Dry Air Oxidation of Commercial Spent Nuclear Fuel

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WHY IS OXIDATION OF CONCERN?

- Dry storage/Transportation
- Fuel handling/Surface facility
- Post-closure

- Fuel integrity/dispersibility
- Retention of radionuclides
- Dissolution kinetics
OXIDATION LEADS TO CLAD UNZIPPING

Fig. 4. Spin defect 559 mm from the top of rod P-64P-124-13 after 3962 h at 229°C in unlimited air.

(a) AXIAL
360°C
51.5 h
A5B

(b) FLAP
325°C
126.6 h
A5C

(c) SPIRAL
325°C
600 h
A4A

Figure 3-11. Types of Cladding Cracks.
OXIDATION INCREASES SURFACE AREA

Opens grain boundaries and can release volatile fission products
GENERALIZED CURVE FOR SPENT FUEL OXIDATION

Figure 3  Generalized Curve Representing the O/M State of SF as a Function of Oxidation Time (Einziger et al., 1992)
CSNF OXIDATION EXHIBITS STRONG TEMPERATURE DEPENDENCE

Turkey Point Fuel (Burnup-27 MWd/kgM), Bare fragment oxidation.
Spent fuel oxidation differs from unirradiated $\text{UO}_2$.

- $\text{UO}_{2.4}$ phase (cubic) vs. $\text{U}_3\text{O}_7$ (tetragonal)
- No "simultaneous" $\text{U}_3\text{O}_8$ formation, i.e., "plateau" behavior
- 5 to 50 times faster initial oxidation rate (open grain boundaries, but Gd-doped unirradiated exhibits the same behavior
Rapid oxidation of the grain boundaries

Oxidation of the bulk grains to $\text{UO}_2^{2+}$ before any $\text{U}_3\text{O}_8$ is observed (true for low burnup?)

Possible intermediate phases

Grain-size dependence

Arrhenius temperature dependence

Resistance to further oxidation at lower temperatures (plateau behavior)

Oxidation to $\text{U}_3\text{O}_8 (\text{OM} \sim 2.70 - 2.75)$ which is $\sim 30\%$ less dense
CHANGES TO FUEL DURING IRRADIATION

- Pellet cracking due to thermal cycling
- Grain growth towards pellet center
- Fission gas bubbles/diffusion to grain boundaries/gap
- Radiation (field, damage to crystal, thermal annealing)
- Densification then pellet swelling
- Oxygen potential dictates phase partitioning, but also diffusion limited
SPENT FUEL ≠ UNIRRADIATED UO₂

- UO₂ with substitutional and interstitial "impurities"
- Increase in oxygen potential with increasing burnup, but buffered by Mo and scavenging of O by Zr
- Charge balance maintained by oxidation of U or loss of O
- Sintered UO₂ behaves differently

Figure from Matzke, JNM 223(1995)1-5
T=750°C
BURNUP DEPENDENCE OF CSNF OXIDATION

Oxidation behavior of LWR fragments of different burnup oxidized at 305°C

![Graph showing burnup dependence of CSNF oxidation.](image-url)
\[ \text{UO}_2 \Rightarrow \text{UO}_{2.4} \]

\[ t_{2.4} = k_{2.4} \exp\left(\frac{Q_{24}}{RT}\right) \]

where

- \( t_{2.4} \) is the time to oxidize from \( \text{UO}_2 \) to \( \text{UO}_{2.4} \) (h)
- \( k_{2.4} \) is the pre-exponential factor for the \( \text{UO}_2 \) to \( \text{UO}_{2.4} \) transition (h)

  Nominal Case: \( 1.40 \times 10^{-8} \)
  Bounding Case: \( 2.93 \times 10^{-9} \)

- \( Q_{24} \) is the activation energy (105 kJ mol\(^{-1}\))
- \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\))

and \( T \) is the temperature (\( K = 273 + T(\degree \text{C}) \)).

Minimal (if any) burnup dependence, mostly temperature and grain size.
$$UO_{2.4} \Rightarrow UO_{2.75}$$

$$t_{2.75} = k_{75} \exp \left( \{Q_{75}^0 + \alpha \times \text{Burnup} \} / RT \right)$$

- $t_{2.75}$ is the time to oxidize from $UO_{2.4}$ to $UO_{2.75}$ (h)
- $k_{75}$ is the pre-exponential factor for the $UO_{2.4}$ to $UO_{2.75}$ transition (h)
- Nominal Case: $4.84 \times 10^{-14}$
- Bounding Case: $1.48 \times 10^{-14}$
- $Q_{75}^0$ is the corresponding Arrhenius activation energy (150 kJ mol$^{-1}$)
- $\alpha = 1.0$ kJ mol$^{-1}$ per MWd/kg M (as high as 1.4 kJ mol$^{-1}$)
- Burnup is the local burnup of the sample (MWd/kg M)
- $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$)
- $T$ is the temperature (K = 273 + T($^\circ$C)).

![Figure 5.11. Time to Oxidize LWR Fragments from $UO_{2.45}$ to $UO_{2.50}$ at 305°C as a Function of Burnup (Burnup from $^{137}$Cs Analysis)](image-url)
Figure 2.4. Radial Profile of Plutonium in ATM-104 Fuel Measured by EPMA [69]

Figure 2.5. Radial Burnup Profile in ATM-104 Fuel with a Pellet Average Burnup of 44.3 MWd/kg M Measured by EPMA [69]
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<tr>
<th>Element</th>
<th>0.06</th>
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<th>0.26</th>
<th>0.36</th>
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RELATIONSHIP OF OXIDATION TO HBS

- NRC limits burnup to 62 MWd/KgM
  - Formation of High Burnup Structure (HBS)
- If soluble dopants can delay or prevent the movement of the uranium planes in oxidation, can they delay or prevent the grain restructuring as well?
  - Pinning of dislocation loops
- Related to lattice parameter?

CRYSTAL LATTICE ENERGY

\[ U = -\frac{ANZ^+ Z^- e^2}{r_0} \left(1 - \frac{1}{n}\right) \]

where

- \( A \) = Madelung constant
- \( U \) = the equilibrium lattice energy
- \( N \) = Avogadro’s number
- \( r_0 \) = the equilibrium distance between ions
- \( n \) = the Born exponent for ionic repulsion.

- Madelung constant is a geometric factor to account for ionic attraction/repulsion from infinite series of nearest neighbor interactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (pm)</th>
<th>Ion</th>
<th>Ionic radius (pm)</th>
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<tr>
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<tr>
<td>Np\textsuperscript{4+}</td>
<td>98</td>
<td>Sm\textsuperscript{2+}</td>
<td>107.9</td>
</tr>
</tbody>
</table>

PELLET FABRICATION (NERI)

Vacuum dry at 100°C for 24 hours

Prepress pellets at 83 MPa
Crush & sieve
Press at 500 MPa

Wet mill for 24 hours

Sinter for 24 hours at 1570°C under 4% H₂
ISOTHERMAL TGA OF La-DOPED UO$_2$ AT 325°C
ISOTHERMAL TGA OF Gd-DOPED UO₂ AT 325°C
CHARGE BLOCKING EFFECT

- Non-uranium cations as substitutions in the U lattice act as net negative charges, making oxidation (and electron transfer) more difficult
  - +2 and +3 are "negative" themselves and lead to oxidation of U to maintain charge balance
  - +4 such as Pu and Zr are "negative" in that they will not/can not oxidize to higher states
- Each substitution affects its 8 nearest neighbor O$_2^-$ and 12 nearest neighbor U ions (Madelung for fluorite)
- Each unit cell of UO$_2$ or U$_4$O$_9$ has 14 U ion clouds
  - At 10 wt% Gd$_2$O$_3$ doping $\Rightarrow$ 14 at% Gd $\Rightarrow$ 2 U in every unit cell have Gd as substitution and 2 U have oxidized to U$^{5+}$
CONCLUSIONS

CSNF oxidation is primarily a function of T, burnup, grain size
Higher burnup fuels show significant resistance to U₃O₈ formation
Lattice energy, charge blocking and electron transfer effects
What are the implications for dissolution rate?

Figures from Tennyson and Godfrey, JACS 56[3](1973)128-133