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Title: Effects of Pressure on Thermal Transport in Plutonium
Oxide Powder

Author(s): Patricia Bielenberg NMT-11
Coyne Prenger ESA-AET
D. Kirk Veirs NMT-11
Jerry Jones Villanova University

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Radial temperature profiles in plutonium oxide (PuO_2) powder were measured in a cylindrical vessel over a pressure range of 0.055 to 334.4 kPa with two different fill gases, helium and argon. The fine PuO_2 powder provides a very uniform self-heating medium amenable to relatively simple mathematical descriptions. At low pressures (<0.1 kPa), the effective thermal conductivity of the powder bed was approximately the same with either helium or argon since the dominant mechanisms are thermal radiation between particles and solid-solid conduction pathways. At high pressures, the effective thermal conductivity of the powder bed is typically assumed in the literature to be dominated by the gas thermal conductivities. However, from experimental measurements at high pressures, the effective thermal conductivity of the powder bed with argon as a fill gas is approximately three times higher than would be predicted from the gas thermal conductivities. Additionally, a significant pressure dependence was measured at pressures greater than atmospheric where the gas thermal conductivity would typically be assumed to be in the continuum limit and independent of pressure.

An analytical model was developed for heat conduction in the fine ceramic powder with conduction pathways in parallel and in series through the gaseous and solid components. Many analytical models in the literature were unsuitable for this system because they make limiting assumptions about the particle dimensions and shape and are developed for packed beds with higher packing fractions. PuO_2 powder has small particle sizes (on the order of 1 to 10 μm), random particle shapes, and high porosity so a more general model was required for this system. The model correctly predicts the temperature profiles of the powder over the wide pressure range for both argon and helium as fill gases. The effective thermal conductivity of the powder bed exhibits a pressure dependence at higher pressures because the pore sizes in the interparticle contact area are relatively small (less than 1 μm) and the Knudsen number remains above the continuum limit at these conditions for both fill gases. Also, the effective thermal conductivity with argon as a fill gas is higher than expected at higher pressures because the solid pathways account for over 80% of the effective powder conductivity. The results obtained from this model help to bring insight to the thermal conductivity of very fine ceramic powders with different fill gases.

Effects of Pressure on Thermal Transport in Plutonium Oxide Powder

Patricia Bielenberg^a, Coyne Prenger^b, Kirk Veirs^a, and Jerry Jones^c

^a Los Alamos National Laboratory, Nuclear Materials Technology Division

^b Los Alamos National Laboratory, Engineering Sciences and Applications Division

^c Villanova University, Dept. of Mechanical Engineering

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Background and Motivation

- The DOE is storing plutonium dioxide (PuO_2) powder in storage containers while awaiting final disposition
- The governing storage standard specifies limits on the safe storage of PuO_2 containers
 - Power generation < 19 W
 - Mass of PuO_2 < 5.0 kg
 - No specific temperature specifications
- Thermal properties of PuO_2 in the storage configuration are important because as temperature increases:
 - outgassing in the container increases
 - fill gas pressure increases
 - vapor pressure of water increases
 - distribution of water between materials changes
 - kinetics of reactions affecting hydrogen gas generation and corrosion changes

Background and Motivation:

Previous modeling efforts

- Finite element models were developed to predict temperature profiles throughout storage containers¹⁻³
- No experimental data for the effective thermal conductivity of the PuO_2 powder were available
- Deissler-Eian correlation used to predict effective thermal conductivities
 - estimated from solid thermal conductivity (k_s), gas thermal conductivity (k_g), and powder porosity (ϵ)
- For $k_{eff}=0.079$ W/m-K and 19 W of PuO_2 ,
 - T_{max} was 229 °C
 - radial ΔT across the PuO_2 bed was 100 °C

PuO_2 powder thermal conductivity(W/m-K) $T=50$ °C			
fill gas	$\epsilon=0$	$\epsilon=0.76$	$\epsilon=1.0$
Helium	1.88	0.31	0.16
Air	1.88	0.082	0.027
Argon	1.88	0.061	0.019

1. T. D. Knight and R. G. Steinke, Thermal analysis of plutonium materials in British Nuclear Fuels, Ltd., containers, Los Alamos National Laboratory Report, LA-UR-97-1866, 1997.

2. S. Hensel, Thermal analysis of the 9975 package as a plutonium storage container, Westinghouse Savannah River Company Report, WSRC-TR-98-00203, 1998a.

3. S. Hensel, Thermal analysis of the 9975 package with the 3013 configuration during normal conditions of transportation, Westinghouse Savannah River Company Report, WSRS-CT-98-00420, 1998b.

Current heat transfer study

Goal: Provide a better prediction of heat transfer rates in PuO_2 powder for use in computing maximum T , P in storage containers

- Experimentally measure temperature profiles in PuO_2 powder
- Develop a model for k_{eff} of the PuO_2 powder and compare predictions to experimental data

PuO₂ powder thermal profile measurements

Radial temperature profiles measured in porous PuO₂ at different pressures

- Porosity=0.774
- $m_{bed}=5.00$ kg
- Wattage=10.3 W
- $V_{bed}=1920$ cm³
- Gases: Argon and Helium
- P range=0.055 to 334 kPa

Experimental results for Ar powder

Radial profiles – Argon powder

Calculated effective thermal conductivities

P (kPa)	ΔT_{bed} (° C)	k_{eff} (W/m-K)
214.0	44	0.090
81.8	52	0.077
38.6	61	0.064
10.8	95	0.041
3.0	164	0.024
1.240	233	0.017
0.570	292	0.013
0.260	330	0.012
0.130	354	0.011
0.070	364	0.011

$$T(r) = -\frac{\dot{q}r^2}{4k_{eff}} + T(r=0)$$

$$k_{eff}\Delta T_{bed} = \frac{\dot{q}R^2}{4}$$

Pressure dependence of k_{eff}

- Gas thermal conductivity (k_g) is pressure dependent depending on operating regime
- Operating regime determined by Knudsen number (Kn)

$$Kn = l/\lambda$$

- λ =pore size
- l =mean free path

$$l = \frac{k_B T}{\sqrt{2} \pi D_m^2 P}$$

- Gas conductivities:
 $k_{cont} = f(T)$ only

$$k_{fm} = \left(\frac{\alpha}{2 - \alpha} \right) \lambda \Lambda_o P \sqrt{\frac{T_{ref}}{T}}$$

He and Ar centerline temperatures

Helium		Argon	
$P(\text{kPa})$	k_{eff} (W/m-K)	$P(\text{kPa})$	k_{eff} (W/m-K)
334.4	0.29	214.0	0.090
277.6	0.28	81.8	0.077
173.2	0.24	38.6	0.064
130.4	0.24	10.8	0.041
82.2	0.22	3.0	0.024
69.8	0.20	1.240	0.017
35.0	0.15	0.570	0.013
7.0	0.066	0.260	0.012
3.6	0.043	0.130	0.011
1.2	0.022	0.070	0.011
0.890	0.019		
0.770	0.018		
0.390	0.015		
0.225	0.013		
0.210	0.012		
0.130	0.012		
0.055	0.011		

k_{eff} predictions from D-E eqn.:

$$k_{eff,He} = 0.31 \text{ W/mK}$$

$$k_{eff,Ar} = 0.063 \text{ W/mK}$$

New model development

- Effective thermal conductivity models in the literature do not correctly predict our experimental results
 - the PuO_2 powder contains random shaped particles with a high porosity
 - many models make limiting assumptions, such as equal sized spheres with a packing fraction of 0.475
 - most models predict that $k_{\text{eff,He}} = 5 * k_{\text{eff,Ar}}$ at high pressure. From our experimental measurements, $k_{\text{eff,He}} = 3 * k_{\text{eff,Ar}}$
- Developed a model with heat conduction through gas and solid pathways in parallel and in series
 - primary difference from similar models in literature^{4,5}: no limiting assumptions about powder porosity or particle shape

4. S. Masamune and J. M. Smith, Thermal conductivity of beds of spherical particles, Industrial and Engineering Chemistry Fundamentals 2(2) (1963) 136-143.

5. S. Hayashi, K. Kubota, H. Masaki, Y. Shibata, and K. Takahashi, A theoretical model for the estimation of the effective thermal conductivity of a packed bed of fine particles, The Chemical Engineering Journal 35(1) (1987) 51-60.

Thermal conductivity model

ϵ =porosity
 $\delta=d/D$ =contact roughness
 L/D =interparticle contact fraction
 $k_{g,o}$ =gas conductivity in outer pore
 $k_{g,in}$ =gas conductivity in gap
 k_{solid} =PuO₂ solid conductivity

D =particle diameter
 d =gap distance
 L =interparticle contact length
 ϕ =sphericity

$$k_{eff} = \epsilon k_{g,o} + (1 - \epsilon) \left(\frac{L}{D} \right) k_s$$

$$\frac{1}{k_s} = \frac{1 - \delta}{k_{solid}} + \frac{\delta}{k_{in}}$$

$$k_{in} = \phi k_{solid} + (1 - \phi) k_{g,in}$$

$$k_{eff} = \epsilon k_{g,o} + \frac{(1 - \epsilon) \left(\frac{L}{D} \right)}{\left[\frac{\delta}{\phi k_{solid} + (1 - \phi) k_{g,in}} + \frac{(1 - \delta)}{k_{solid}} \right]}$$

Parameters to calculate k_{eff}

- To calculate k_{eff} , we need to estimate:
 - the parameters δ , ϕ , and L/D
 - the pore sizes (λ_o and λ_{in}) to calculate $k_{g,o}$ and $k_{g,in}$ for each gas

Parameter	Value
δ	3.7×10^{-3}
ϕ	1.8×10^{-4}
L/D	0.10
$\lambda_{in}(\mu\text{m})$	0.68
$\lambda_o(\mu\text{m})$	17

$$k_{eff} = \varepsilon \underline{k_{g,o}} + \frac{(1-\varepsilon)(\underline{L/D})}{\left[\frac{\delta}{\underline{\phi} k_{solid} + (1-\underline{\phi}) \underline{k_{g,in}}} + \frac{(1-\delta)}{k_{solid}} \right]}$$

k_g free molecular expressions
(shown for argon)

$$k_{gAr,o} = \left(\frac{\alpha_{Ar}}{2 - \alpha_{Ar}} \right) \underline{\lambda_o} \Lambda_{Ar} P \sqrt{\frac{T_{ref}}{T}}$$

$$k_{gAr,in} = \left(\frac{\alpha_{Ar}}{2 - \alpha_{Ar}} \right) \underline{\lambda_{in}} \Lambda_{Ar} P \sqrt{\frac{T_{ref}}{T}}$$

Gas-dependent parameters	Ar	He
α	0.9	0.5
$\Lambda(\text{W/m}^2\text{-K-Pa})$	0.697	2.202

Modeling results: importance of interparticle contact area

Complex behavior captured due to small pore size in interparticle contact area

- P dependence at high P:
 $Kn_{in} < 0.01$ until $P = 1200$ kPa
- $k_{eff,He} = 3 * k_{eff,Ar}$ at high P

in interparticle contact area,

$k_{g,He} = 4 * k_{g,Ar}$
compared to

$k_{cont,He} = 8 * k_{cont,Ar}$

Radial profile results for argon

- Predicted radial profiles agree well with expt. measurements at all pressures
- Indicates that contributions of thermal radiation and heat conduction are correctly captured by model
 - thermal radiation most important at high T (T^4 dependence)
 - at low P, thermal radiation important in center of container and solid-solid conduction dominates near container wall

Conclusions

- Measured temperature profiles of PuO_2 powders at varying pressures with argon and helium fill gases
- Developed thermal conductivity model that agrees well with experimental data
 - determined that including interparticle area and pore size was necessary to predict high pressure powder behavior
 - thermal conductivity expression can be used for a wide variety of powders
- Compared predictions from new conductivity expression with thermal conductivity values used in previous PuO_2 modeling studies
 - previous PuO_2 thermal conductivity value:
 - $k_{eff}=0.0796$ W/m-K for air
 - predicted value with new model:
 - $k_{eff}=0.155$ W/m-K for air
 - ΔT across PuO_2 bed decreases by approximately half

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