  - Mineral solid solutions implemented as stoichiometric species

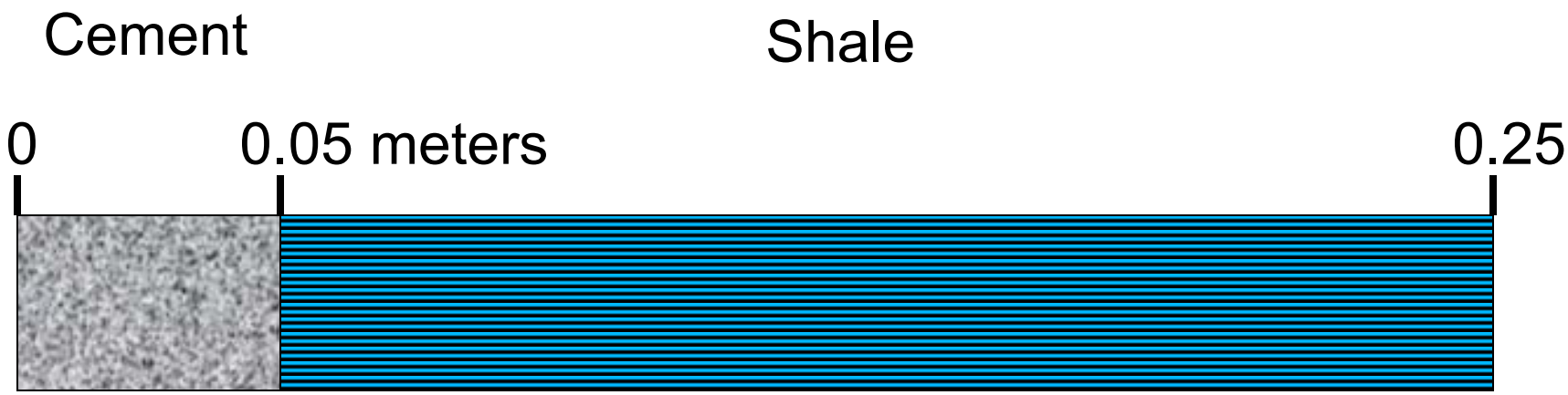
- C-S-H solid solution based on experimental solubility data
  - Endmembers: $Ca(OH)_2$ and SiO_2
  - Mol-fraction X_{SiO2} = 1 / (1+R), R = Ca/Si
  - Excess mixing model:

$$G^E = x(1-x)RT[a_0 + a_1(x-(1-x)) + a_2(x-(1-x))^2]$$

  - Parameter estimation: $\mu_{Ca(OH)2}$, μ_{SiO2}, a_0, a_1, a_2, (a_3)

Ca/Si Ratio


10.0
3.0
2.0
1.0
0.5
0.25
0.10
Experimental data of Chen et al. (2004)
-2
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
0
0.2
0.4
0.6
0.8
1
X_{SiO_2} (in solid or solvent)
$Log([a_{Ca^{2+}} * a_{OH^-}^2] + a_{SiO_2(aq)})$
solidus 5
solutus 5
solidus 6
solutus 6
1: solid
1: liquid
2: solid
2: liquid
3: solid
3: liquid
4: solid
4: liquid
5: solid
5: liquid
6: solid
6: liquid



38% C-S-H (x_{SiO2}=0.36, Ca/Si = 1.78)

15% portlandite

14% monosulfate

3% hydrogarnet

30% porosity

20% illite

7% quartz

1% kaolinite

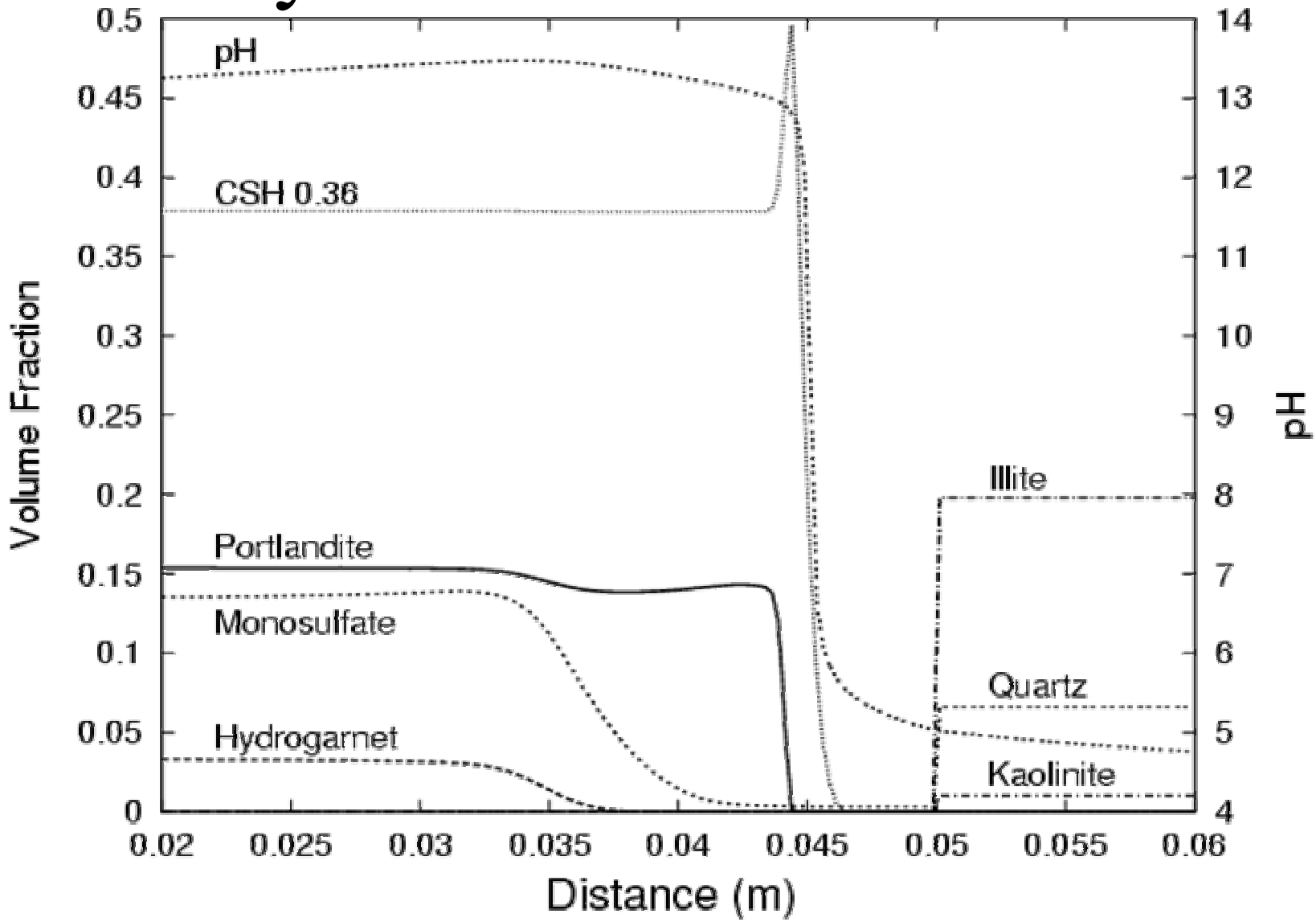
1% calcite

1% dolomite

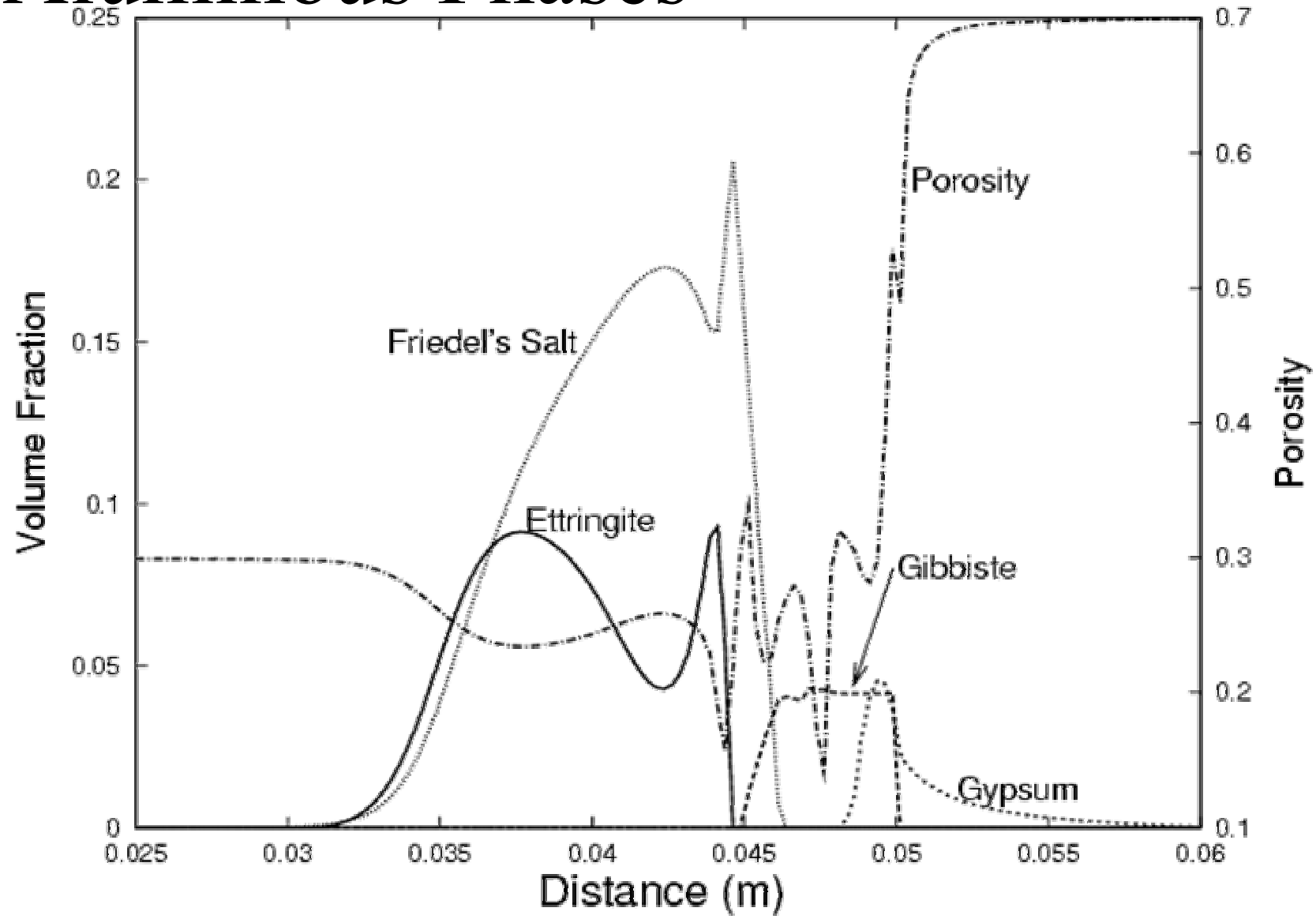
70% porosity

- 1-D diffusion of CO_2-saturated brine into cement
- 25 ^{o}C and 179 bars P(CO_2)

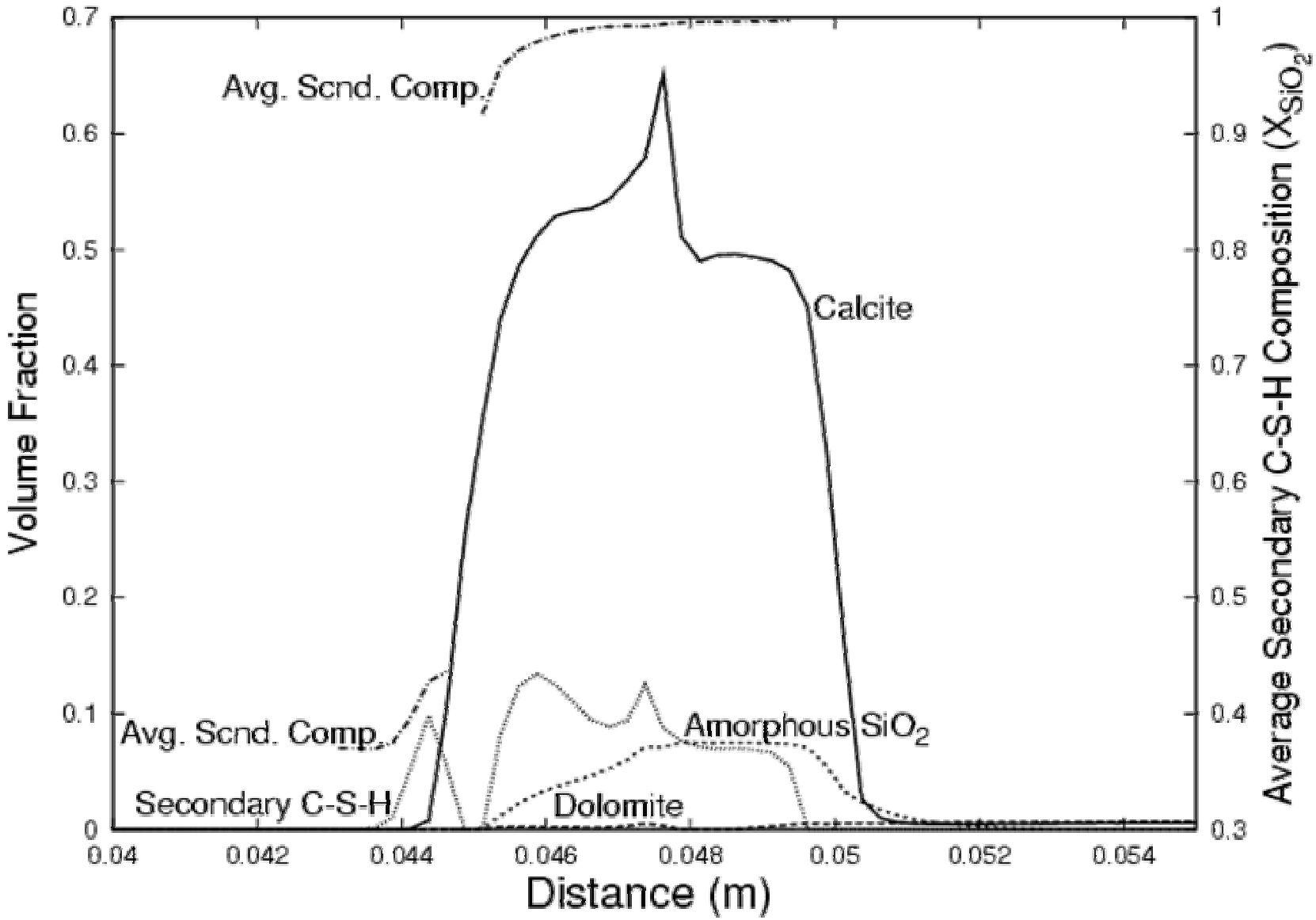
Primary Phase Behavior



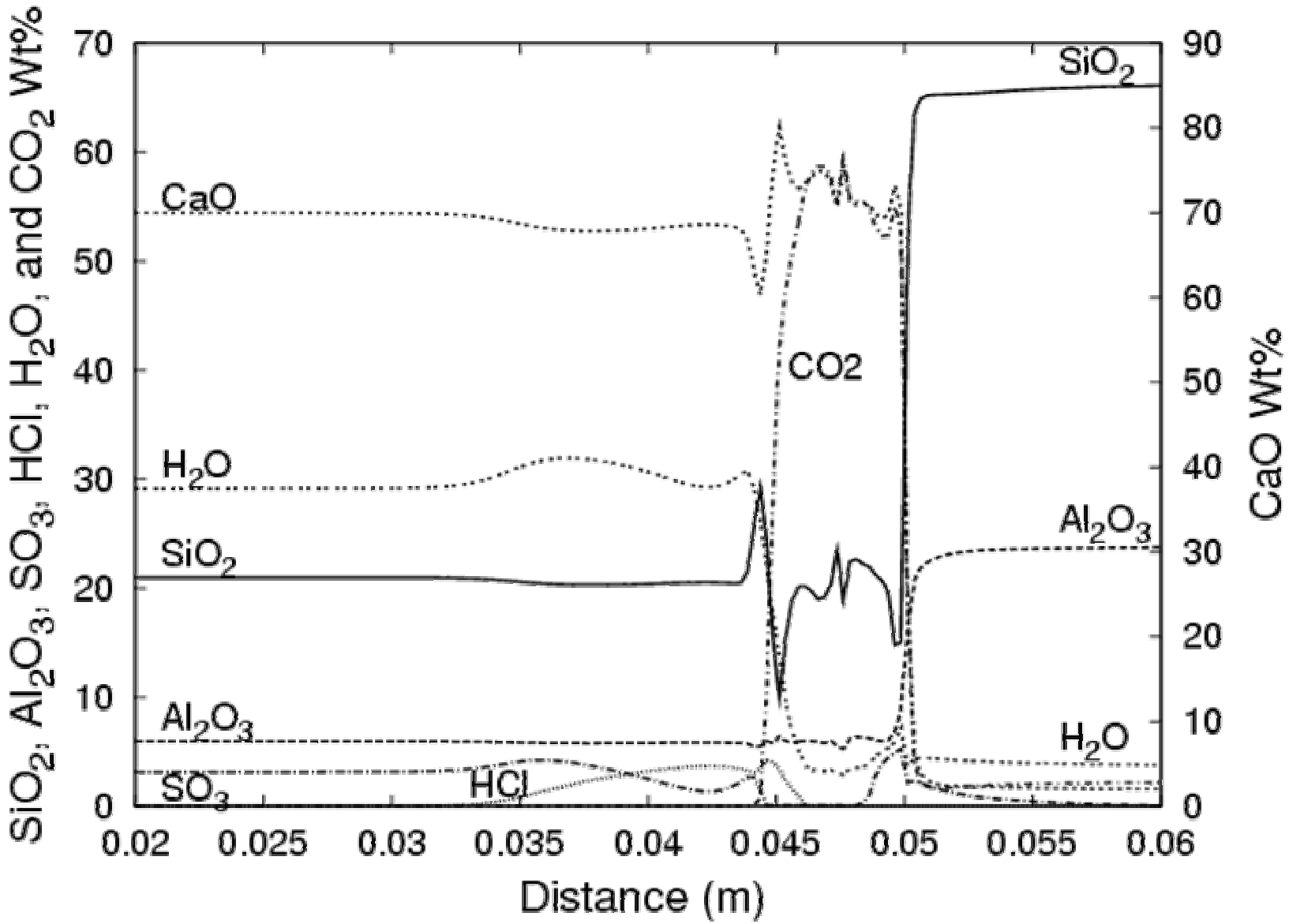
Aluminous Phases



Secondary Phases



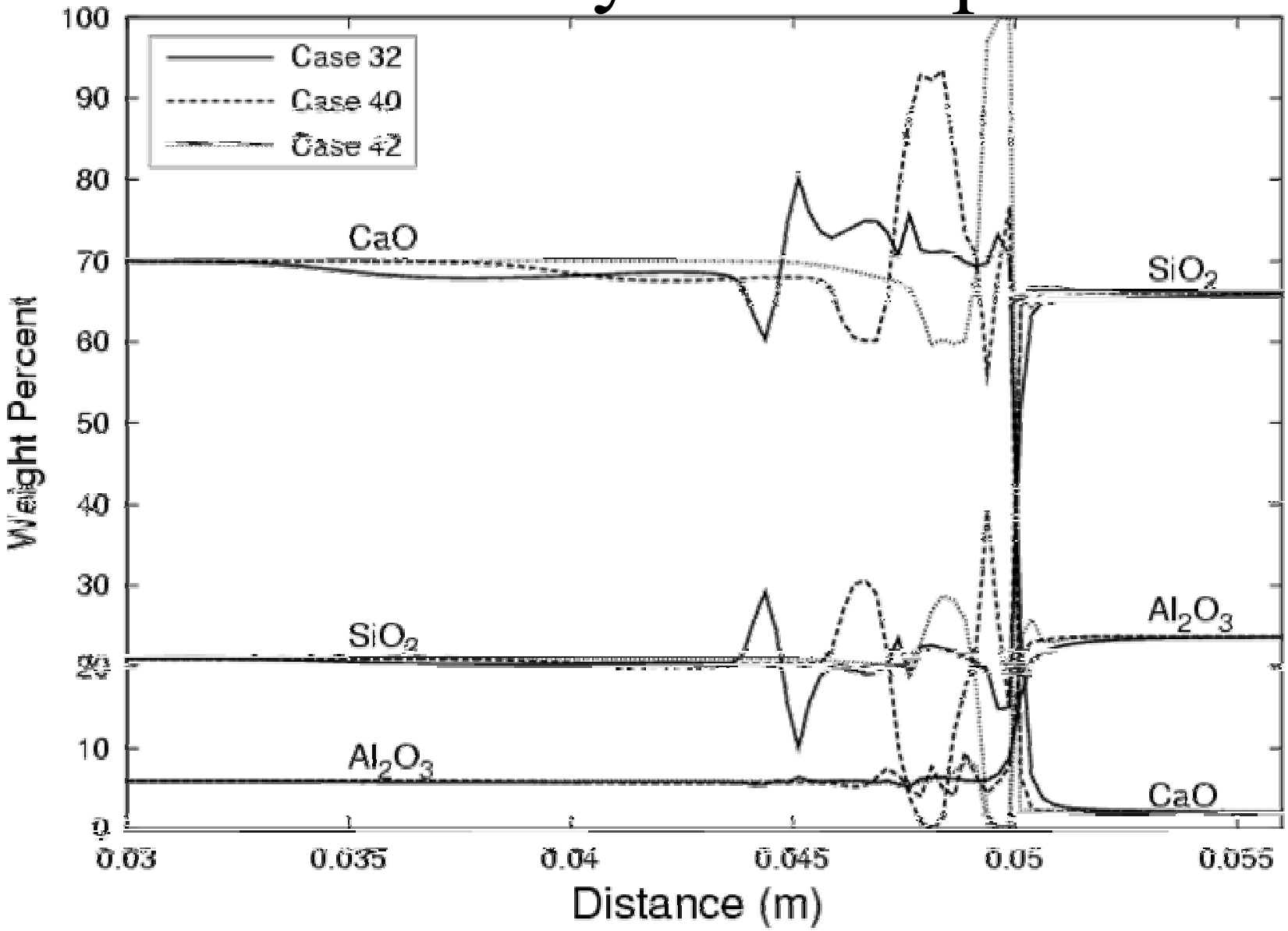
Bulk Composition



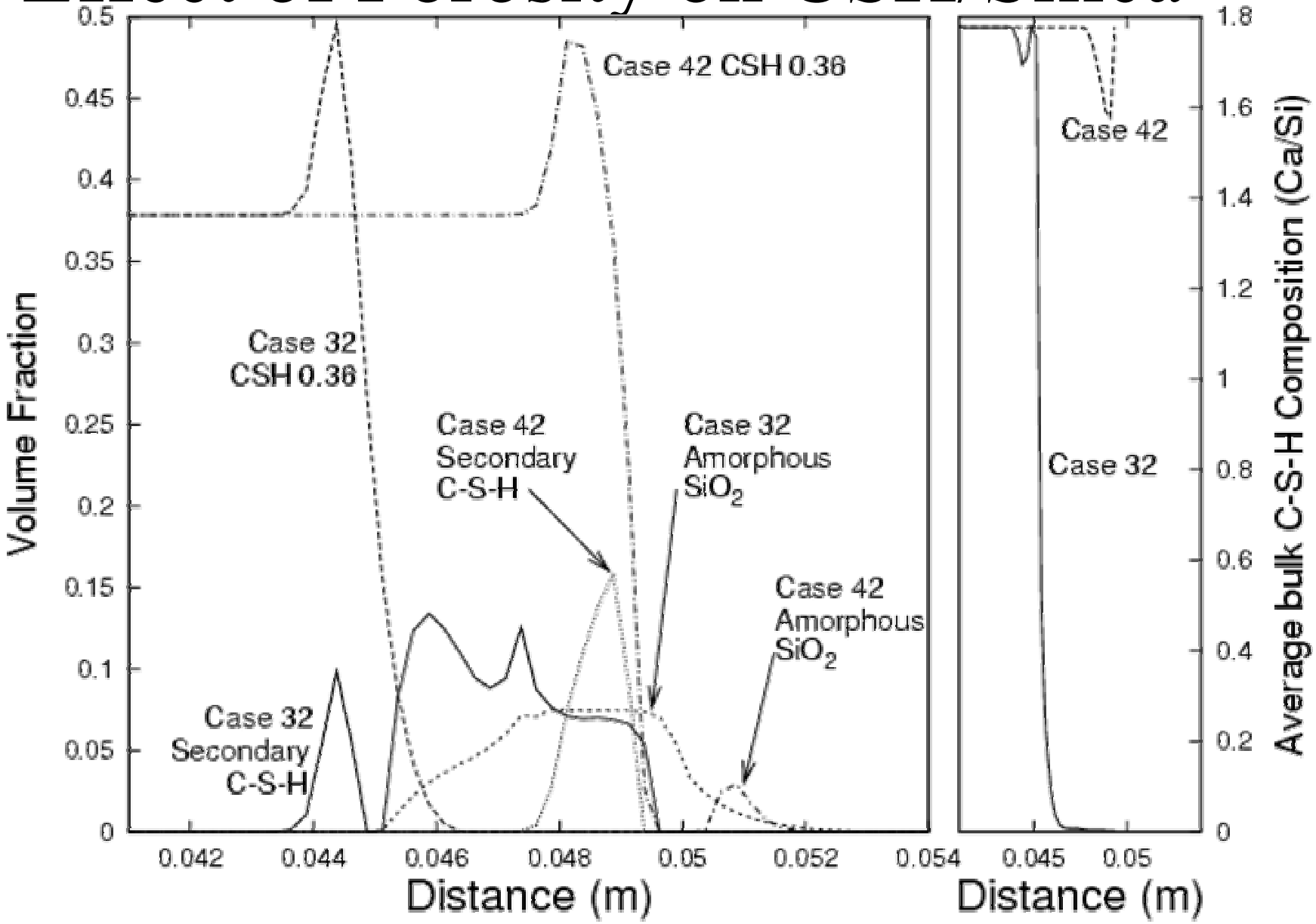
Variables

Case	Cement	Shale	Tort.	Other
32	0.3	0.7	0.0004	
40	0.3	0.3	0.0004	
42	0.3	0.09	0.0004	
34	0.3	0.7	0.004	
35	0.3	0.7	0.00004	
36	0.3	0.7	0.0004	No SS
37	0.3	0.7	0.0004	No SS or SiO_2(am)
38	0.3	0.7	0.0004	Rates/100
39	0.3	0.7	0.0004	Rates * 100
44	0.3	0.7	0.0004	Species dependent diffusion

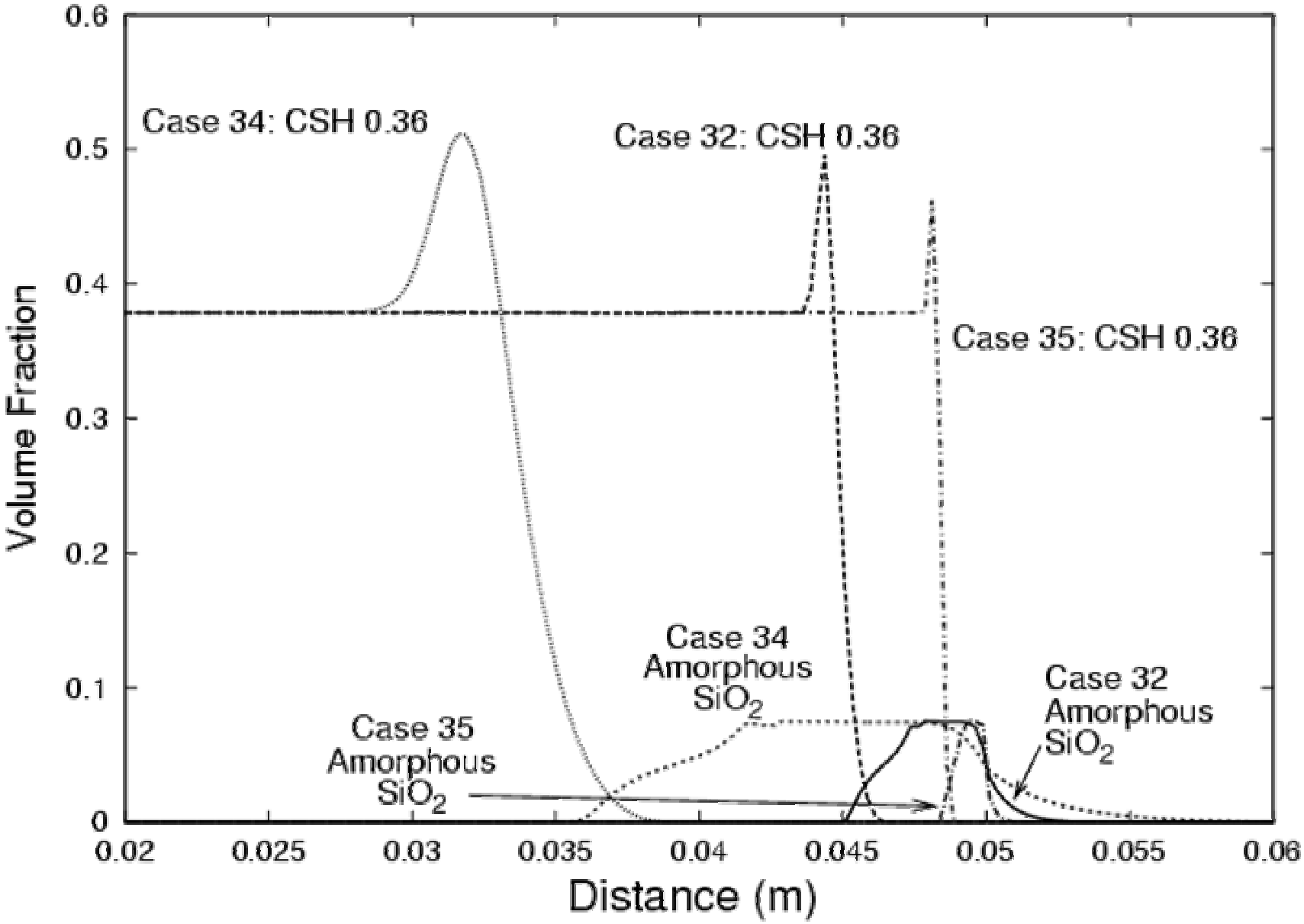
Effect of Porosity on Composition



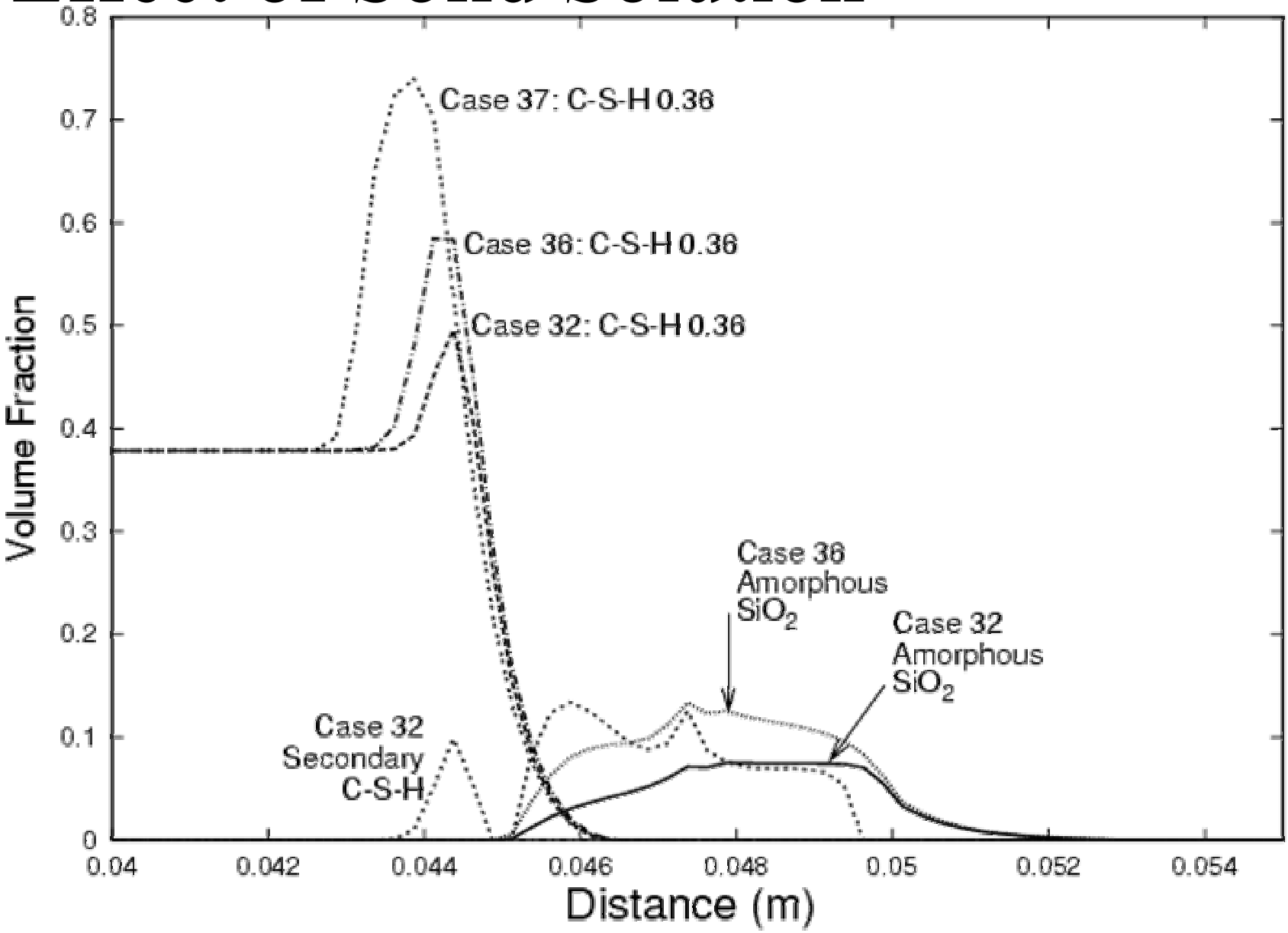
Effect of Porosity on CSH/Silica



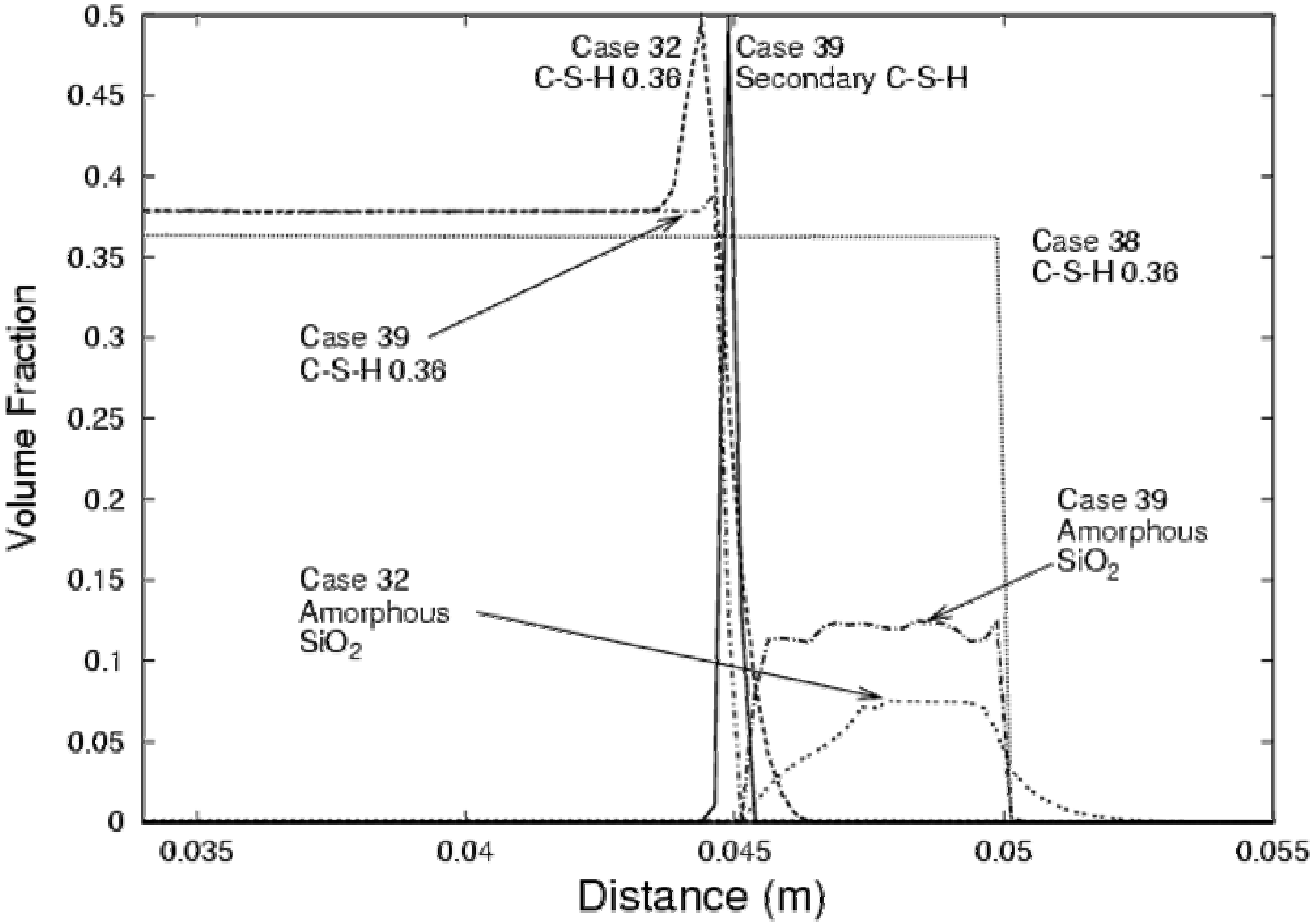
Effect of Tortuosity



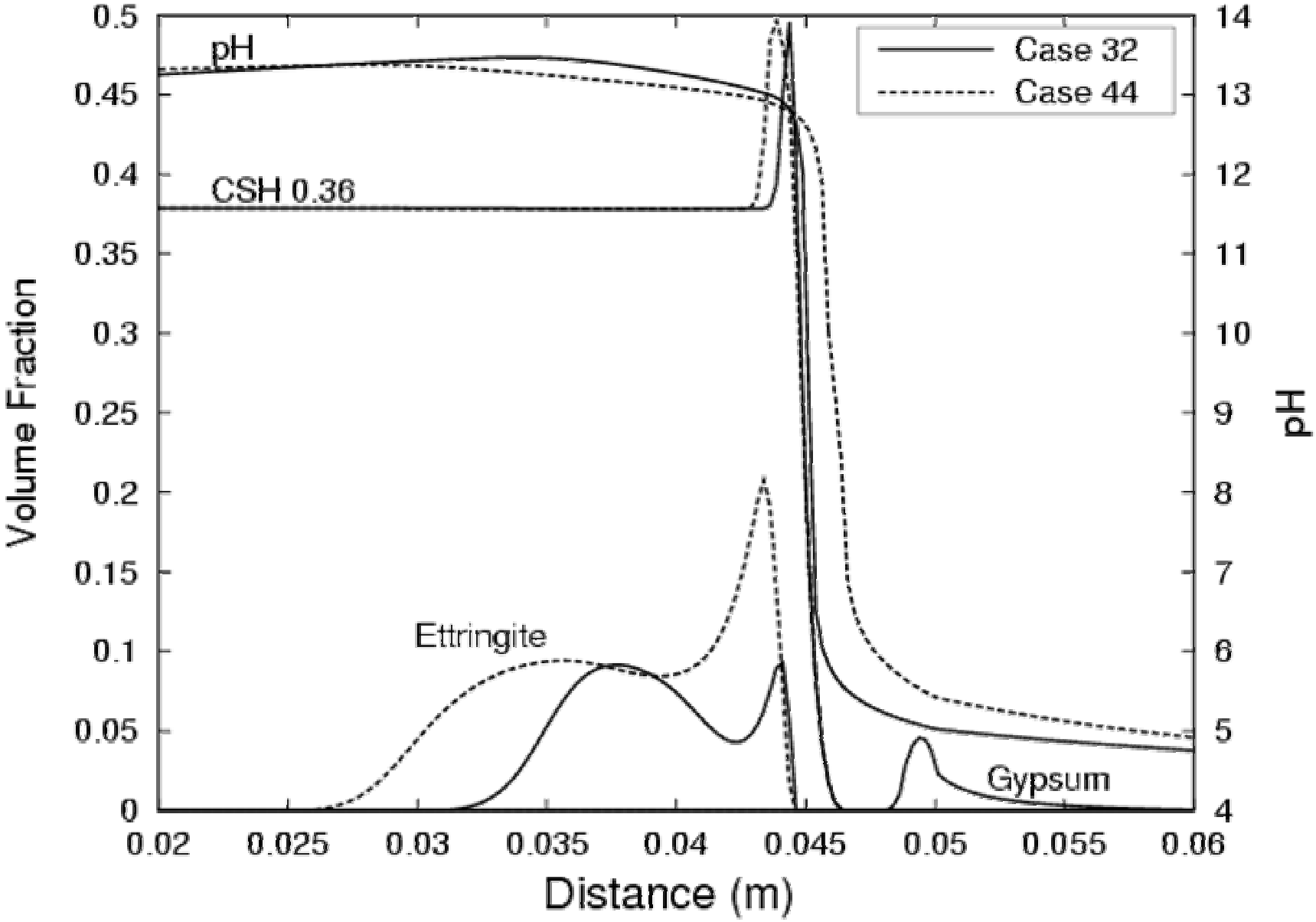
Effect of Solid Solution



Effect of Reaction Rate



Species Dependent Diffusion



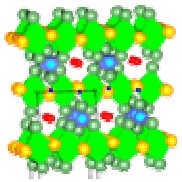
SACROC snapshot:
Amount of CO_2 transport?
Interface opening or sealing?

1 cm

1 cm

Conclusions

- Diffusion-based models capture key features of cement degradation
- System behavior is a sensitive function of tortuosity and reaction rate
- Much higher (1000X) rates and much higher tortuosity (100X) necessary to explain depth penetration of 1 atm acid experiments
  - pH typically accelerates rates $\propto pH^{0.5}$
  - Tortuosity strong function of age, w/c
- Challenge: translate cement degradation into effective leak rates:
  - Fracture versus matrix vs annulus flow
  - Self-sealing or self-propagating interfaces



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