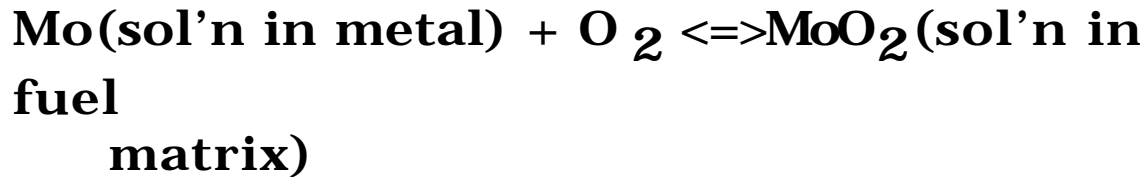


## 12.4.2 Partitioning of Mo

As shown earlier, the free energy of formation of  $\text{MoO}_2$  is close to stoichiometric fuel



With ideal solutions, we can replace activities with fractions to give;

$$G_{\text{Mo}}^{\circ} = RT \ln a_{\text{O}_2} - RT \ln \frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m}$$

Free Energy in of Formation $\text{MoO}_2$ $\text{MoO}_2$	$\overline{G_{\text{O}_2}}$ Oxygen Potential Fuel	Fraction of Mo Metal Matrix as
---	--	--------------------------------------

-----  
Set up expressions for  $y_{\text{Mo}}^f$  (12.22) &  $y_{\text{Mo}}^m$  (12.23)

$$G_{\text{Mo}}^{\circ} = \overline{G_{\text{O}_2}} - RT \ln \frac{f_{\text{Mo}}}{1 - f_{\text{Mo}}} \frac{Y_{\text{NM}} + (1 - f_{\text{Mo}}) Y_{\text{Mo}}}{1 - Y_{\text{Y-Re}} + f_{\text{Mo}} + Y_{\text{ZrNb}} - Y_{\text{BaSr}}}$$

Unknowns,  $f_{\text{Mo}}$  = frac of oxidized Mo as  $\text{MoO}_2$   
 $V_{\text{U}}, V_{\text{Pu}}$  to determine  $\overline{H_{\text{O}_2}}, \overline{S_{\text{O}_2}} \rightarrow \overline{G_{\text{O}_2}}$

### 12.4.3 Oxygen Balance

- Recognize that oxygen can exist in both HM oxides and FP oxides (Zr, Ba, Sr, Y, ....)

$$N_o^{Ba-Sr} + N_o^f$$

$$3N_{Ba-Sr} (BaZrO_3, SrZrO_3)$$

- Charge balance is maintained by reduction of Pu or oxidation of U

---

### Charge Balance

#### Hypostoichiometric Fuel Only

$$(V_U = 4, V_{Pu} < 4)$$

$$2N_o^f = 4N_U + V_{Pu}N_{Pu} + 4(N_{Zr-Nb} - N_{Ba-Sr})$$

$$+ 6N_{Ba-Sr} + 3N_{Y-RE} + 4f_{Mo}N_{Mo}$$

---

#### Hyperstoichiometric Fuel Only

$$(V_U > 4, V_{Pu} = 4)$$

$$2N_o^f = V_U N_U + 4N_{Pu} + 4(N_{Zr-Nb} - N_{Ba-Sr})$$

$$+ 6N_{Ba-Sr} + 3N_{Y-RE} + 4f_{Mo}N_{Mo}$$

Dividing through by  $N_U$  and using burn up def.,

$$2 \frac{O}{M} = 4(1 - q)(1 - ) + V_{Pu} q(1 - ) +$$

$$(2Y_{Ba-Sr} + 4Y_{Zr-Nb} + 3Y_{Y-Re} + 4f_{Mo}Y_{Mo})$$

similar for hyper fuel.

- Use oxygen balance to solve for  $f_{Mo}$  and  $V_U$  or  $V_{Pu}$

fraction of Mo oxidized to  $MoO_2$

- Knowing  $V_U$  or  $V_{Pu}$ , we can solve for  $\overline{G_{O_2}}$  from figures 11.13 and 11.14

=====  
 Note figure 12.10 for hypo fuel !

Note difference from figure 11.12  
 (Mo holds oxygen content down)

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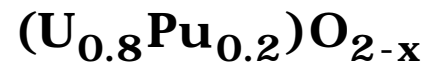
$$crit = \frac{1 - \frac{O}{M} \frac{1}{2}}{1 - \frac{(2Y_{Ba-Zr} + 4Y_{Zr-Nb} + Y_{Y-Re})}{4}}$$

when

$$O/M = 1.99 \quad crit = 1.5\%$$

$$O/M = 1.97 \quad crit = 4.8\%$$

For



$$O/M = 1.95 \quad \text{crit} = 6.7\%$$

## 12.4

### The Effect of Burnup on the Oxygen Potential of the Fuel.

The burnup of Pu ( or U) causes oxygen to be released and the FP's, even though there are 2 of them , cannot combine with all of the oxygen liberated (Hypo--> Hyper)

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To find  $\overline{G_{O_2}}$  (function of r) need;

- 1.) decrease of U, Pu and increase in oxygen consuming FP's
  - 2.) Chemical and Physical States of FP's
  - 3.) Redistribution of O<sub>2</sub> and FP's in fuel
  - 4.) Thermochemistry of solid -gas phase
  - 5.) Effectiveness of cladding to remove oxygen and FP's
- 

#### 12.4.1 Concentration Changes During Burnup

Orlander shows

$$N_U = (1 - q)(1 - \lambda)(N_U^\circ + N_{Pu}^\circ)$$
$$N_{Pu} = q(1 - \lambda)(N_U^\circ + N_{Pu}^\circ)$$

where  $q$  = cation fraction of Pu

= burnup

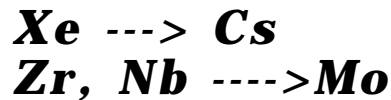
$$q = \frac{q^\circ}{1 - \dots} \quad \text{if conversion ratio} = 1.0$$

also,

$$N_i = Y_i (N_U^\circ + N_{Pu}^\circ)$$

# 12.5 Fission Product Migration

*In addition to vapor transport, solid state diffusion can transport solid fission products around fuel pins. Note that the precursors may be important.*



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**Cesium is classic example which is usually found in colder portions of the fuel**

<u>Bad</u>		<u>Good</u>
• Accelerates potential corrosion SS	$\text{Cs}_2\text{O}$	• Reduces $\text{O}_2$
• Removes Cs so it can't tie up Iodine	$\text{Cs}_2\text{MoO}_4$ $\text{Cs}_2\text{UO}_4$	• Oxide less volatile
• Swelling	$\text{CsI}$	• Usually all I is tied up with Cs ( $Y_{\text{Cs}} \approx 6Y_{\text{I}}$ )

- 
- Figure 12.11, note log scale
  - Movement of Mo -Figure 12.1
- 

- Columnar grains concentrate  $\text{Cs}_2\text{MoO}_4$  at fuel surface



## 12.6 Fuel Cladding Interaction

***Major problem for high burnup fuels in 316 SS cladding (Not as bad for lower B.U. LWR fuel)***

### 12.6.1

**Important thing is to keep  $O_2$  low to resist oxide formation - Table 12.4**

***Can do this by keeping fuel hypostoichiometric but that is hard because of vapor transport***

**Note: If one could keep the O/M ratio at 1.96, then the oxygen partial pressure is so low that  $Cr_2O_3$  can't form. This is one reason oxide fuel is fabricated in the hypostoichiometric state.**

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### **12.6.2 Observations of Cladding Corrosion by Irradiated Mixed Oxide Fuels**

**Two types of cladding attack**

- a.) Corrosion of inner clad wall**
- b.) Transport of clad constituents to fuel**

#### **Attack of Cladding**

- 1.) Worst "actors"**

**Cs, Mo, I, Oxygen**

- 2.) Depends on T and  $O_2$  potential**

**Figure 12.16**

**Note threshold at 550°C**

## Mechanism



Low melting point medium to  
attack  $\text{Cr}_2\text{O}_3$

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### 12.6.3 Transport of Cladding Components to Fuel---- Read

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### 12.7 Fuel Swelling Due to Solid Fission Products

$$\frac{V}{V_{\text{solid.FP}}} = \frac{V - V^\circ}{V^\circ} = \frac{\sum \text{Partial Volume of } i}{V_U} - 1$$

Volume of  $\text{UO}_2$

Does **not** include gases !!!

---

#### Qualifications for Table 12.6

- *It overestimates the DV in hot part and underestimates it in the cold part.*
- *As oxygen potential increases, more  $\text{MoO}_2$  forms, increasing DV*

0.15 - 0.45 % per % B.U.

## Problem 12.4

After irradiation it was found that where the  $T=2000^\circ\text{K}$ , the Mo was distributed as follows;

- 0.08 mole%  $\text{MoO}_2$  in oxide fuel
  - 10 at% Mo in metallic inclusions
  - 0.01 g of metallic inclusions per gram of irradiated fuel
- 

a.) Assuming ideal solutions, calculate  $p_{\text{O}_2}$

$$G_{\text{Mo}}^\circ = -574 + 164 \frac{T}{1000} \dots \frac{\text{kJ}}{\text{mole}}$$

for  $\text{Mo}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{MoO}_2(\text{s})$

$$K = \exp \frac{-G_{\text{Mo}}^\circ}{RT} = \frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m \cdot p_{\text{O}_2}} \quad (\text{eq. 12.17})$$

12.17)

@ 2000 °K,

$$G_{\text{Mo}}^\circ = -574 + 164 \cdot 2 = -246 \text{ kJ/mole}$$

Then oxygen potential is;

$$G_{\text{O}_2}^\circ = RT \ln(p_{\text{O}_2}) = G_{\text{Mo}}^\circ + RT \ln \frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m}$$

$$8.28 \cdot 2 \cdot \ln(0.08/10) = -80 \text{ kJ/mole}$$

$$G_{O_2}^\circ = -246 - 80 = -326 \text{ kJ/mole}$$

$$p_{O_2} = \exp \frac{-326}{R \cdot 2000} = 2 \times 10^{-9} \text{ atm}$$

b.) Assuming that all the noble metals are in metallic inclusions, calculate the burnup of the fuel. ( Assume all At. Wts. of elements in metallic inclusions are 100)

There are 0.01 g of metallic inclusions per g of fuel, or,

$$\frac{0.01}{100} \text{ g atoms of metallic inclusions}$$

per 0.1 cm<sup>3</sup> of fuel

-----

However, only 10% (at) of inclusions are of Mo

The Noble Metal (NM) conc. (g atom/cm<sup>3</sup> fuel) is

$$N_{NM} = \frac{0.00009}{0.1} = 0.0009 \frac{\text{g - atom.NM}}{\text{cm}^3 \cdot \text{fuel}}$$

=====

$$N_U^\circ + N_{Pu}^\circ = \text{initial heavy metal Conc}$$

$$= 10 \frac{\text{g}}{\text{cc}} \cdot \frac{1}{270 \frac{\text{g}}{\text{g - atom. HM}}}$$

**= 0.037 g atom HM /cc of fuel**

using eq. 12.16

$$= \frac{N_{NM}}{Y_{NM} \cdot (N_U^\circ + N_{Pu}^\circ)} = \frac{0.0009}{0.456 \cdot 0.037} = 0.053$$

$$= 5.3 \%$$

c.) Find the Mo content of the metallic inclusion that should have been found if no Mo had been lost from or gained by the unit volume of fuel under consideration.

From eq. 12.16, total Mo conc. after 5.3% BU ;

$$N_{Mo}^* = (0.206) \cdot (N_U^\circ + N_{Pu}^\circ)$$

table 12.1 Part b

$$= 0.0004$$

$(N_{Mo}^{incl})^*$  = Mo in metallic inclusions (\f(g

atom,cc fuel)) =

$$0.001 \left( \frac{\text{g atom incl}}{\text{cc fuel}} \right) \cdot (y_{Mo}^m)^*$$

assume metallic inclusion are principally NM, use b.)

$$\begin{aligned} (N_{Mo}^f)^* &= \text{Mo in fuel matrix, } \frac{\text{g atom}}{\text{cc fuel}} \\ &= 0.037 \frac{\text{g atom HM}}{\text{cc fuel}} \cdot (y_{Mo}^f)^* \end{aligned}$$

$$N_{Mo}^* = (N_{Mo}^{incl})^* + (N_{Mo}^f)^* = 0.001 (y_{Mo}^m)^* + 0.037 (y_{Mo}^f)^*$$

But the ratio  $\frac{(y_{Mo}^f)^*}{(y_{Mo}^m)^*}$  is fixed by  $G_{O_2}$  and is

the same as the measured value, therefore,

$$(y_{Mo}^f)^* = \frac{0.08}{10} (y_{Mo}^m)^*$$

and

$$N_{Mo}^* = (y_{Mo}^m)^* \cdot 0.001 + \frac{0.037 \cdot 0.08}{10}$$

$$= 0.0013 (y_{Mo}^m)^*$$

$$(y_{Mo}^m)^* = \frac{N_{Mo}^*}{0.0013} = \frac{0.0004}{0.0013}$$

$$= 0.31$$

Metallic inclusions should have contained 31% Mo if none is lost from this spot in the fuel. The fact that only 10 at% of the inclusion was Mo means that 2/3 of the Mo produced by fission at the radial location where the measurements were made was

**removed by some migration process to other radial positions in the fuel pin.**