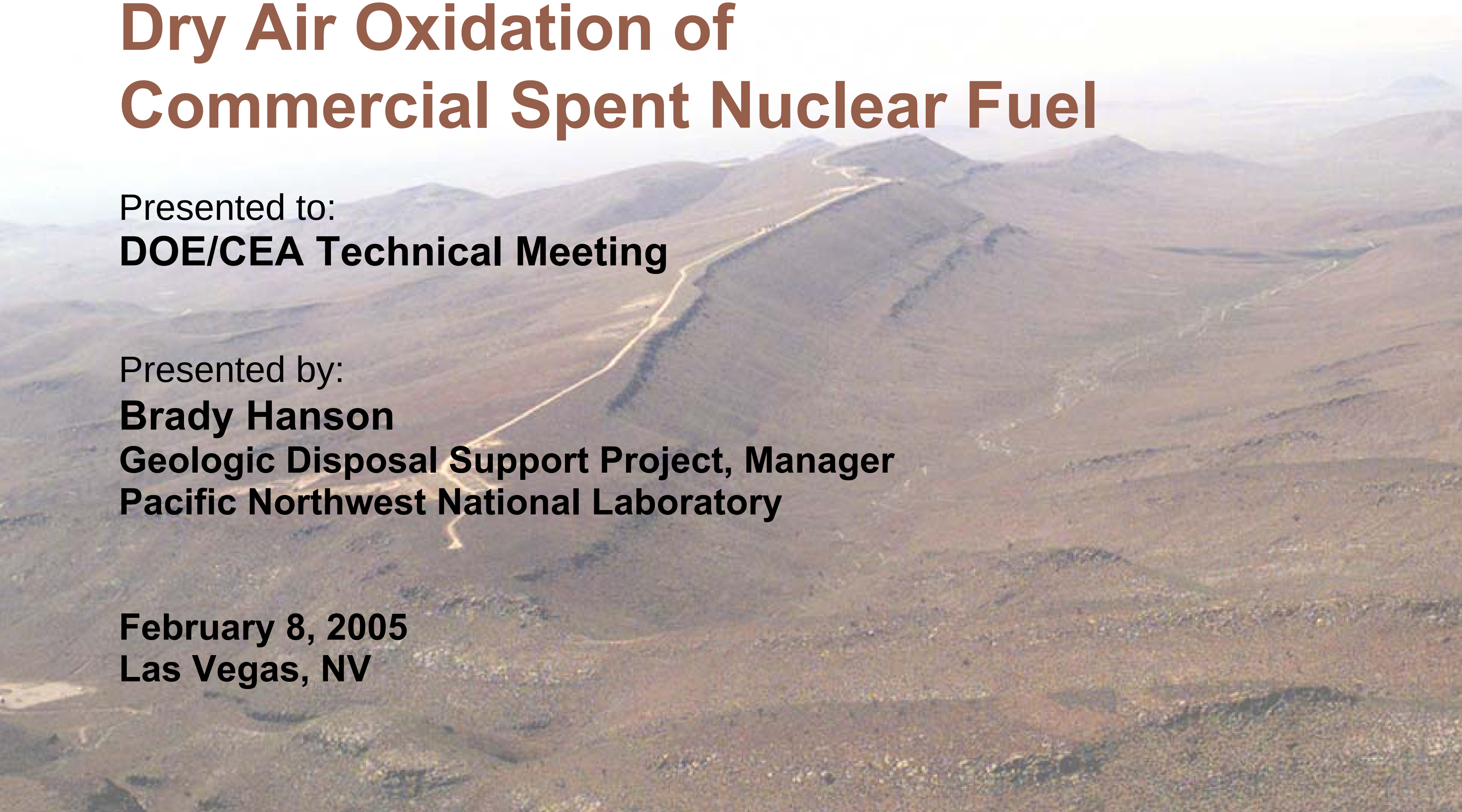

Dry Air Oxidation of Commercial Spent Nuclear Fuel

Presented to:
DOE/CEA Technical Meeting

Presented by:
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Pacific Northwest National Laboratory

February 8, 2005
Las Vegas, NV

WHY IS OXIDATION OF CONCERN?

- Fuel integrity/dispersibility
  - Clad unzipping
  - Increase surface area
- Retention of radionuclides
- Dissolution kinetics

OXIDATION LEADS TO CLAD UNZIPPING

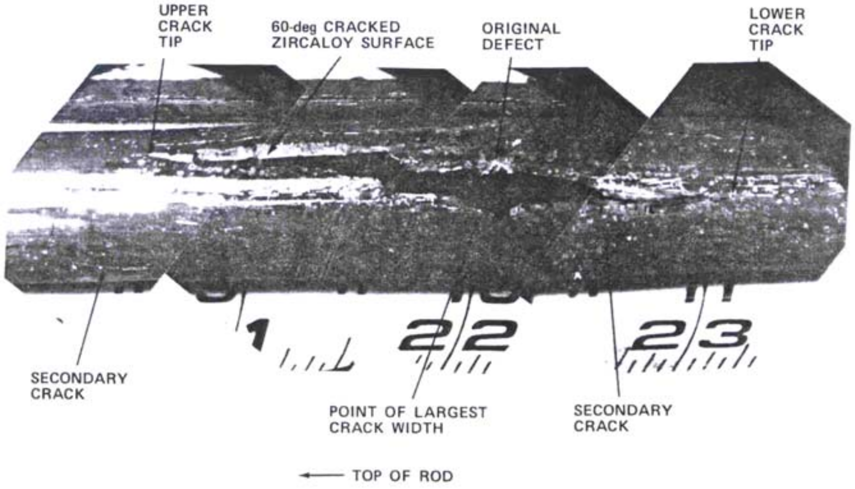
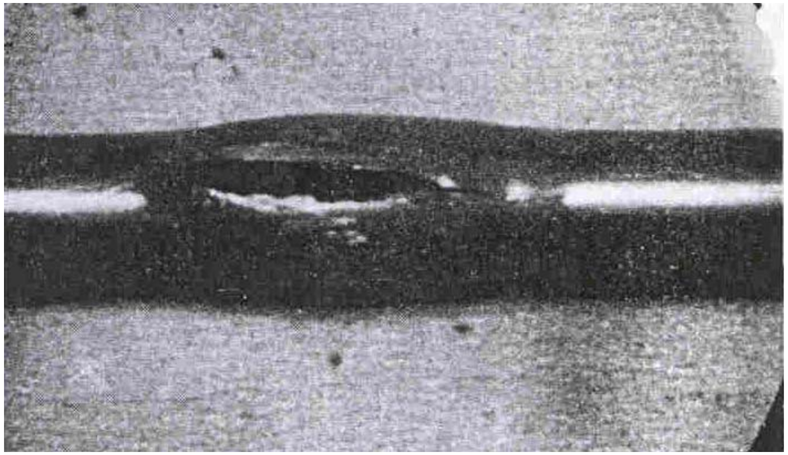
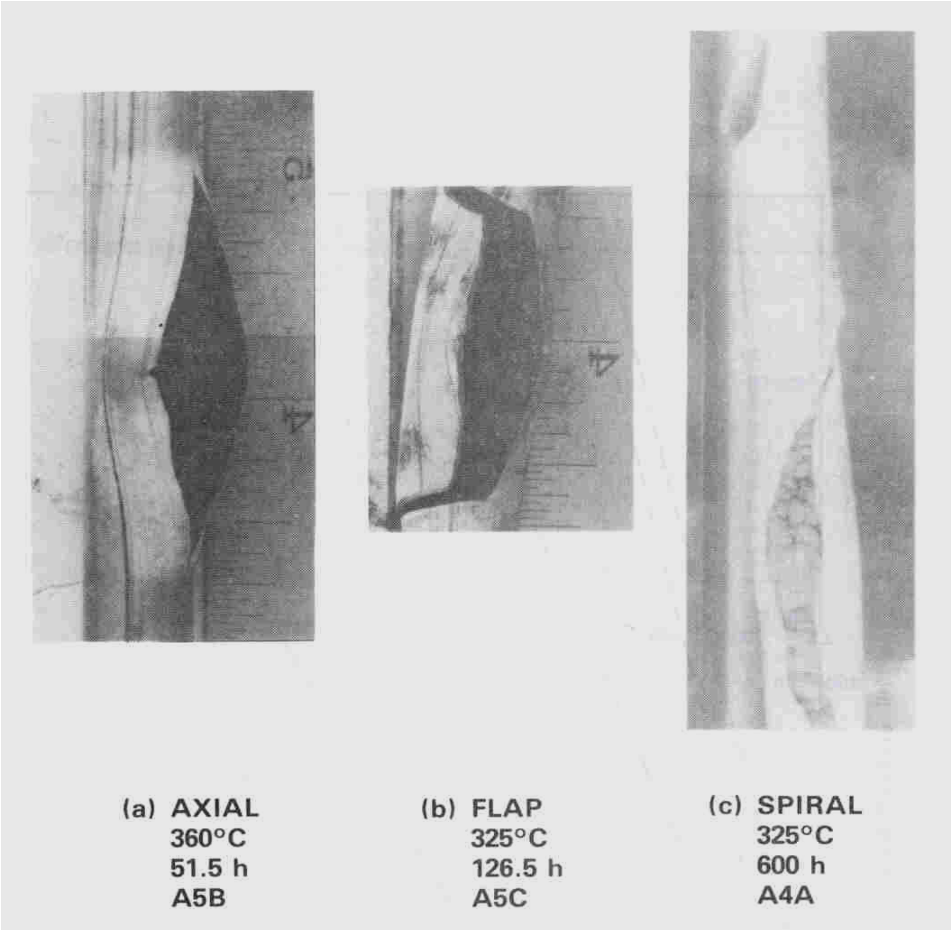


Fig. 4. Split defect 559 mm from the top of rod PB-PH462-E3 after 5962 h at 229°C in unlimited air.

Einziger and Cook, *Nuc. Tech.* 69(1985)55-71.



Kohli et al., Nuc. Tech. 69(1985)186-197



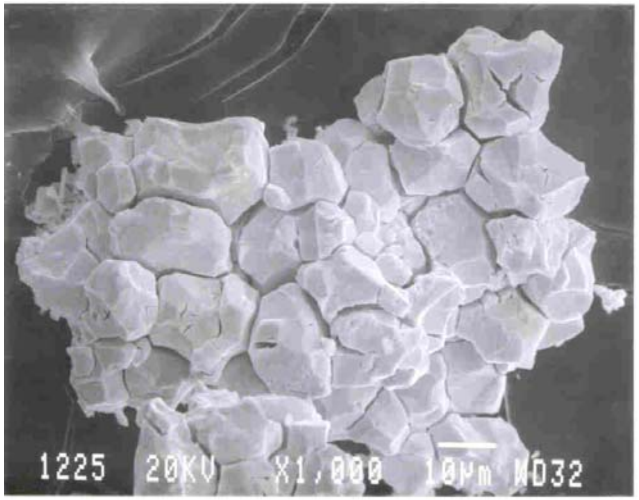
(a) AXIAL
360°C
51.5 h
A5B

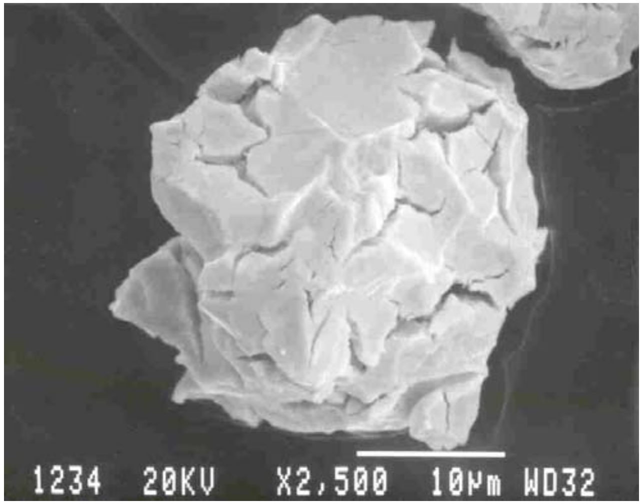
(b) FLAP
325°C
126.5 h
A5C

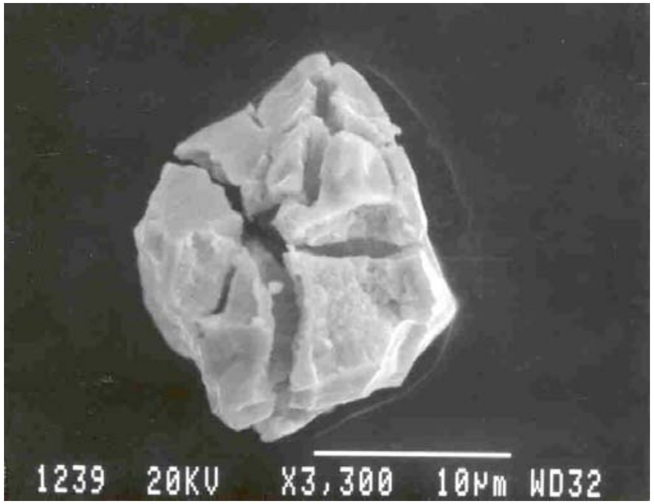
(c) SPIRAL
325°C
600 h
A4A

EPRI NP-4524, April 1986, p. 3-20

OXIDATION INCREASES SURFACE AREA

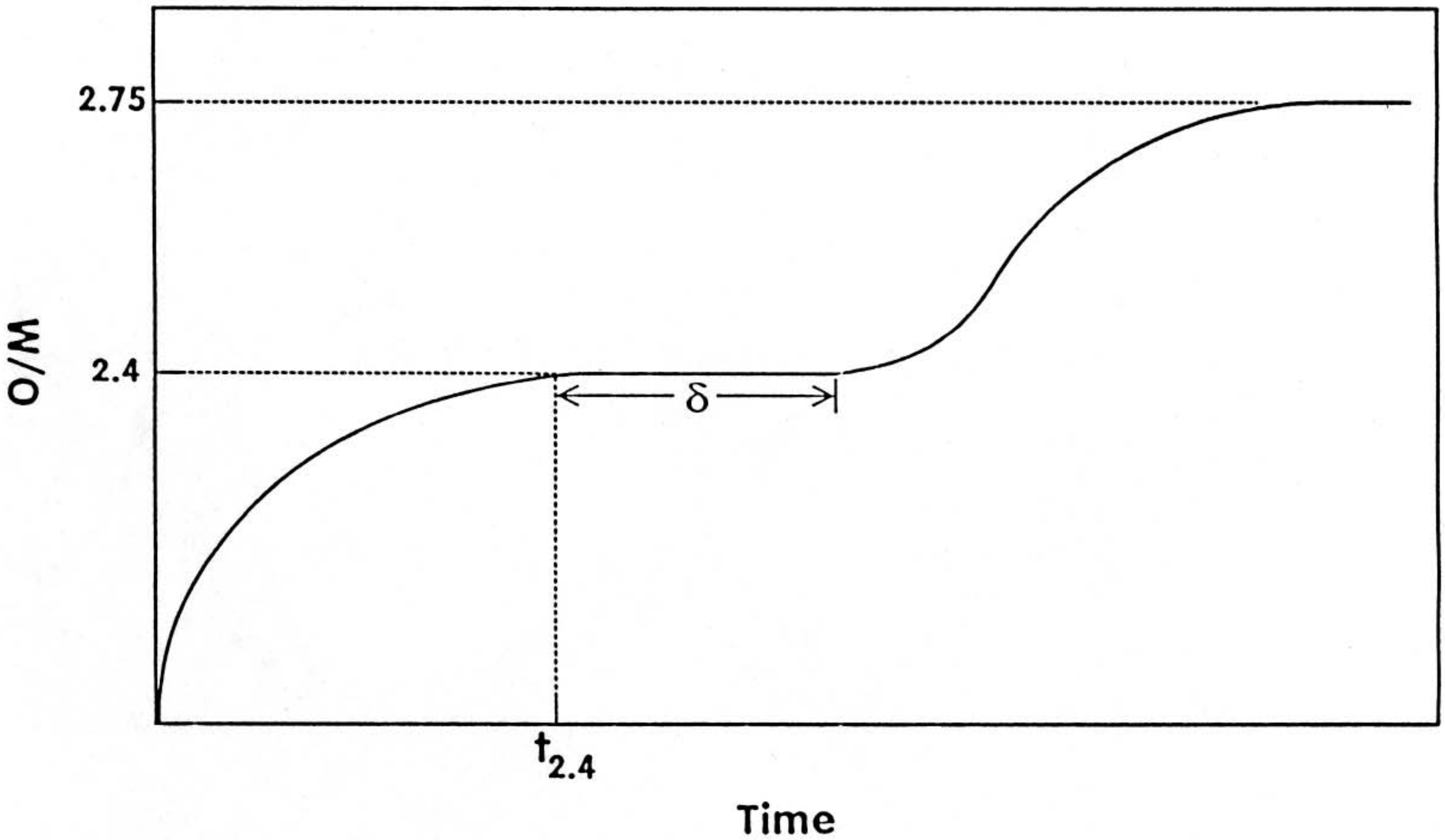






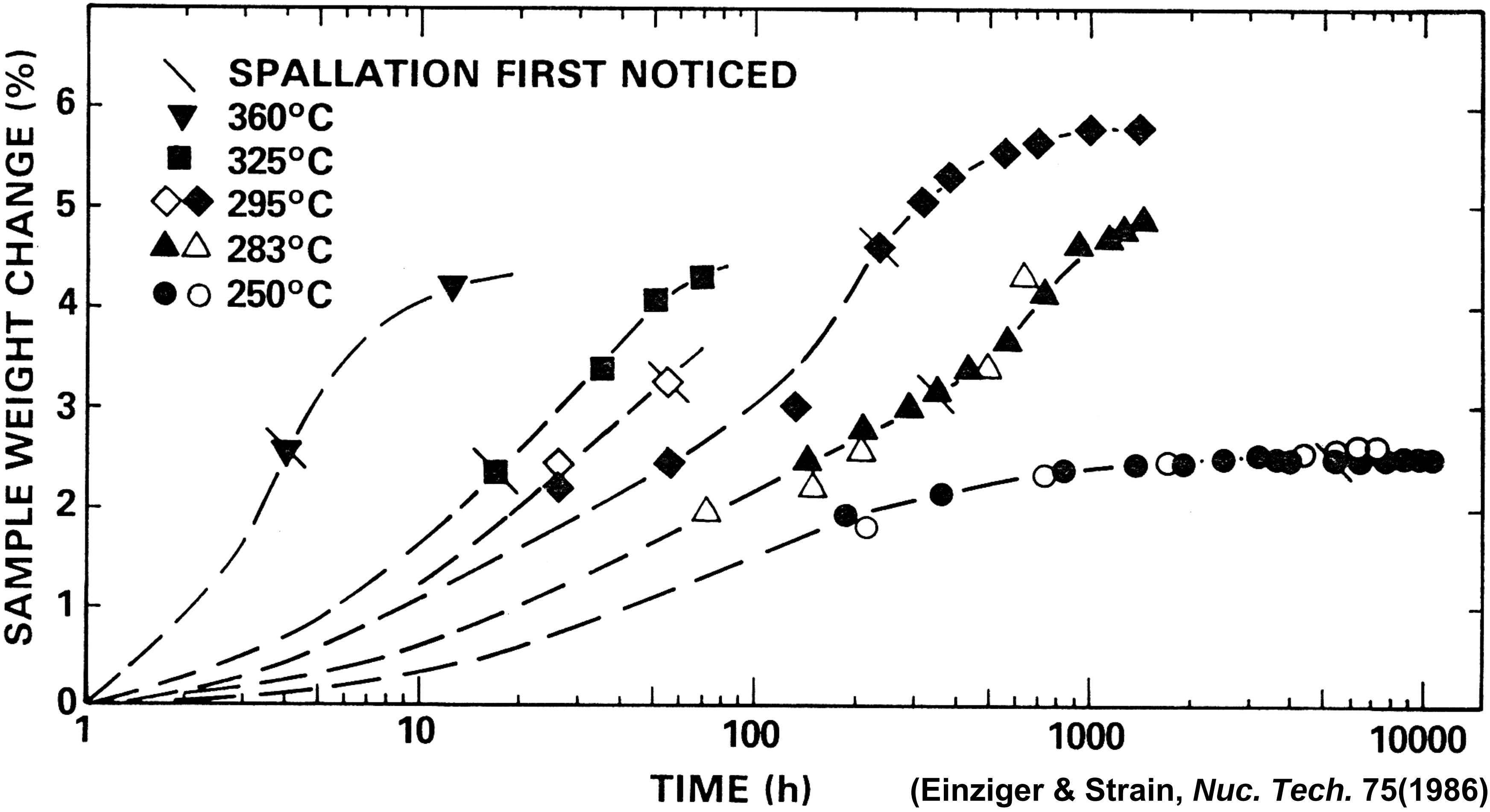
Opens grain boundaries and can release volatile fission products

GENERALIZED CURVE FOR SPENT FUEL OXIDATION



(Hanson, PNNL-11929, July 1998)

CSNF OXIDATION EXHIBITS STRONG TEMPERATURE DEPENDENCE



(Einziger & Strain, *Nuc. Tech.* 75(1986)82-95)

Turkey Point Fuel (Burnup~27 MWd/kgM), Bare fragment oxidation. Duplicate tests run at 250, 283, and 295°C

REVIEW OF UO_2/CSNF OXIDATION

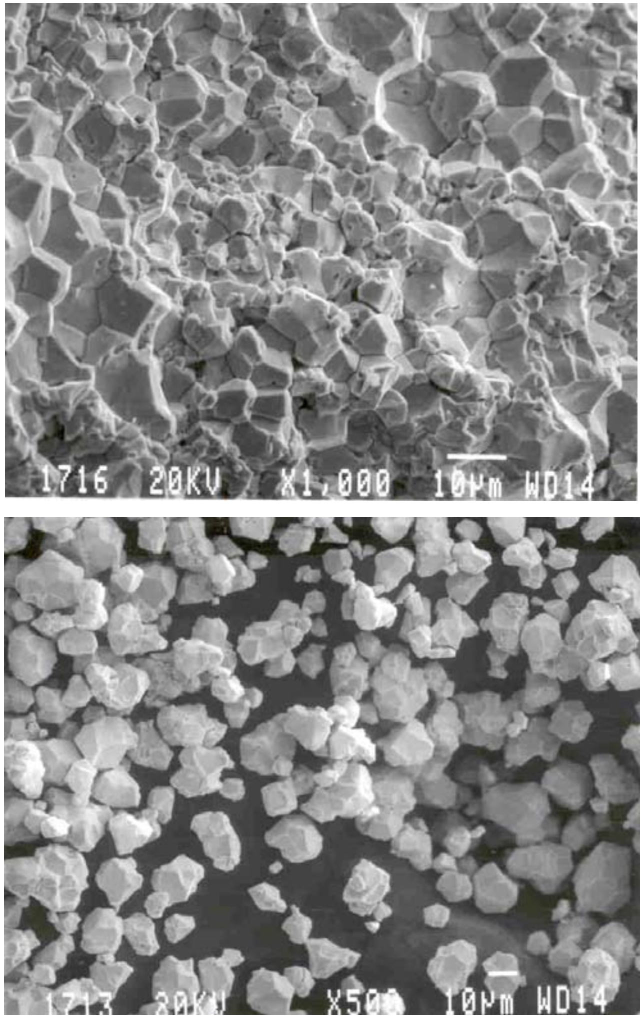
- **Spent fuel oxidation differs from unirradiated UO_2**
  - **$UO_{2.4}$ phase (cubic) vs. U_3O_7 (tetragonal)**
  - **No “simultaneous” U_3O_8 formation, i.e., “plateau” behavior**
  - **5 to 50 times faster initial oxidation rate (open grain boundaries, but Gd-doped unirradiated exhibits the same behavior)**

CSNF OXIDATION CHARACTERISTICS

- Rapid oxidation of the grain boundaries
- Oxidation of the bulk grains to $UO_{2.4}$ before any U_3O_8 is observed (true for low burnup?)

$$UO_2 \Rightarrow U_4O_9 \Rightarrow U_3O_8$$

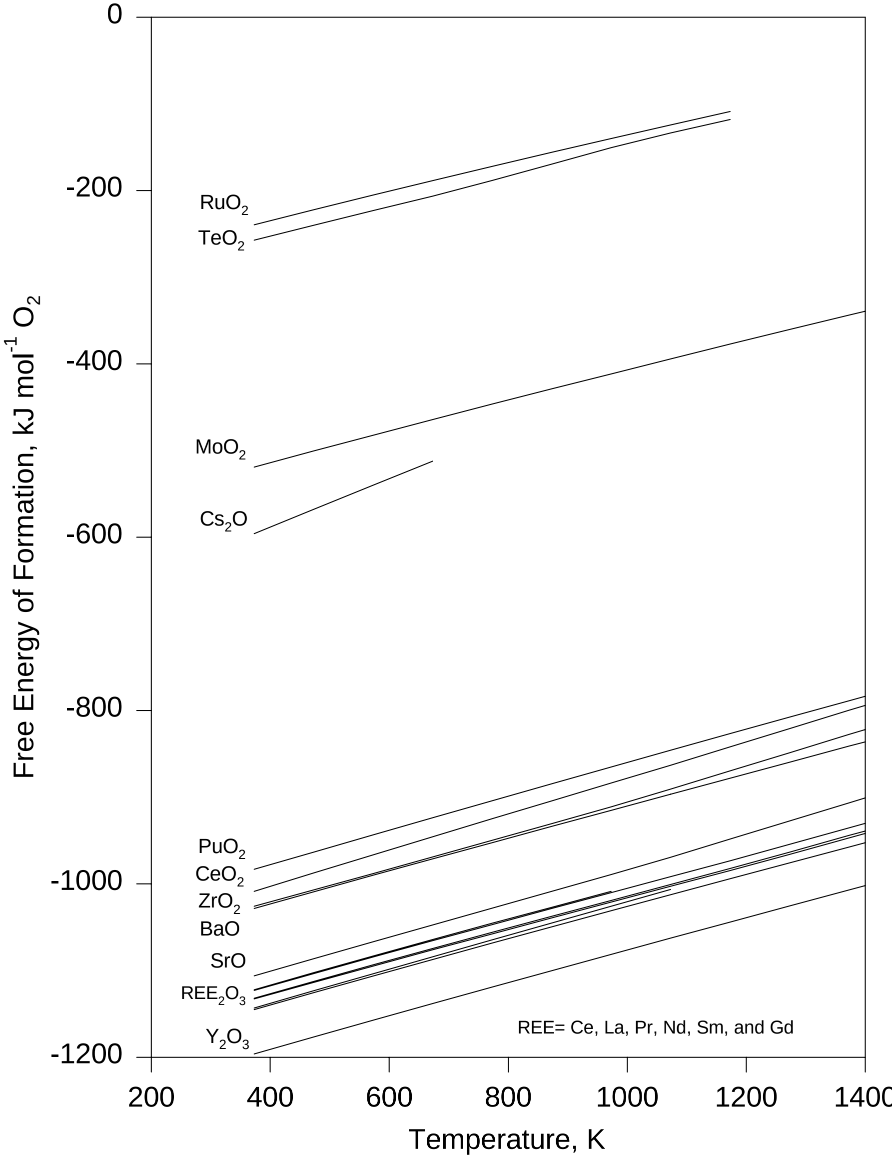
- Possible intermediate phases
- Grain-size dependence
- Arrhenius temperature dependence
- Resistance to further oxidation at lower temperatures (plateau behavior)
- Oxidation to U_3O_8 (O/M~2.70-2.75) which is ~30% less dense



Note grain boundary oxidation and fragment friability at $UO_{2.41}$ (255°C)

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



(Hanson, PNNL-11929, July 1998)

SPENT FUEL ≠ UNIRRADIATED UO_2

- UO_2 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 UO_2 behaves differently

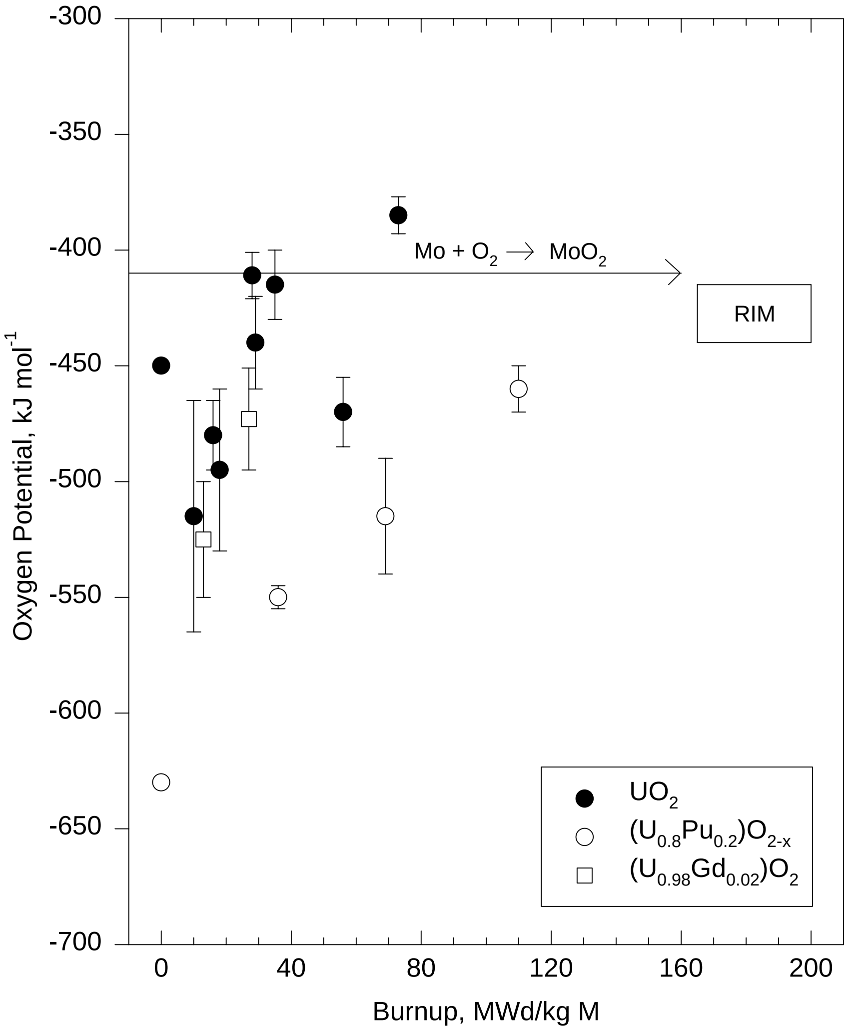
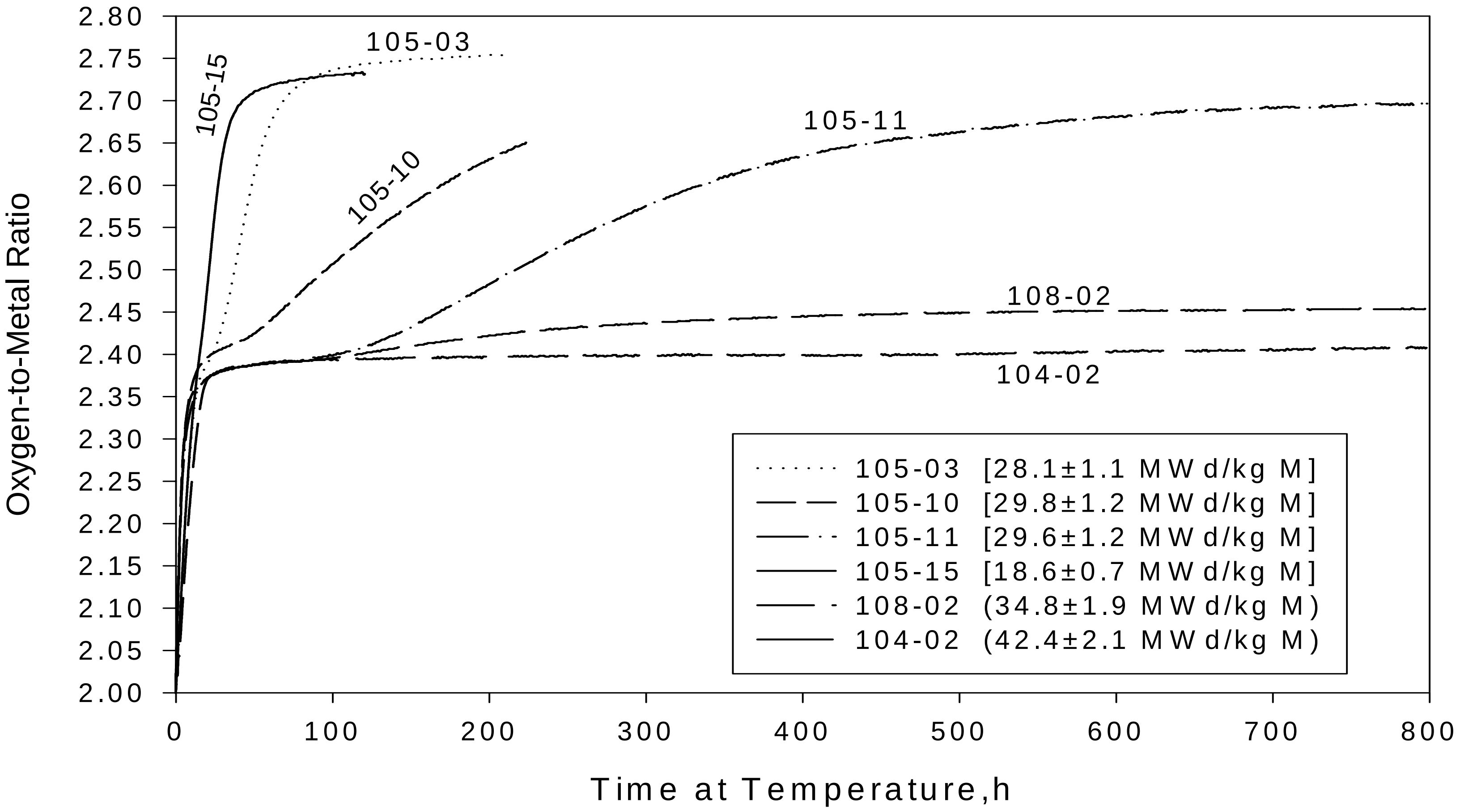


Figure from Matzke, JNM 223(1995)1-5

T=750°C

BURNUP DEPENDENCE OF CSNF OXIDATION

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



$UO_2 \Rightarrow UO_{2.4}$

$$t_{2.4} = k_{2.4} \exp(Q_{24}/RT)$$

where

$t_{2.4}$ is the time to oxidize from UO_2 to $UO_{2.4}$ (h)

$k_{2.4}$ is the pre-exponential factor for the UO_2 to $UO_{2.4}$ transition (h)

Nominal Case: 1.40×10^{-8}

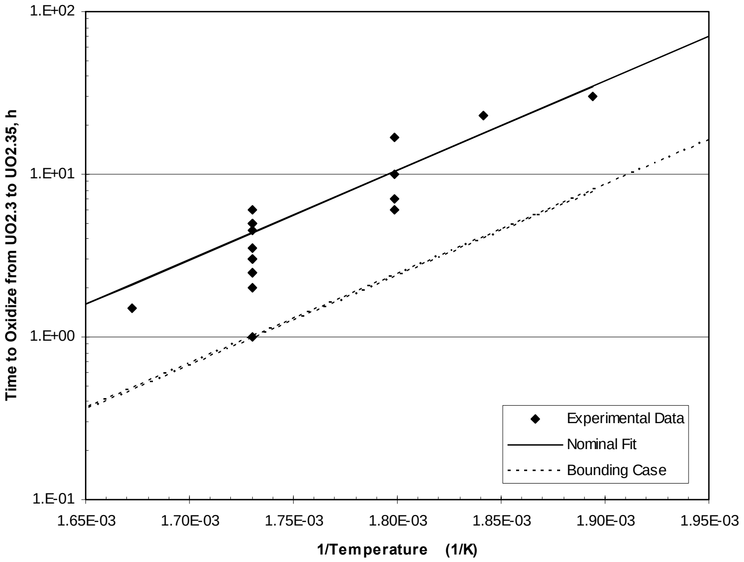
Bounding Case: 2.93×10^{-9}

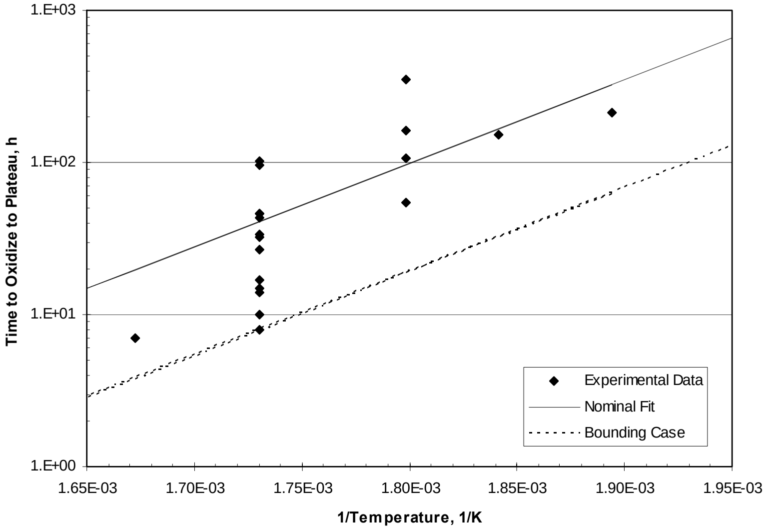
Q_{24} is the activation energy (105 kJ mol^{-1})

R is the universal gas constant (8.314 J mol^{-1} K^{-1})

and T is the temperature (K =273+T(°C)).

Minimal (if any) burnup dependence, mostly temperature and grain size.





(ANL-EBS-MD-000013, Rev. 00)

$UO_{2.4} \Rightarrow UO_{2.75}$

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

$t_{2.75}$ 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: 4.84×10^{-14}

Bounding Case: 1.48×10^{-14}

Q_{75}^{0} is the corresponding Arrhenius activation energy (150 kJ mol^{l-1})

α=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(°C)).

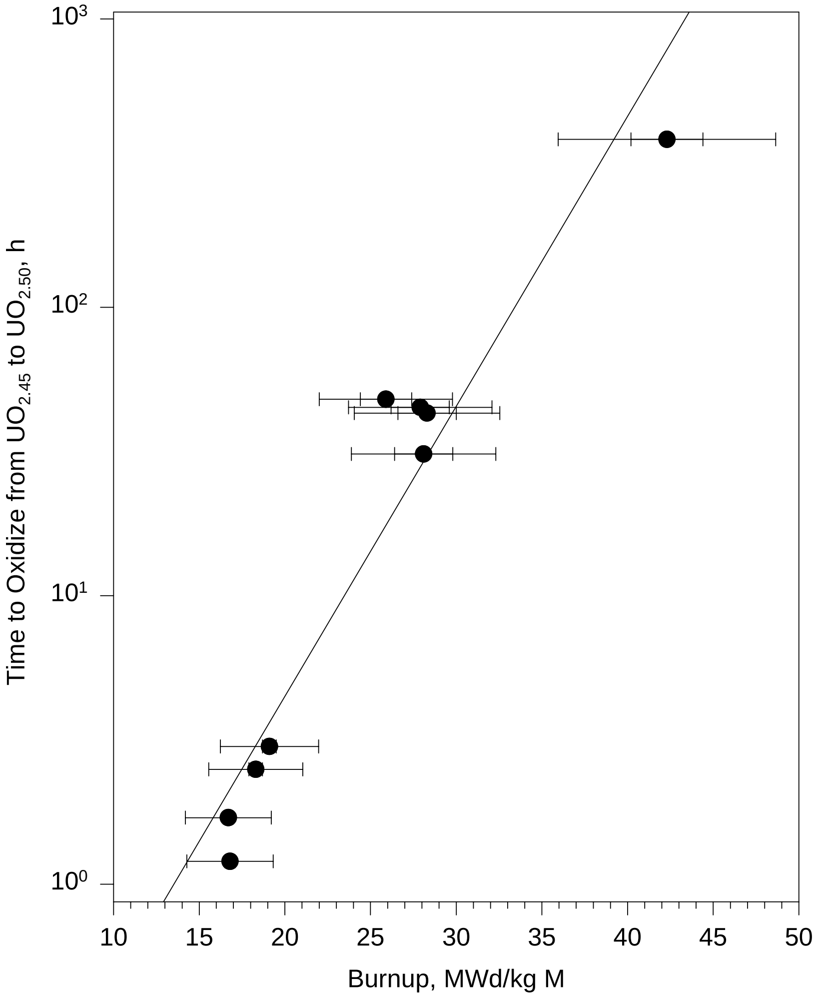


Figure 5.11. Time to Oxidize LWR Fragments from $UO_{2.45}$ to $UO_{2.50}$ at 305°C as a Function of Burnup (Burnup from ^{137}Cs Analysis)

(Hanson, PNNL-11929, July 1998)

RESONANCE ABSORPTION ⇒ HBS

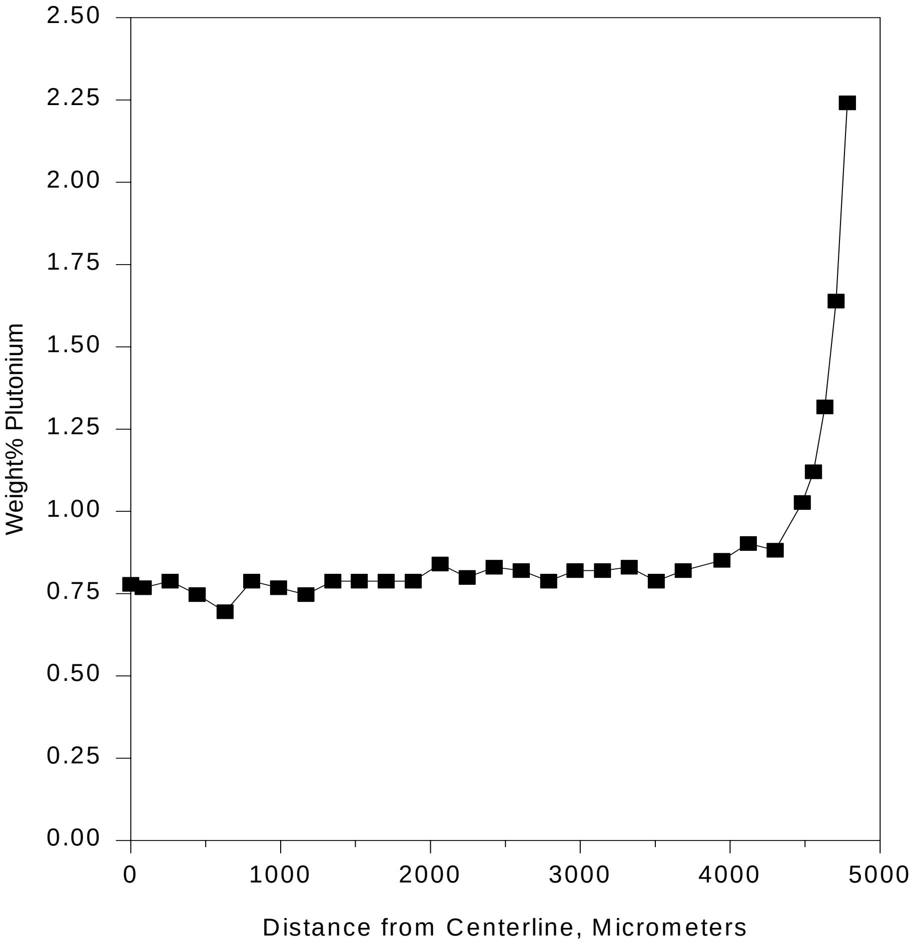


Figure 2.4. Radial Profile of Plutonium in ATM-104 Fuel Measured by EPMA [69]

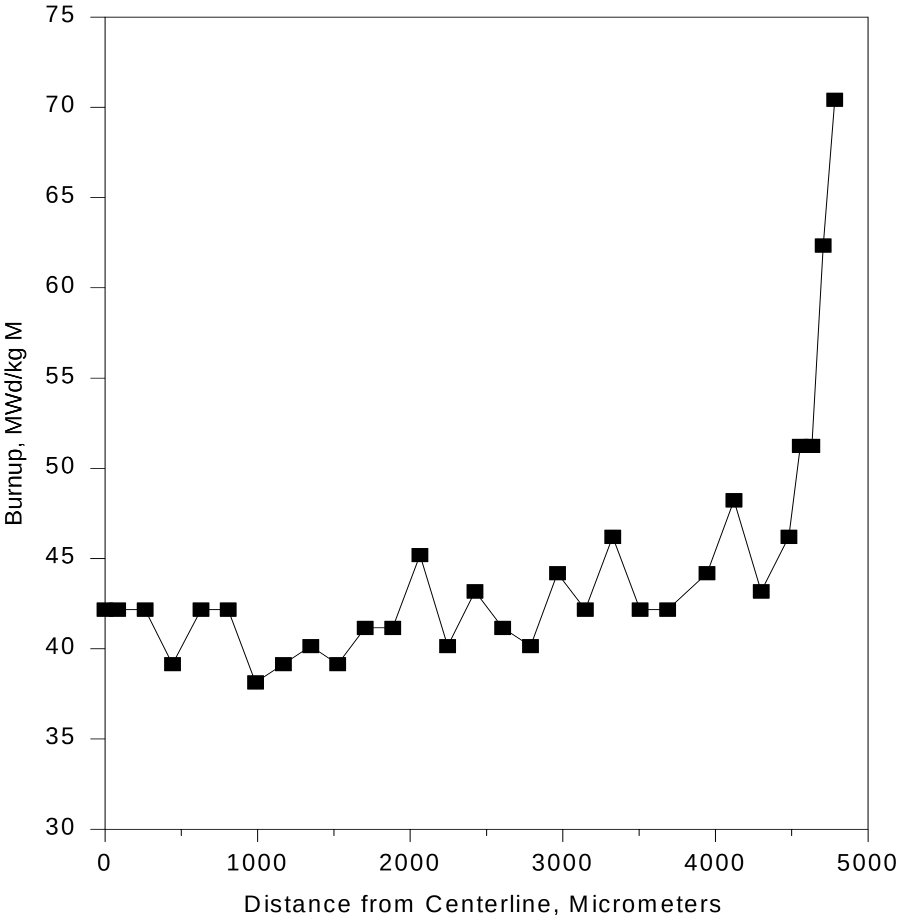


Figure 2.5. Radial Burnup Profile in ATM-104 Fuel with a Pellet Average Burnup of 44.3 MWd/kg M Measured by EPMA [69]

(Hanson, PNNL-11929, July 1998)

CUMULATIVE ELEMENTAL YIELDS (%)

Element	^{235}U	^{239}Pu	^{241}Pu
Sr	9.35	3.45	2.52
Y	4.82	1.69	1.22
Zr	36.76	21.03	16.58
Mo	24.47	22.96	19.92
Tc	6.07	6.16	6.08
Ru	11.44	17.83	20.04
Rh	3.03	6.94	6.73
Pd	1.60	15.79	22.44
Cs	19.41	21.26	20.67
Ba	12.90	12.86	13.31
La	6.36	5.54	6.22
Ce	12.05	10.31	10.48
Nd	20.72	16.22	18.03

RELATIONSHIP OF OXIDATION TO HBS

- **Formation of High Burnup Structure (HBS)**
  - **Local burnup ~65 MWd/kg M**
  - **Average burnup ~45 MWd/kg M**
  - **Restructure of grains, change porosity characteristics**
- **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?**

Figures from Allen and Homes, *Journal of Nuclear Materials* 223(1995)231-237

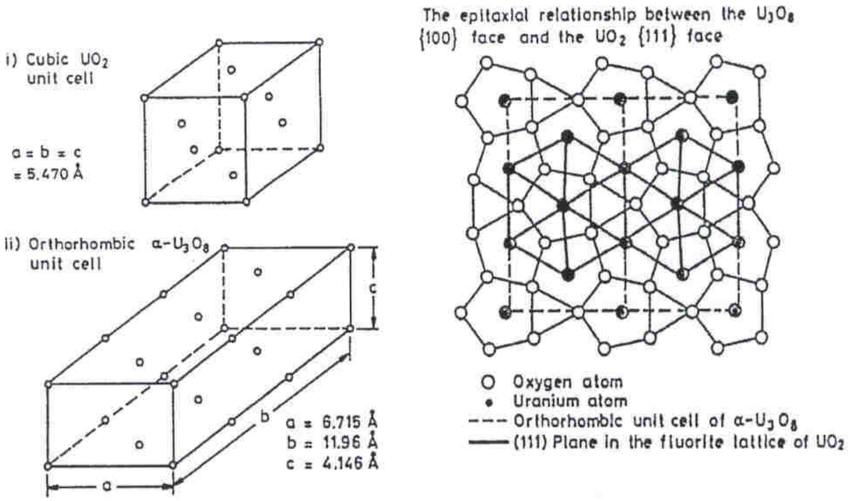


Fig. 1. Comparison of the UO_2 and α-U_3O_8 unit cells (to same scale).

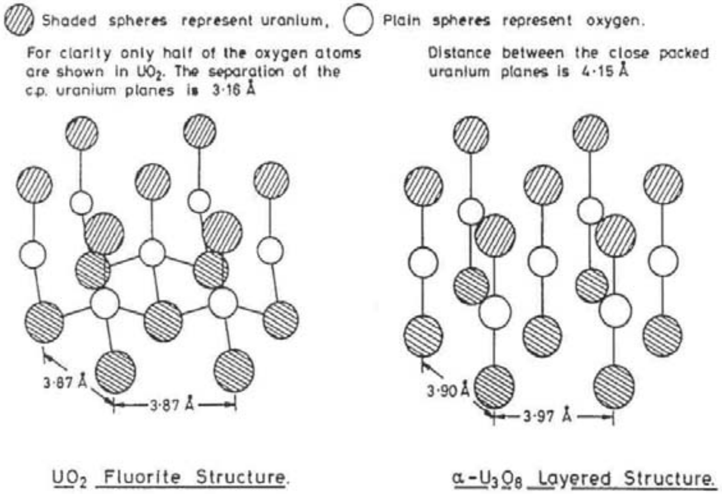


Fig. 2. The oxygen concentration and packing sequence of the atoms in UO_2 and α-U_3O_8.

CRYSTAL LATTICE ENERGY

$$U = -\frac{A\,N\,Z^{+}\,Z^{-}\,e^{2}}{r_0}\left(1-\frac{1}{n}\right)$$

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**

Ionic Radii from RD Shannon, *Acta Cryst*. A32(1976)751-767.

Ion	Ionic radius (pm)	Ion	Ionic radius (pm)
Am^{3+}	109	O^{2-} (IV)	138
Ba^{2+}	142	Pr^{4+}	96
Ce^{4+}	97	Pu^{4+}	96
Cm^{3+} (VI)	97	Rb^{1+}	161
Cs^{1+}	174	Sr^{2+}	126
Eu^{3+}	106.6	U^{4+}	100
Gd^{3+}	105.3	U^{5+} (VII)	84
La^{3+}	116.0	U^{6+}	86
Mo^{4+} (VI)	65.0	Y^{3+}	101.9
Nd^{3+}	110.9	Zr^{4+}	84
Np^{4+}	98	Sm^{3+}	107.9

PELLET FABRICATION (NERI)

Wet mill for 24 hours

Vacuum dry at 100°C for 24 hours

⇒

Prepress pellets at 83 MPa

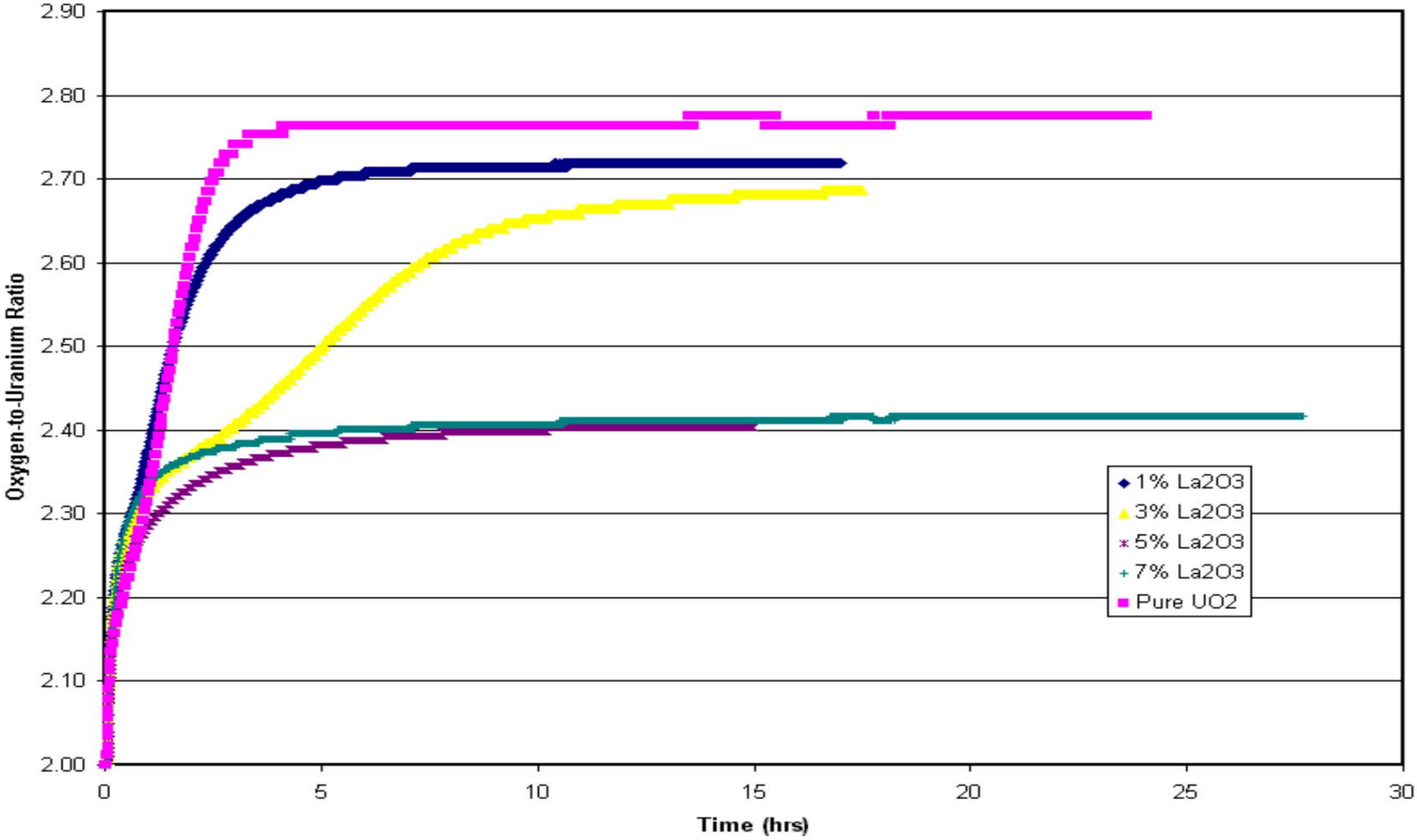
Crush & sieve

Press at 500 MPa

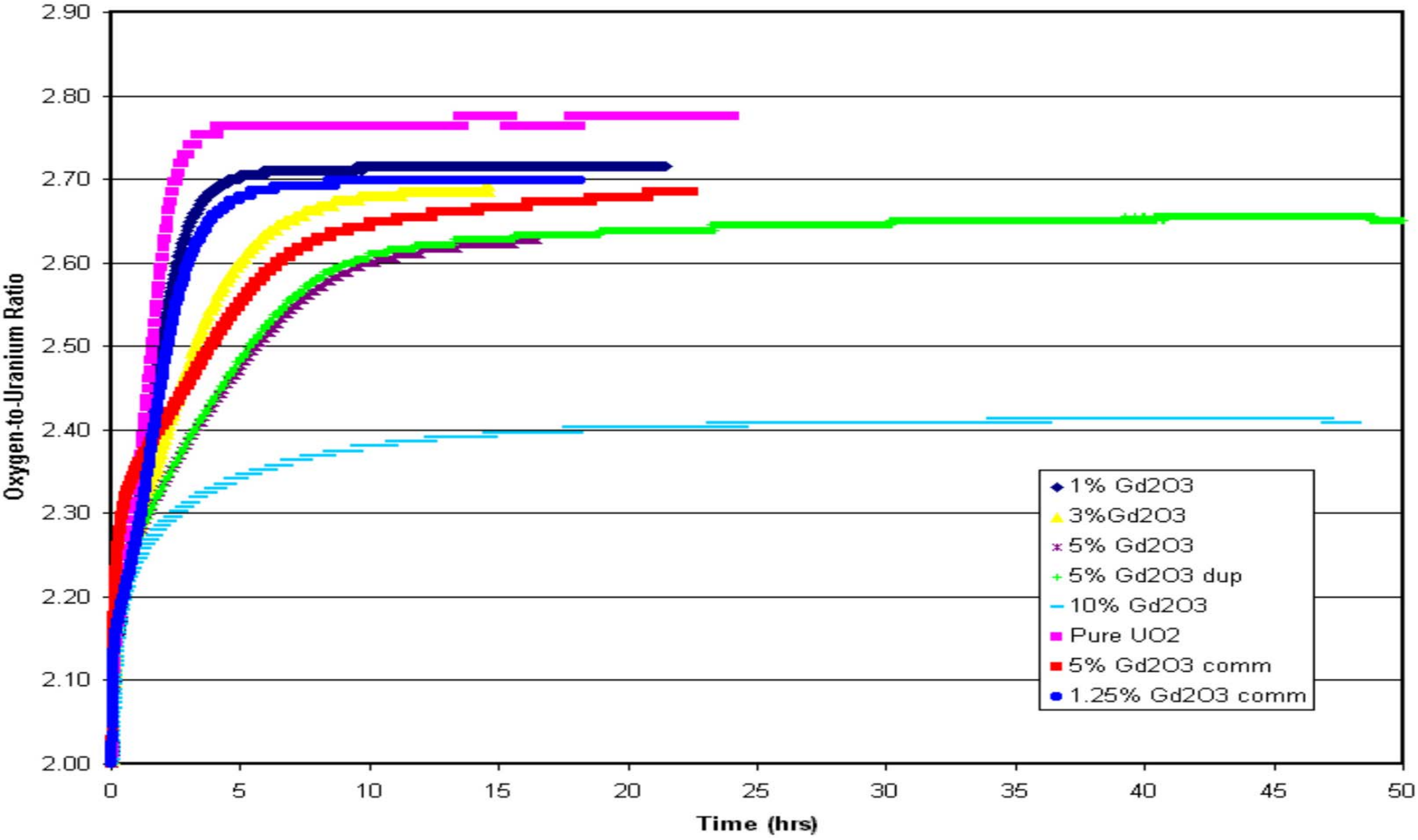
⇓

Sinter for 24 hours at 1570°C under 4% H_2

ISOTHERMAL TGA OF La-DOPED UO_2 AT 325°C

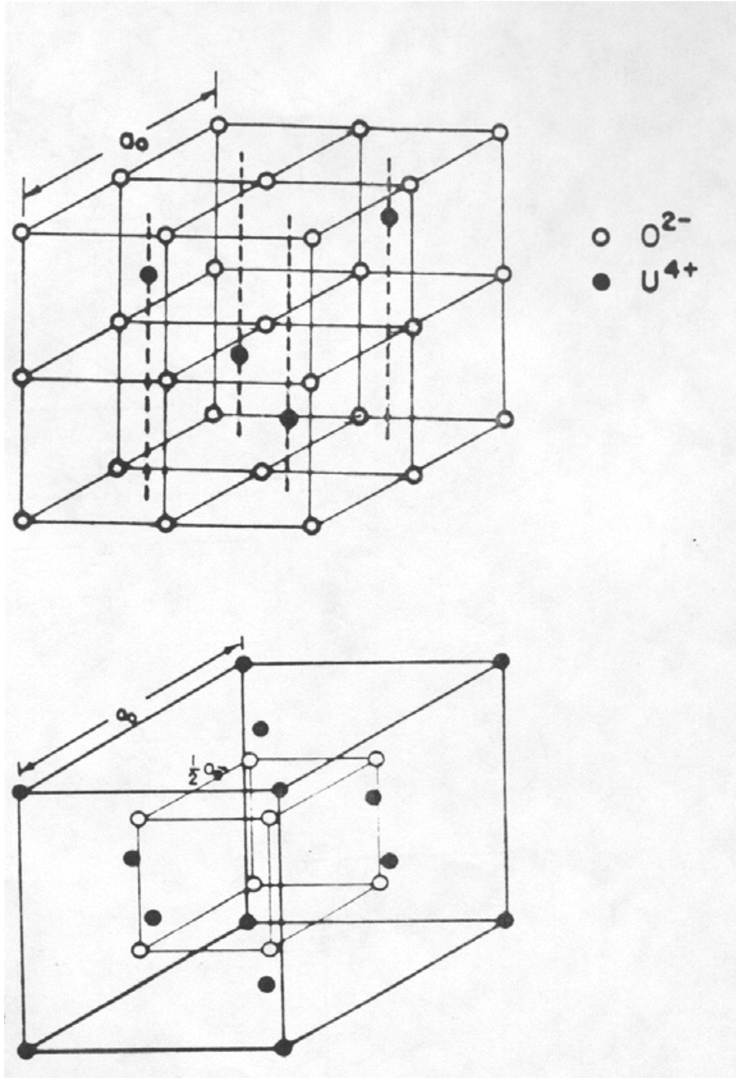


ISOTHERMAL TGA OF Gd-DOPED UO_2 AT 325°C



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_4O_9 has 14 U ion clouds**
    - **At 10 wt% Gd_2O_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+} (or possible oxygen vacancy)**



CONCLUSIONS

- **CSNF oxidation is primarily a function of T, Burnup, grain size**
- **Higher burnup fuels show significant resistance to U_3O_8 formation**
- **Lattice energy, charge blocking and electron transfer effects**
- **What are the implications for dissolution rate?**

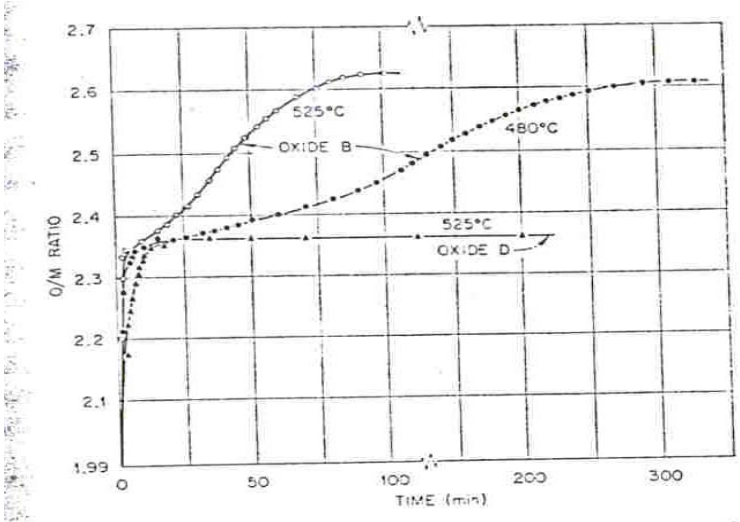


Fig. 3. Isothermal oxidation of (U,Pu)O_2, oxides B and D.

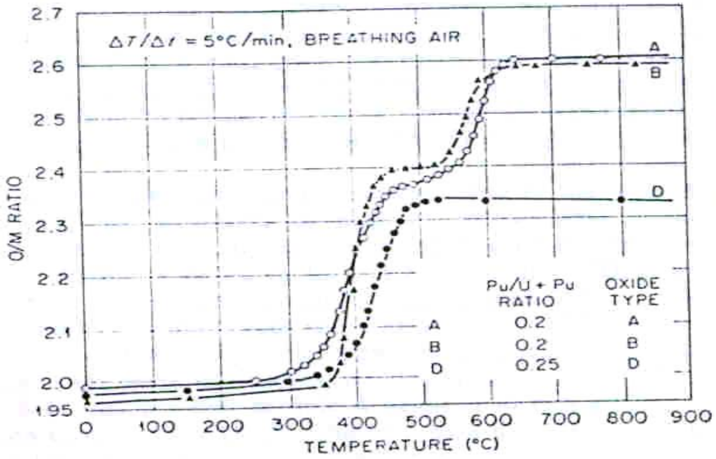


Fig. 6. Oxidation of (U,Pu)O_2, oxides A, B, and D, with programed heating.

Figures from Tennery and Godfrey, *J Am. Cer. Soc.* 56[3](1973)129-133