Corrosion of Cement by CO2

Evaluating the Risk of Leakage
Leakage Program

- Mike Celia & Co.
  - Assess risk of leakage on the scale of oil field

- Jean Prévost & George Scherer & Co.
  - Analyze leakage process from a single well
Overview of Leakage Model

508 wells, 7 permeable layers
Injection rate $\sim 1.6$ Mt/yr
(Depth $\sim 1750$ m)

Formation properties assigned deterministically

Effective permeability of wells assigned stochastically

Permeability of each vertical segment of each well is independent and uncorrelated
Assumed distributions of permeability in wells

Intact cement: $K \sim 10^{-20} \text{ m}^2$

Degraded cement: $K \sim 10^{-16} \text{ m}^2$
Monte Carlo Simulation

- Maximum leakage (95% confidence level) above injection layer
We need a carefully-designed field experimental program to measure current conditions (quantitative properties!) in old wells.

This will reduce the largest uncertainty in current risk analysis models.

We have proposed and analyzed one such test.
Field Measurements for Wells Properties
Conclusions

Semi-analytical models provide relatively fast computational tools for leakage analysis.

Monte Carlo analysis provides limits for leakage variance.

Combined modeling and field experiments are required to provide defensible, quantitative leakage estimates.

To identify permeability distribution, need field campaign.

- Re-enter existing (abandoned) wells.
- Use statistical mix of wells (location, depth, age, etc.).

Lynn Orr and Sally Benson (CMI Advisory Board) and Michael Celia and Jan Nordbotten (Princeton University) are participating.

Panel on "Scientific Challenges for Geological Carbon Sequestration" led by Sally Benson and Michael Celia.

- Identify and prioritize "Proposed Research Directions for geological storage of carbon.
- The workshop report is intended "to shape competitiveness of energy alternatives and to inform the scientific, technical, and policy communities."
Injection & Leakage

- Greatest risk of leakage is through cement sealing cap rock
Potential Leakage Routes

- Interfacial cracks / annuli through cap rock

Well plug

Well casing

Annulus is primarily fault sealed.
leakage

- Model of injection & transport
  - What is the fluid that reaches the cement?

- Experimental study of cement corrosion
  - How does cement respond to acidic brine?

- Model of acidic brine in annulus
Cement paste with 0 or ½ bentonite

Flow-through to find maximum reaction rate

Batch reactions to study transport control

Thesis now complete

Publications in progress

Andrew Duguid
Acidified brine passes over rod of cement

Provides maximum rate of reaction (i.e., no limitation from saturation of solution or diffusion of reaction products)
Under conditions corresponding to limestone formation (calcium-saturated brine, pH5, 50°C), no reaction is seen over 26 days.
Flow Through Experiment (Continuous fresh acid)

Sandstone formation: pH 3, 50°C

0 hours      6 hours      24 hours      30 hours      2 days

3 days      4 days      6 days      7 days      8 days
Flow Through Experiment (Continuous fresh acid)

- Corrosion is strongly accelerated by
  - lower pH
  - higher temperature

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<thead>
<tr>
<th>Temperature</th>
<th>pH 2.4</th>
<th>pH 3.7</th>
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<td>50°C</td>
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Under typical conditions of a sandstone formation at ~1 km depth, the rate of attack would be roughly 2 - 3 mm per month if fresh acid flowed over the cement.

Constant rate of attack (not diffusion controlled)
Added geochemistry to the reactive transport module in Dynaflow

Accounts for all phases in cement paste, reaction with carbonic acid (or dry CO$_2$), precipitation and redissolution of calcium carbonate, change in porosity

Includes chemistry from EQ3/6 plus new data

Next: include advection from Bruno Huet.
Simulation of Experiment

Model predicts appropriate minerals with sharp boundaries.
Simulation of Experiment

Calcium carbonate (white) layer appears where C-S-H gels
Simulation of Experiment

- pH varies sharply across reaction zone

![Graph showing pH and concentrations of CaCO₃, Ca(OH)₂, and Calcium-Silicate-Hydrate](attachment:image.png)
Assume power-law dependence of $D$ on porosity

Diffusivity rises by $\sim 20x$ as corrosion transforms cement to silica gel

$$D = D_0 \left[ \frac{\phi(t) - \phi(\infty)}{\phi(0) - \phi(\infty)} \right]^m$$
Diffusivity dips where CaCO$_3$ forms, slowing (but not stopping) corrosion of interior
CaCO₃ layer is diffusion barrier with constant thickness so it does not produce $\sqrt{t}$ kinetics.

Diffusivity in CaCO₃ layer is $\sim$1000 times less than in silica gel (or still water), so it dominates transport until gel layer thickness is $\sim$3 mm.

Transport through gel dominates kinetics after a few months, leading to $\sqrt{t}$ kinetics.
Corrosion w/o Leak

Itme to dissolve:

m of cement ~100 yrs,

m of cement ~1000 yrs

Therefore, leakage unlikely without pre-existing annulus or crack exists.
If attack is slow compared to flow rate, gap width increases uniformly. Rapid increase in leak rate.
Concentrated Attack

- If attack is rapid compared to flow rate, corrosion localized at bottom → slow/no increase in leak rate.

Flow rate controlled by original gap width.
Movement Upward

- Phase change (boiling) of CO2/brine
- Thermal effects (contraction/cracking)
- Vapor blocking?
- Corrosion of cement
- Precipitation/erosion of corrosion products
- Requires geochemistry, flash/phase equilibration
As fluid leaks upward through the well, the drop in $p$ and $T$ causes phase changes (boiling) influences acidity, transport, corrosion rate.

Dick Fuller is developing module to predict phase assemblage during leakage.

Flash Fuller
What is unique?

Modular CO2 + water + salt flash module

Modular cement geochemistry module

Extensive cement thermodynamic database (0-100°C)

Can be incorporated into other reservoir reactive transport models
Deflection of Cap Rock

Injection pressure deflects cap rock upward.

Potential cracking of cement and/or shale.

Analysis requires poromechanics, including cracking, possible with Dynaflow (J.H.).
Conclusions

- Reaction rate is fast - several mm per month - under steady flow of acidic brine
- Much less rapid attack in limestone
- Initial rate of attack slowed by calcite layer
- Escape takes centuries in absence of crack/annulus
- Probability & severity of annuli unknown
- Geochemistry module permits modeling of attack
- Flash module predicts phase assemblage