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Title: Aerosol Physics Considerations for Using Cerium Oxide CeO2 as a Surrogate for Plutonium Oxide PuO2 in Airborne Release Fraction Measurements for Storage Container Investigations

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Aerosol Physics Considerations for Using Cerium Oxide CeO2 as a Surrogate for Plutonium Oxide PuO2 in Airborne Release Fraction Measurements for Storage Container Investigations

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Abstract: Cerium oxide (CeO2) dust is recommended as a surrogate for plutonium oxide (PuO2) in airborne release fraction experiments. The total range of applicable particle sizes for PuO2 extends from 0.0032 µm (the diameter of a single PuO2 molecule) to 10 µm (the defined upper boundary for respirable particles). For particulates with a physical particle diameter of 1.0 µm, the corresponding aerodynamic diameters for CeO2 and PuO2 are 2.7 µm and 3.4 µm, respectively. Cascade impactor air samplers are capable of measuring the size distributions of CeO2 or PuO2 particulates. In this document, the aerodynamic diameters for CeO2 and PuO2 were calculated for seven different physical diameters (0.0032, 0.02, 0.11, 0.27, 1.0, 3.2, and 10 µm). For cascade impactor measurements, CeO2 and PuO2 particulates with the same physical diameter would be collected onto the same or adjacent collection substrates. The difference between the aerodynamic diameter of CeO2 and PuO2 particles (that have the same physical diameter) is 39% of the resolution of a twelve-stage MSP Inc. 125 cascade impactor, and 34% for an eight-stage Andersen impactor. An approach is given to calculate the committed effective dose (CED) coefficient for PuO2 aerosol particles, compared to a corresponding aerodynamic diameter of CeO2 particles. With this approach, use of CeO2 as a surrogate for PuO2 material would follow a direct conversion based on a molar equivalent.

In addition to the analytical information developed for this document, several US national labs have published articles about the use of CeO2 as a PuO2 surrogate. Different physical and chemical aspects were considered by these investigators, including thermal properties, ceramic formulations, cold pressing, sintering, molecular reactions, and mass loss in high temperature gas flows. All of those US national lab studies recommended the use of CeO2 as a surrogate material for PuO2.

Definitions

Activity Median Aerodynamic Diameter (AMAD) ICRP Definition - Fifty per cent of the activity in the aerosol is associated with particles of aerodynamic diameter greater than the AMAD.

Aerodynamic Diameter –The diameter of a hypothetical (spherical) particle of unit density (1.0 g/cc) that has the same (terminal) settling velocity as the particle under consideration.

Introduction

Worker protection is a primary consideration for situations involving airborne plutonium (and other transuranic) contamination. The size of radioactive aerosols has a significant impact on the fraction of inhaled activity that is ultimately absorbed into the body (ICRP 66, 1994). During inhalation, in general, very small particles are likely to penetrate to and deposit in the deepest parts of the lung, while large particles tend to be trapped in the upper airway and ultimately swallowed. This effect is especially important in the case of plutonium (ICRP 67, 1994). Lung deposition of aerosol particulates is expressed in terms of the aerodynamic diameter, d_a, which is defined as the diameter of a hypothetical (spherical)

particle of unit density (1.0 g/cc) that has the same (terminal) settling velocity as the particle under consideration. The physical diameter, d_p, of the particle in question applies to a spherical shape. Non-spherical particle shapes (e.g. fibers, flat flakes, etc.) are not considered in this document.

Figure 1 and Table 1 show the 50 year committed effective dose (CED) in mrem/Bq of inhaled Pu-239 as a function of the activity median aerodynamic diameter (AMAD), where fifty per cent of the activity in the aerosol is associated with particles of aerodynamic diameter greater than the AMAD (ICRP 67, 1994). For example, the CED is an order of magnitude greater (CED = 21.0 mrem/Bq) for an AMAD of 0.03 µm, compared to a CED = 2.0 for an AMAD of 10 µm.

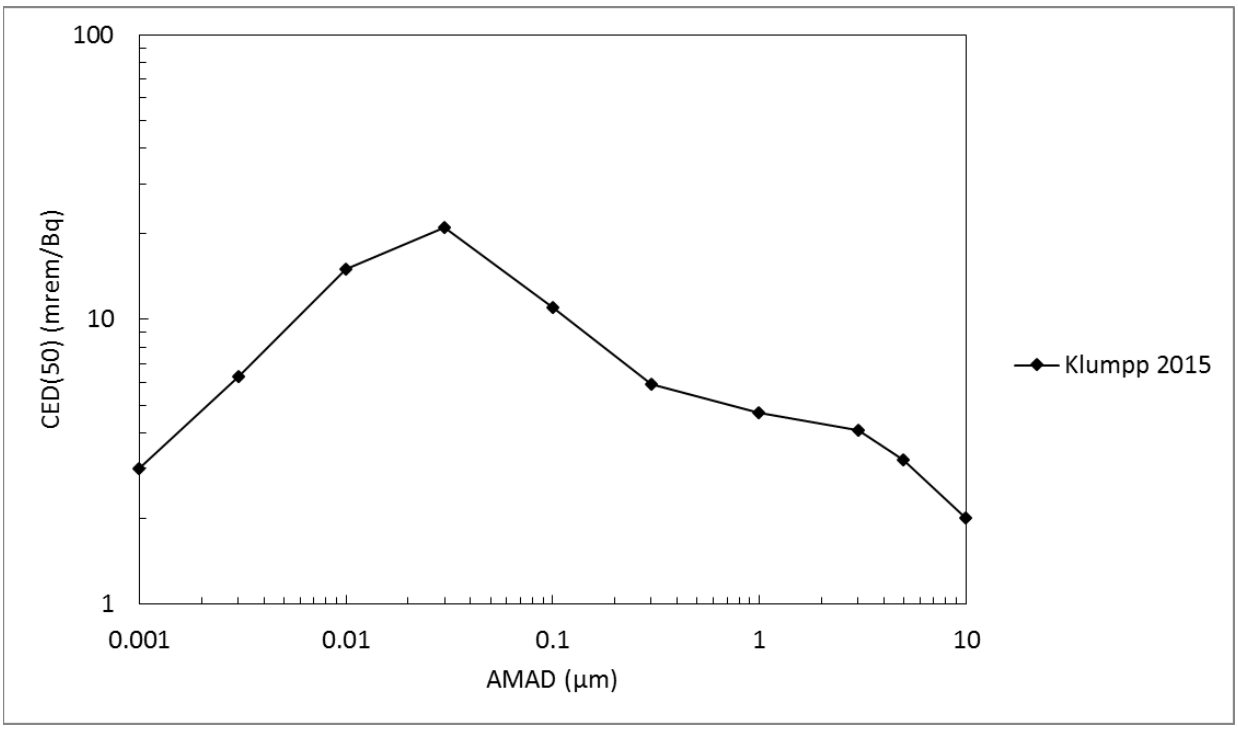


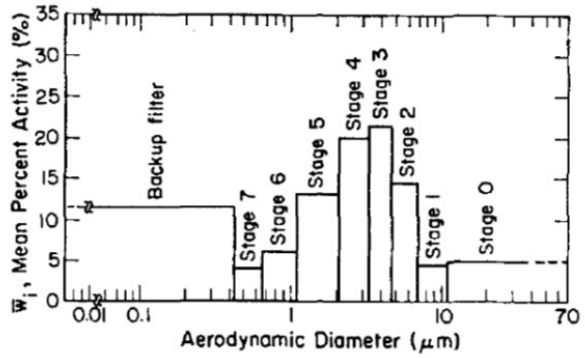
Figure 1. Committed effective dose (CED) coefficients for Type M Pu-239 (medium solubility) by inhalation over a range of aerodynamic median activity diameter (AMAD).

Table 1. Dose coefficients for Type M Pu-239 by inhalation.

AMAD (µm)	CED(50) (mrem/Bq)
0.001	3.0
0.003	6.3
0.01	15.0
0.03	21.0
0.1	11.0
0.3	5.9
1	4.7
3	4.1
5	3.2
10	2.0

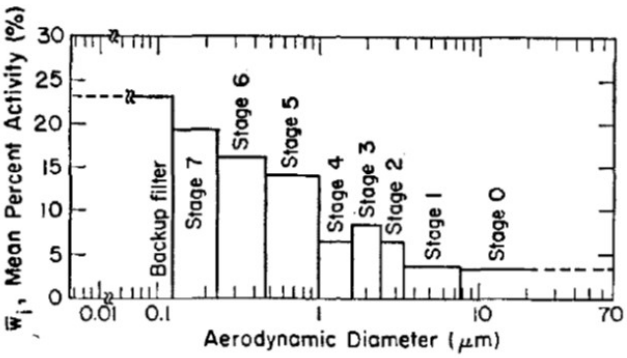
Note the size of a single PuO2 molecule is 0.0032 µm (Delagard 2011), and that 10 µm is the aerodynamic diameter of respirable aerosol (US DOE 2008).

As a point of comparison, measurements of the PuO2 AMAD at Los Alamos National Laboratory (Elder et al 1974) indicated the presence of two distinct size distributions, depending on the sample location. At a LANL "fabricating facility", PuO2 showed a large activity peak at about 4 µm AMAD, with about 22% of the activity located in the submicron size range. In a LANL "chemical recovery facility", about 74% of the measured activity was located in the submicron size range. In the smallest size range, about 23% of the activity was collected on the final collection stage (the collection filter).



In a LANL "fabricating facility", about 22% of the activity is in the submicron size range.

Elder et al 1974



In a LANL "chemical recovery facility", about 74% of the activity is in the submicron size range.

Elder et al 1974

Figure 2a and 2b. Cascade impactor measurements of PuO2 AMAD at LANL facilities.

A cascade impactor collects aerosol particles by size differentiation onto multiple independent stages (Figure 3). The stages are fitted with collection substrates (e.g. aluminum foil disks) that may be individually analyzed (e.g. radioactivity measurements, mass balance, mass spectrometry, etc.).

After passing through an inlet jet, the first stage collects the largest particles by impaction, and the next stage has an increased number of narrower jets to accelerate the air flow, where smaller aerosol particles can be impacted onto the next collection substrate. Successive stages have increasing numbers of acceleration jets with smaller diameters, and aerosol particles are collected stage by stage until any remaining particulates are collected on an absolute (high efficiency) filter.

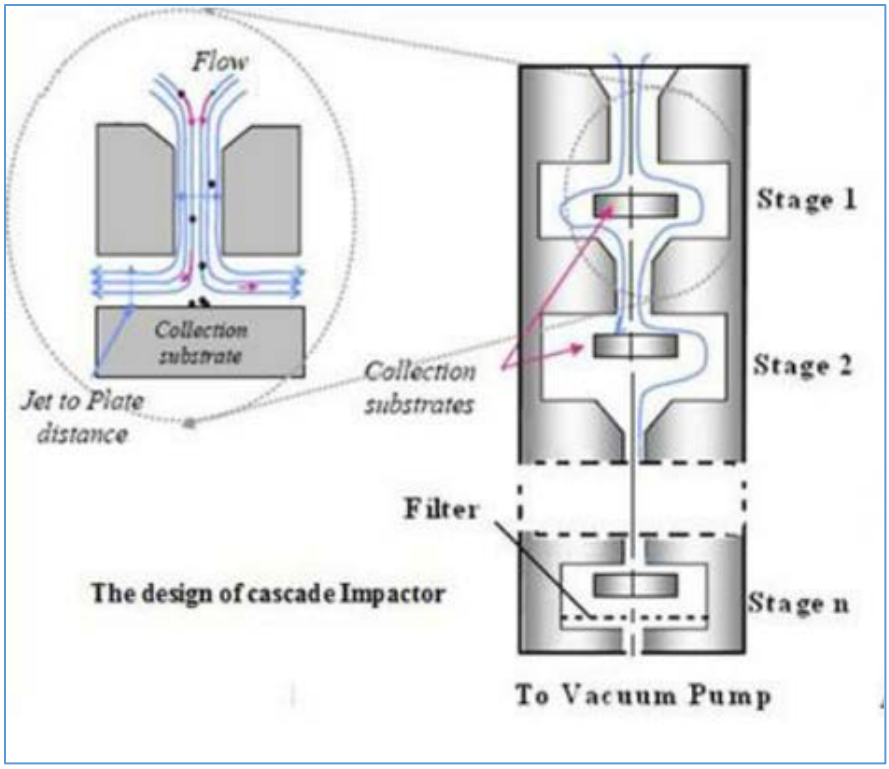


Figure 3. Schematic of a generic cascade impactor. (Ahmed et al.)

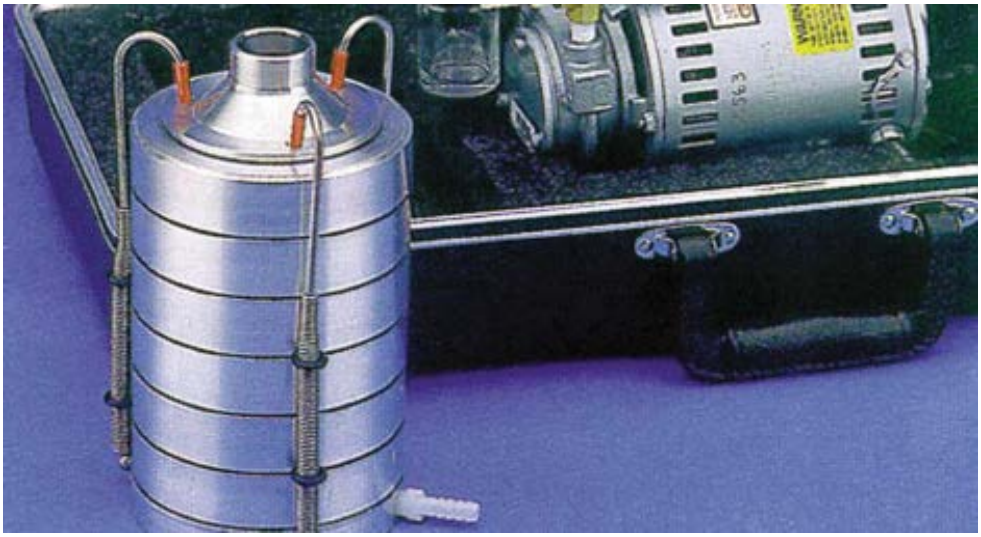


Figure 4. Photograph of a typical (6-stage) Andersen impactor. The aluminum body is 3.75" diameter and an external applied vacuum supplies the required air flow.

Comparison of aerodynamic diameters of CeO2 to PuO2 particles

Particle density affects the aerodynamic diameter is shown in Figure 5. The calculations for this figure take into account the Cunningham slip correction factor, C_C, which is necessary for aerosol particles with a physical diameter smaller than about 3 µm, where the slip correction factor is $C_C(d_p=3$

μm) = 1.05. The details of these calculations are beyond the scope of this document, but Figure 5 uses the following form of the slip factor:

$$C_C = 1 + \frac{\lambda}{d}\left[2.34 + 1.05\, exp\left(-0.39\frac{d}{\lambda}\right)\right]$$

where
d = the diameter of the particle, and
λ = the mean free path between air molecules.

The calculation for Figure 5 requires an iterative procedure, since the slip correction must be applied to the physical and the aerodynamic diameters. The Excel spreadsheet used for the Figure 5 results were compared with representative tabulated results (Hinds 1999).

$$d_a = d_p\left(\frac{C_C(d_p)}{C_C(d_a)}\right)^{\frac{1}{2}}\left(\frac{\rho_p}{\rho_0}\right)^{\frac{1}{2}}$$

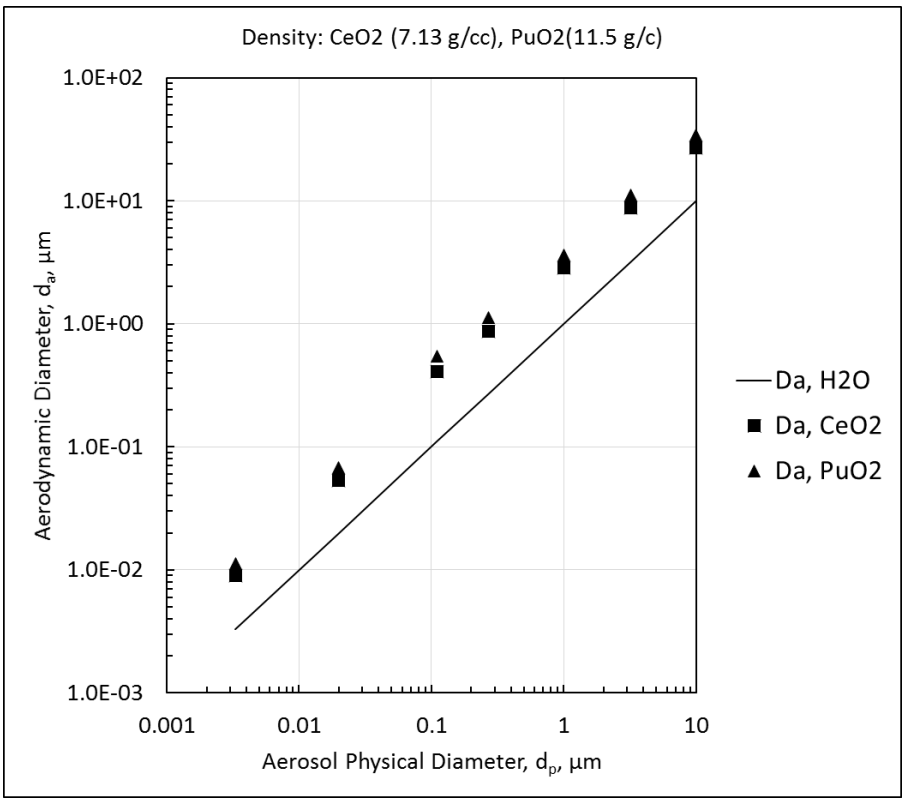


Figure 5. If a CeO2 and a PuO2 particle have the same physical diameter, the densities of the two particles produce different aerodynamic diameters. A unit density (1.0 g/cc) spherical water droplet is included for comparison.

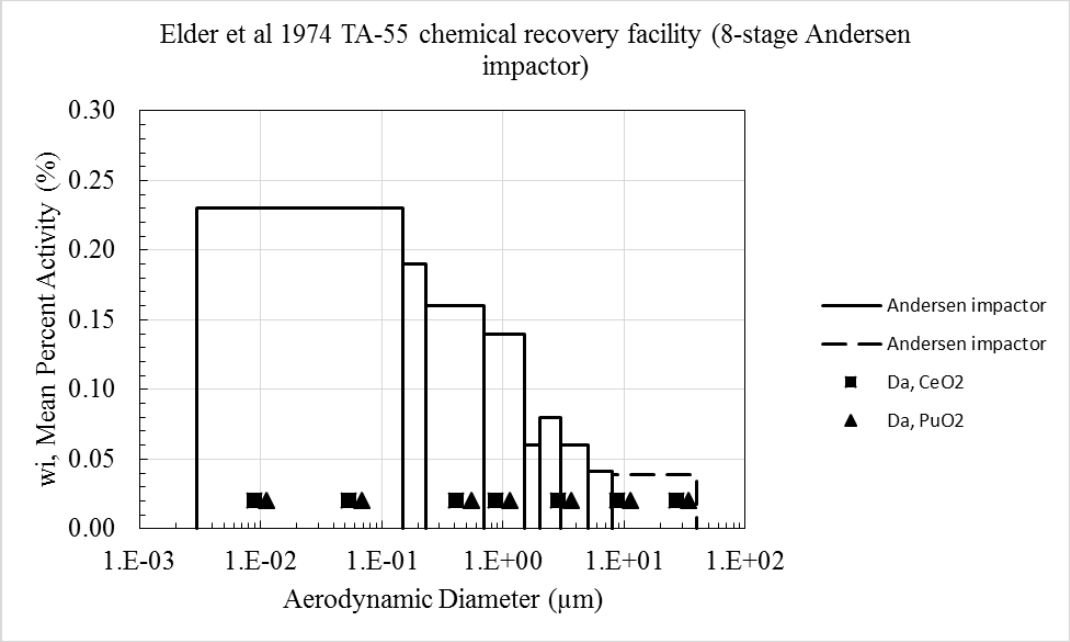


Figure 6. The calculated aerodynamic diameters from Figure 5 are overlaid onto (Elder et al 1974) experimental results. For a given physical diameter of particles, the cascade impactor would tend to collect CeO2 or PuO2 particulates (with the same physical diameter) onto the same respective collection stage. (A default value of w_i=0.02 was assigned for sake of the graph illustration.)

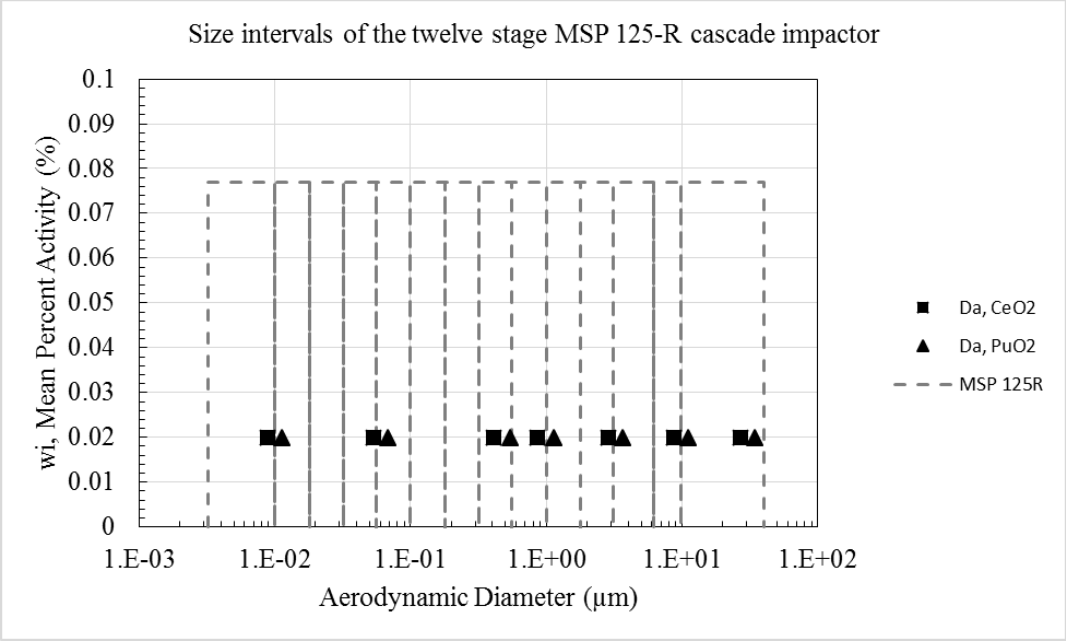


Figure 7. The Radiation Protection group is proposing new PuO2 measurements in the LANL plutonium facility that would use a twelve-stage cascade impactor. If CeO2 particles and PuO2 particles have the same physical diameter, they would be collected on the same or adjacent cascade impactor stages. The indicated data points are preselected calculations, and contrary to the location of these calculated numbers, it should not be concluded that the majority of aerosol particles are collected on adjacent substrate stages.

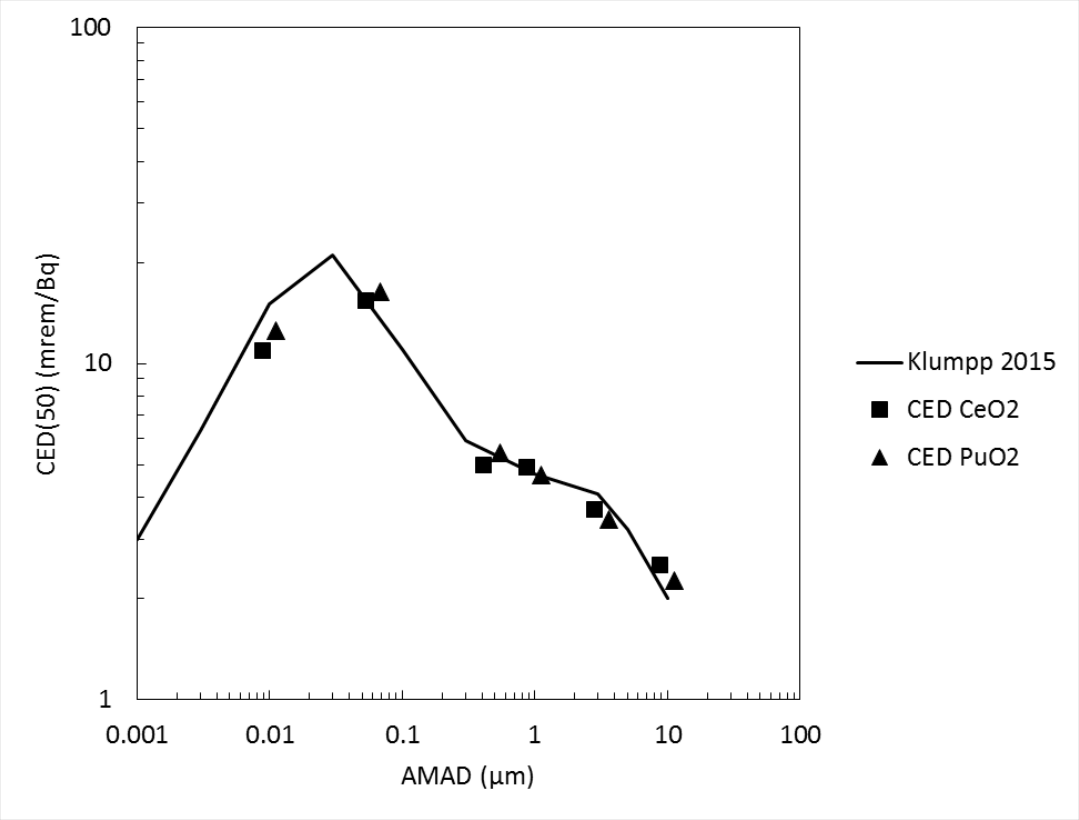


Figure 8. A representative calculation of the committed effective dose (CED) coefficient for representative AMAD values. Future use of CeO2 as a surrogate for PuO2 material can be directly compared by calculation, using a molar equivalent approach.

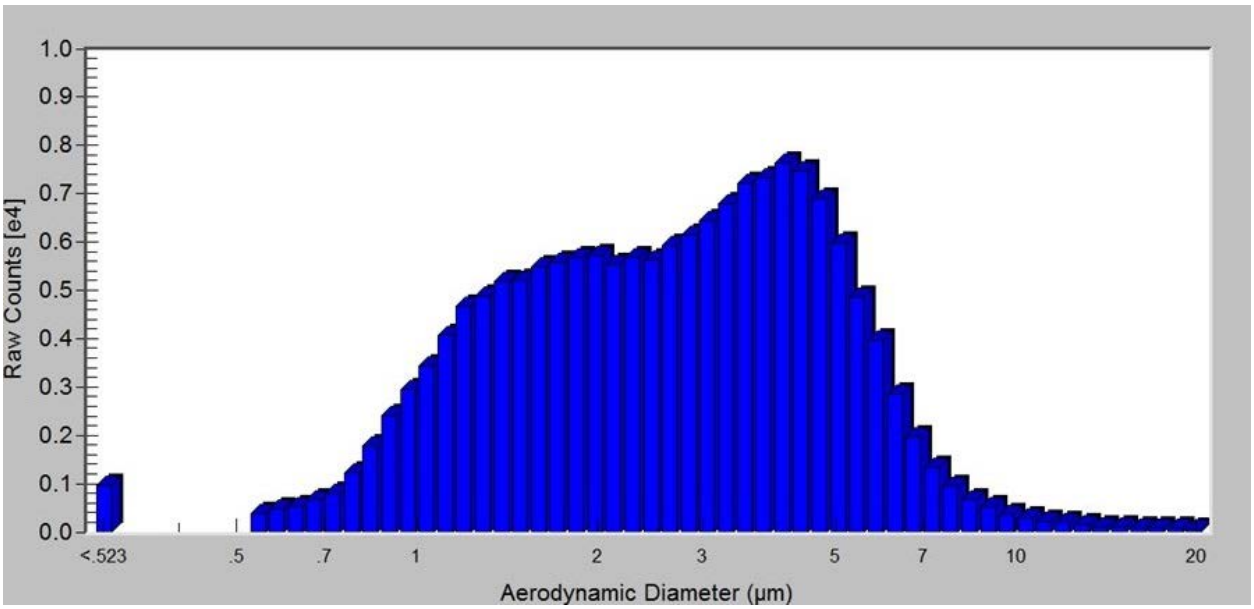


Figure 9. Low-energy impact dispersal of ambient humidity CeO2 test dust. For this measurement, CeO2 dust (1 µm physical diameter) was dispersed from the fibers of a small brush, with a low energy impact, compared to Figure 10. (In Figures 9 and 10, the fibers of a small artist brush were dipped into a container of CeO2 dust, and then the dust was dispersed by tapping the brush against a hard surface that was located adjacent to the air-sampling inlet of an aerosol spectrometer.) (Berg and Moore 2016)

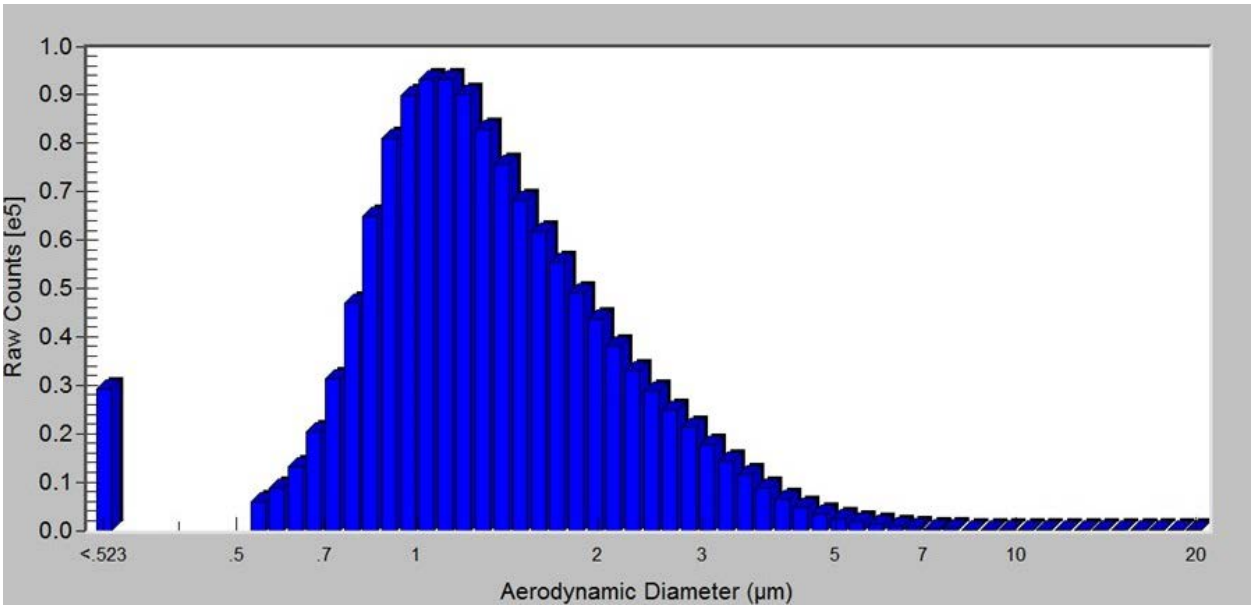


Figure 10. High-energy impact dispersal CeO2 test dust that was stored in ambient humidity conditions. Compared to Figure 9, a high-energy impact is necessary to dislodge small particulate from the fibers of the small brush. Figures 9 and 10 indicate that tests with a one-micron (1 µm) CeO2 test dust will produce different results, based on test input conditions. It is assumed that PuO2 aerosols would agglomerate and de-agglomerate in a similar fashion to CeO2 test dust. (Berg and Moore 2016)

Chemical and physical considerations for using CeO2 as a surrogate for PuO2

A description of the similarity of CeO2 to PuO2 was published in a study of the explosive dispersal of spent reactor fuel. The description is quoted verbatim,

> *"Cerium, a lanthanide element, is quite similar chemically, i.e., a good surrogate or homologue to the chemistry of uranium and plutonium, both actinide elements. Cerium has multiple oxidation states (+3, +4), similar to those of uranium and plutonium (+3, +4, +5, and +6). CeO2 is also an oxide quite chemically similar to the UO2 and PuO2 in nuclear fuel -- and the DUO2 in the Phase 3 surrogate tests. CeO2 and UO2 have the same ionic crystal, fluorite-type structure. For these reasons, CeO2 was used in multiple decontamination studies performed at Sandia National Laboratories [19-21]. CeO2 is commercially available in powder form, relatively inexpensive, and has a low hazards identification rating (Material Safety Data Sheet, MSDS). Cerium oxide has a theoretical density of about 7.13 g/cc compared to about 10.96 g/cc for UO2.*
>
> *Cerium oxide is a refractory oxide with a very high melting point, approximately 2600 °C, compared to 2878 °C for UO2. CeO2 is an oxide ceramic like UO2, and has similar physical properties (e.g., elastic moduli and Poisson's ratio, plus other thermal and mechanical properties), that have been comprehensively assessed and documented in the literature. From a shock physics viewpoint, the material properties important to shock aerosolization in our explosive, HEDD jet-impact tests, e.g., bulk modulus, bulk speed of sound, fracture toughness, and strength, compare reasonably well for both CeO2 and UO2. Therefore, the participants in the WGSTSC concluded that CeO2 is a good surrogate for uranium oxide fuel pellets from chemical, thermal, and physical or mechanical points of view."*
>
> (Molecke et al 2008)

The following two figures are examples from a different study, where a direct comparison of CeO2 and PuO2 was performed.

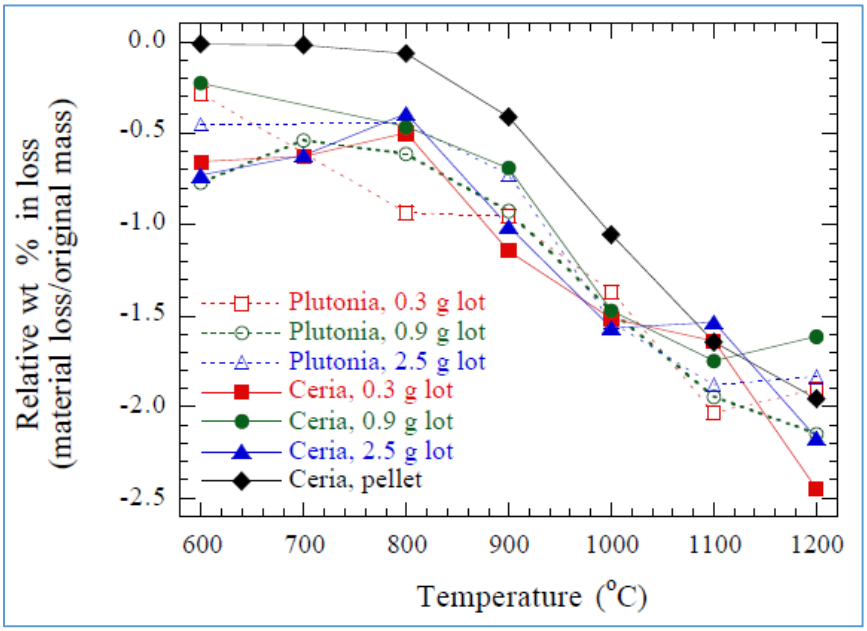


Figure 11. Weight loss from ceria and plutonia exposed to Ar-6%H2 for 0.5 h as a function of temperature and lot size. "The MOX ceria surrogate is composed of CeO2 that is initially doped with approximately 2 wt% Ga2O3." (Kolman et al 1999)

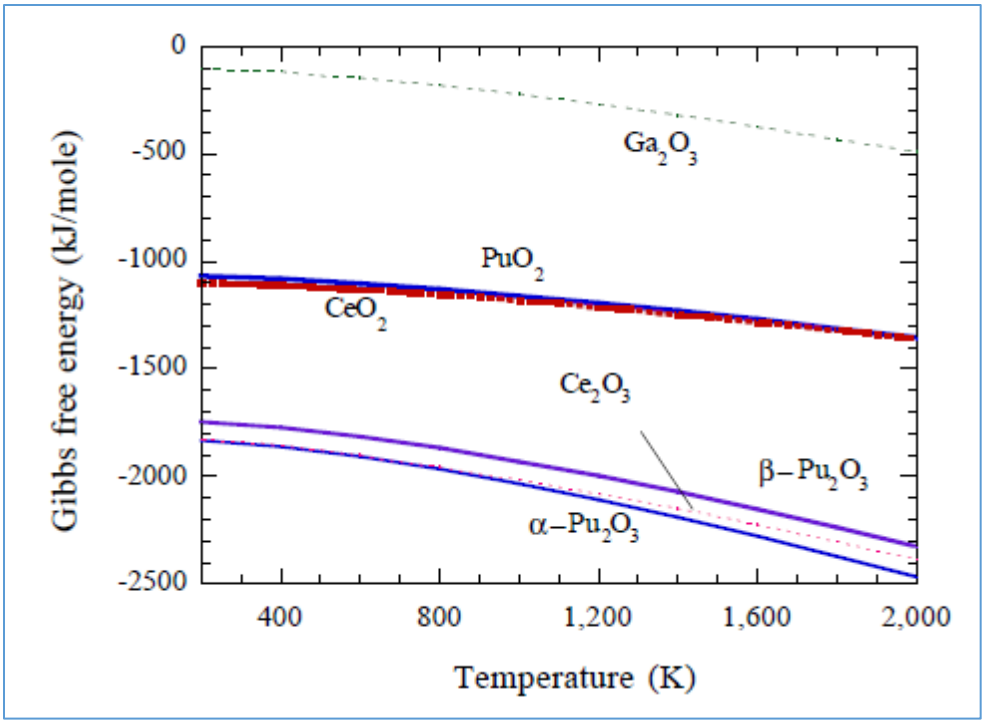


Figure 12. The Gibbs free energy of several plutonium and cerium oxides systems. (Kolman et al 1999)

In reference to Figure 6, it must be noted that the Gibbs free energy comparison has a range of application, such that,

"*In thermodynamics, the Gibbs free energy is a thermodynamic potential that can be used to calculate the maximum or reversible work that may be performed by a thermodynamic system at a constant temperature and pressure. According to the second law of thermodynamics, if the Gibbs free energy change of a chemical reaction ΔG< 0, the reaction is spontaneous. This only means this reaction is thermodynamically favorable. For example, The reaction $C_{(s)}$diamond → $C_{(s)}$graphite has a negative change in Gibbs free energy and is therefore thermodynamically favorable at 25°C and 1 atm. However, even though favorable, it is so slow that it is not observed. <u>Whether a reaction is thermodynamically favorable does not determine its rate</u>*". (Mortimer 2000).

Therefore, the comparison of Gibbs free energy can only tell us that CeO2 and PuO2 have similar thermodynamic potential, but cannot tell us that they have similar chemical reactivity.

Table 2. Published studies that investigated CeO2, PuO2, or both substances

(Ko, Yang et al. 2014)Test Method	CeO2 Only	PuO2 Only	CeO2 and PuO2	Did the authors recommendation the use of CeO2?
Thermal Property evaluation			Hoyt, R.C. (2002)	Yes
Ceramic formulation, cold press and sintering			Marra, J. C. et al (2002)	Yes
Chemical reaction with small molecules (H2O, H2, and O2)			Brady, J. T. et al (2000)	No conclusion or opinion
Thermal behavior and crystallization kinetics	(Ko, Yang et al. 2014)			N/A
Particle properties		Machuron-mandard, X. et al (1995)		N/A
Selective oxidation	(Beckers and Rothenberg 2010)			N/A
Mass loss in Ar-H2 gas flow; Gibbs free energy			Kolman, D. G. et al 1999	Yes

A quote from one of these studies is pertinent to this document:

"*Cerium oxide as a surrogate for the actinide oxides in the Pu immobilized form is adequate from many perspectives and is, thus, a suitable "stand-in" for process development studies. Although not discussed here, cerium oxide performed well as a physical surrogate for batching, powder handling and compaction. In both systems, the major phase formed was pyrochlore and the dissolution behavior of cerium oxide and plutonium oxide into the crystalline assemblage generally coincided. Finally, the overall shrinkage of the two systems under the baseline sintering conditions was essentially identical.*" (Marra JC et al 2002)

Conclusions

This document presents the calculations of aerodynamic diameter for CeO2 and PuO2 aerosol particles. Future experiments would be capable of accounting for the different aerodynamic diameters of CeO2 and PuO2, based on experimental design. For example, cascade impactor air samplers and aerodynamic particle sizers (APS) both measure the size of aerosol particulates based on the aerodynamic diameter. A cascade impactor is solely a mechanical device that separates one aerosol particle from another, due to inertial impaction when one particle has a different aerodynamic diameter (e.g. Figures 2a and 2b) compared to the other. An aerodynamic particle sizer is an electronic instrument (Figures 9 and 10) that uses laser based time-of-flight measurements.

For indoor laboratory experiments, an APS could be a suitable device to gather numerical information, but a cascade impactor would be more practical for outdoor applications where a rugged system is required. In addition, a cascade impactor gathers size-differentiated samples onto collection

substrates. The collection substrates (e.g. aluminum foil disks) can be post-processed to determine the relative size distribution of test dust aerosol compared to other materials that may be present in an experimental scenario. By comparison, an APS device cannot be used to differentiate between test dust and extraneous background material.

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