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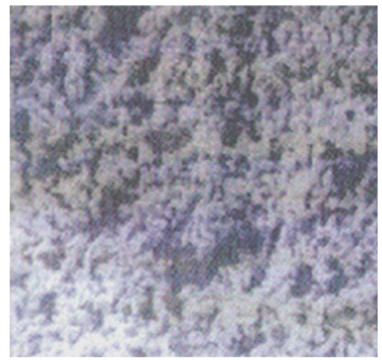

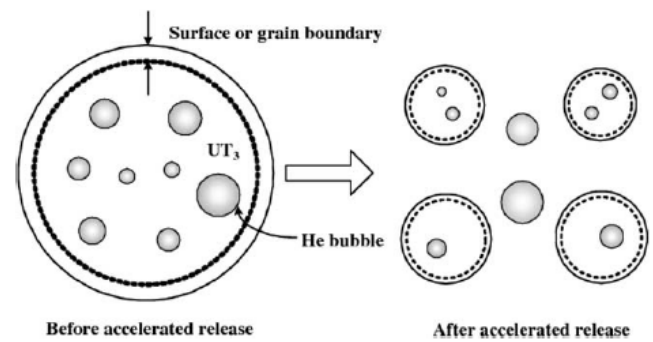


# Effect of helium-3 formation on the thermal decomposition of uranium tritide particle beds

Ryan Keedy and Patricia Gharagozloo
Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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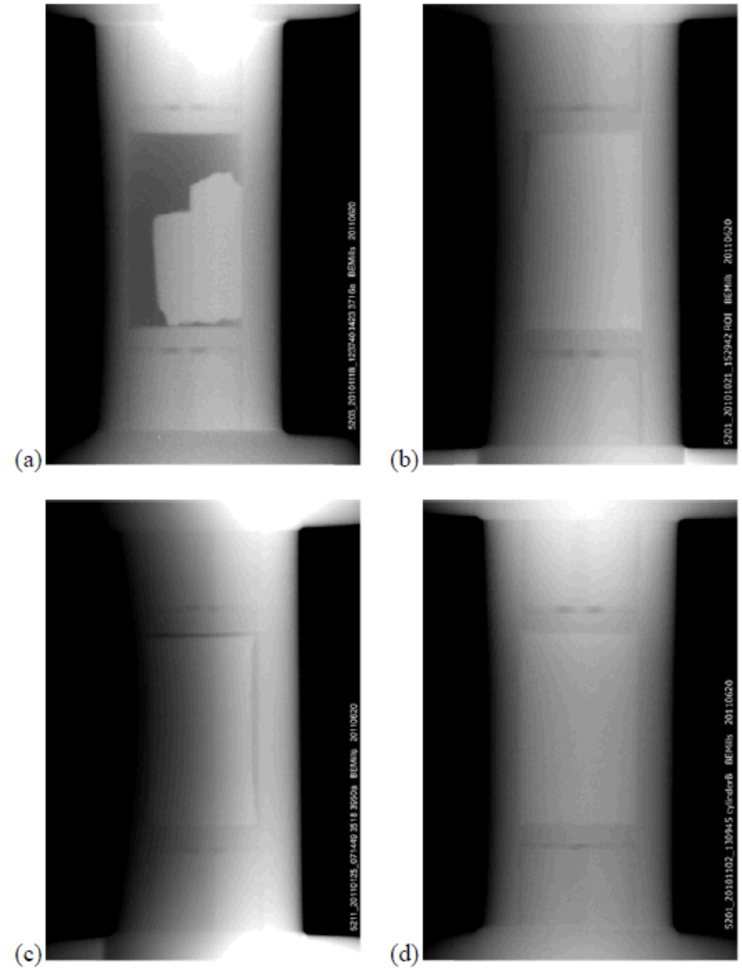
# Introduction

- Metal hydrides are used for hydrogen storage
- Uranium has advantages versus other hydriding metals
  - Very quick uptake/release rate
  - Very high hydrogen:metal atomic ratio
  - Tolerant of impurities
- Because uranium hydride is hazardous, experimental studies have been limited
- Goal is to simulate the behavior of dehydration as a function of bed temperature and age

# $UH_3$ is less dense than U

- Hydrided uranium nearly doubles in volume
  - Not an interstitial compound



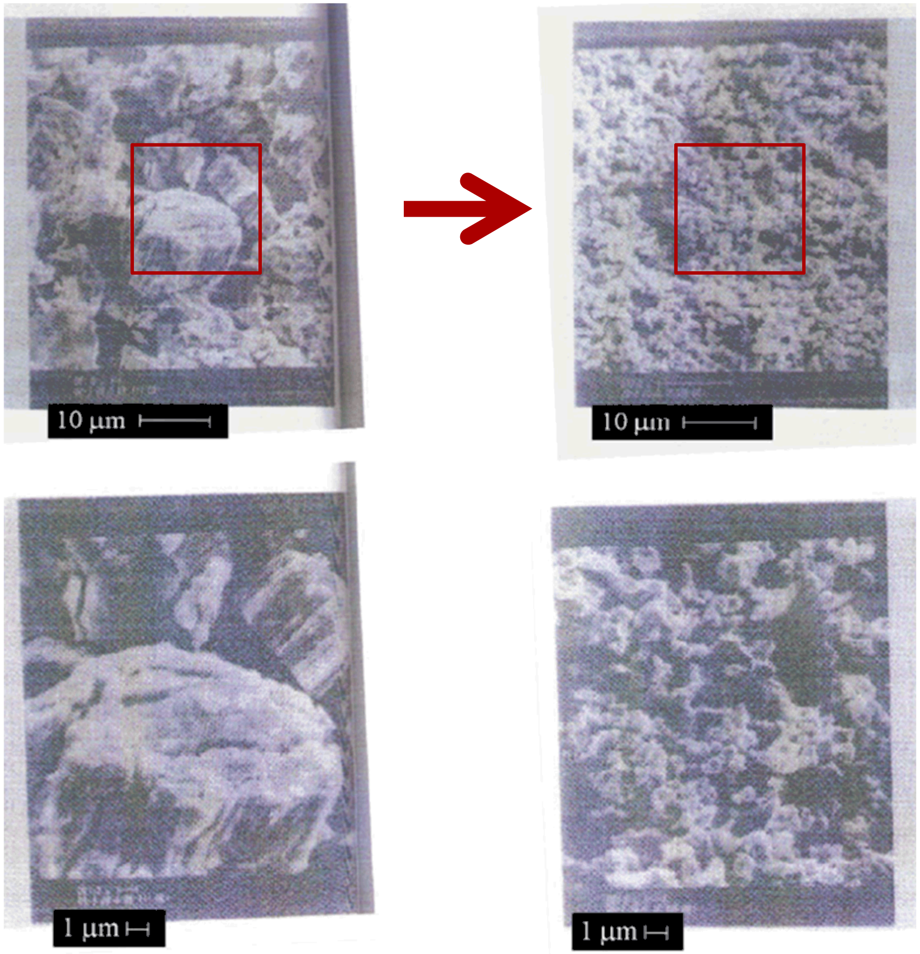

Shugard, et al, 2011. *Rapid hydrogen gas generation using reactive thermal decomposition of Uranium hydride.* SAND2011-6939, Sandia National Laboratories

# Uranium hydride breaks into particles

- Uranium metal exposed to hydrogen gas leads to embrittlement
  - Formation of uranium hydride ($UH_3$)

$$2U + 3H_2 \rightarrow 2UH_3$$

  - Stress from repeated cycling typically results in a fine powder (~0.5-0.75 µm diameter)
  - Uniform, equilibrium bed properties are reached after ~3 cycles



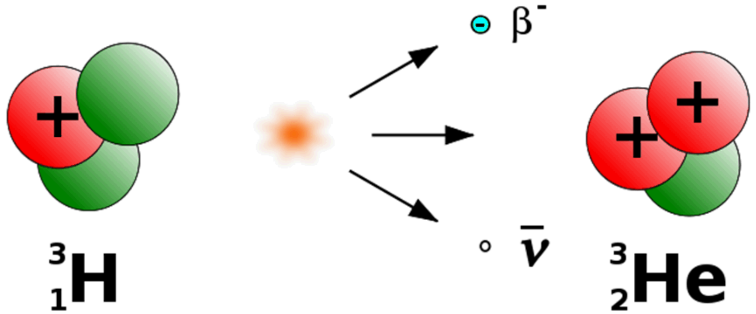

1 hydride cycle

5 hydride cycles

Downs, Tucker, and Jones. "*A Review of the Mound Sem Facility for Radioactive and Pyrophoric Materials*". Conference presentation. *Unpublished Studies.* Sandia National Labs. (1982).

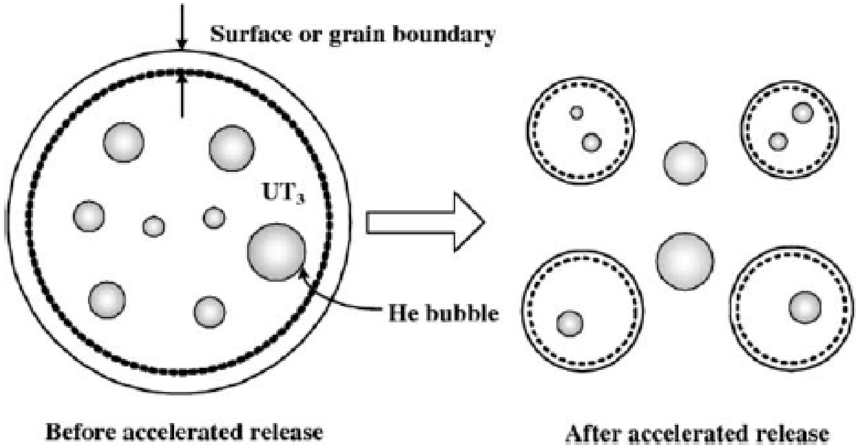
# Helium formation

- Tritium is a hydrogen isotope with a half-life of ~12 years
- Tritium beta decays to helium-3
- Tritium in $UT_3$ is assumed to be replaced by ambient pressure



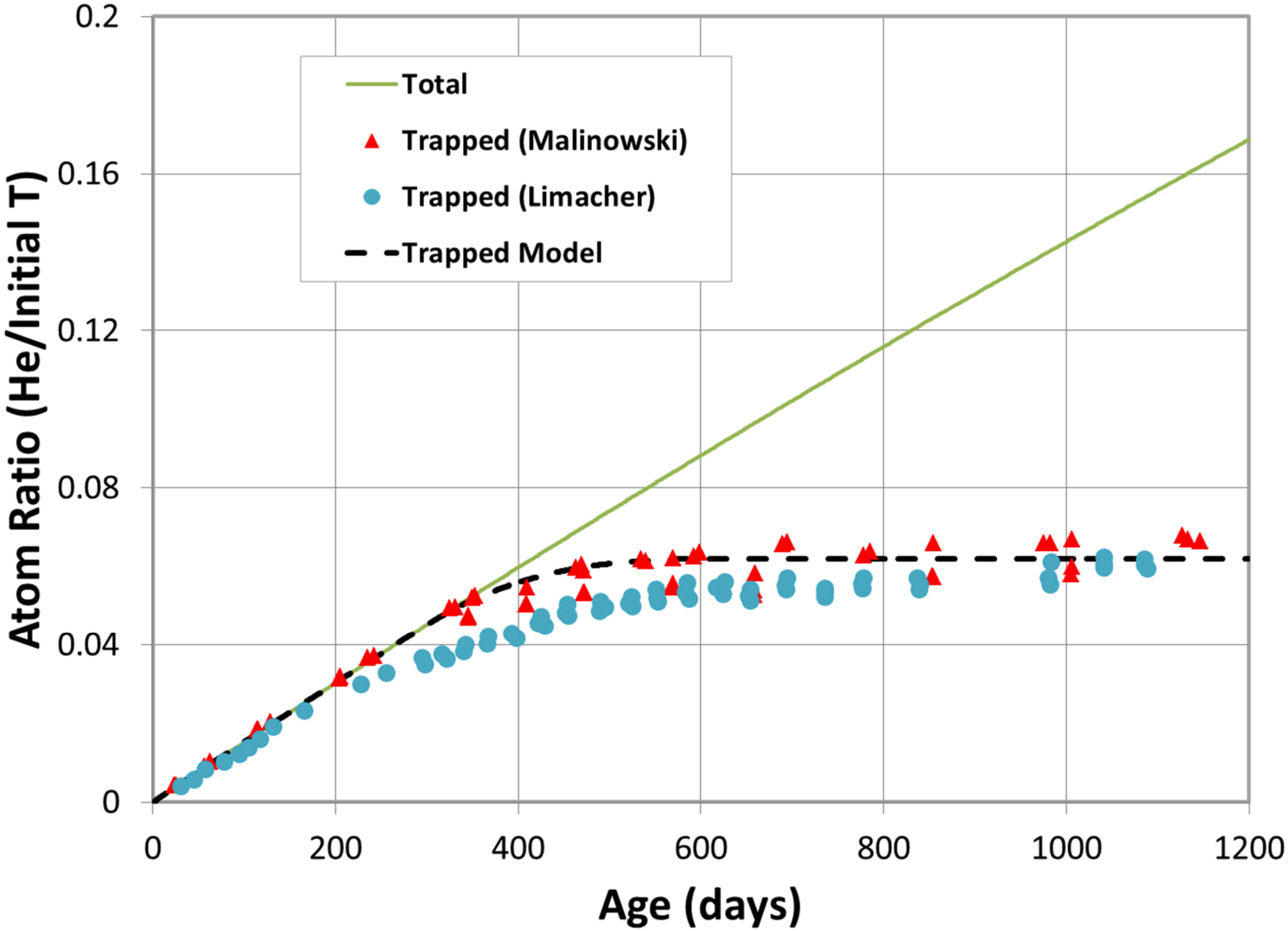
# Helium is trapped in bubbles

- Helium is believed to form "bubbles" in the metal under very high pressures
- Bubble size grows as tritium continues to decay
- Amount of trapped helium follows isotope decay behavior before leveling off



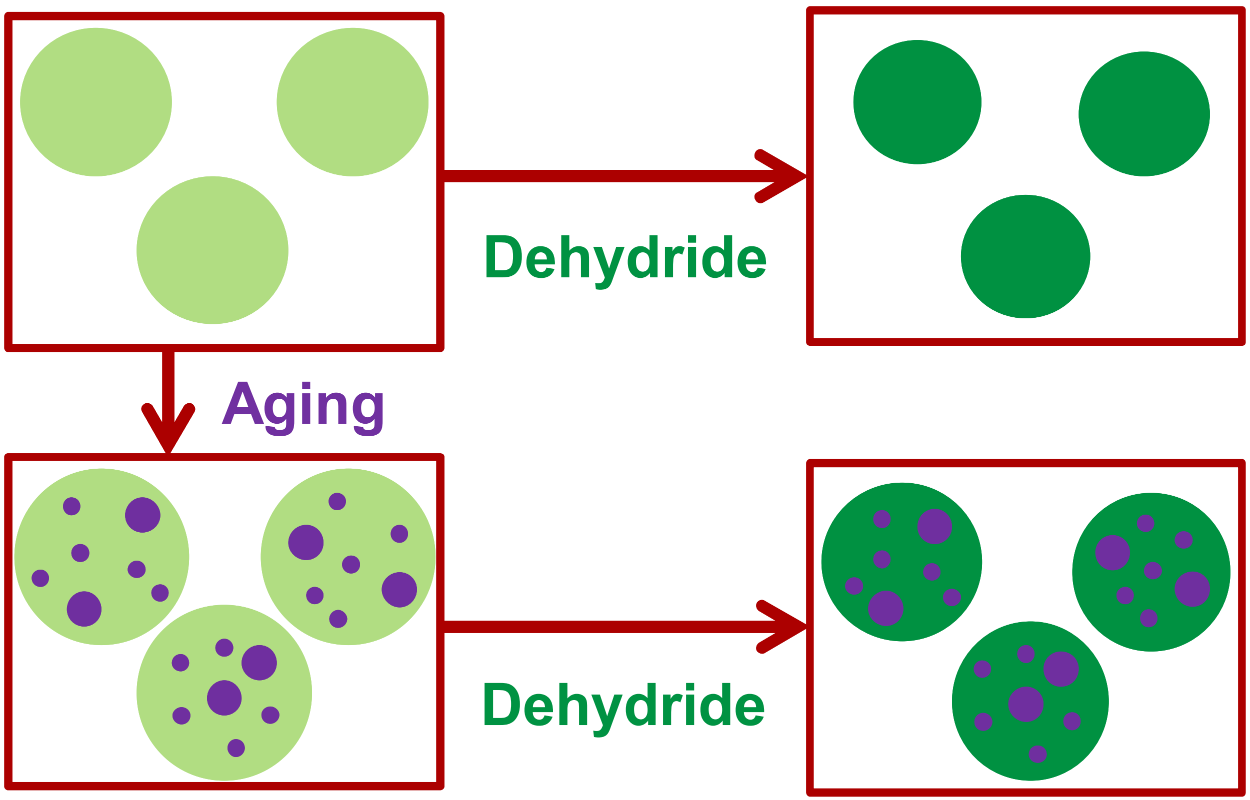

Ao, et al, 2009. *X-ray diffraction analysis of uranium tritide after aging for 420 days*.

# Helium bubble mass plateaus



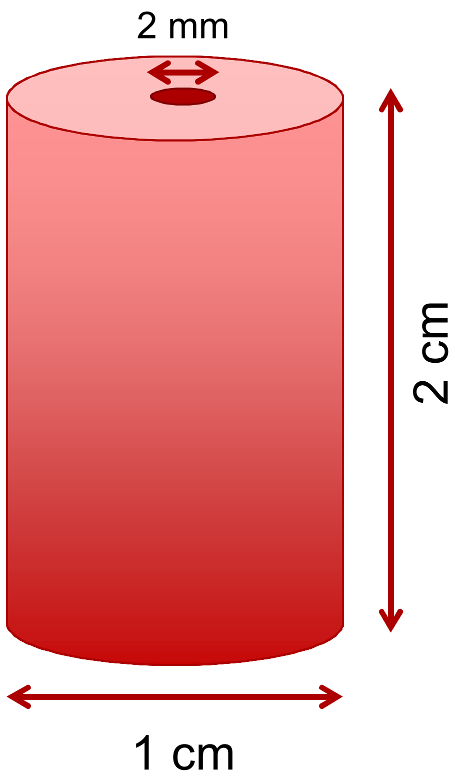
# Helium bubbles decrease porosity

- The helium bubbles swell the uranium particles, decreasing porosity
- Dehydrided particle bed is also less porous when helium bubbles are present



# Problem geometry

- Uranium powder bed
  - Sealed cylindrical container
  - Low ambient pressure
- Temperature is set uniformly throughout the domain
- Hydrogen gas is allowed to flow out of an opening at one end of the cylinder
- Predict evolution of hydride mass fraction



# Modeling assumptions

- Helium volume is a function of bed age
- Trapped helium assumed to remain in situ during release
  - Volume will remain constant
- Bed particles are assumed to be spherical
- As metal particles de-hydride, their density increases, and volume decreases
- Decreasing particle volume results in higher porosity
  - Spatially resolved as a function of tritium content

# Model formulation

- Solve a system of PDEs:
  - Mass/species balance
  - Continuity
- Additional equations required:
  - Chemistry
  - Porosity
  - Permeability
  - Gas EOS
  - Velocity (Darcy’s Law)
- Simulation is conducted with Aria
  - Part of the SIERRA suite of codes developed and used by Sandia National Laboratories

# Permeability is a function of porosity

- Function of porosity and Knudsen number
  - $Kn = \lambda / d_p$ (function of total pressure)
  - Spatially resolved as a function of hydrogen content and total pressure
- Tortuosity ($\tau$) and pore diameter ($d_p$) are both taken to be functions of porosity

$$\tau = \frac{1.25}{\phi^{1.1}}$$

$$d_p = 2R\left[\frac{\phi}{1-\phi}\right]^{1/3}$$

$$\lambda = \frac{\mathcal{R}T}{\pi\sqrt{2}N_A P d_{H_2}^2}$$

$$\kappa = \frac{\phi d_p^2}{\tau^2}\left(\frac{1}{32} + \frac{5}{12}Kn\right) = 1.28R\phi^{3.2}\left[\frac{\phi}{1-\phi}\right]^{1/3}\left(\frac{R}{16}\left[\frac{\phi}{1-\phi}\right]^{1/3} + \frac{5\sqrt{2}}{24}\frac{\mathcal{R}T}{\pi N_A P d_{H_2}^2}\right)$$

Young and Todd, 2005. *Modelling of multi-component gas flows in capillaries and porous solids.* International Journal of Heat and Mass Transfer

# Chemistry equations

$$2U + 3H_2 \leftrightarrow 2UH_3$$

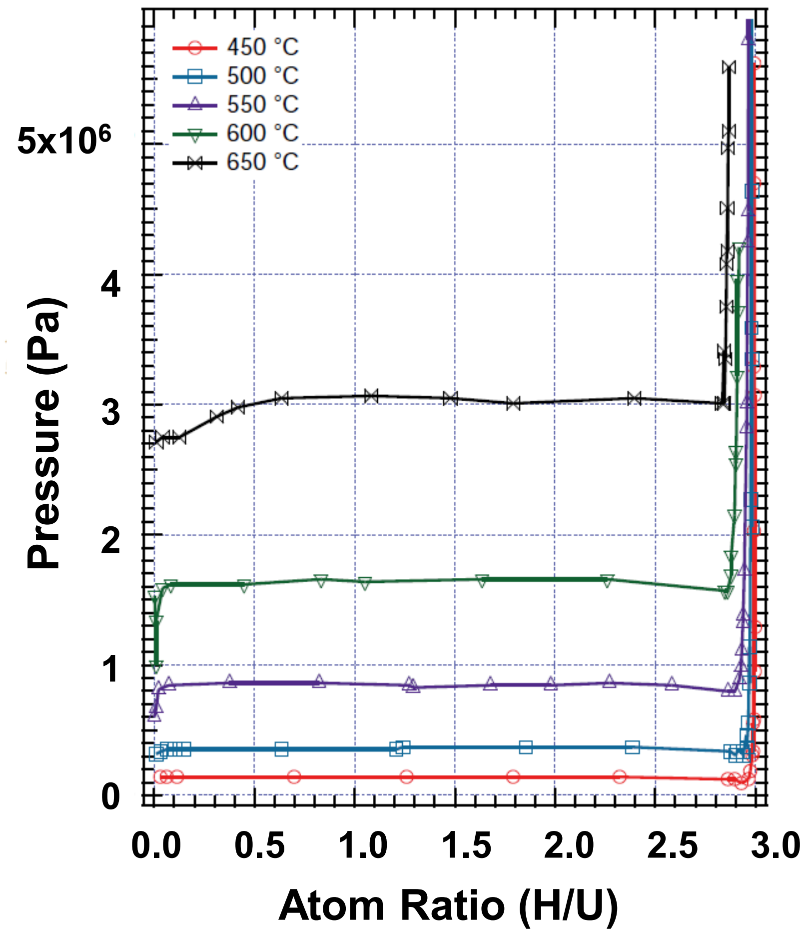
- Equilibrium pressures have been established in the literature:

$$P_0[torr] = 10^{9.47 - \frac{4700}{T\,[K]}}$$

- Rate of decay for hydration is fitted to

$$\frac{\partial U}{\partial t} = k(1-U)^{2/3} ln\left(\frac{P_0}{P}\right)$$

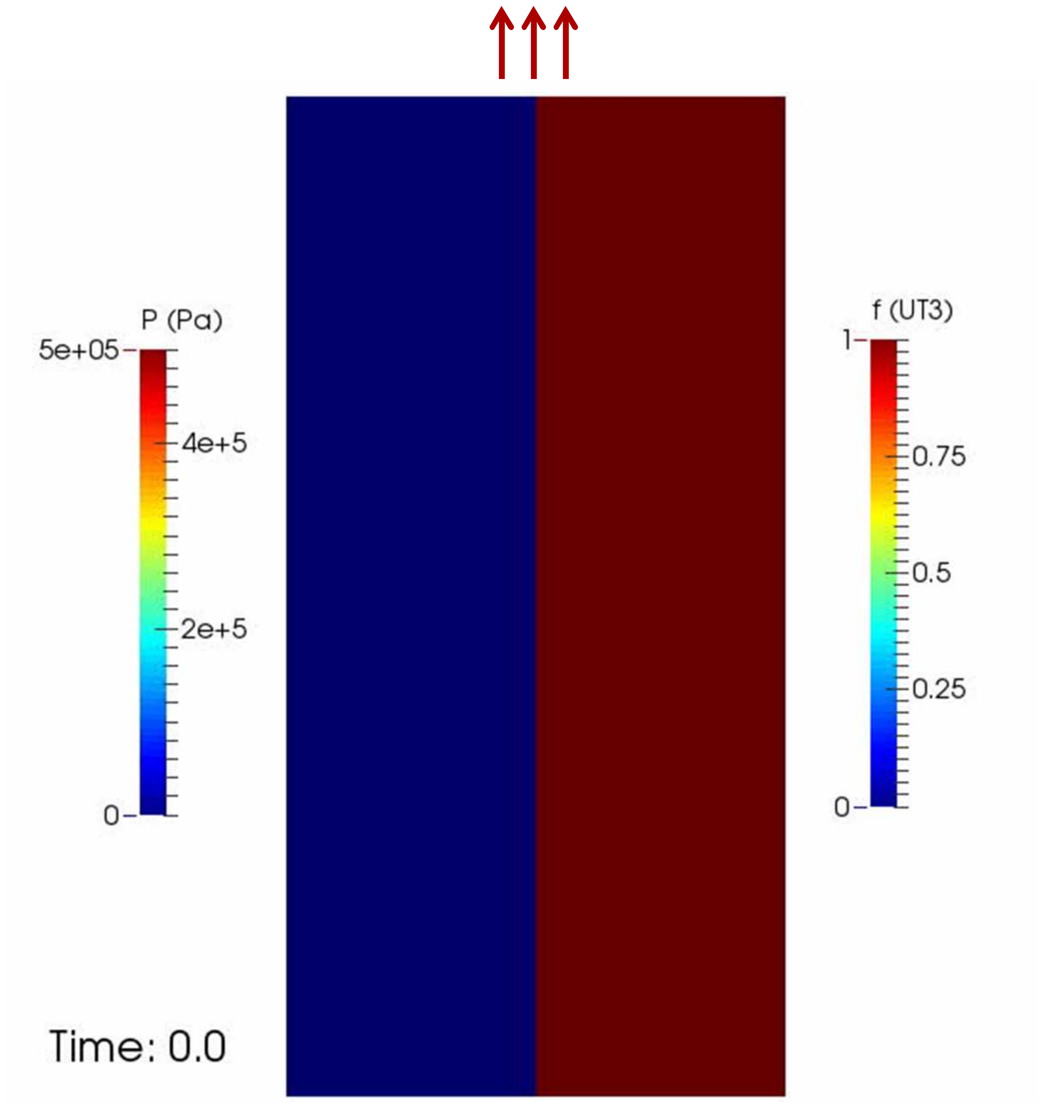
$$k(\mathrm{T}) = Ae^{-E_a/(RT)}$$

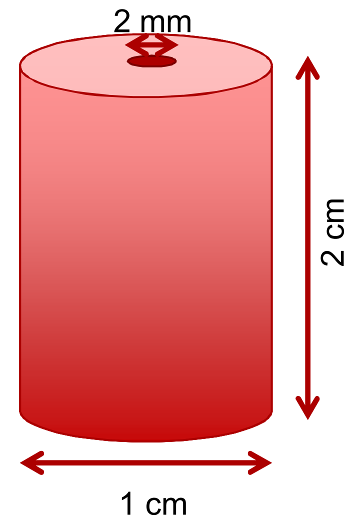



Lindner, D.L, 1990. *Isothermal Decomposition of Uranium Hydride*. Journal of the Less-Common Metals

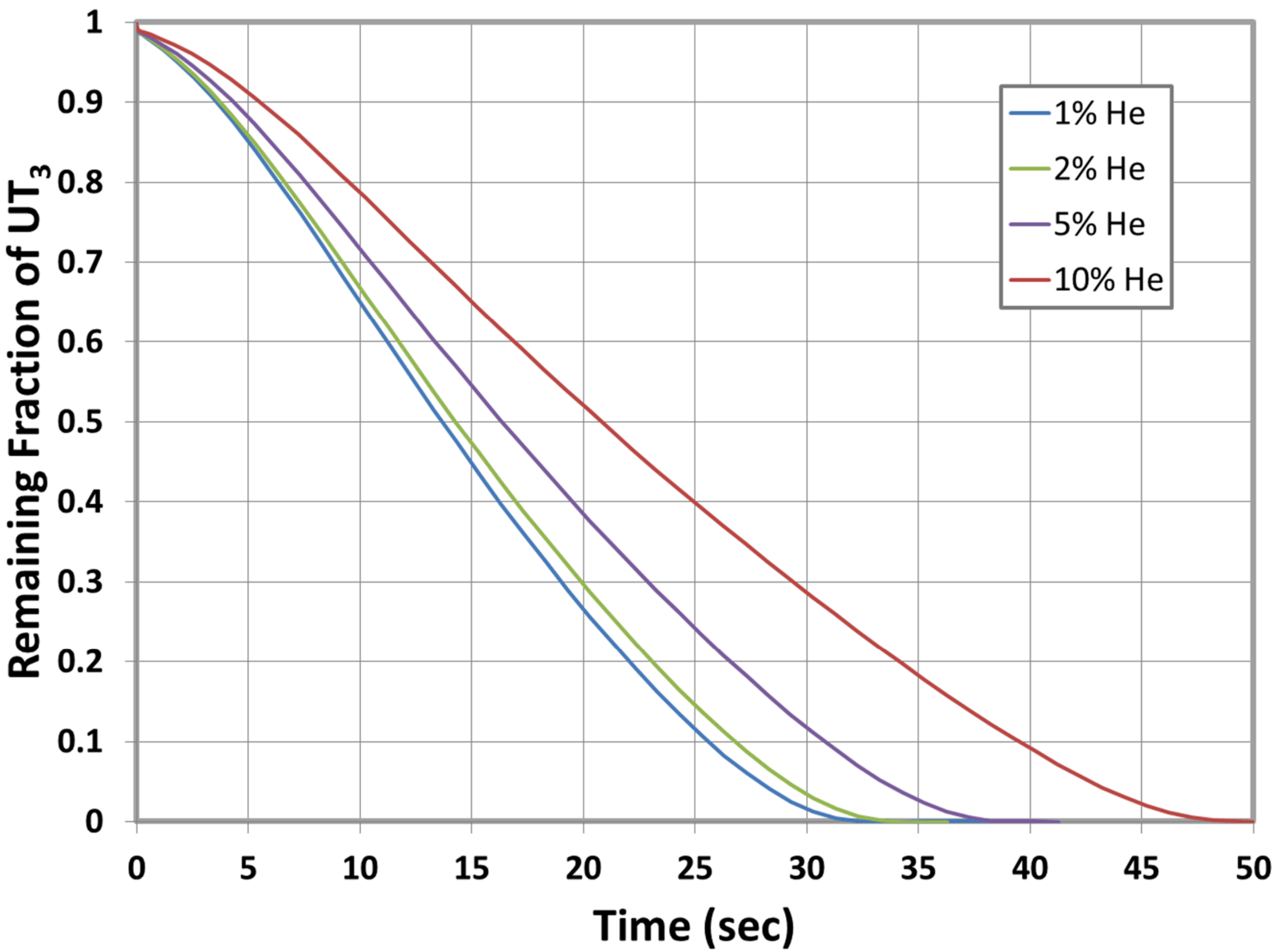
Libowitz and Gibb, 1957. *High Pressure Dissociation Studies of the Uranium Hydrogen System.* Journal of Physical Chemistry.

# Gas flows out as $UT_3$ decays

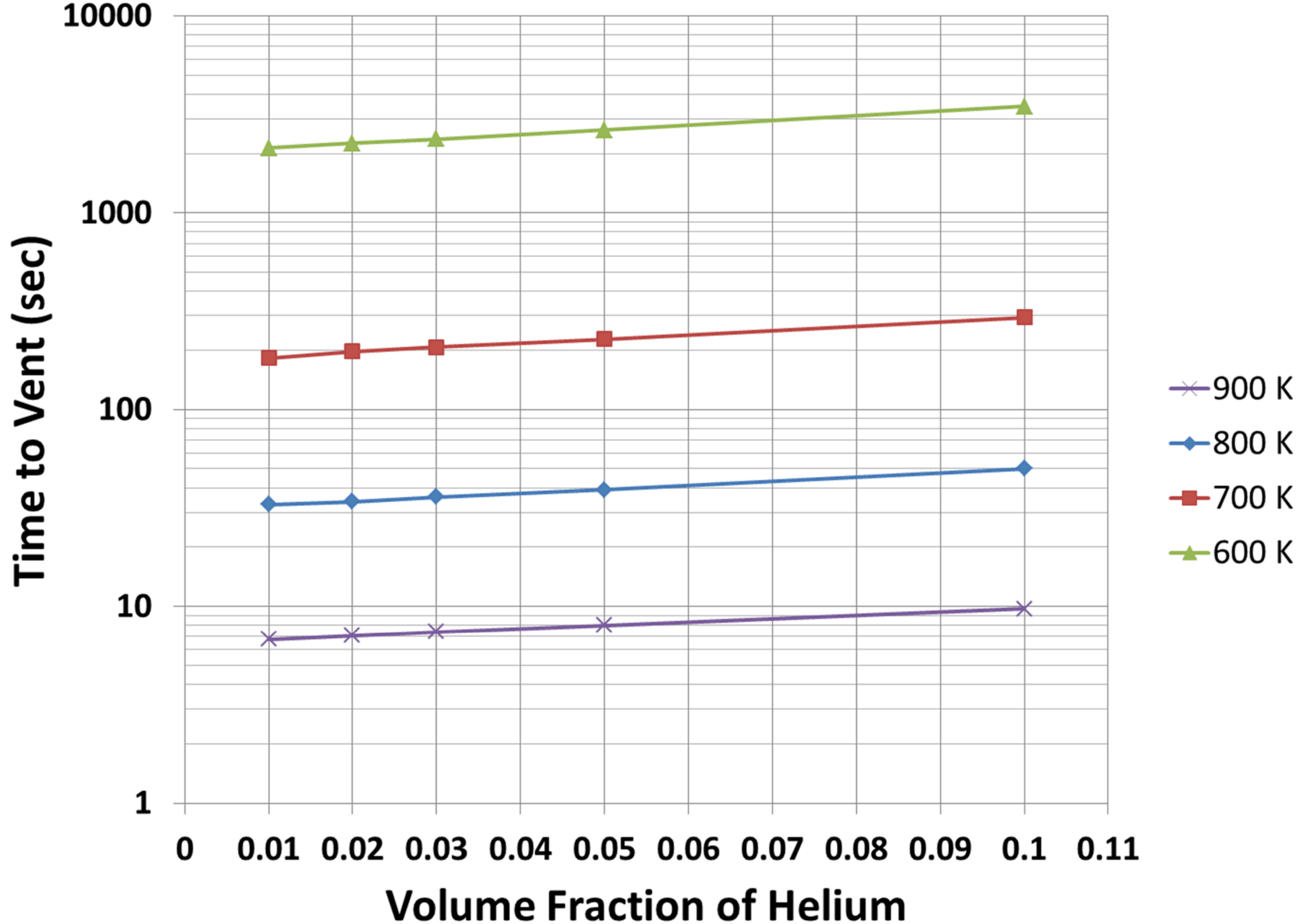


# Aged $UT_3$ increases venting time



# Temperature and aging effects on venting



# Conclusions and future work

- Fresh uranium hydride bed empties ~1.5x faster than aged bed
- Venting time is a strong function of temperature
- Incorporate additional physics into model
  - Energy equations
  - Helium gas source terms
  - Oxidation
- Comparison to experiments

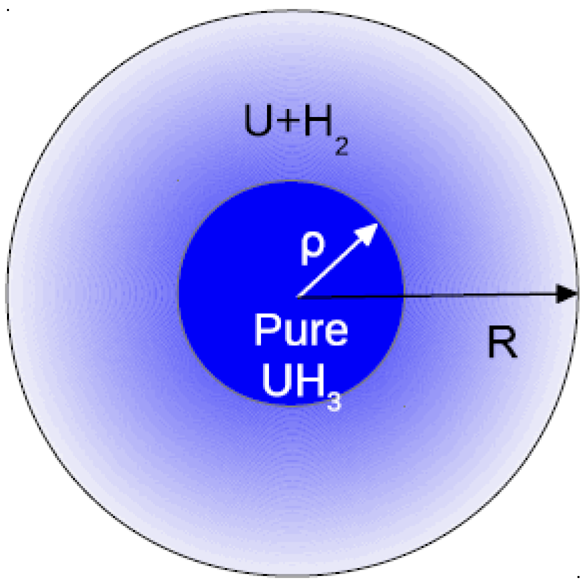
# SUPPLEMENTAL SLIDES

# Physics-based model

- Combine PDE's for diffusion within the particle

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

$$-D\frac{\partial c}{\partial r} = \Gamma \frac{\partial \rho}{\partial r}$$




- COMSOL model solves for *k*:

$$R_{UH_3} = 3k([UH_3]_0 - [U])^{2/3}[UH_3]_0^{1/3} log\left(\frac{P_0}{P}\right)$$

- Equilibrium pressure described by

$$log_{10}(P_0) = -\frac{A}{T} + B$$

# Model consistent with experiments