

Chapter 12

Behavior of Solid Fission Products in Oxide Fuel Elements

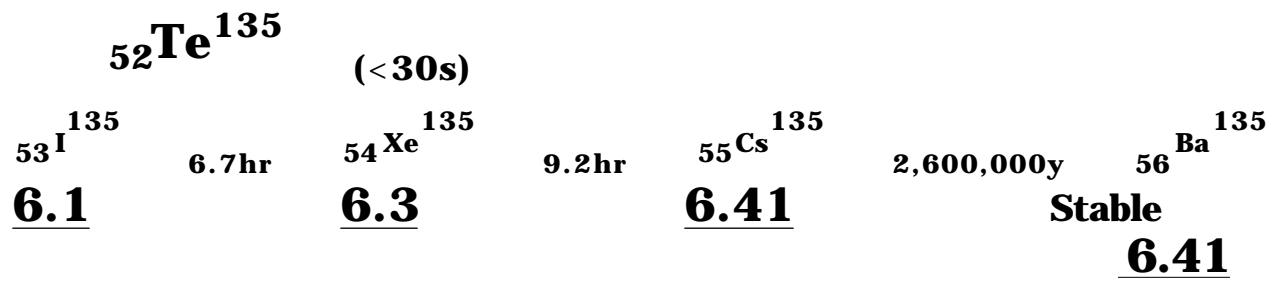
Why are fission products so important?

- 1.) They influence the availability of oxygen
- 2.) Their volume is different
- 3.) Fission gases like Xe and Kr escape increasing pressure in fuel
- 4.) Solid FP can change the thermal conductivity and melting point
- 5.) Gaseous FP can change the thermal conductivity of gas in gap.

Since target burnups are 10%, we can have as much as 20% in FP in the fuel

12.1 Elemental Yield of Fission Products From nuclear physics;

$$\begin{array}{ccc}
 & & Z \\
 & & | \\
 (\text{cy})_{ZM}^A & = & (\text{iy})_{Z'M}^A \\
 & & | \\
 & & Z' \\
 \text{Cumulative Yield} & & \text{Independent Yield}
 \end{array}$$



Chain Yield $Y_A = (\text{cy})_{zMA}$

Three Things effect the final distribution;

- 1.) Fissile isotope (note Pu shift)
- 2.) Neutron energy
- 3.) Neutron flux (burnout)

See figures, 12.2 and 3.16

Fission Product yield

Elemental Yield $Y_i = \frac{1}{F t_{\text{irr}}} N_{i,A}$

Fission Rate **Concentration of
element i resulting
from the decay chain at
mass # A**

Note also;

$$Y_i = 2$$

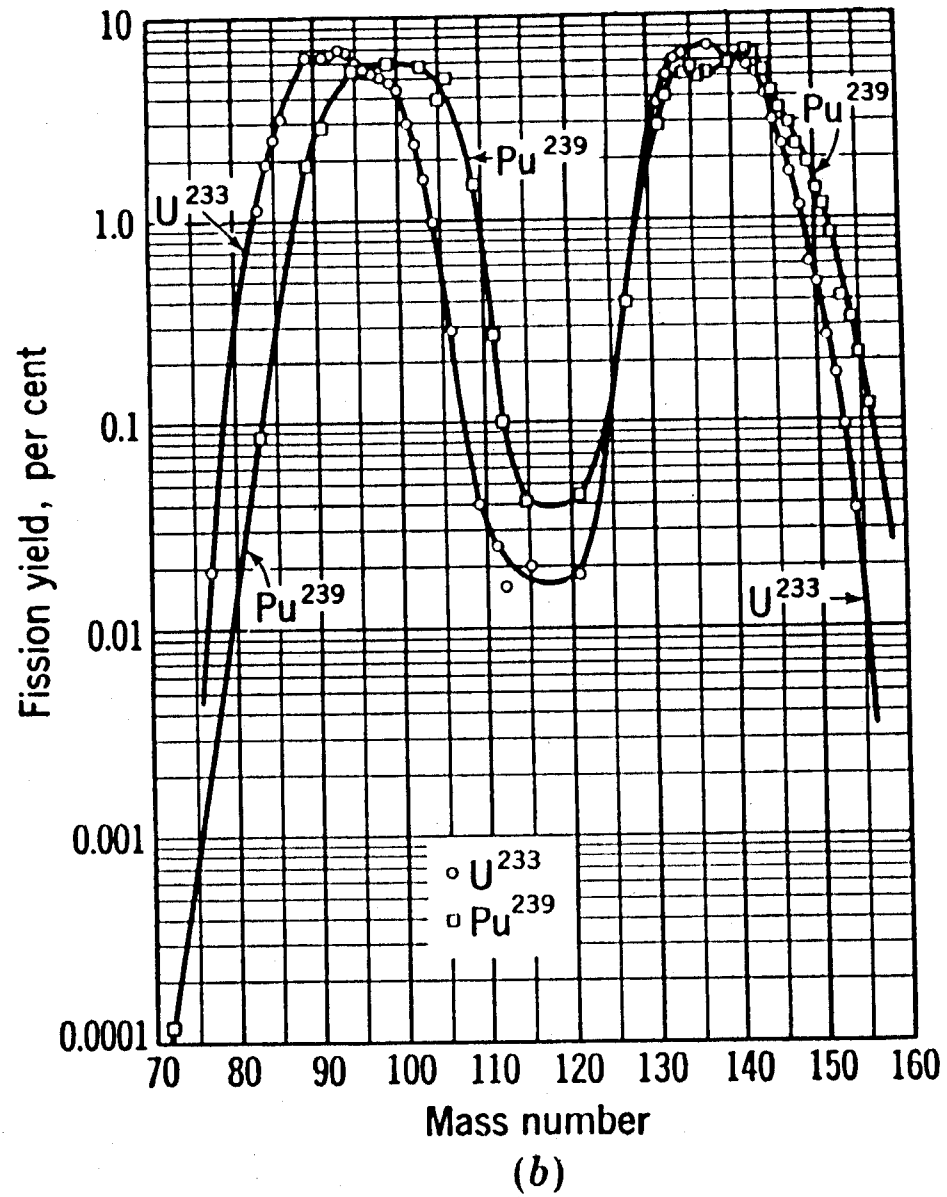
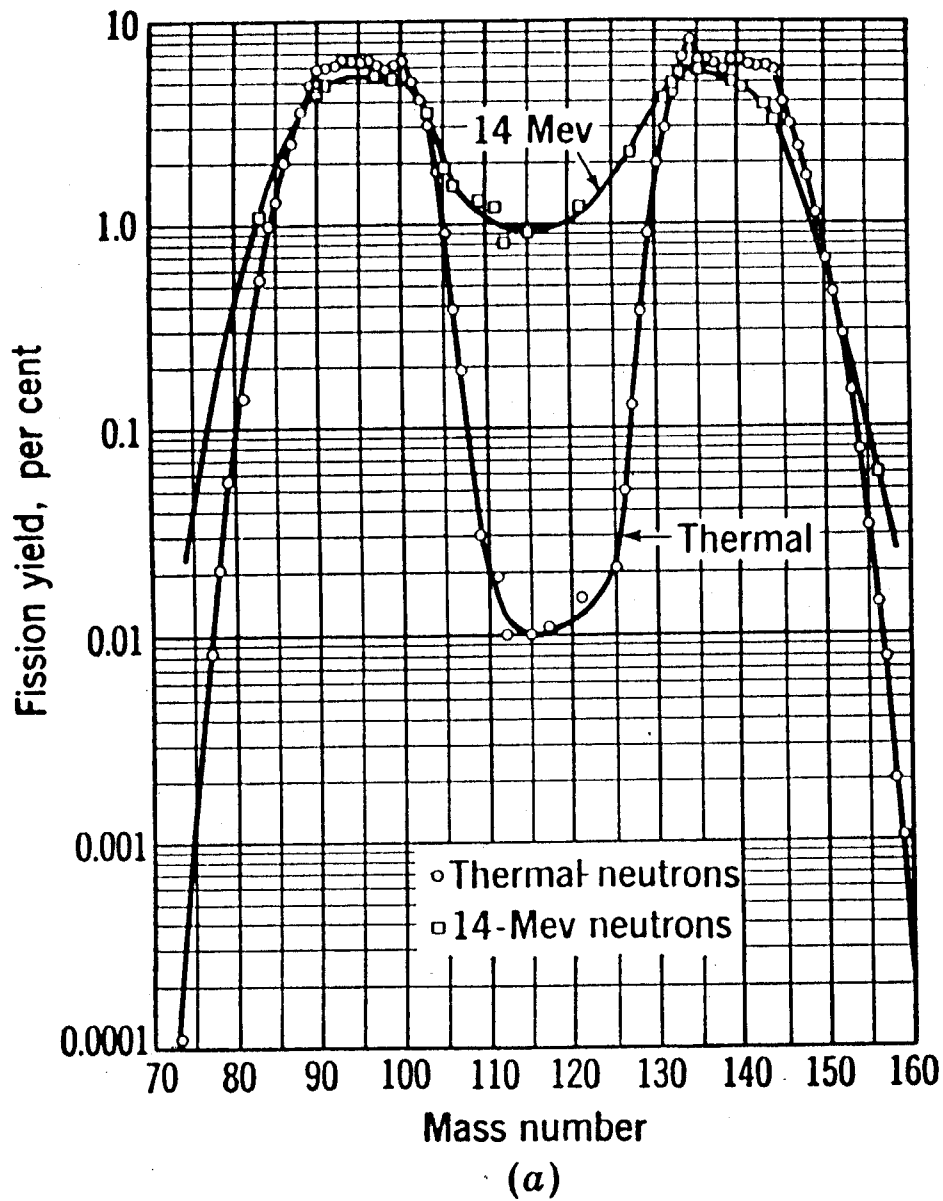


Fig. 3-16. Fission-product yield data for (a) U^{235} by thermal and 14-Mev neutrons and (b) U^{233} and Pu^{239} by thermal neutrons. (From Ref. 27.)

Table 12.1 Elemental Fission-Product Yields in a Fast-Neutron Spectrum

Chemical group	Elemental yield		
	$^{235}\text{U}^*$	$^{239}\text{Pu}^*$	15% $^{239}\text{Pu}^\ddagger$ 85% ^{238}U
Zr + Nb	0.298	0.204	0.219
Y + rare earths ‡	0.534	0.471	0.493
Ba + Sr	0.149	0.096	0.109
Mo	0.240	0.203	0.206
Ru + Tc + Rh + Pd	0.263	0.516	0.456
Cs + Rb	0.226	0.189	0.209
I + Te	0.012	0.070	
Xe + Kr	0.251	0.248	

*All elements with elemental yields greater than 1% are included. The groups shown in the table account for all but about 2% of the fission products. [After L. Burris and J. Dillon, Estimation of Fission Product Spectra in Discharged Fuel from Fast Reactors, USAEC Report ANL-5742, Argonne National Laboratory, June (1957).]

‡ J. H. Davies and F. T. Ewart, *J. Nucl. Mater.*, 41: 143 (1971).

‡ Lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, and gadolinium.

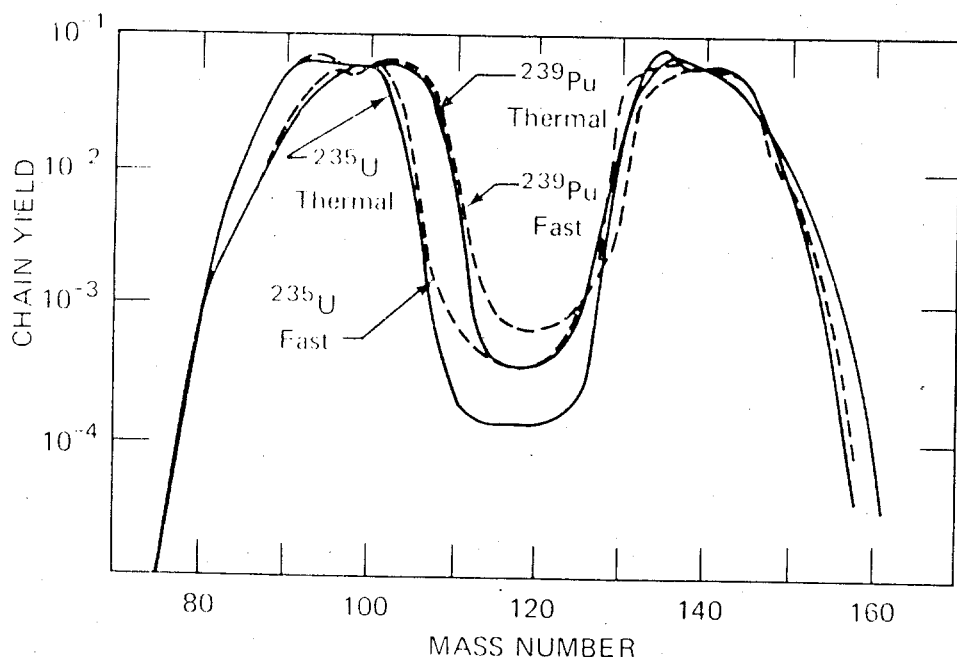


Fig. 12.2 Chain yields as a function of mass number of the chain for fast- and thermal-neutron flux spectra and for ^{235}U and ^{239}Pu . [From J. H. Davies and F. T. Ewart, *J. Nucl. Mater.*, 41: 143 (1971).]

One is not usually interested in the isotopes, but rather the elements. See Olander for a calculation of

$$Y_{Cs} = y_{133} + y_{135} + y_{137} \quad (\text{figure 12.1})$$

$$N_{Cs^{133}} = y_{133} \dot{F} t_{irr} \left[1 - \frac{\{1 - \exp[-\lambda_{Xe} t_{irr}]\}}{\lambda_{Xe} t_{irr}} \right]$$

Since $t_{1/2} = 5.3$ d for Xe_{133}

$$N_{Cs^{133}} \approx Y_{133} \dot{F} t_{irr} \quad \text{for times} > 5 \text{ days}$$

See table 12.1

Importance of Various FP's

- Zr + Nb**
 - Zr can combine with $O_2 \rightarrow ZrO_2$
 - Zr, Nb can take C away from UC
- Y + rare earths** • High crosssections, oxides
- Ba + Sr** • Sr radioactivity, zirconates
- Mo, Ru, Tc** • Volatile oxide, oxygen buffer
- Rh, Pd** • Reprocessing
- Cs + Rb** • Volatile, corrosive
- I + Te** • I is volatile, corrosive
- Xe + Kr** • Gases, pressure on cladding, thermal conductivity of gap

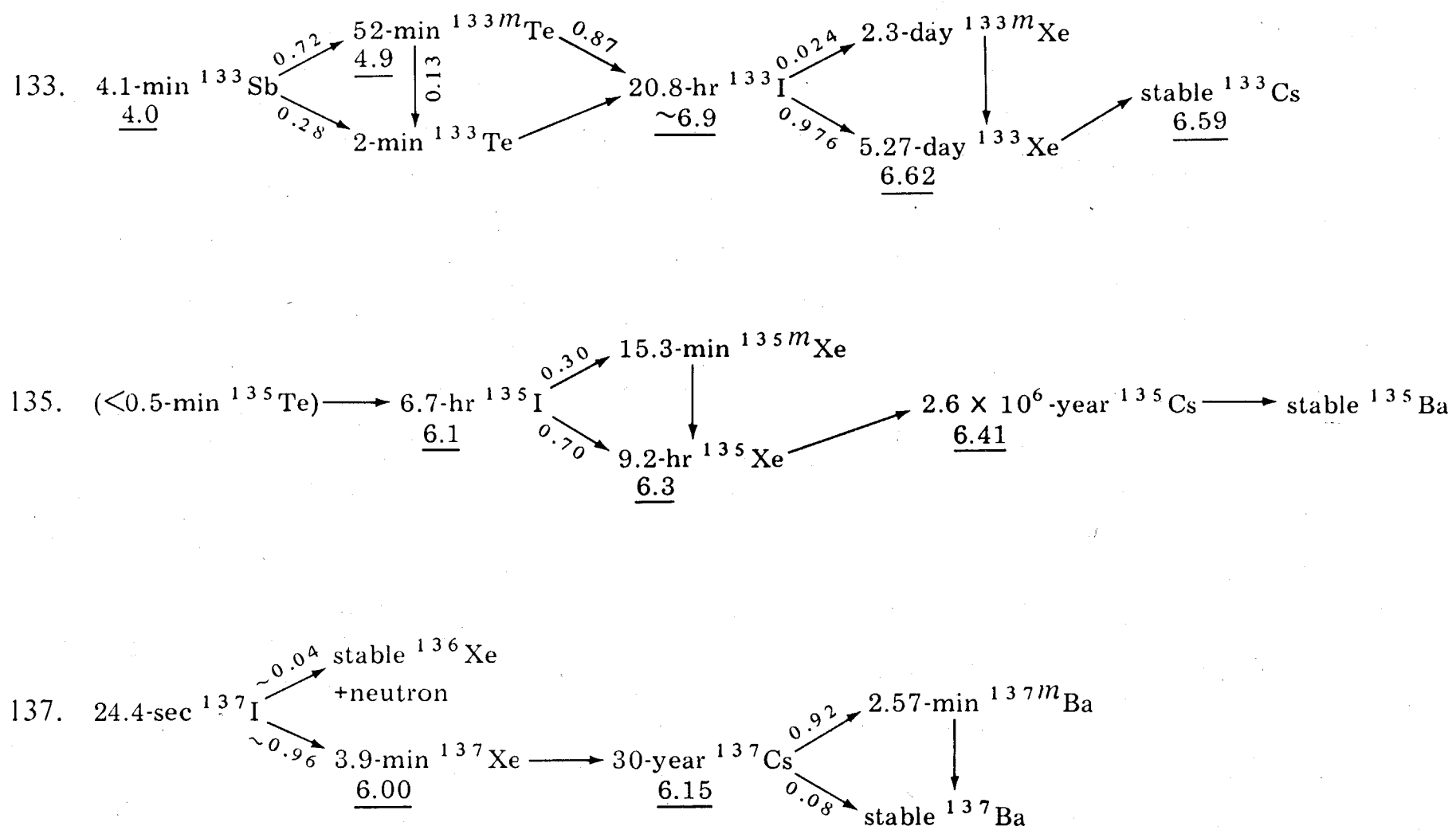


Fig. 12.1 Decay chains containing cesium (mass numbers 133, 135, and 137) from thermal-neutron fission of ^{235}U . Underlined numbers give the cumulative fission yields. The last yield of the chain represents the chain yield. Lower yields for earlier chain members may be due to (1) direct formation in fission of later chain members, (2) chain branching, or (3) experimental uncertainty. The last reason accounts for instances in which an early chain member has a higher yield than a subsequent member. Where more than one decay mode has been observed, the branching ratios are shown on the arrows. Parentheses indicate that the nuclide probably occurs in fission but has not been observed. [From S. Katkoff, *Nucleonics*, 18: 201 (1960).]

Fast ²³⁵U

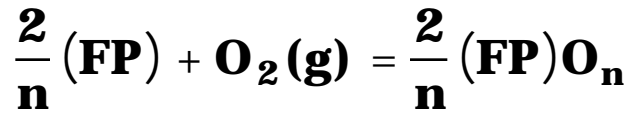
Fast (Mixed Oxide)

1.) Y + Rare Earths	Y + Rare Earths (0.493)
2.) Zr + Nb	Noble metals (0.456)
3.) Noble Metals	Xe + Kr (0.25)
4.) Xe + Kr	Zr + Nb (0.219)
5.) Mo	Cs + Rb (0.209)
6.) Cs + Rb	Mo (0.206)
7.) Ba + Sr	Ba + Sr (0.109)
8.) I + Te	I + Te (0.07)

12.3

Chemical State of Fission Products in Oxide Fuels

Big question is, Do the FP's form Oxides?



Valence of FP Cation = 2n

Key is the oxygen partial pressure

The oxygen partial pressure at which the element and oxide coexist comes from the Law of Mass Action

$$p_{\text{O}_2} = \exp \frac{G_{\text{FP}}^\circ}{RT}$$

where G_{FP}° = Free energy of formation of FP oxide at T, per mole of oxygen

If G is positive or only slightly negative, it will take a high p_{O_2} from the fuel to cause an oxide to form.

If G is strongly negative, then even small oxygen partial pressure from the fuel will form oxide

The oxides from $\text{UO}_{2\pm x}$ have oxygen potentials ranging from;

-170 kJ/mole (Hyper)

[Figure 11.12]

to - 670 kJ/mole (Hypo)

Figure 12.6

Figure 12.7

If the free energy of formation of the oxide is more negative than the fuel, then the oxide will form

If the free energy of formation of the oxide is less negative than the fuel, then the elemental form will remain.

Note the case for Mo:

The G_{FP} is close to stoichiometric fuel

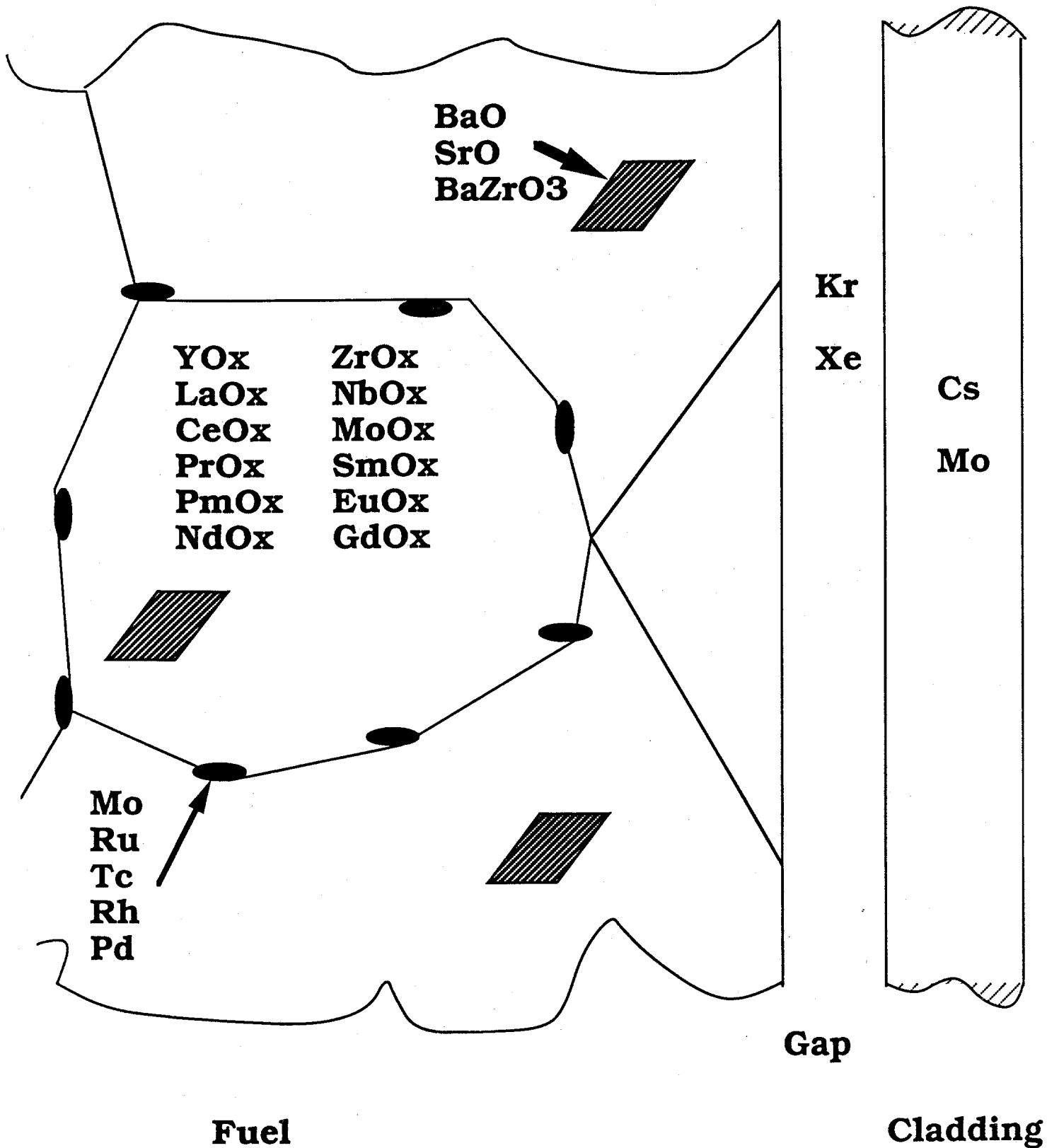
Hypo - Mo Metal

Hyper- MoO_2

Mo Can Buffer Oxygen Content

see Table 12.3

12.2 Physical State of Fission Products



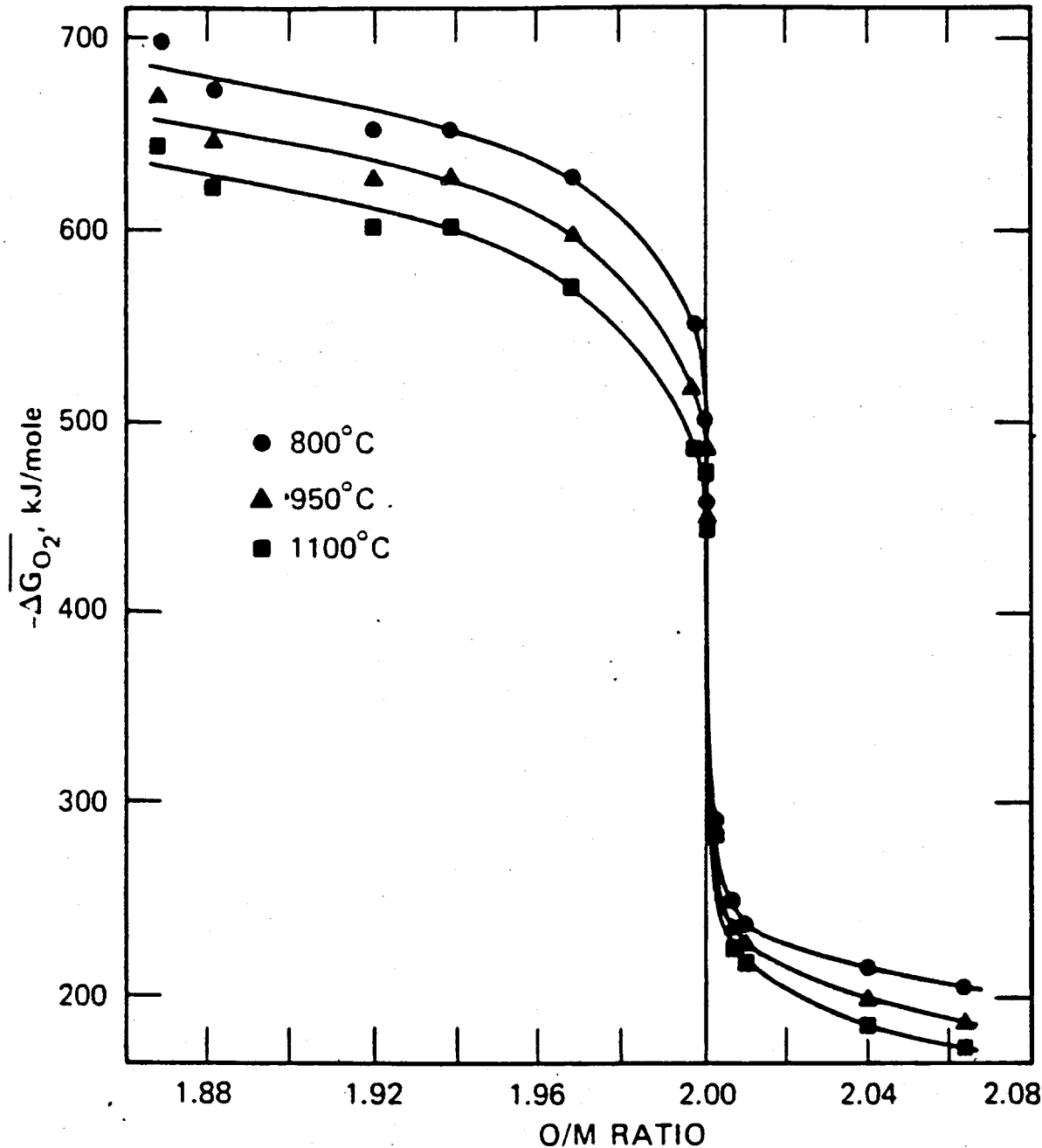


Fig. 11.12 $\overline{\Delta G_{O_2}}$ vs. O/M ratio for $U_{0.70}Pu_{0.30}O_{2 \pm x}$. (From T. L. Markin and E. J. McIver, *Plutonium 1965*, A. E. Kay and M. D. Waldron (Eds.), p. 845, Chapman and Hall, London, 1965.)

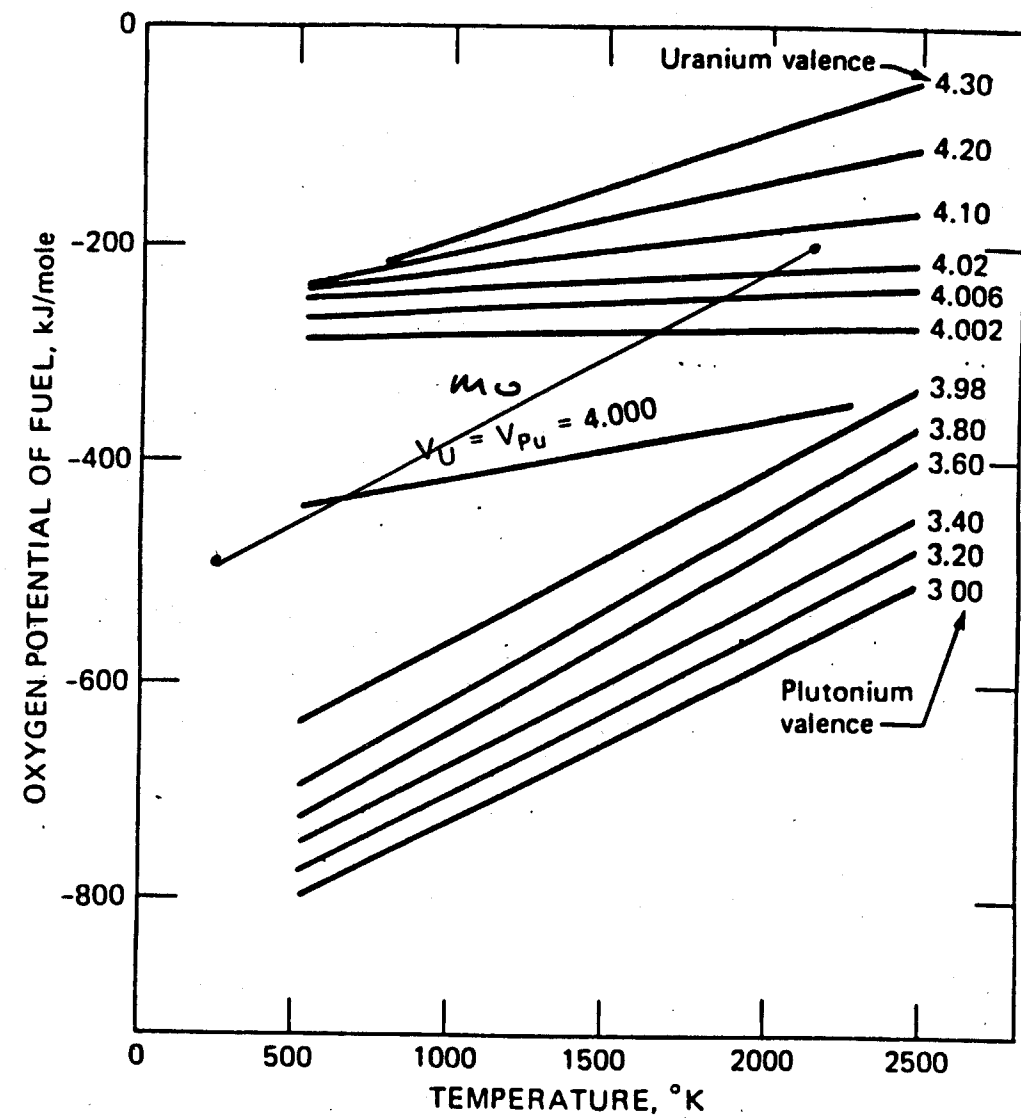
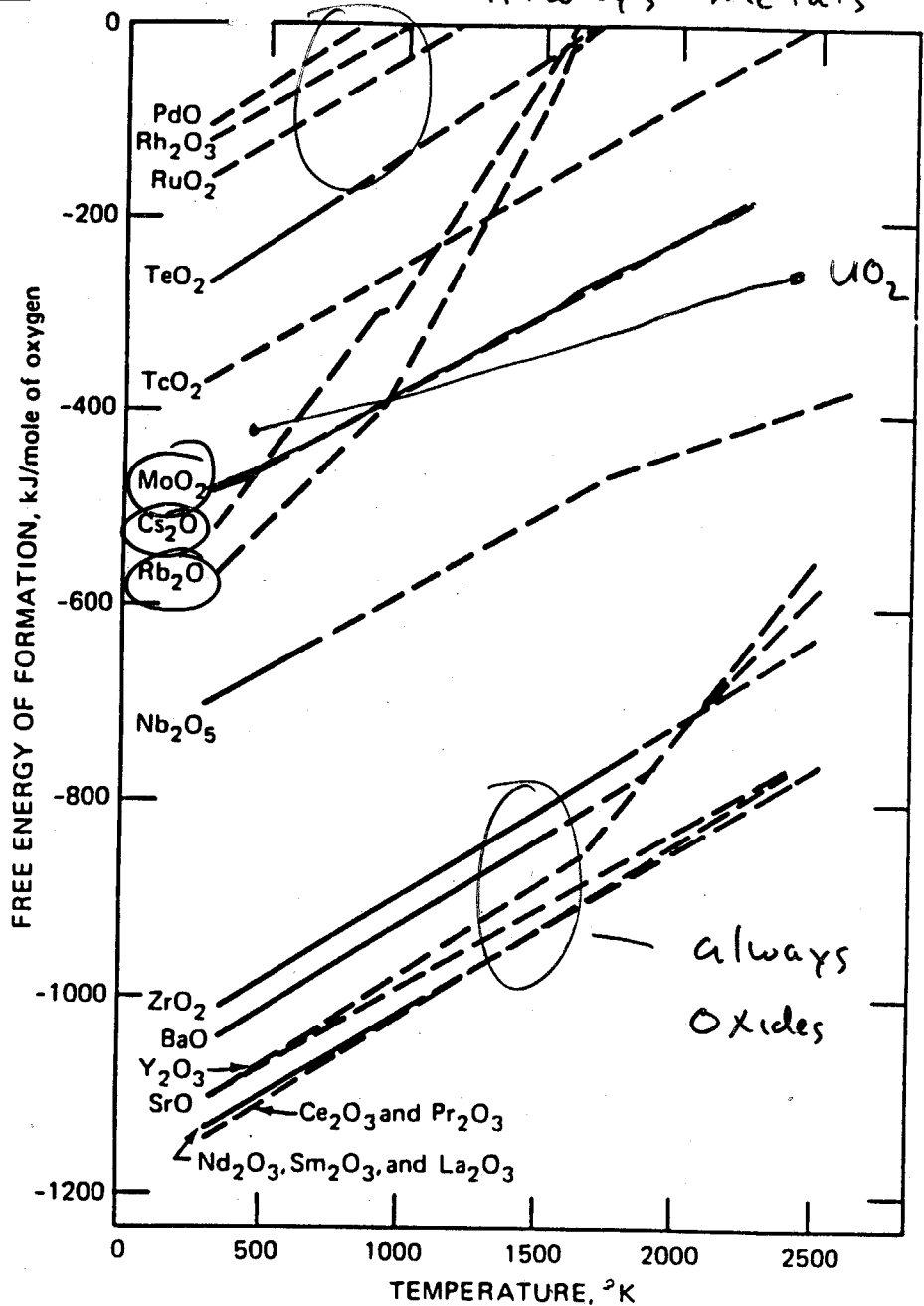


Fig. 12.6 Oxygen potentials of mixed-oxide fuels (taken from Figs. 11.13 and 11.14 and Eq 11.14).

Fig. 12.7 Standard free energies of formation of high-yield fission products. ---, extrapolations of data. [From D. R. O'Boyle et al., *J. Nucl. Mater.*, 29: 27 (1969).]

FUNDAMENTAL ASPECTS OF NUCLEAR REACTOR FUEL ELEMENTS

Table 12.3 Probable Chemical and Physical States of Fission Products in Near-Stoichiometric Mixed-Oxide Fuel

Chemical group	Physical state	Probable valence
Zr and Nb*	Oxide in fuel matrix; some Zr in alkaline earth oxide phase	4+
Y and rare earths†	Oxide in fuel matrix	3+
Ba and Sr	Alkaline earth oxide phase	2+
Mo	Oxide in fuel matrix or element in metallic inclusion	4+ or 0
Ru, Tc, Rh, and Pd	Elements in metallic inclusion	0
Cs and Rb	Elemental vapor or separate oxide phase in cool regions of fuel	1+ or 0
I and Te	Elemental vapor; I may be combined with Cs as CsI	0 or 1-
Xe and Kr	Elemental gas	0

*Although the most common oxide of niobium is Nb_2O_5 , the dioxide NbO_2 has been assumed to be stable in the fuel. The choice of niobium valence is not critical since its elemental yield is only 4%.

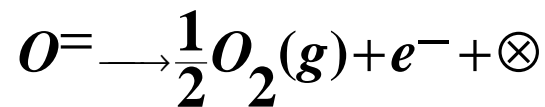
†Cerium has a 4+ valence state and may be stable as CeO_2 in fuels of high oxygen potential. This element has also been found in the alkaline earth oxide phase.

How Do FP Oxides Actually Fit into the Oxide?

When oxidation state = 4, no problem!

When sesquioxides form, M_2O_3 , and charge is +3, then electric neutrality is required;

1.) Produce oxygen vacancy (fig. 12.8b)



2.) U atoms oxidize to U^{+5} or U^{+6} (fig.12.8c)



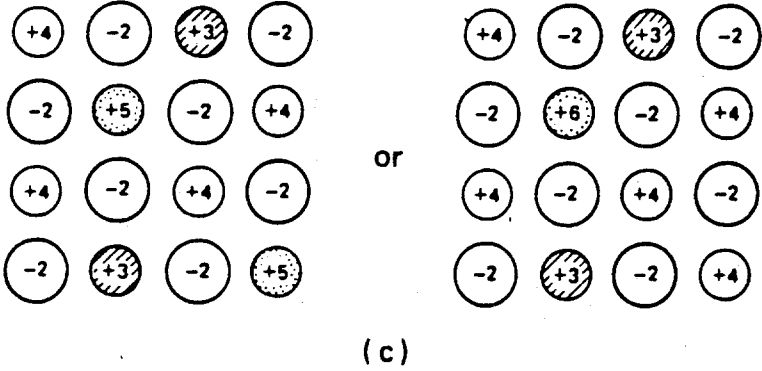
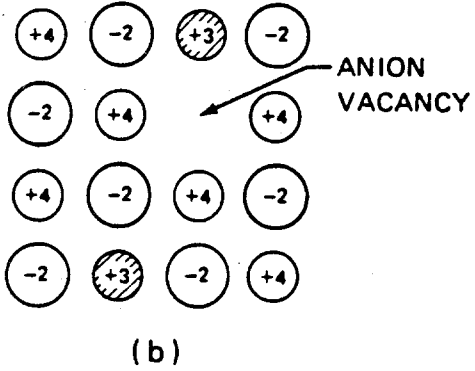
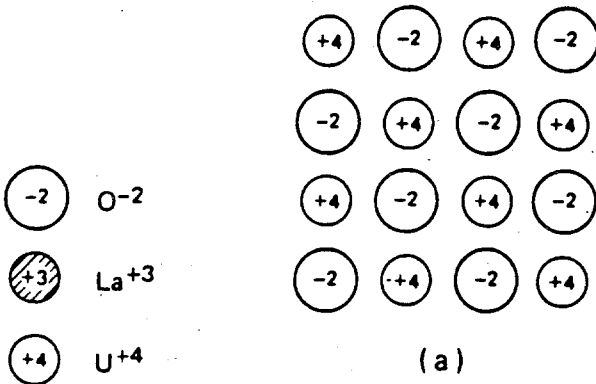


Fig. 12.8 Two-dimensional representation of methods of maintaining electrical neutrality when La^{3+} is introduced into UO_2 . (a) Perfect UO_2 lattice. (b) Removal of oxygen ions. (c) Oxidation of U^{4+} to U^{5+} or U^{6+} .