Comparative Study Using Some Advanced Simulation Methods for Leaching of Cementitious Materials Over Ten Thousands of Years


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Background (1/3)

Nuclear power generation covers 30 percents of power generation in Japan.

Method for disposing radioactive waste is very important.

**RADIOACTIVE WASTE**

- High-level radioactive waste
  - Geological disposal
    (~-300m)
- Low-level radioactive waste
  - Concrete Pit
    (-10 ~ -5m)
  - Sub-surface Disposal
    (-100 ~ -50m)

Underground
(-100 ~ -50m)
Cross sectional view of sub-surface disposal repository

Concrete pit: Maintaining stability of the repository
Mortar: Preventing radioactive nuclides to leak
Bentonite: Preventing underground water to permeate to the repository
Long-term durability (over 10,000 years) is demanded for this repository. Evaluating long-term durability of concrete is necessary.

**Issues for cementitious material**

- Crack
- Chemical degradation

- Calcium leaching to underground water
- Chemical reaction between mortar and bentonite
Target of this study

Simulation-code for evaluating calcium leaching

for example… DuCOM, LIFE D.N.A., CCT-P

 ※ Method of simulation is different.

Evaluating calcium leaching of cement hydrates by 3 codes.

• What kind of deterioration will occur in sub-surface disposal repository?
• How fast is the deterioration speed?
Evaluating method for calcium leaching

**Numerical Simulations**

- Dissolution/Precipitation of Hydrates
  - Thermodynamic database
  - Solid-liquid equilibrium for calcium

&

- Mass Transfer
  - Advection
  - Diffusion
  - Electrical potential

**Experimental Models**

\[ L = a \times t^{1/n} \]

- \( n \); parameter (generally \( n=2 \))
- \( a \); constant parameter
## Comparison of 3 codes

<table>
<thead>
<tr>
<th>Code</th>
<th>Model of diffusion coefficient</th>
<th>Chemical reactions</th>
<th>Cementitious material</th>
<th>Bentonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuCOM</td>
<td>$D_{eff} = \frac{\phi \cdot S}{\Omega} \cdot \delta \cdot D_{ion}$</td>
<td>* Solid/liquid equilibrium for calcium</td>
<td></td>
<td>Absorption of Ca ions</td>
</tr>
<tr>
<td>LIFE D.N.A.</td>
<td>$D_{eff}^i = \eta \cdot \beta \cdot f(\phi) \cdot D_0^i$</td>
<td>* Solid/liquid equilibrium for calcium (considering with Na, K) * precipitation of CaCO$_3$, Mg(OH)$_2$, Friedel’s salt.</td>
<td></td>
<td>Absorption of Ca ions</td>
</tr>
<tr>
<td>CCT-P</td>
<td>$D(t) = D(0) \cdot (\frac{\phi(t)}{\phi(0)})^n$</td>
<td>* Thermodynamic database * Incongruent dissolution of C-S-H * Dissolution/ precipitation of CaCO$_3$</td>
<td></td>
<td>Ion exchange reactions of Na, K, Ca and Mg</td>
</tr>
</tbody>
</table>
Simulation model

migration of Calcium ion

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Rock</th>
<th>Concrete</th>
<th>Bentonite</th>
<th>Mortar</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Boundary line (constant)

Composition of underground water (mmol/l)

<table>
<thead>
<tr>
<th>Ion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+}</td>
<td>0.13</td>
</tr>
<tr>
<td>Na^{+}</td>
<td>0.77</td>
</tr>
<tr>
<td>K^{+}</td>
<td>0.03</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>0.16</td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>0.14</td>
</tr>
<tr>
<td>Cl^{-}</td>
<td>0.44</td>
</tr>
<tr>
<td>CO_3^{2-}</td>
<td>0.62</td>
</tr>
<tr>
<td>pH</td>
<td>8.6</td>
</tr>
</tbody>
</table>
Mix proportions of concrete and mortar

<table>
<thead>
<tr>
<th></th>
<th>W/B ( % )</th>
<th>Air (%)</th>
<th>Unit Quantity (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>Concrete</td>
<td>45</td>
<td>2.5</td>
<td>160</td>
</tr>
<tr>
<td>Mortar</td>
<td>45</td>
<td>2.5</td>
<td>230</td>
</tr>
</tbody>
</table>

Cement hydrates using in calculation

DuCOM ; Portlandite, C-S-H
LIFE D.N.A. ; Portlandite, C-S-H, Calcite, Brucite, Friedel’s salt, NaOH, KOH
CCT-P ; All hydrates in database
Simulation result of calcium leaching rate at 50,000 years

Leaching depth: DuCOM > LIFE D.N.A. > CCT-P

Precipitations → decrease of diffusion coefficient

Faced to Bentonite

Faced to Rock
Evaluating for calcium leaching speed

Calcium leaching speed of concrete (faced to rock)

Leaching speed: DuCOM > LIFE D.N.A. > CCT-P
Evaluating for calcium leaching speed

Calcium leaching speed of concrete (faced to rock & bentonite)

Na+, K+ from Bentonite control Calcium leaching from concrete
Degradation process of cement hydrates

DuCOM

Rock

Concrete

D increase

Bentonite

Concrete

D increase

LIFE

D.N.A.

Rock

Precipitate (Calcite, Brucite, Friedel’s salt)

D decrease

Bentonite

D increase

CCT-P

Rock

Precipitate (Calcite)

D increase

Bentonite

Na+, K+

D increase

D; diffusion coefficient
Changing in diffusion coefficient

Dissolution/precipitation of cement hydrates
  ... Porosity increase/decrease
  ... Diffusion coefficient increase/decrease

\[ D_{eff} = \frac{\phi \cdot S}{\Omega} \cdot \delta \cdot D_{ion} \]

\[ D_{eff}^i = \eta \cdot \beta \cdot f(\phi) \cdot D_0^i \]

\[ D(t) = D(0) \left( \frac{\phi(t)}{\phi(0)} \right)^n \]

Graph showing diffusion coefficient versus Calcium leaching rate.
Influential factor for Calcium leaching

• Changing in diffusion coefficient

• Chemical reaction (especially, precipitation)

• Degradation process of cement hydrate is different

• Calcium leaching speed is different
Conclusions

Evaluating calcium leaching of cement hydrates by 3 codes.

- What kind of deterioration will occur in sub-surface disposal repository?
  - Portlandite & C-S-H leach from cementitious material
  - Secondary minerals would precipitate
  - Degradation process is different in 3 codes

- How fast is the deterioration speed?
  - Calcium leaching speed is DuCOM > LIFE D.N.A. > CCT-P
  - Calcium leaching depth at 50,000 years are 130~500mm
  - The reason why simulation result is different…
    Changing in diffusion coefficient
    Chemical reaction (especially, precipitation)
Appendix
Dissolution/Precipitation of Hydrates

Calcium liquid/Solid equilibrium

Mass Transfer

- Transport by solution flow
- Transport by diffusion

\[ D_{\text{eff}} = \frac{\phi S}{\Omega \cdot \delta \cdot D_{\text{ion}}} \]

Calcium leaching = Porosity increase = D increase
Dissolution/Precipitation of Hydrates

Calcium liquid/Solid equilibrium

\[ C_{p0Ca} \]

\[ C_{p1Ca} = A_{cp1} \cdot C_{p0Ca} \]

\[ C_{p2Ca} \]

\[ C_{pCa} = A_{cp1} \left( \frac{C_{Ca}}{C_{0Ca}} \right) \]

\[ \text{Ca}^{2+} \text{ Concentration in liquid} \]

\[ \text{Ca}^{2+} \text{ Concentration in Solid} \]

\[ C_{1Ca} \]

\[ C_{0Ca} \]

\[ f(\phi) = 0.001 + 0.07\phi^2 \{1.8(\phi - 0.18) \cdot H(\phi - 0.18)\} \]

\[ \beta = \frac{1 - c \cdot G_{vol}}{1 - d \cdot S_{vol}} \cdot P_{vol} \]

Mass Transfer

\[ D_{eff}^i = \eta \cdot \beta \cdot f(\phi) \cdot D_0^i \]

- Transport by solution flow
- Transport by diffusion
- Electric force

Transition zone
Dissolution/Precipitation of Hydrates

- the thermodynamic database
  (Chemical reaction code HARPHRQ)
- Incongruent dissolution of C-S-H
  \[
  \log K_i = \frac{x}{1 + x} \log K_{0i} - \frac{x}{1 + x} \log \left( \frac{x'}{1 + x} \right) + \frac{x}{(1 + x)^2} \left\{ A_{0i} + A_{1i} \frac{1 - x}{1 + x} + A_{2i} \left( \frac{1 - x}{1 + x} \right)^2 \right\}
  \]

\( \log K_{sp} \) of C-S-H gel depend on the rate of Ca/Si

Mass Transfer

- Transport by solution flow
- Transport by diffusion

\[
D(t) = D(0) \cdot \left( \frac{\phi(t)}{\phi(0)} \right)^n
\]
Investigation result of the old structures

- Lagerblad (2001)
- Yokozeki (2002)
- Saito et al. (2003)

The most deteriorated data:
- \[ Y = 2.42 \sqrt{t} \] Leaching depth at 50,000 years = 541 mm

Average of all data:
- \[ Y = 0.94 \sqrt{t} \] Leaching depth at 50,000 years = 210 mm

Simulation results = 130 ~ 500 mm at 50,000 years
Comparison DuCOM to LIFE D.N.A.

- **DuCOM**
  - Graph showing the rate of Ca concentration in solid/initial vs. Ca concentration in liquid (mmol/l).
  - Different types of cement affect Na ions & K ions.

- **LIFE DNA**
  - Graph illustrating the Ca concentration in solid vs. Ca concentration in liquid.
  - Model change indicators:
    1. Ca(OH)$_2$
    2. LIFE DNA (model change)
    3. C-S-H

- **Leaching depth**
  - Bar chart showing leaching depth (mm) for 1,000 and 10,000 years:
    - LIFE D.N.A.
    - LIFE D.N.A. (model change)
    - DuCOM

Values:
- LIFE D.N.A.: 42.5, 97.5 (1,000 year), 200 (10,000 year)
- DuCOM: 0, 5, 10, 15, 20, 25