Modeling the Development of Locally Acidified Sites within Corroding Nuclear Fuel Surfaces

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Nuclear Energy

- There were 441 nuclear plants in 32 countries supplying about 21.2% of the world's electricity*.
- It is a green energy that does not produce global warming gases.
- Spent fuel must be safely stored and eventually disposed of.

Nuclear Waste Disposal

- Cladding tube
- Spent nuclear fuel
- Bentonite clay
- Surface portion of deep repository
- Fuel pellet of uranium dioxide
- Copper canister with cast iron insert
- Crystalline bedrock
- Underground portion of deep repository

500 m
Local acidity may develop as a consequence of the hydrolysis of uranyl ions within defect sites (pores/flaws).
Local Acidity and Corrosion

At low pH (<5), UO$_2$ dissolution rate increases drastically.

Build-up of acidity inside a defect site would accelerate local fuel dissolution.

Experimental Observation

- Current decrease indicates a film formation leading to partial passivation.
- The eventual rise of current indicates an increase in the dissolution rate at locally acidified sites.

For example:

\[ \frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + R_i \]

For example:

\[ R_{UO_2^{2+}} = k_f[UO_2^{2+}][OH^-] - k_b[UO_2OH^+] \]
Boundary and Initial Conditions

Bulk Concentration (Outside)

Initial Concentration (Inside)

Swept-away:

\[
\hat{n} \cdot D_i \nabla C_i = \alpha (C_{bi} - C_i)
\]

Insulative:

\[
\hat{n} \cdot D_i \nabla C_i = 0
\]

pH = 9.5

\[
\begin{align*}
[UO_2^{2+}] & \\
[UO_2OH^+] & \\
[UO_2(OH)_2^-] & \\
[UO_2(OH)_3^-] & \\
[UO_2(OH)_4^{2-}] &
\end{align*}
\]

0 M

\[\text{UO}_2^{2+} \text{ Flux}\]

\[
\hat{n} \cdot D \nabla C = J
\]
**UO₂ Dissolution Flux**

Dissolution at the base of the pore/flaw

\[ \text{UO}_2 \rightarrow \text{UO}_2^{2+} + 2e^- \]

\[
J_{UO_2^{2+}} = \frac{10^{-6}}{nFA_{\text{active}}} \exp(-4.4 + 16 \times E_{\text{applied}})
\]

COMSOL Multiphysics is a modeling package based on FEM.
A multiphysics is the name of the game, PDE’s set the rules.
Localized Attack

- Initial simulations performed assuming uniform dissolution across the whole surface showed no pH depression
- Experiments demonstrated localized attack
- Degree of localized dissolution was incorporated into the $\text{UO}_2^{2+}$ flux as *Attenuation Factor* ($\text{FA} = \text{apparent area/active area}$)

Uranyl-silicate deposits indicate the active regions during the dissolution
Effect of Flux Attenuation

- FA is a measure of the degree of localization of dissolution.
- Local acidification observed at $E > 250 \text{mV}$ suggesting $FA \approx 1000$ (equivalent to 0.1% active area on the surface).
- The higher the potential, the lower FA required for a depression in pH.
- A plateau in pH looks like a ‘buffering’ effect.
Effect of Applied Potential

- The input flux increases as the $E$ increases
- pH depression occurs when $E > \sim 0V$ (SCE), and the shallower the pore, the higher the potential required
- Sigmoidal curves appear similar to a weak acid titration. (pH vs volume of acid compared with pH vs potential)
- That pH does not reach a plateau may suggest an inability to achieve an acid-base equilibrium in deep pores
Effect of Pore Depth

- The effective diffusion path increases as the pore depth increases.
- Higher potential required to cause pH depression in shallower pores.
- pH depression is not possible for a potential $<-250\text{mV}$.
- pH sensitive region shifts to smaller depth as $E$ increases.
  This may suggest mixed diffusional-chemical equilibrium control.
Summary: pH Threshold Diagram

- Threshold pH (=5) below which UO₂ dissolution rate increases drastically.
- Regions above each line pH<5 (aggressive region).
- Aggressive region increases as E increases.
- Lower potential requires combination of deeper pores and higher FA to achieve aggressive conditions.
- Higher potential, fewer and deeper sites will be subject to acidified dissolution.
Sensitivity Analysis: D, k and $\alpha$

D = $10^{-8}$ cm$^2$/s
$\Delta k_f = 10^4$
$\square k_f = 10^6$
$\bigcirc k_f = 10^8$

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$\bigcirc k_f = 10^8$

$\alpha = 1$
$\bigcirc \alpha = 0.1$
$\times \alpha = 0.01$
$\bigtriangleup \alpha = 0.001$
Further improvement of FCAD Model
Electrochemical and Corrosion Studies at Western

http://publish.uwo.ca/~ecsweb/

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