Nuclear Fuel Performance

NE-533

Spring 2024

Exam 2

- Average: 90.7
- Stdev: 8.6
- No curve this time
- If you have any questions or comments, observed discrepancies, etc., let me know

MOOSE Project Notes

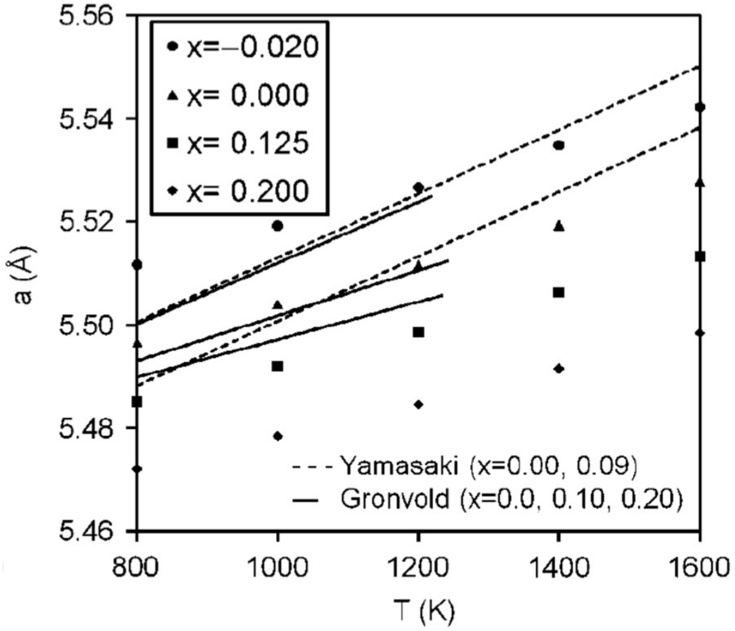
- For part 2, I want everyone to use contact and gap heat transfer
- You can compare your results from part 1 and the analytical solution as an initial stage of verification
- Some of you may have done this, I have not worked through all input files yet
- Make sure your executable has contact compiled, and you have a thermal contact block
- The rest I leave for you to figure out

Last Time

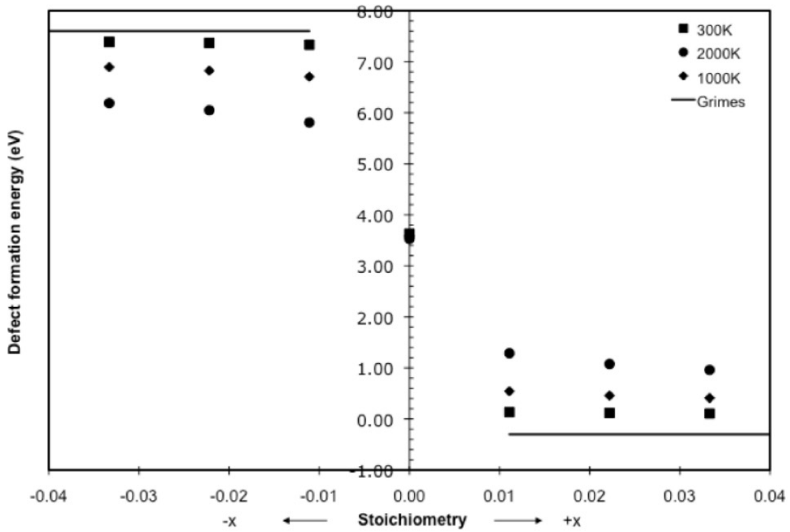
- The average grain size in UO_2 impacts fuel behavior and performance
- The material wants to reduce its energy by having large grains grow at the expense of small grains
- Fuel densification is driven by reduction in surface area of pores – continuation of sintering process
- Started fuel chemistry

Fuel Stoichiometry/Properties

- The lattice constant of the material decreases with increasing stoichiometry



- The vacancy formation energy also changes with stoichiometry



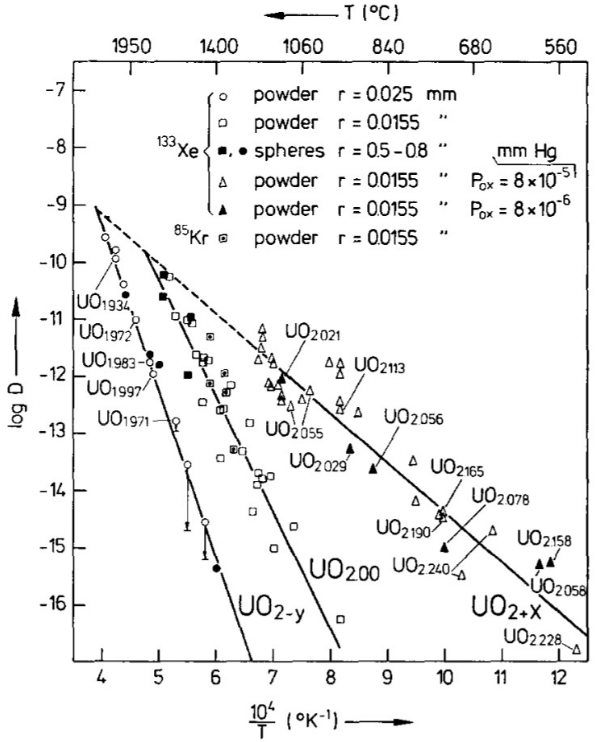
Fuel Stoichiometry/Properties

- The solution energy of Xe, Cs, and Sr in UO_2 depends on stoichiometry as well

- The coefficient defining Xe diffusion also changes with stoichiometry

- **Though stoichiometry matters, most fuel performance codes ignore it**

Fission product	$UO_{1.97}$	UO_2	$UO_{2.03}$
Xe	3.88 eV	3.88 ev	2.61 eV
Cs	1.7 eV	-0.04 eV	-3.29 eV
Sr	-3.71 eV	-6.03 eV	-9.55 eV



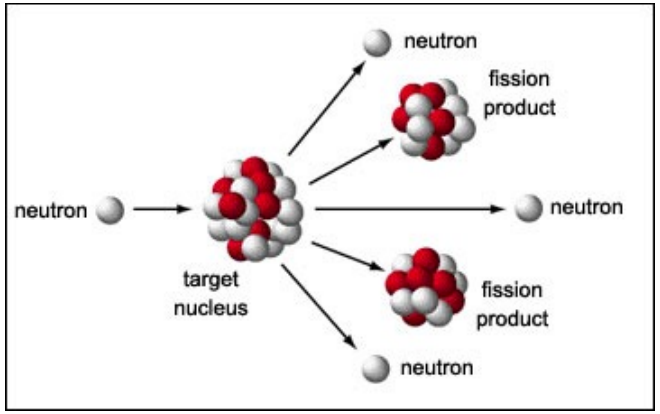
Fuel Chemistry Summary

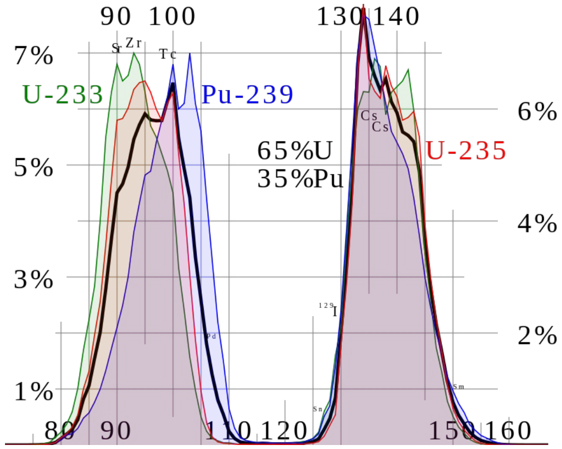
- UO_2 has a cubic fluorite structure that is very stable
- The charges are balanced with a U^{4+} valence state
- However, the ratio of oxygen to uranium can change. We call this the stoichiometry and abbreviate it as O/M ratio
- The O/M ratio changes during reactor operation, but it is complicated
- The O/M ratio impacts many properties of the fuel

FISSION PRODUCTS

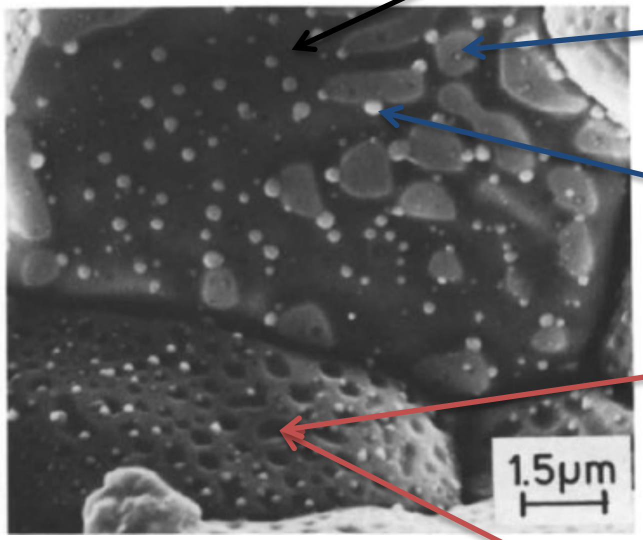
Fission Product Generation

- Fission releases around 200 MeV
  - The fission fragments have 169 MeV of kinetic energy
  - 2 to 3 neutrons with an average energy of 2 MeV
  - 7 MeV of prompt gamma ray photons
  - The remaining energy is released by beta decay
- Every fission product that is produced is now in the crystal lattice of the fuel, changing the chemistry/microstructure





There are various types of fission products that form



Soluble oxides (Y, La and the rare earths)
- Dissolved in the cation sublattice

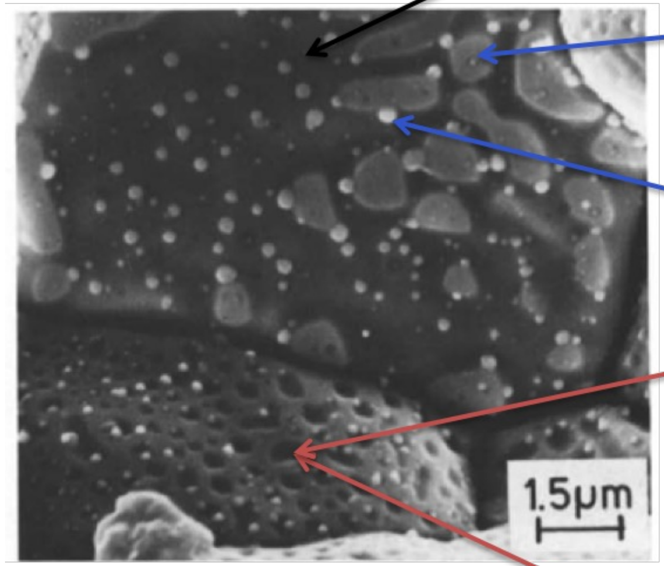
Insoluble oxides (Zr, Ba and Sr)
- Form insoluble oxides in the fluorite lattice

Metals (Mo, Ru, Pd, and Tc)
- Form metallic precipitates

Volatiles (Br, Rb, Te, I and Cs)
- Exist as gases at high temperatures of the pellet interior
- Also exist as solids at the cooler pellet exterior

Noble gases (Xe, Kr)
- Essentially insoluble in the fuel matrix
- Form either intragranular (within grain) voids or bubbles or intergranular (grain boundary) bubbles

All fission products impact the behavior of the fuel



Soluble oxides (Y, La and the rare earths)
- Cause swelling, decrease thermal conductivity

Insoluble oxides (Zr, Ba and Sr)
- Can cause swelling

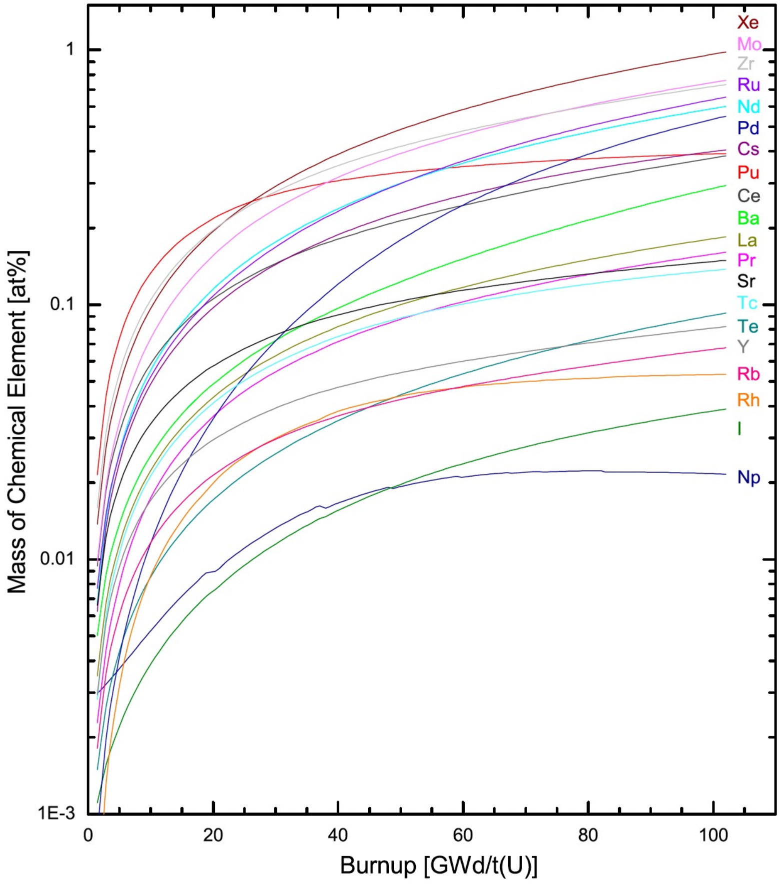
Metals (Mo, Ru, Pd, and Tc)
- Slightly raise thermal conductivity,

Volatiles (Br, Rb, Te, I and Cs)
- Cause swelling, decrease thermal conductivity
- Escape from fuel, corrode the cladding

Noble gases (Xe, Kr)
- Cause swelling
- Decrease thermal conductivity
- After release, raise gap pressure and lower thermal conductivity

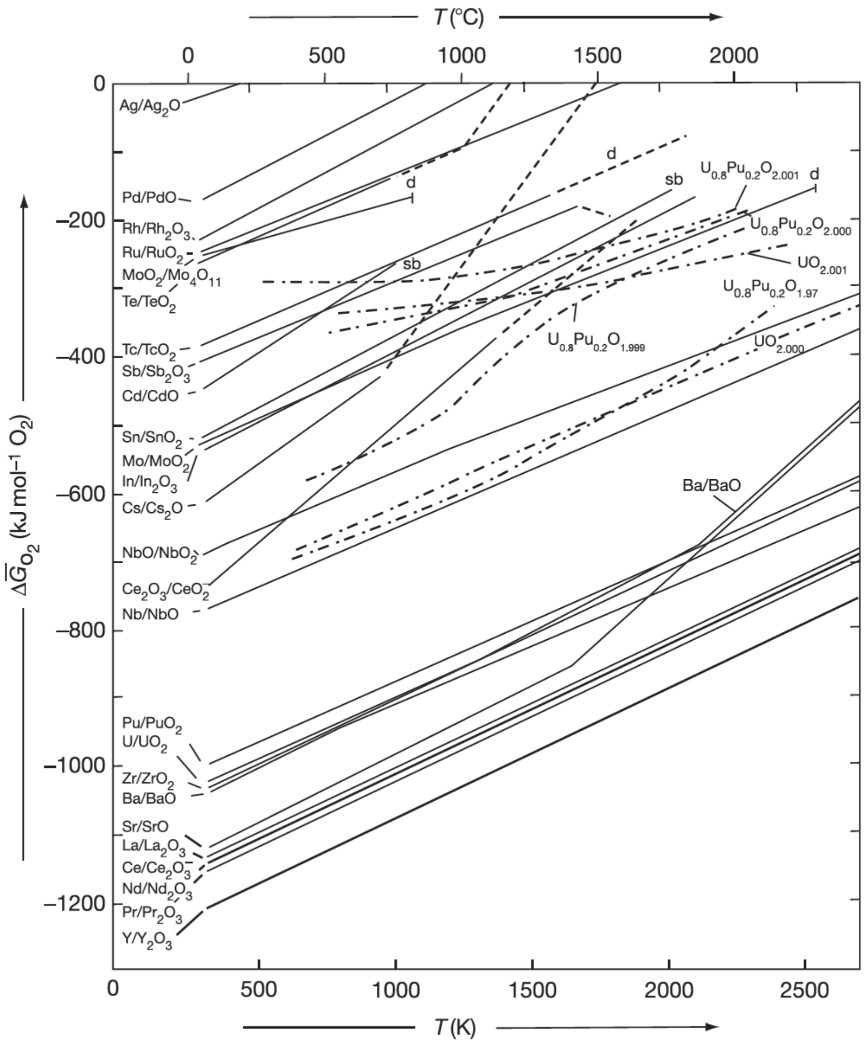
Fission Product Evolution

- Not only are the absolute proportion of fission products accumulating with time, but the relative proportions are changing with respect to one another
- There are continuous transitions between the groups as the critical concentration conditions for new phase development are surpassed because of increased burnup
- Since fission releases two oxygen but only one metal atom, and not all metal atoms will react to bond the oxygen, the O/M ratio of the fuel slowly increases during burnup



Oxide Formation

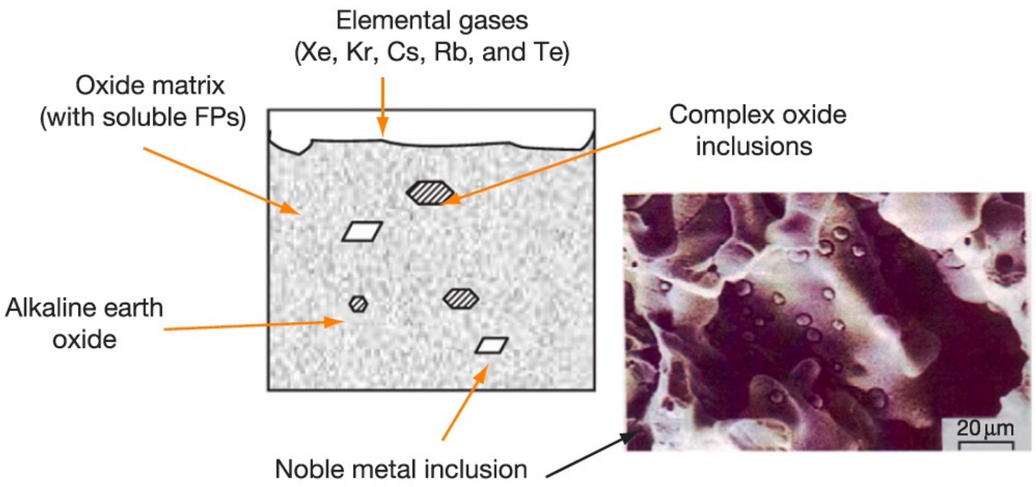
- With burnup, the liberated oxygen will associate with U, Pu, and La but may not be in sufficient supply to combine with Pd and other less oxidizing elements
- If the Gibbs energy of formation of the given fission product lies below the fuel oxygen potential, the element will be capable of forming an oxide (Ce, Sr, Ba)
- If the reaction line is above the oxygen potential in the fuel, the fission product will exist as an element in the fuel (in a separate metallic phase) (Ru, Pd, Tc)



Soluble/Insoluble Fission Products

- When a 4+ valence fission product (e.g.,Zr4+) enters the lattice, there is no change in the electrical neutrality
- If the charge of the fission-product cation is lower than U+4, the site occupancy of the lattice is altered to achieve electrical neutrality
- The alkaline earth cations Ba+ and Sr2+ have large ionic radii and form a separate oxide phase
- Fission products that have limited solubility in UO2 will segregate to the grain boundaries and voids

Chemical group	*Physical state*	*Probable valence*
Zr and Nb	Oxide in fuel matrix; some Zr in alkaline earth oxide phase	4+
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 and CsI	0 or 1−
Xe and Kr	Elemental gas	0

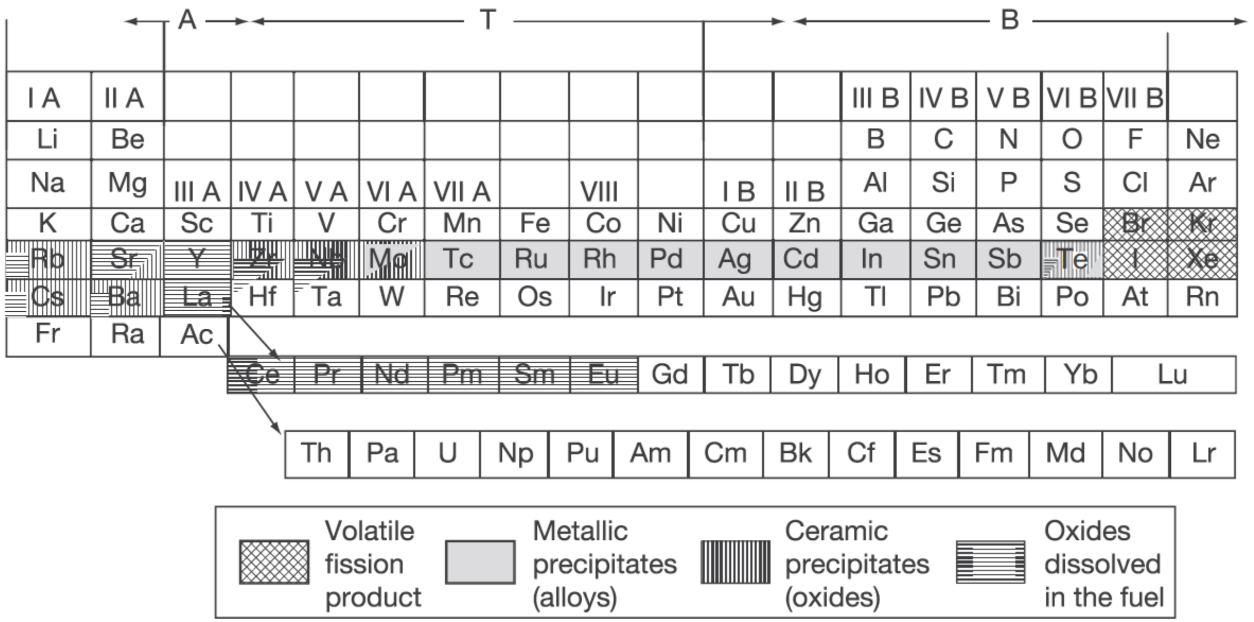


Fission Product Segregation/Precipitation

- Fission products can be segregated because of their migration to specific locations such as intragranular segregations, grain boundaries, or pellet surfaces
- Metallic inclusions are commonly observed in ceramographs from irradiated samples
- They are formed by isotopes of Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Te
- These inclusions are found at the surface of the grain boundaries and are associated, in general, with grain boundaries and intragranular bubbles
- Some of the components of these precipitates can be oxidized or reduced forming other compounds that can be released from the fuel matrix
- Cs, Ru, Te, and Ba have been consistently found at the cracks in the pellet and on the clad inner surface
- The white inclusions are metallic precipitates, which are composed of Mo, Tc, Rh, Ru, and Pd, form a quinary alloy in an hcp structure
- A "gray oxide phase" perovskite structure containing different combinations of Ba, Cs, Zr, Mo, and U can also form

Volatile/Gaseous Fission Products

- Xe release occurs at the central region of the pellet where the highest temperatures were achieved during irradiation
- Volatile FPs are released from the fuel matrix similar to that of the noble gases
- Volatile fission products in the gap can react among themselves, resulting in a changing chemical speciation
- The kinetics of formation/decomposition of CsI and Zr iodides are possible factors in the mechanism of SCC



FP Interaction with Zr Cladding

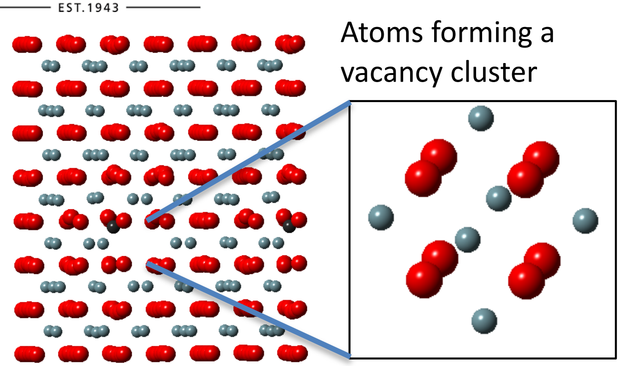
- Fission fragments will deposit on the inner surface of the cladding
- Some of these species can diffuse into the cladding, while others can attack the cladding thereby initiating cracks that can later progress with the formation of through-wall cracks
- Oxygen will diffuse into the cladding and contribute to its oxidation state
- Measurements have shown deposits of Sr, Cs, Pu, and Am
- The corrosion behavior of zirconium by Te has been reported
- The chemical reaction between some corrosive fission products and the cladding can lead to PCI
- Fission products such as Cs, Cd, or I can attack the cladding inducing crack initiation, which then progress through the cladding by intragranular and transgranular cracking modes

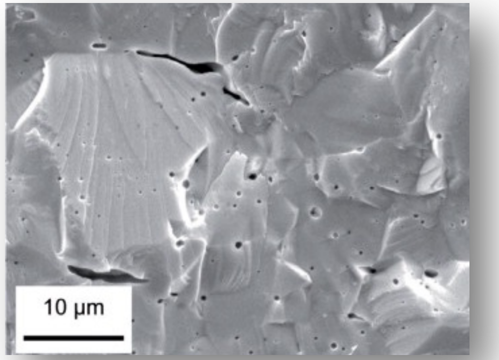
FISSION GAS RELEASE

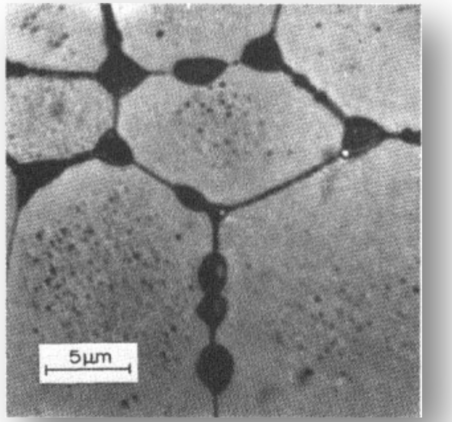
Fission Gas Release

- Fission gases (Xe, Kr) are released in a process composed of three stages in UO2
- Stage 1: Gas atoms are produced throughout the fuel due to fission and diffuse towards grain boundaries
- Small intragranular bubbles form within the grains, but never get larger than a few nm radius due to resolution from energized particles
- Gas atoms that don't get trapped within the intragranular bubbles migrate to grain boundaries

Los Alamos NATIONAL LABORATORY EST. 1943

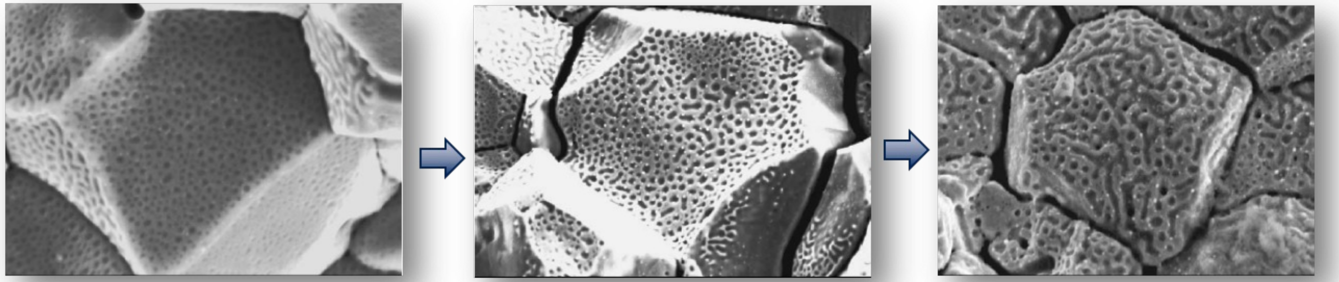






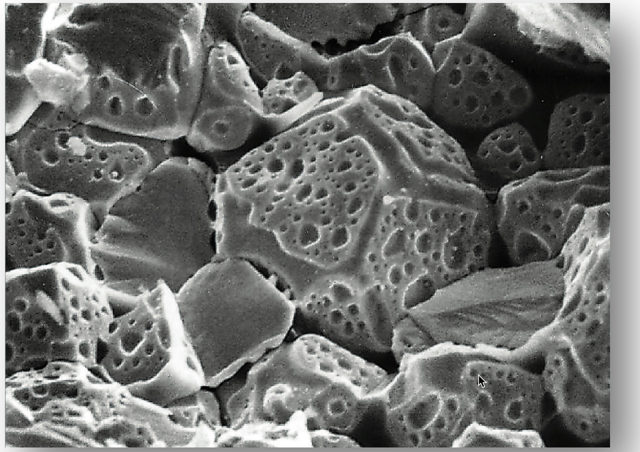
Fission Gas Release

- Stage 2: Gas bubbles nucleate on grain boundaries, growing and interconnecting



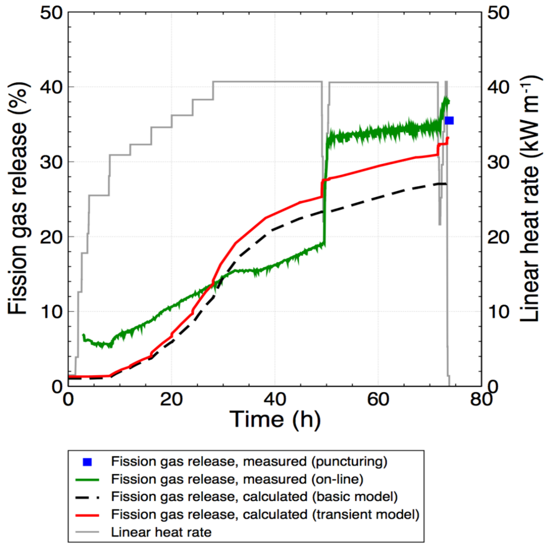
Nucleation Growth Percolation

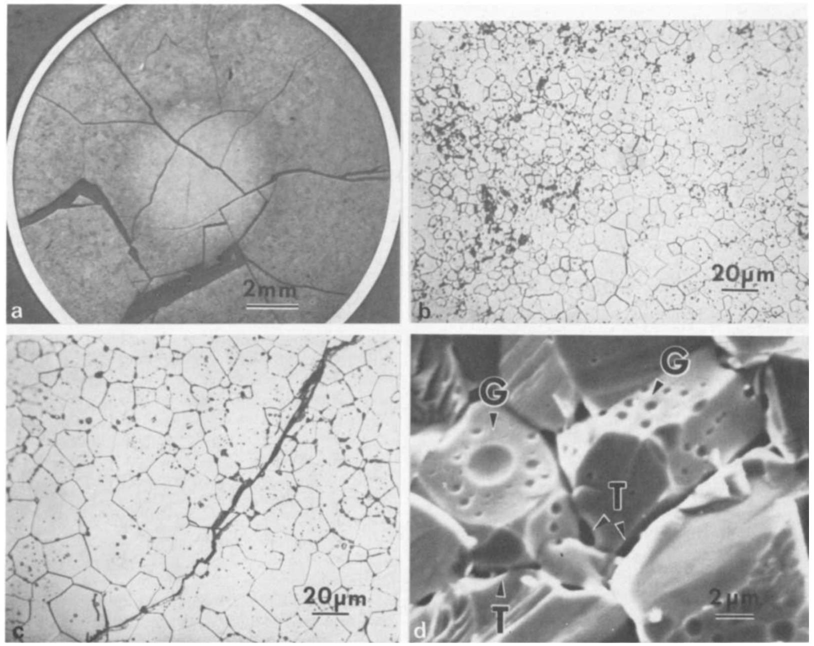
- Stage 3: Gas travels through interconnected bubbles to a free surface



Fission Gas Release

- Fission gas release also occurs due to mechanisms that don’t depend on diffusion
- Release can occur to particle recoil and knockout at low temperature
- It can occur due to fracture during rapid transients





Fission Gas Release

- Released fission gas enters the gap and plenum, causing various problems
- Xe and Kr have very low thermal conductivities, reducing the gap conductance
- The plenum pressure increases
- The volatile fission gases corrode the cladding
- They are also radioactive and hazardous, causing problems when the cladding is breached
- Fission gas release experiments:
  - Post irradiation annealing
    - Fuel is irradiated at low temperature; Fuel is then placed into a furnace and heated; Gas atom release is then measured
  - In-pile release
    - Gas release is measured during reactor operation; It is much more difficult than post-irradiation annealing; Total amount released is measured by puncturing cladding after irradiation; Release with time can be estimated using a pressure transducer inside an instrumented fuel rod

Fission Gas Release

- Fission gas release models attempt to predict the rate at which gas is released from the fuel
- To model fission gas release, ideally, we must model all three stages of gas release
  - Diffusion of gas atoms to grain boundaries
  - Growth and interconnection of grain boundary bubbles
  - Transport of gas atoms through interconnected bubbles to free surfaces
- The earliest models only considered Stage 1
- Most models now consider stage 1 and 2
- There are no models that consider all three stages, but some are under development

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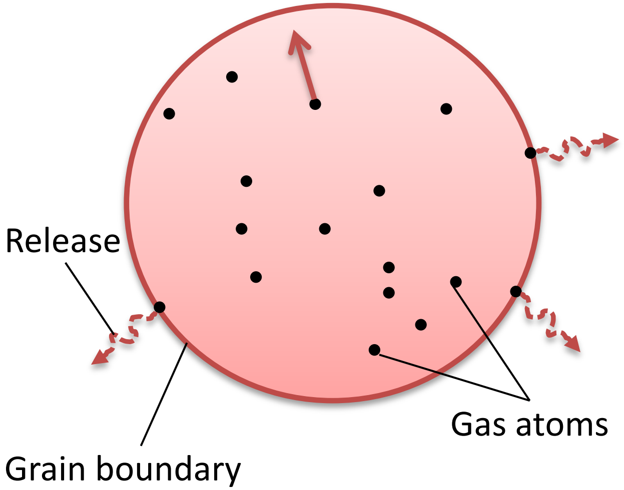
Booth Model

$$\dot{c}_g = k_{c_g} + \nabla \cdot D \nabla c_g$$

$$\dot{c}_g = k_{c_g} + D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_g}{\partial r} \right)$$

- The Booth model is the earliest model of fission gas release and only considers stage 1
- A grain is considered as a simple sphere
- Gas atoms are released at the grain boundary
- The model solves the diffusion equation in 1D spherical coordinates
- Assumptions
  - $c_g(r, t)$
  - All grains are spheres of radius *a*
  - D is constant throughout the grain
  - Gas is produced uniformly throughout the grain
  - Gas is released once it reaches the grain boundary



<u>ICs and BCs</u>

$c_g(r, 0) = 0$

$c_{g,r}(0, t) = 0$

$c_g(a, t) = 0$ (release)

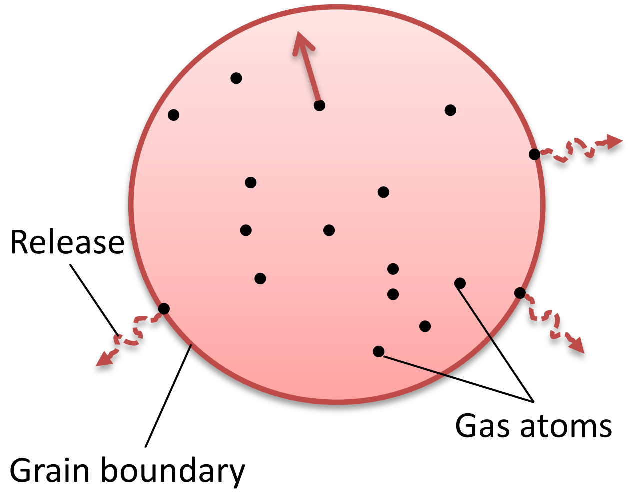
Modeling post-irradiation annealing

- The initial gas concentration is c_g^0
- No gas is produced

$$\dot{c}_g = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_g}{\partial r}\right)$$

- Solving this equation tells us the value of c_g at any radius or time
- However, we want to know the fraction of gas atoms that have made it to the grain boundary
- We use the flux at the grain boundary

$$J_a = -D\left(\frac{\partial c_g}{\partial r}\right)_a \qquad f = \frac{4\pi a^2 \int_0^t J_a dt}{4/3\pi a^3 c_g^0} = \frac{3}{a c_g^0}\int_0^t J_a dt$$



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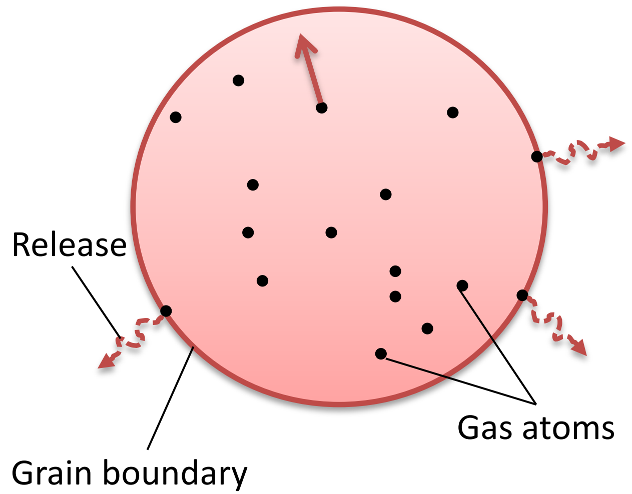
$c_g(r, 0) = c_g^0$

$c_{g,r}(0, t) = 0$

$c_g(a, t) = 0$ (release)

Solving the Booth Model

- This equation is solved using a Laplace transform after nondimensionalization
- Will not go through the derivation (shown in Olander)
- $\tau = D \times t / a^2$



$$f = 6\sqrt{\frac{Dt}{\pi a^2}} - 3\frac{Dt}{a^2} \qquad \tau < \pi^{-2}$$

$$f = 1 - \frac{6}{\pi^2} e^{-\pi^2 \frac{Dt}{a^2}} \qquad \tau \geq \pi^{-2}$$

Booth Example

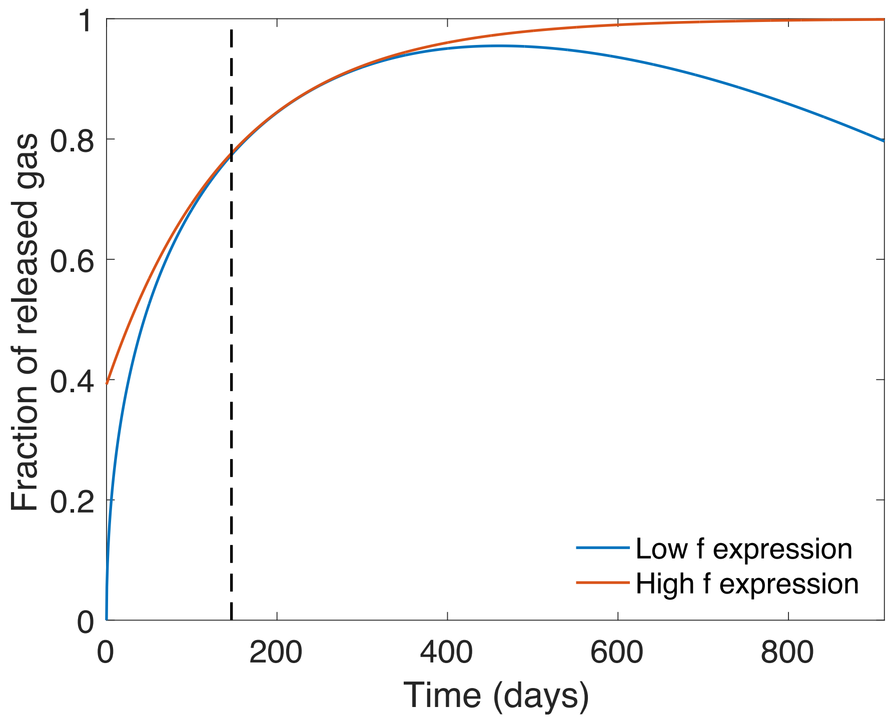
- For a diffusion coefficient for Xe of D = 8e-15 cm^2/s, what fraction of the fission gas trapped in an post-irradiation annealed fuel pellet has escaped after one hour? It has an average grain size of 10 microns
  - D = 8e-15 cm^2/s
  - a = 10e-4 cm
  - t = 3600 s
- Which f? $\tau = D \times t/a^2 = 2.88E\text{-}4 < \pi^{-2} = 0.101$

$$f = 6\sqrt{\frac{Dt}{\pi a^2}} - 3\frac{Dt}{a^2}$$

  - f = 6*sqrt(8e-15*3600/(pi*(10e-4)^2)) – 3*8e-15*3600/(10e-4)^2 = 0.0181

Different expressions for fission gas release

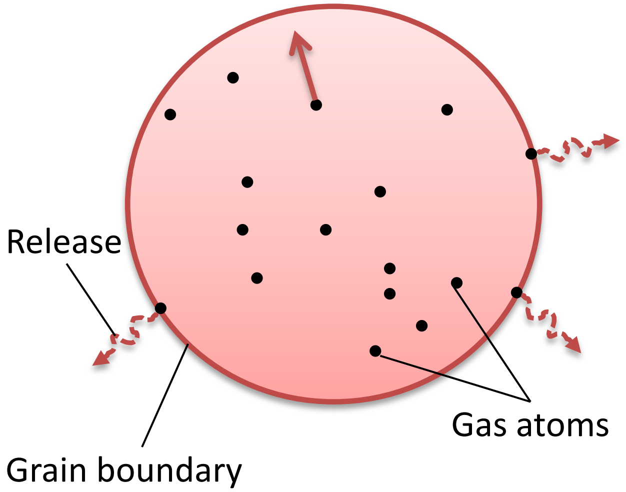
- Given the data from the previous example, can plot both
  - $\tau < \pi^{-2}$ $\quad f = 6\sqrt{\frac{Dt}{\pi a^2}} - 3\frac{Dt}{a^2}$
  - $\tau > \pi^{-2}$ $\quad f = 1 - \frac{6}{\pi^2}e^{-\pi^2 \frac{Dt}{a^2}}$



Modeling in-pile release

$$\dot{c}_g = y\dot{F} + D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_g}{\partial r}\right) - \lambda c_g$$

- The initial gas concentration is 0
- Gas is produced due to fission, where y is the chain yield (y = 0.3017 for Xe and Kr) and the fission rate
$$\dot{F} = qN_U\sigma_{f235}\phi_{th}$$
- Gas can also decay, where λ is the decay constant
  - If we only consider stable stable products, λ = 0
- For in pile release, the fraction is equal to
$$f = \frac{3}{ay\dot{F}t}\int_0^t J_a\,dt$$
- After solving with with a Laplace transform
$$f = 4\sqrt{\frac{Dt}{\pi a^2}} - \frac{3}{2}\frac{Dt}{a^2} \qquad \tau < \pi^{-2}$$
$$f = 1 - \frac{0.0662}{\frac{Dt}{a^2}}\left(1 - 0.93e^{-\pi^2\frac{Dt}{a^2}}\right) \qquad \tau \geq \pi^{-2}$$
- The total gas production is $y\dot{F}t$ gas atoms/cm^3



<u>ICs and BCs</u>

$c_g(r, 0) = 0$

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$c_g(a, t) = 0$ (release)

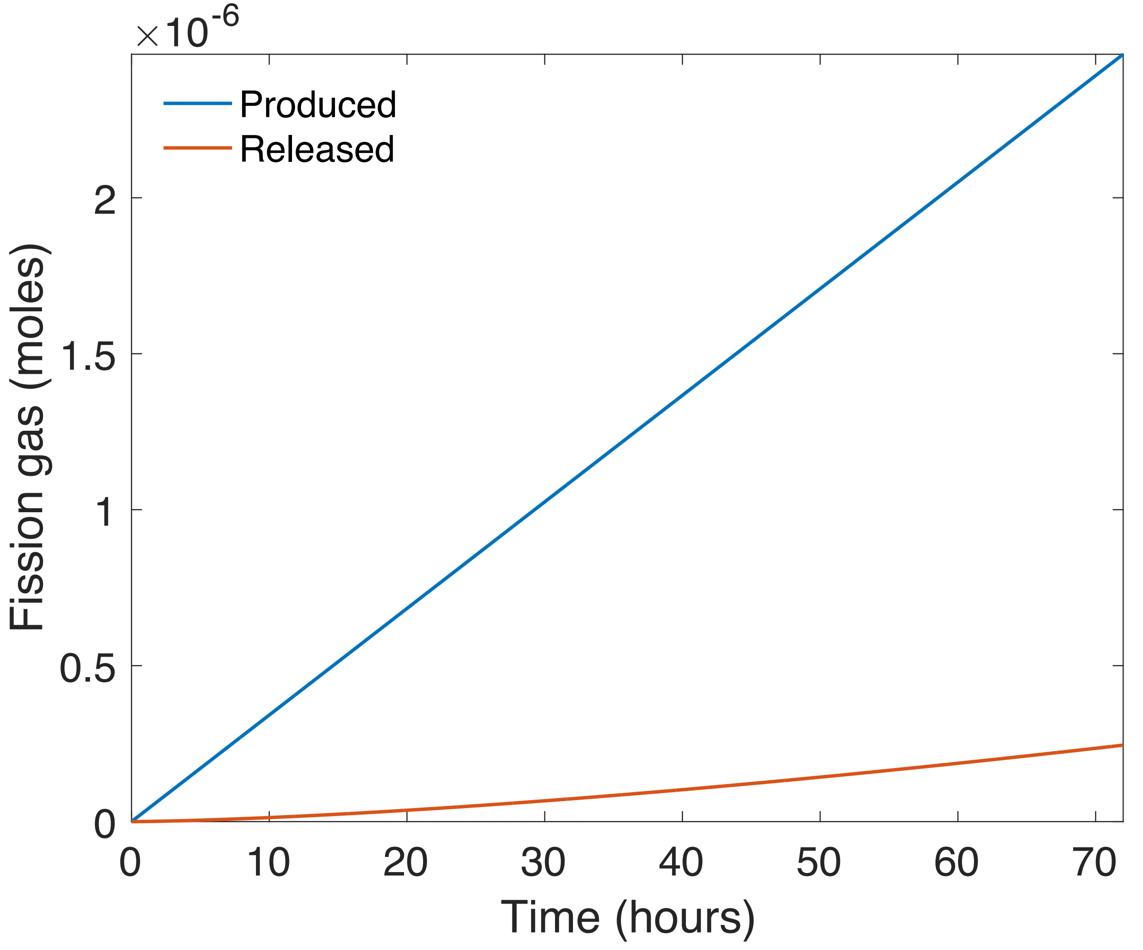
Example

- For a diffusion coefficient for Xe of D = 8e-15 cm^2/s, what fraction of the fission gas trapped in an in-pile fuel pellet has escaped after one hour? It has an average grain size of 10 microns.
  - D = 8e-15 cm^2/s
  - a = 10e-4 cm
  - We have a short time (t=3600 s), so we can use:

$$f = 4\sqrt{\frac{Dt}{\pi a^2}} - \frac{3}{2}\frac{Dt}{a^2}$$

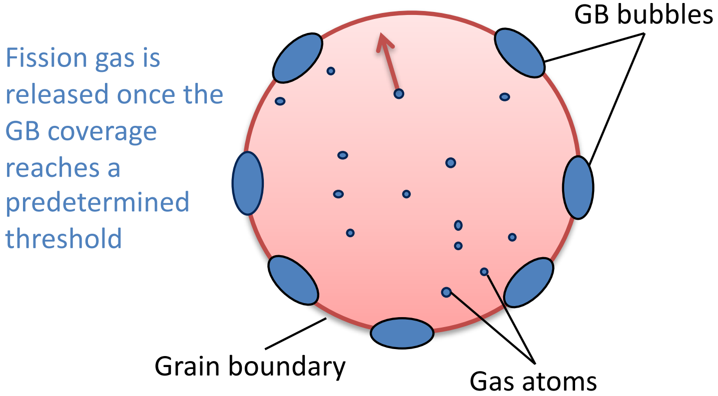
  - f = 4*sqrt(8e-15*3600/(pi*(10e-4)^2)) – 3/2*8e-15*3600/(10e-4)^2 = 0.0121

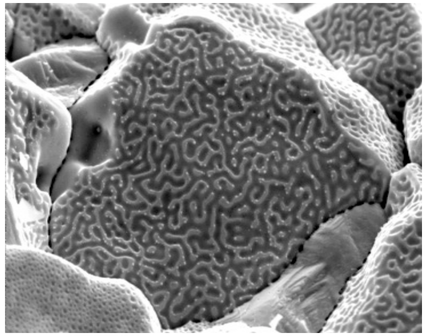
As time progresses, both the fraction released and the produced gas increase



Forsberg-Massih model

- The Booth model ONLY considers stage one of fission gas release
- Two stage Forsberg-Massih mechanistic model
  - Considers intragranular diffusion diffusion to grain boundaries (stage 1)
  - Also, grain boundary gas accumulation, resolution back into grain, saturation (stage 2)
  - Assumes that once the bubbles on the grain face are interconnected, it is released (no stage 3)





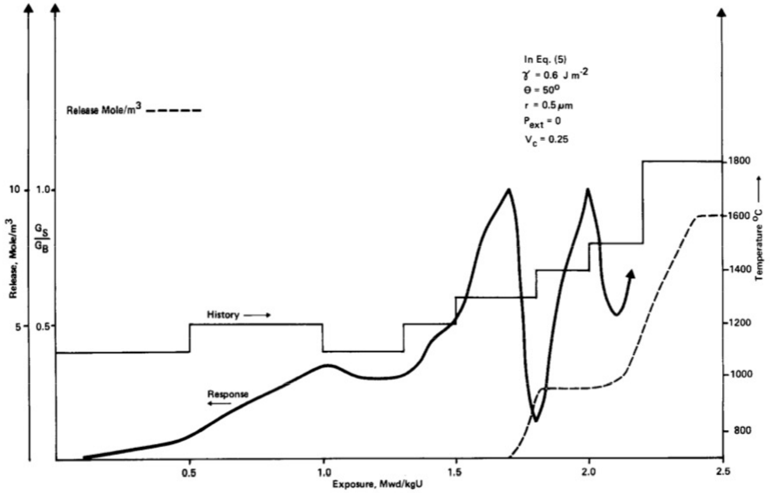
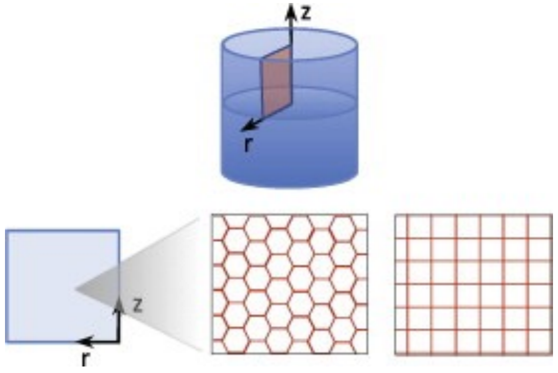
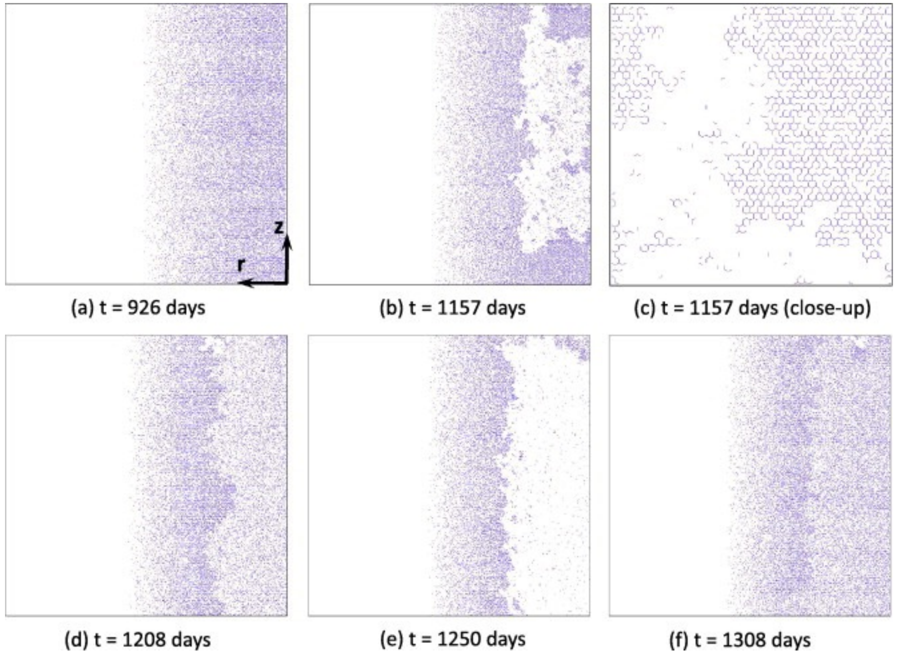


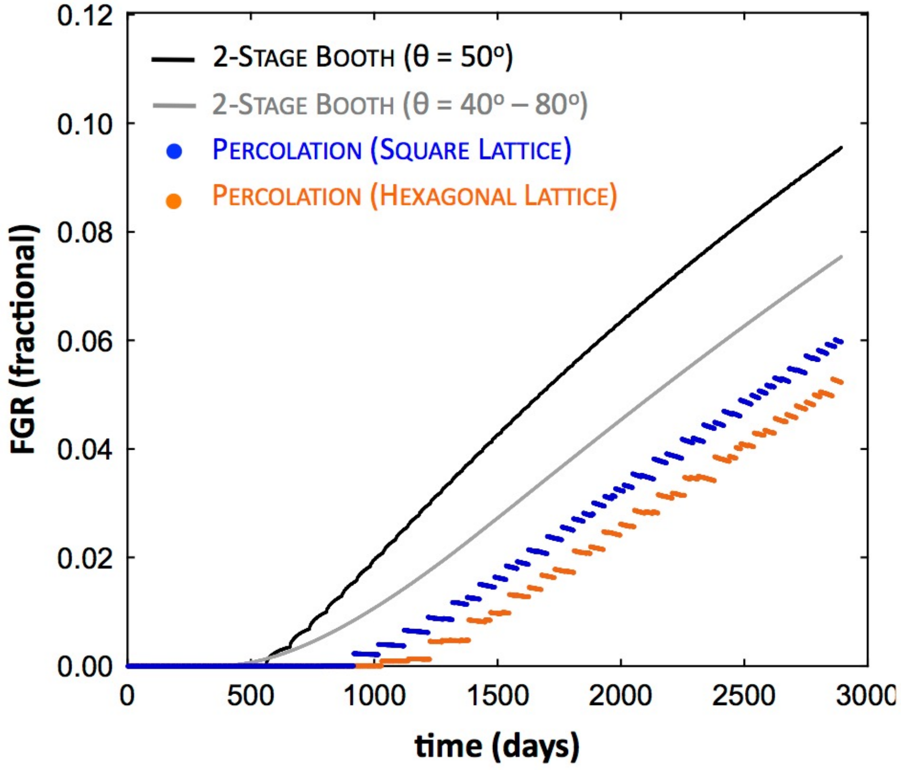
Fig. 1. Fraction of gas atoms on grain boundary, G_s/G_B, as a function of exposure for downward fuel cascading temperature history. γ is the bubble surface tension, 2θ is the angle where two free surfaces meet at a grain boundary, r is average bubble radius, V_c is the fractional coverage of the grain boundaries at saturation and the grain radius is taken to be 5 μm.

Forsberg-Massih model

- 2-stage F-M model over-predicts gas release because it neglects grain boundary bubble percolation (Stage 3)



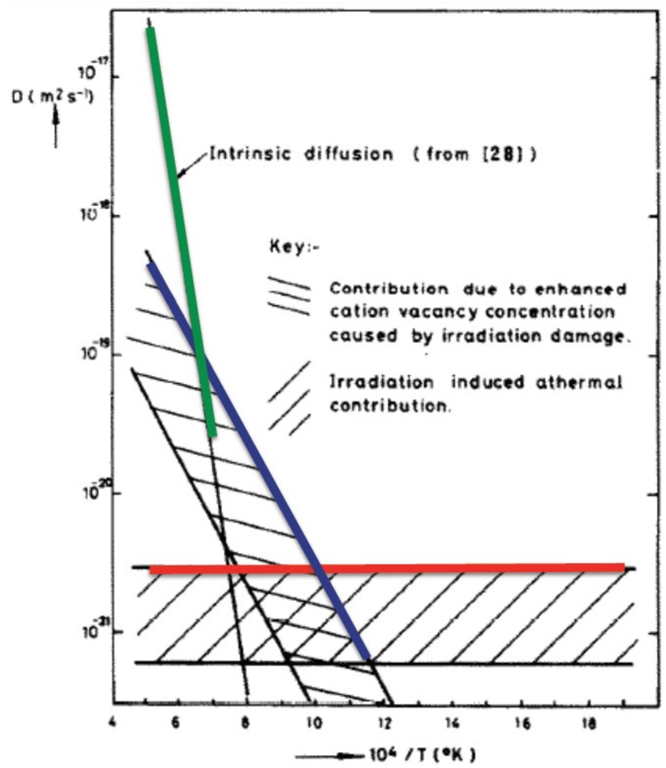




Millett, Tonks, and Biner. JNM, 424.1 (2012): 176-182.

Gas diffusion

- The diffusivity of the fission gas depends on temperature and on irradiation
- Experimental data shows three different regimes for the diffusivity

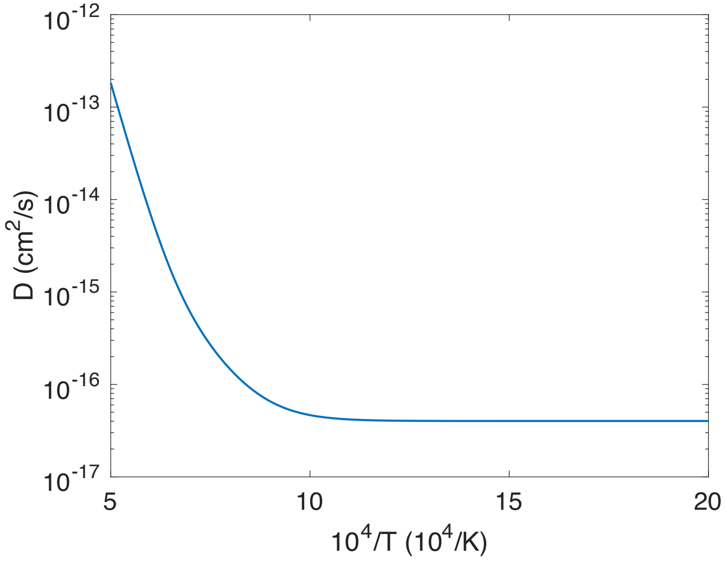


$$D = D_1 + D_2 + D_3 \text{ cm}^2/\text{s}$$

$$D_1 = 7.6 \times 10^{-6} e^{-\frac{3.03 \text{ eV}}{k_b T}}$$

$$D_2 = 1.41 \times 10^{-18} e^{-\frac{1.19 \text{ eV}}{k_b T}} \sqrt{\dot{F}}$$

$$D_3 = 2.0 \times 10^{-30} \dot{F}$$



Gas diffusion

- The effective fission gas diffusivity is slower due to trapping by intragranular bubbles
- As the gas atoms diffuse towards the grain boundary, some are trapped by the small intragranular bubbles
- Some are later knocked out by energized particles (called resolution)
- The effective diffusion constant depends on the trapping rate r_t and the resolution rate r_r

$$D_{eff} = \left(\frac{r_r}{r_r + r_t}\right) D$$

Summary

- Five families of fission products, which change the fuel behavior
  - soluble oxides, insoluble oxides, noble metals, volatiles, noble gases
- Fission gas is released in three stages
  1. Fission gas production and diffusion to grain boundaries
  2. Grain boundary bubble nucleation, growth, and interconnection
  3. Gas transport through interconnected bubbles to free surfaces
- There are models which include 2^{nd} and 3rd stages of fission gas release
- Fission gas diffusivity behavior changes with temperature and fission rate