QA: NA

U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Dry Air Oxidation of Commercial Spent Nuclear Fuel

Presented to:
DOE/CEA Technical Exchange Meeting

Presented by:
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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

Einziger and Cook BREACHED LWR SPENT FUEL RODS

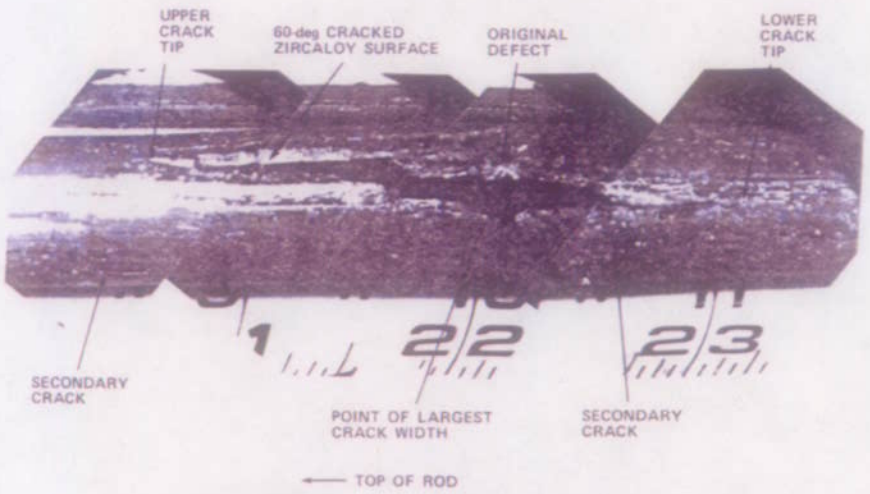
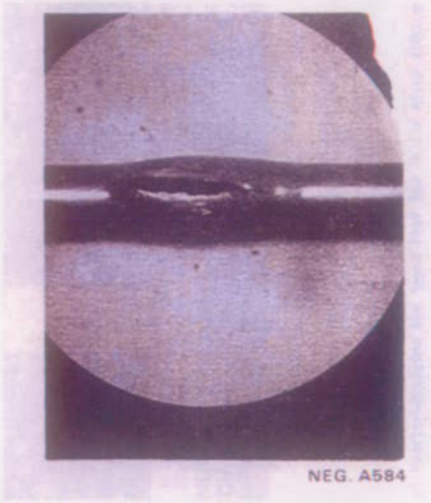
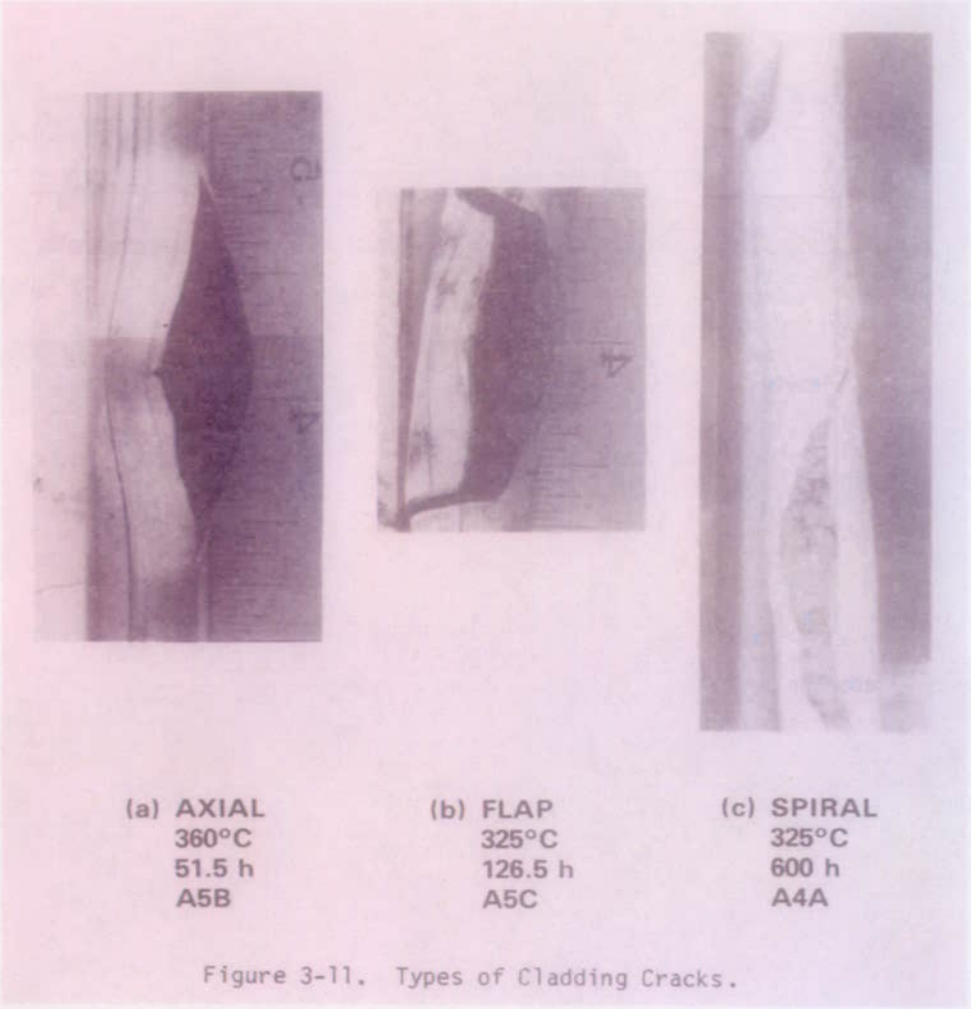


Fig. 4. Split defect 559 mm from the top of rod PB-PH462-E3 after 5962 h at 229°C in unlimited air.





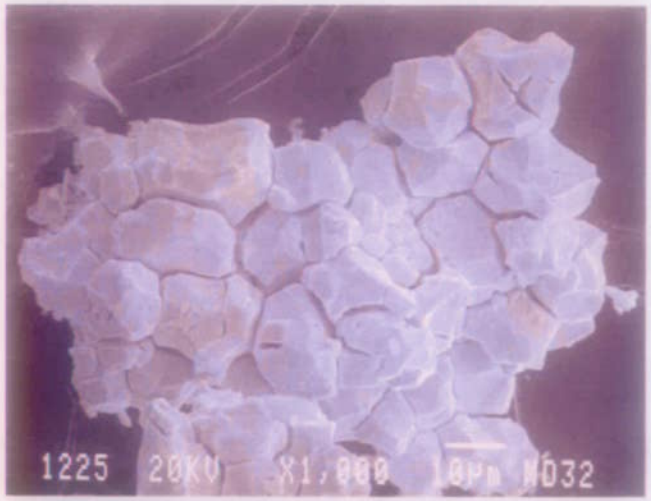
(a) AXIAL
360°C
51.5 h
A5B

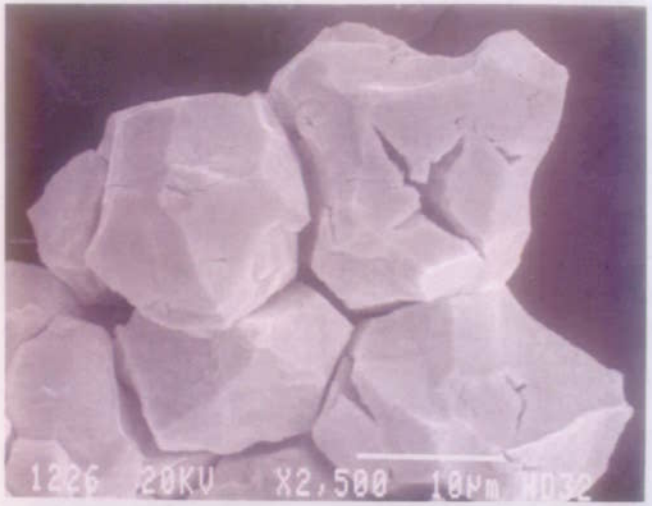
(b) FLAP
325°C
126.5 h
A5C

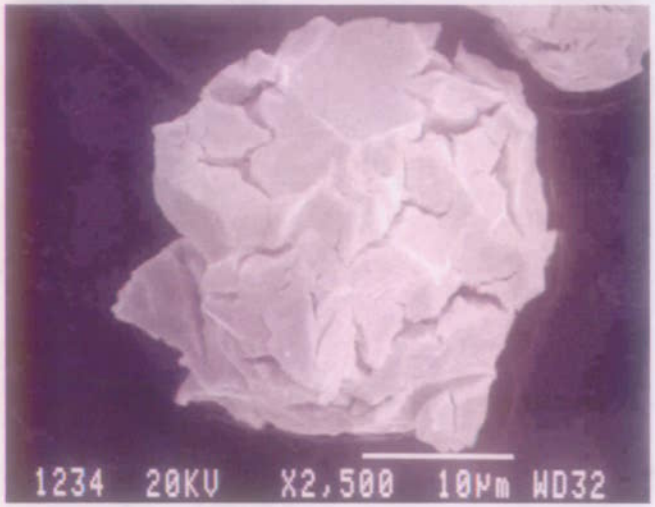
(c) SPIRAL
325°C
600 h
A4A

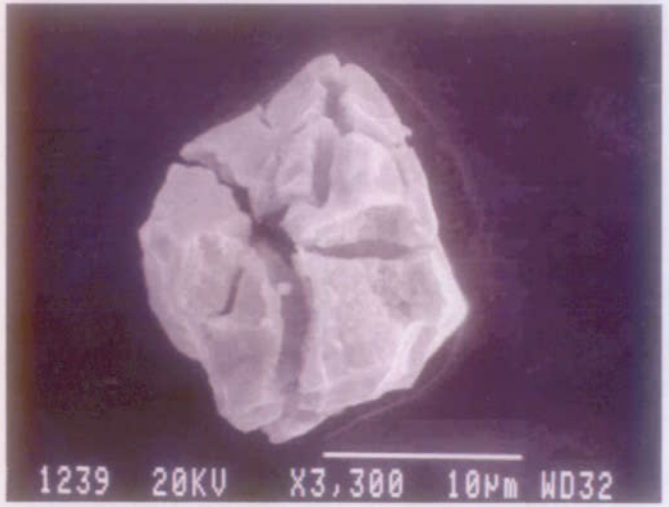
Figure 3-11. Types of Cladding Cracks.

OXIDATION INCREASES SURFACE AREA





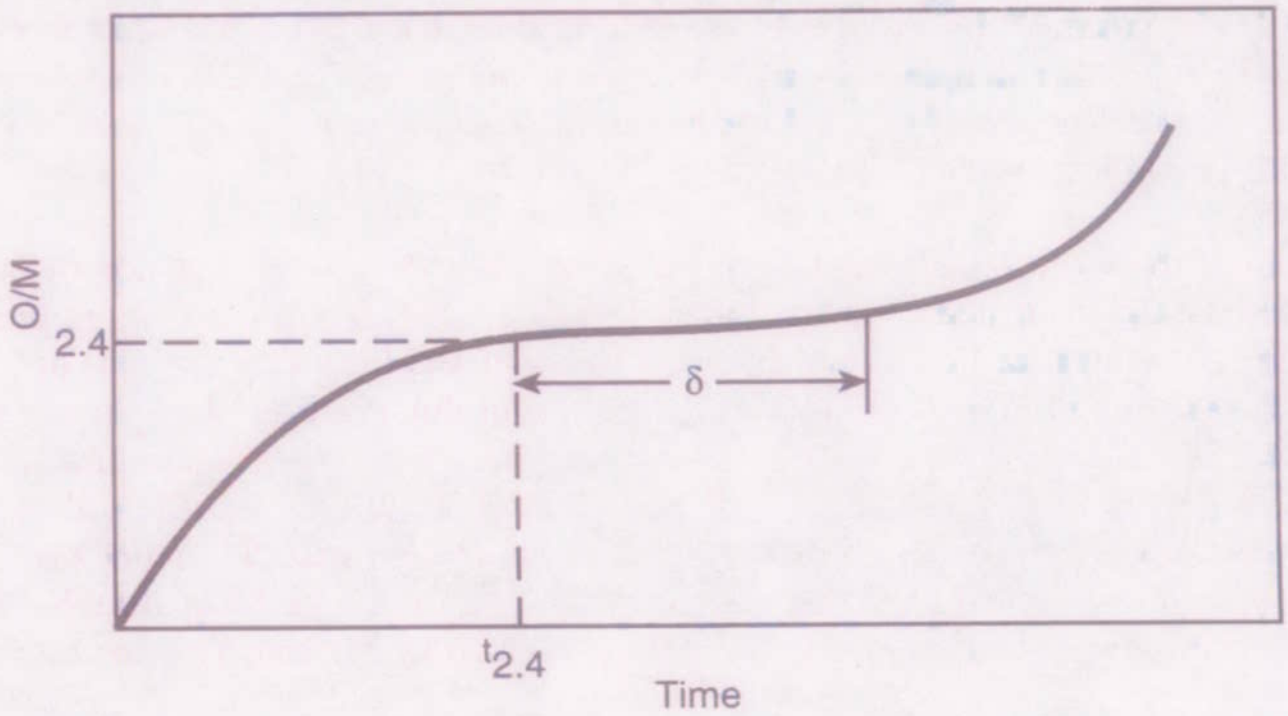




Opens grain boundaries and can release volatile fission products

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)



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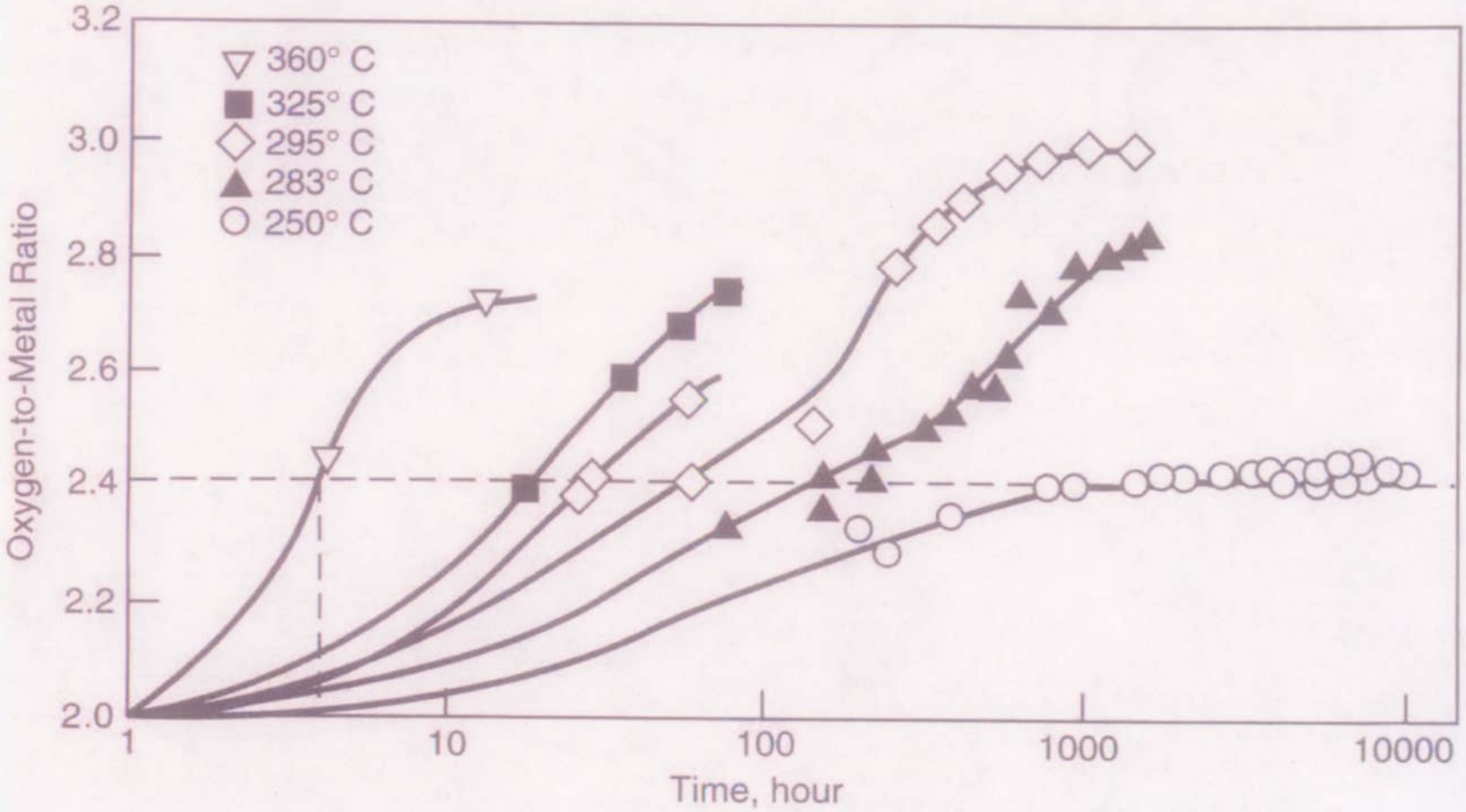
CSNF OXIDATION EXHIBITS STRONG TEMPERATURE DEPENDENCE



Turkey Point Fuel (Burnup~27 MWd/kgM), Bare fragment oxidation.

REVIEW OF UO_2/CSNF OXIDATION

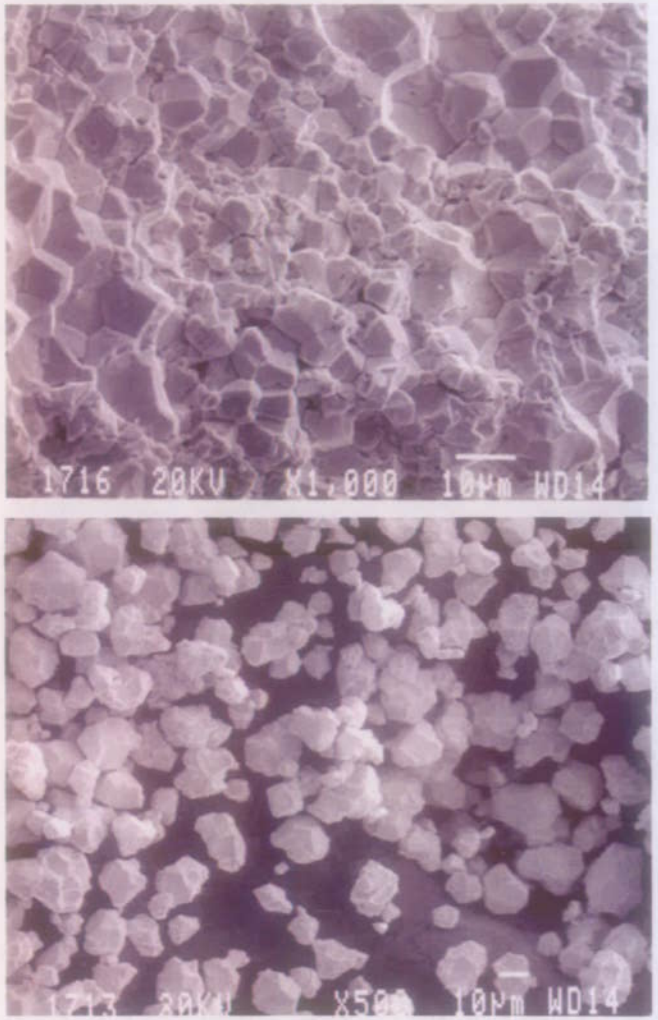
- Spent fuel oxidation differs from unirradiated UO_2
  - $UO_{2.4}$ phase (cubic) vs. U_3O_7 (tetragonal)
  - No "simultaneous" U_3O_8 formation, i.e., "plateau" behavior
  - 5 to 50 times faster initial oxidation rate (open grain boundaries, but Gd-doped unirradiated exhibits the same behavior

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?)

$$UO_2 \Rightarrow U_4O_9 \Rightarrow U_3O_8$$

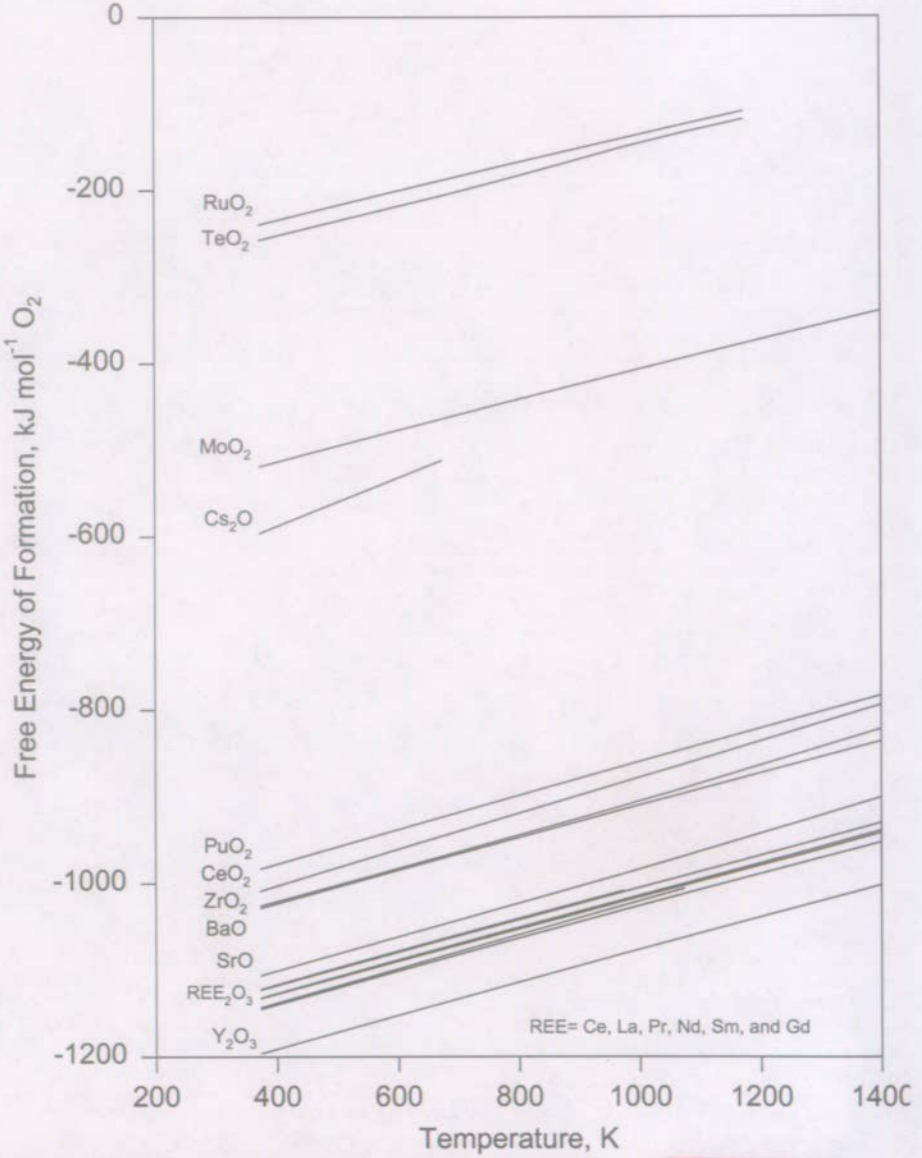
- Possible intermediate phases
- Grain-size dependence
- Arrhenius temperature dependence
- Resistance to further oxidation at lower temperatures (plateau behavior)
- Oxidation to U_3O_8 (O/M~2.70-2.75) which is ~30% less dense



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



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

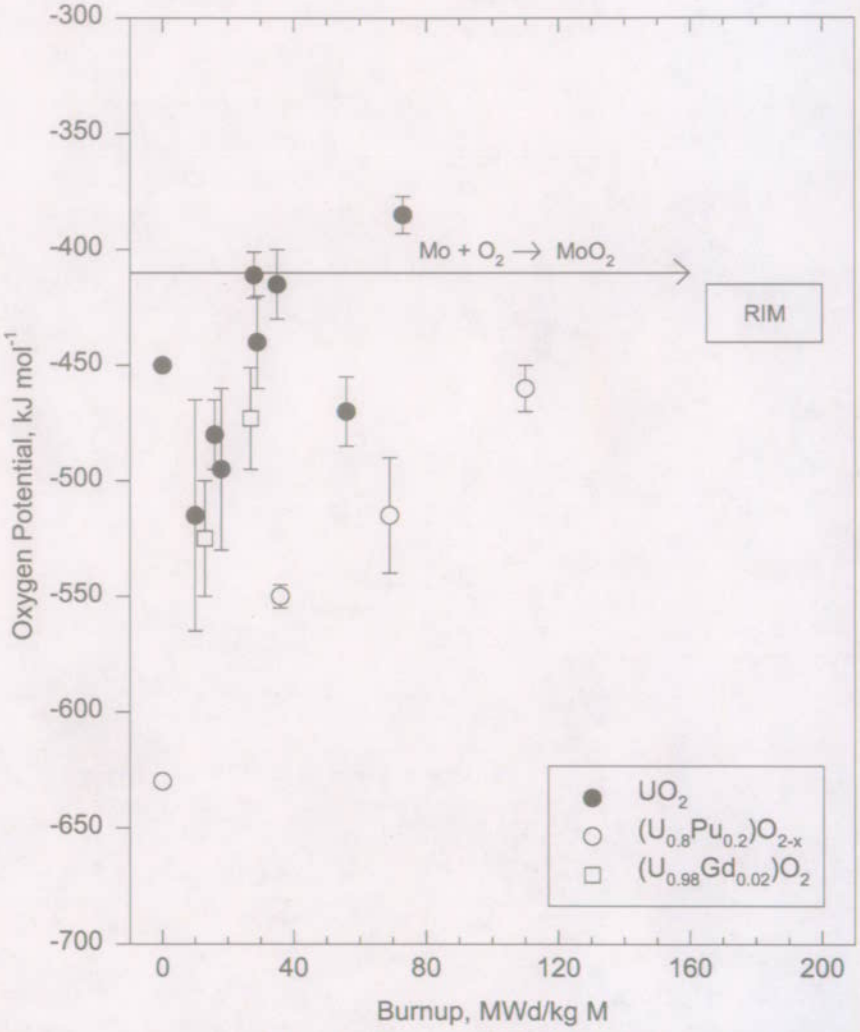
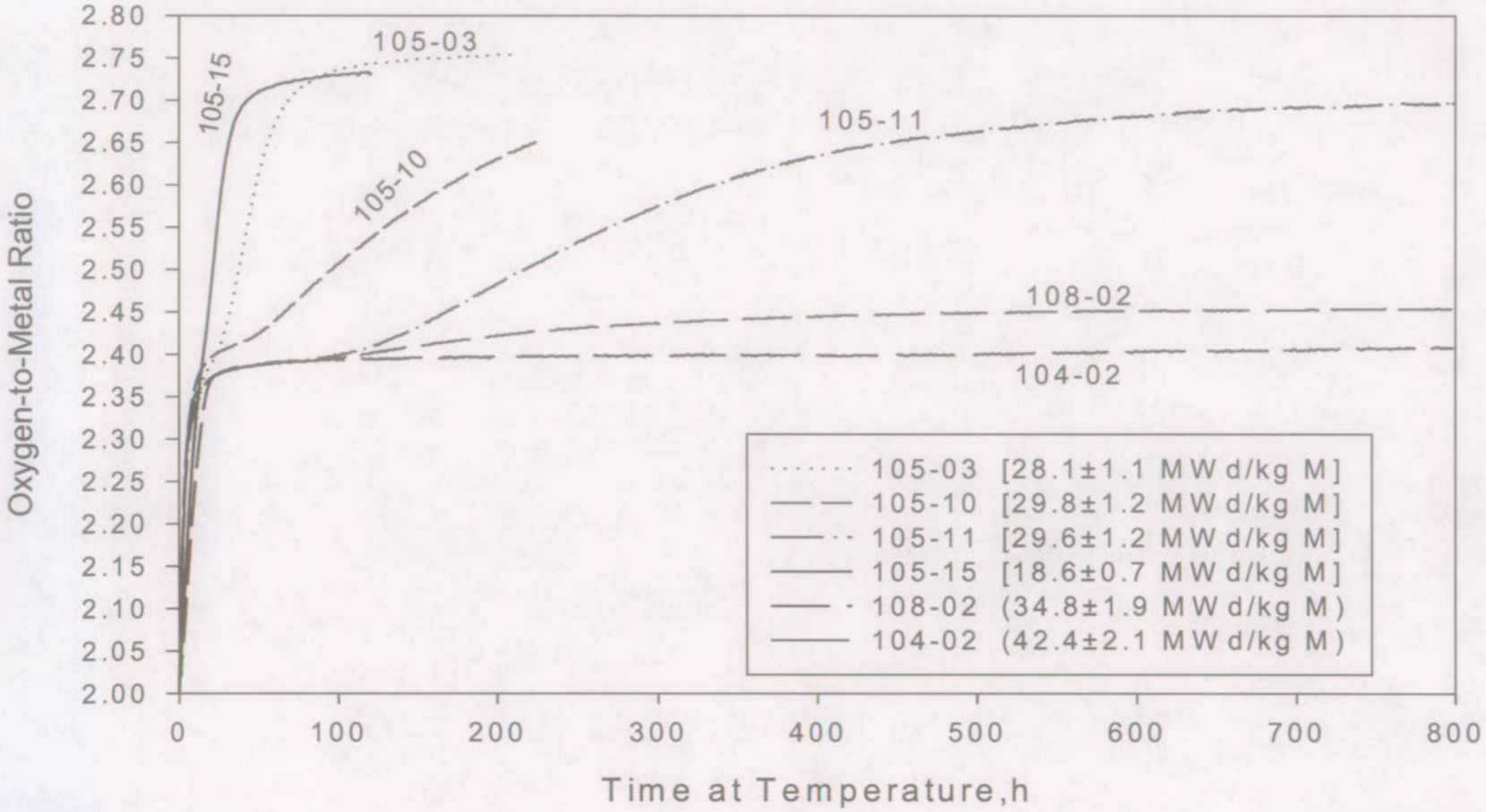


Figure from Matzke, JNM 223(1995)1-5
T=750°C

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}

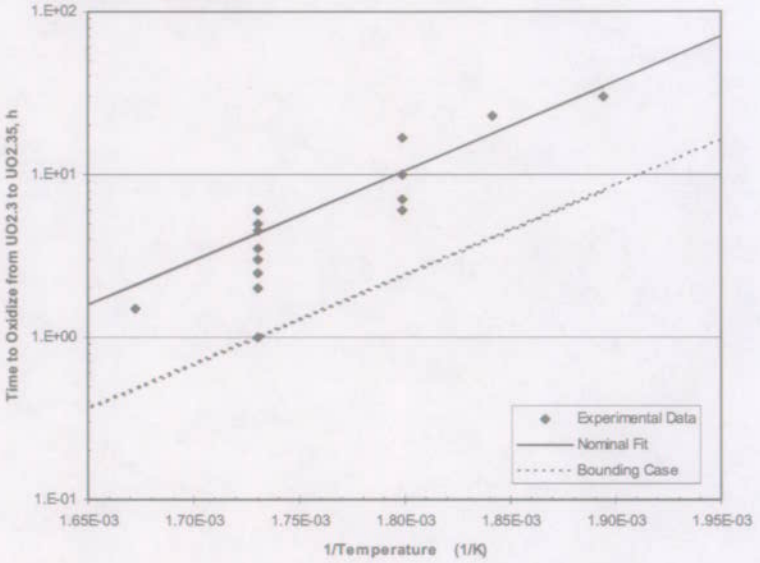
Bounding Case: 2.93×10^{-9}

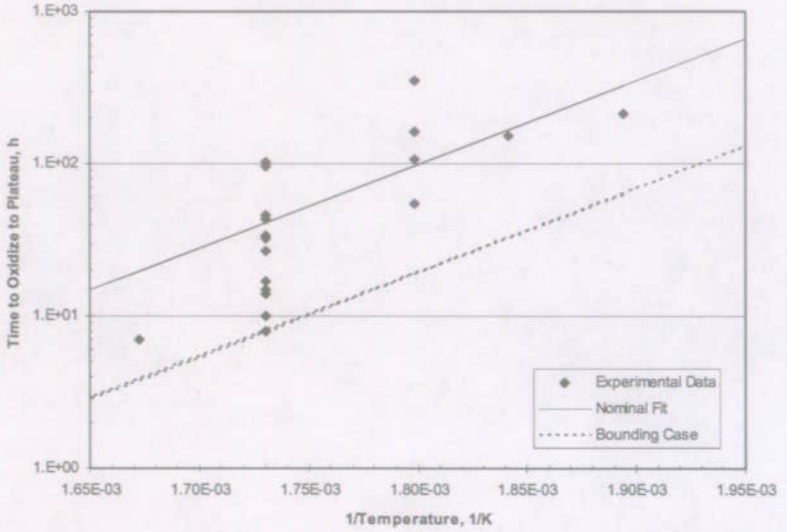
Q_{24} is the activation energy (105 kJ mol^{-1})

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.





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

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

$t_{2.75}$ 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 mo^{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)).

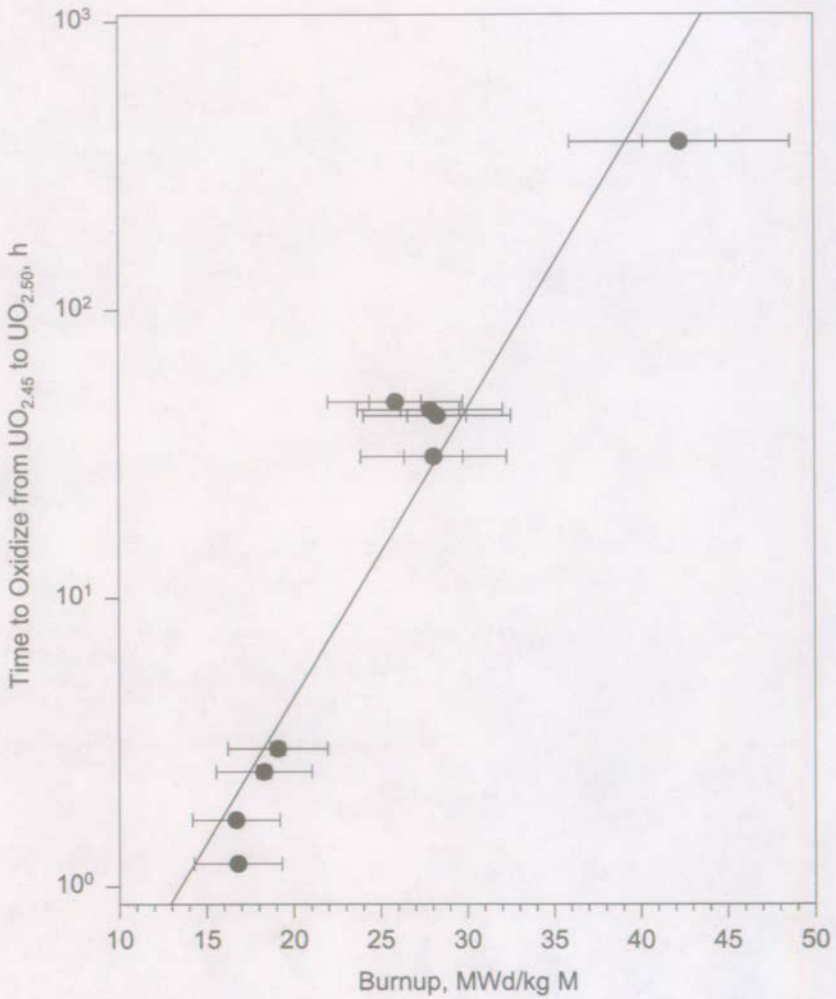


Figure 5.11. Time to Oxidize LWR Fragments from $UO_{2.45}$ to $UO_{2.50}$ at 305°C as a Function of Burnup (Burnup from ^{137}Cs Analysis)

RESONANCE ABSORPTION ⇒ HBS

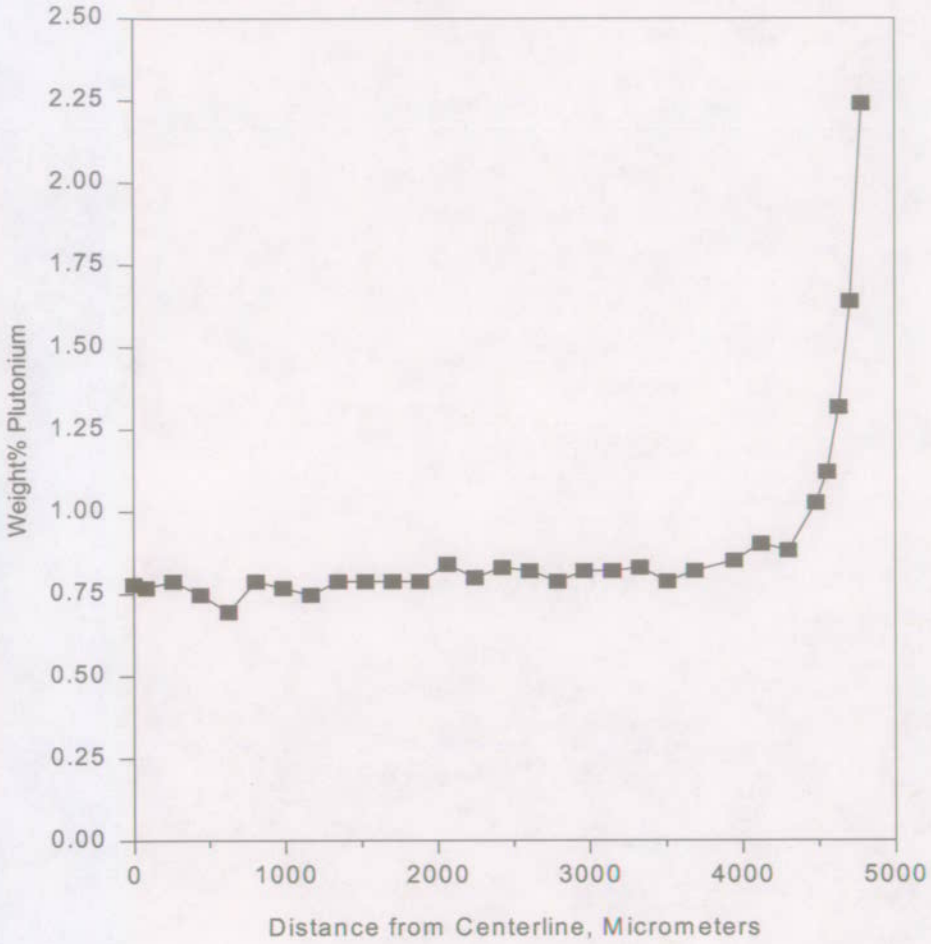


Figure 2.4. Radial Profile of Plutonium in ATM-104 Fuel Measured by EPMA [69]

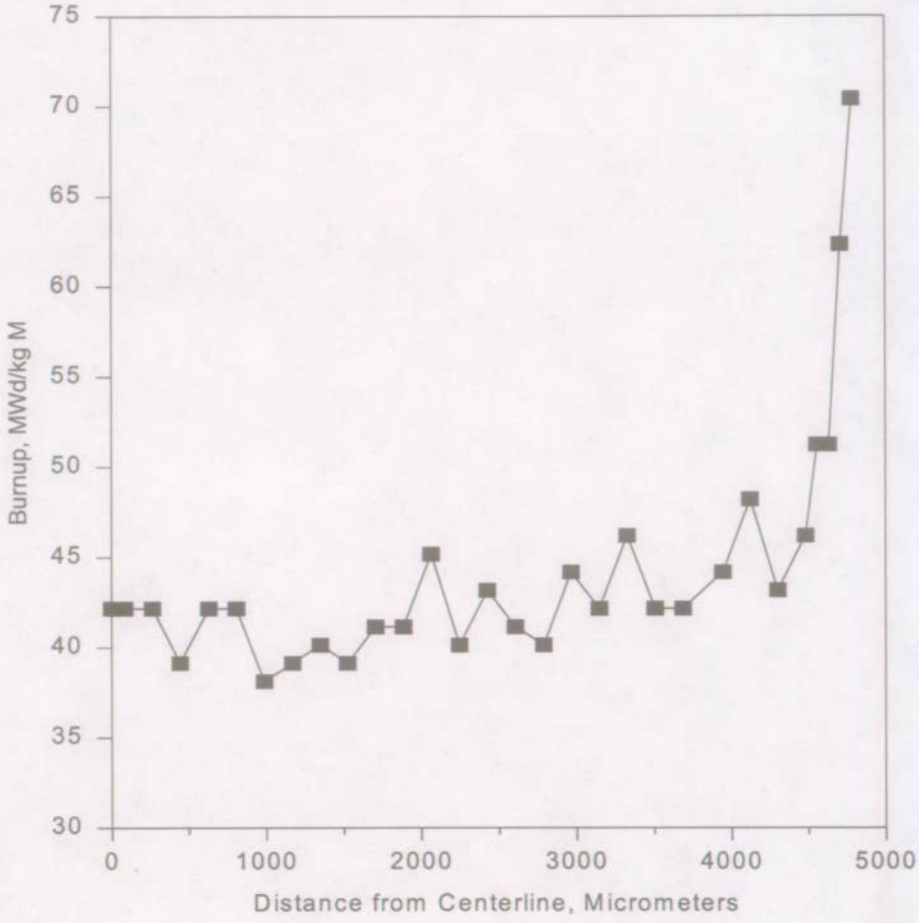


Figure 2.5. Radial Burnup Profile in ATM-104 Fuel with a Pellet Average Burnup of 44.3 MWd/kg M Measured by EPMA [69]

CUMULATIVE ELEMENTAL YIELDS (%)

Z	Element	^{235}U	^{239}Pu	^{241}Pu
37	Rb	3.88	1.60	1.16
38	Sr	9.35	3.45	2.52
39	Y	4.82	1.69	1.22
40	Zr	36.76	21.03	16.58
42	Mo	24.47	22.96	19.92
43	Tc	6.07	6.16	6.08
44	Ru	11.44	17.83	20.04
45	Rh	3.03	6.94	6.73
46	Pd	1.60	15.79	22.44
52	Te	2.24	3.37	2.33
55	Cs	19.41	21.26	20.67
56	Ba	12.90	12.86	13.31
57	La	6.36	5.54	6.22
58	Ce	12.05	10.31	10.48
59	Pr	5.79	5.29	4.91
60	Nd	20.72	16.22	18.03
62	Sm	4.17	4.84	5.77
63	Eu	0.16	0.36	0.54
64	Gd	0.06	0.41	0.66

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?

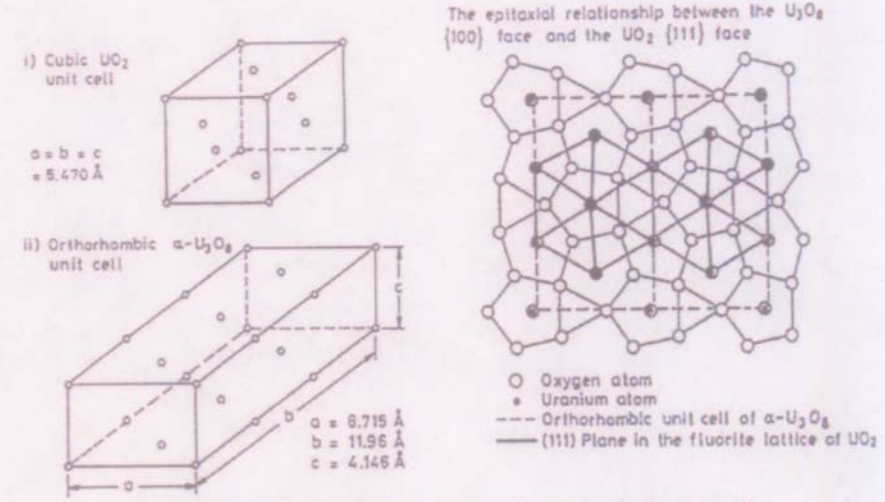


Fig. 1. Comparison of the UO_2 and α-U_3O_8 unit cells (to same scale).

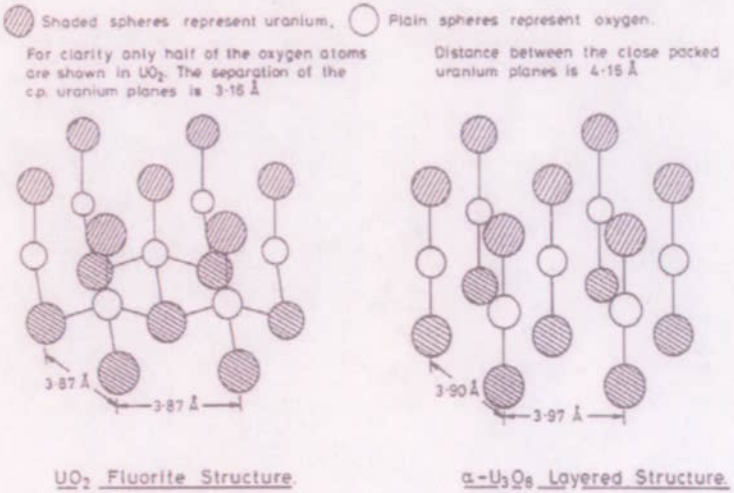


Fig. 2. The oxygen concentration and packing sequence of the atoms in UO_2 and α-U_3O_8.

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

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

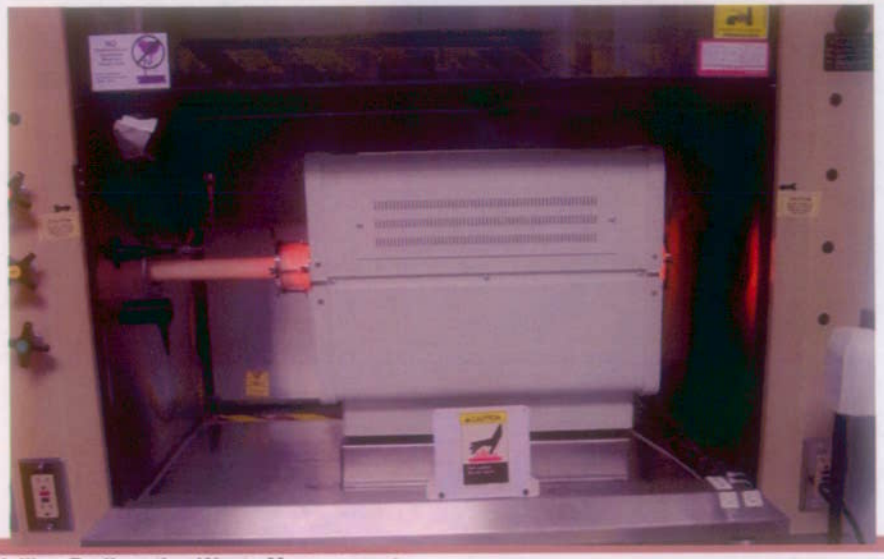
⇒

Prepress pellets at 83 MPa

Crush & sieve

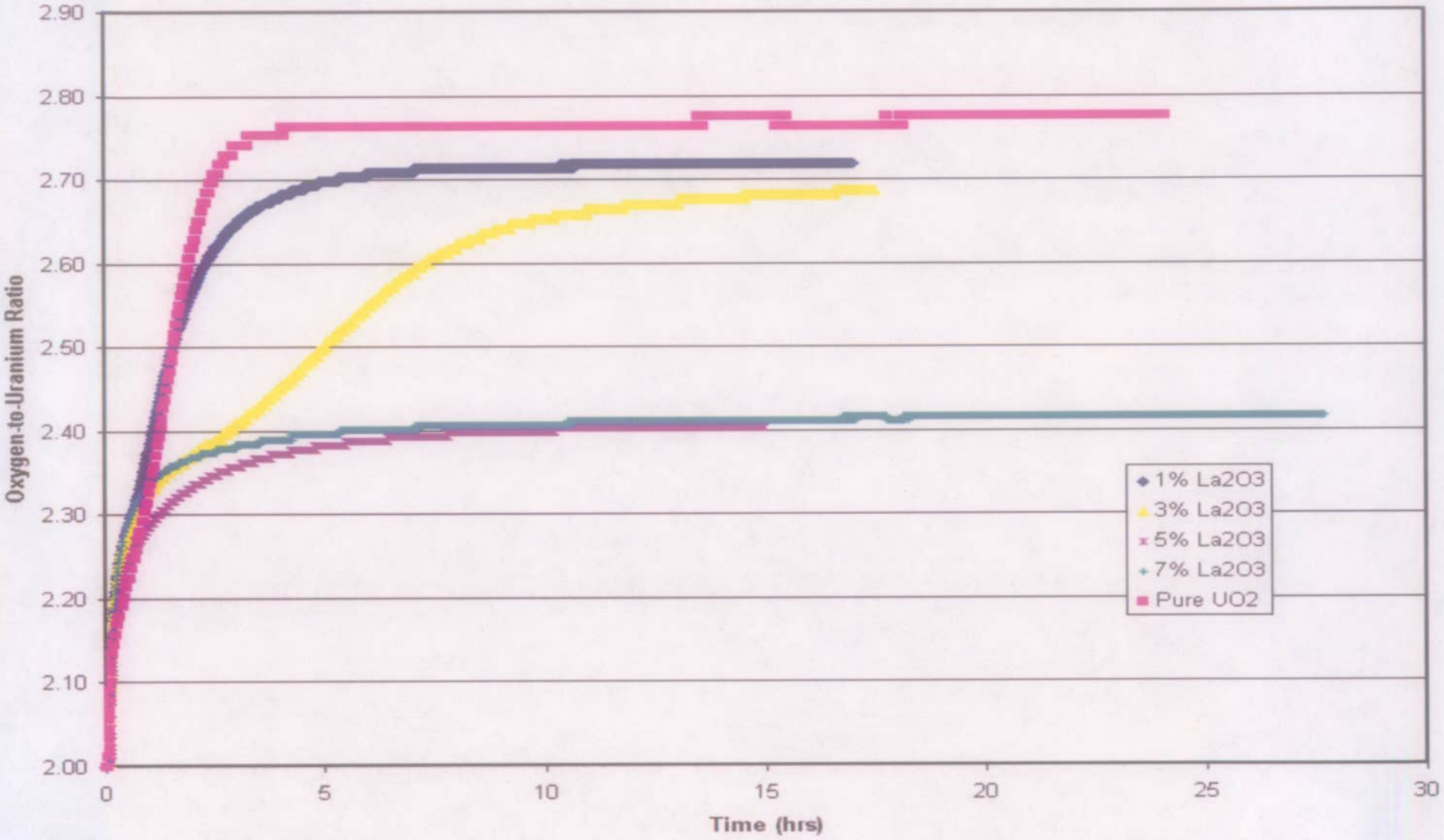
Press at 500 MPa

⇓

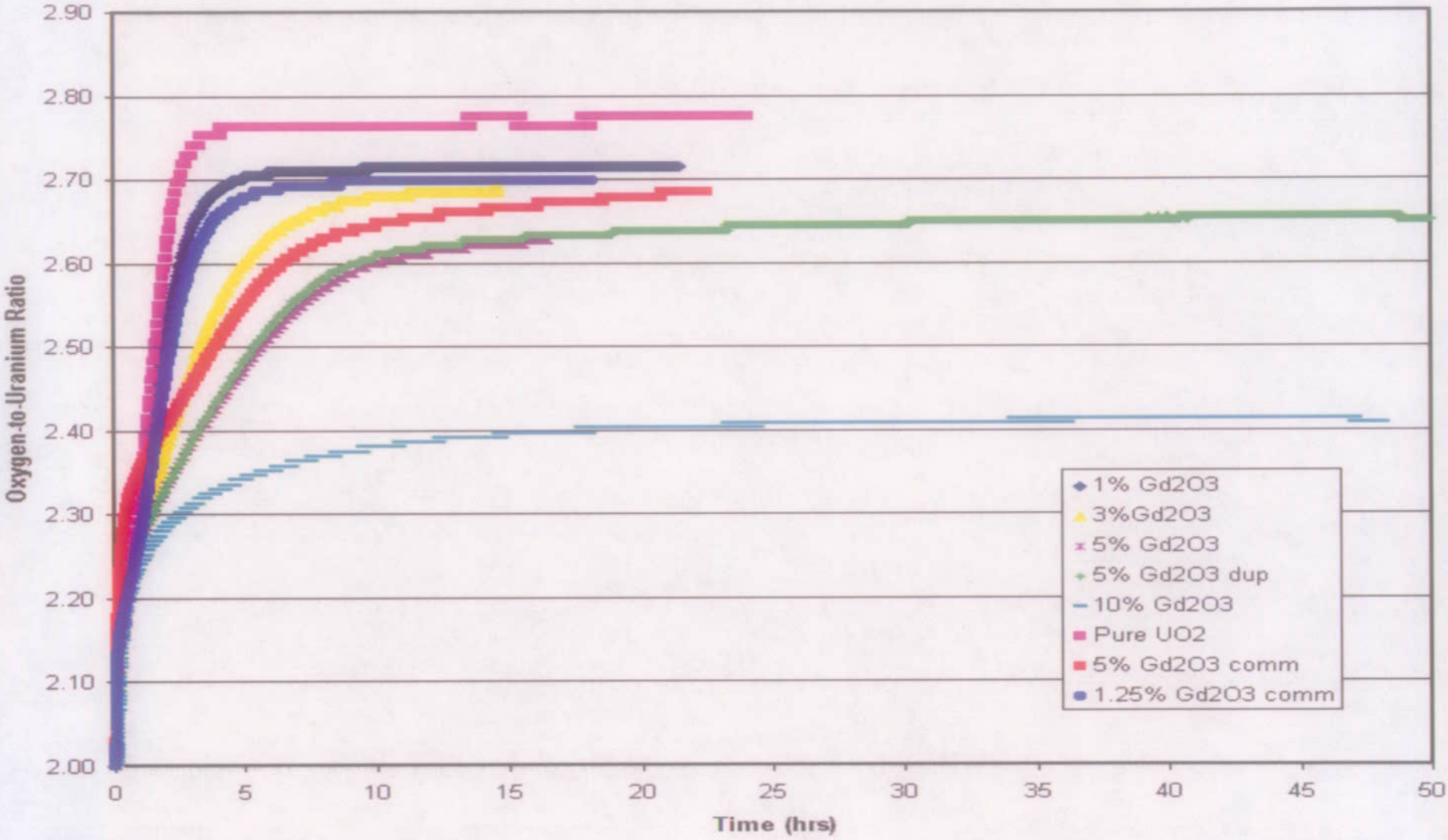


Sinter for 24 hours at 1570°C under 4% H_2

ISOTHERMAL TGA OF La-DOPED UO_2 AT 325°C

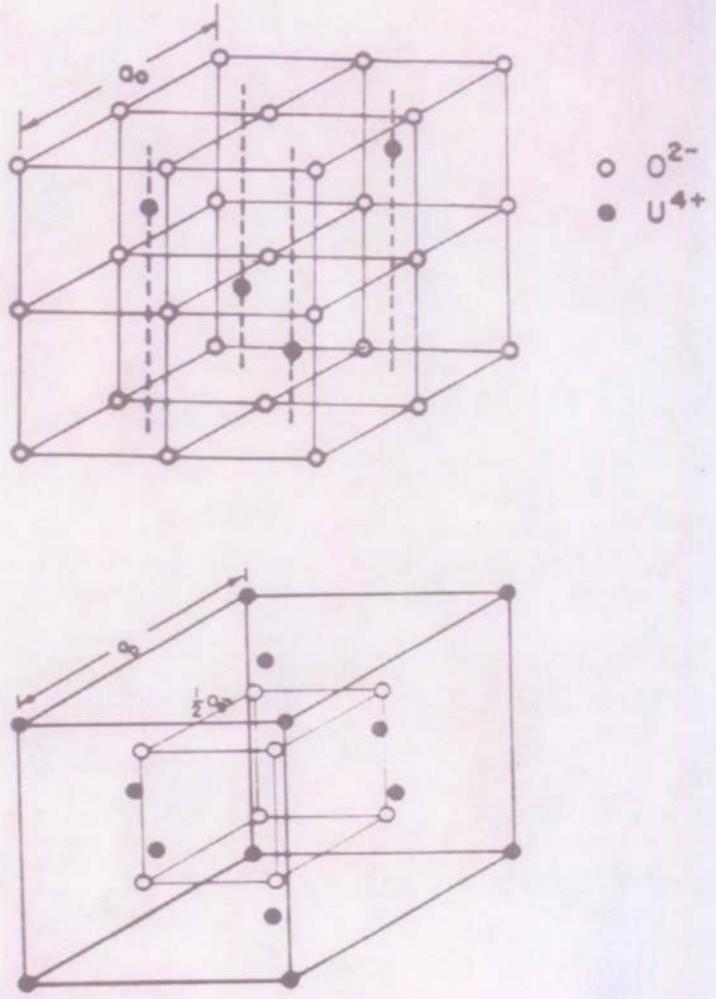


ISOTHERMAL TGA OF Gd-DOPED UO_2 AT 325°C



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+}



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?

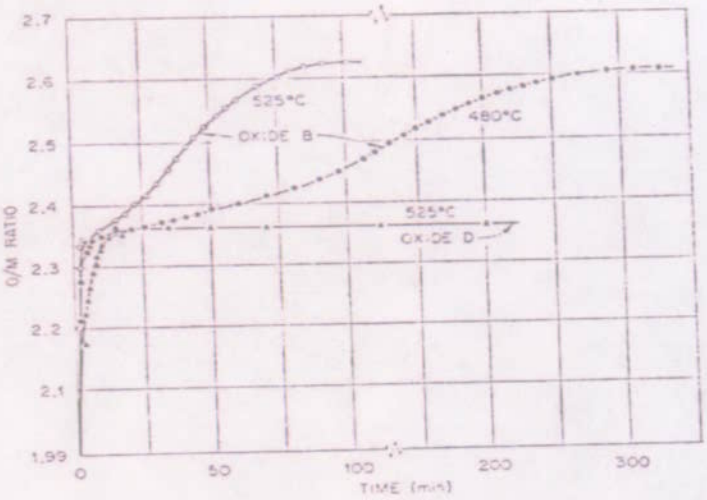


Fig. 3. Isothermal oxidation of $(U,Pu)O_2$, oxides B and D.

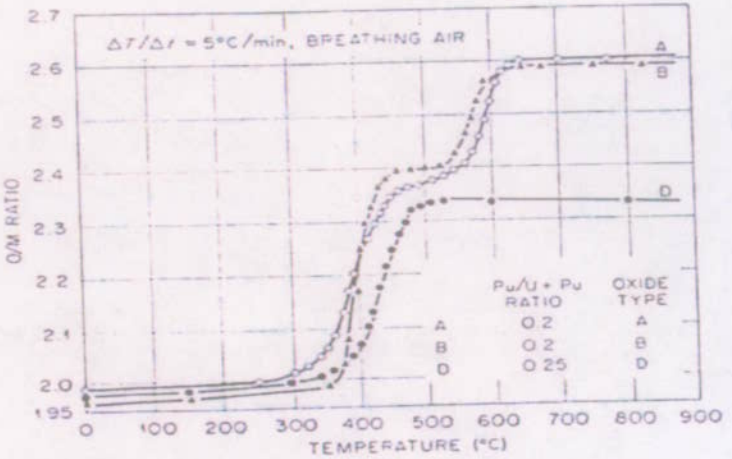


Fig. 6. Oxidation of $(U,Pu)O_2$, oxides A, B, and D, with programed heating.

Figures from Tennery and Godfrey, JACS 56[3](1973)129-133