

*White Paper on Possible Inclusion of
Mixed Plutonium-Uranium Oxides in
DOE-STD-3013-96*

Los Alamos
NATIONAL LABORATORY

*Los Alamos National Laboratory is operated by the University of California
for the United States Department of Energy under contract W-7405-ENG-36.*

Edited by Margaret Burgess, Group CIC-1

*This work was supported by the US Department of Energy,
Office of Environmental Management.*

An Affirmative Action/Equal Opportunity Employer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither The Regents of the University of California, the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by The Regents of the University of California, the United States Government, or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of The Regents of the University of California, the United States Government, or any agency thereof. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

*White Paper on Possible Inclusion of
Mixed Plutonium-Uranium Oxides in
DOE-STD-3013-96*

John M. Haschke

*Ted Venetz**

*Rich Szempruch**

*James W. McClard***

**Babcox and Wilcox Hanford Company*

***Westinghouse Savannah River Corporation*

WHITE PAPER ON POSSIBLE INCLUSION OF MIXED PLUTONIUM-URANIUM OXIDES IN DOE-STD-3013-96

by

John M. Haschke, Ted Venetz,
Rich Szempruch, and James W. McClard

ABSTRACT

This report assesses stabilization issues concerning mixed plutonium-uranium oxides containing <50 wt % Pu. It recommends that these materials be stored under a revision to DOE-STD-3013-96 "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," which addresses long-term storage of materials >50 mass % Pu. Possible consequences of uranium substitution on thermal stabilization, specific surface areas, moisture readsorption behavior, loss-on-ignition analysis, and criticality safety of the oxide are examined and discussed.

INTRODUCTION

The Department of Energy (DOE) plutonium storage standard, "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," (DOE-STD-3013-96) applies to storage of plutonium-bearing metals and oxides containing at least 50 mass % Pu.¹ However, certain materials that do not satisfy this purity requirement may be suitable for storage according to the criteria of DOE-STD-3013. This assessment addresses issues that should be considered if mixed plutonium-uranium oxides (MOX) with less than 50 mass % Pu are to be included in DOE-STD-3013. Appropriate consideration of this possibility is merited. An ability to store MOX under DOE-STD-3013 eliminates the need to separate the plutonium oxides from the uranium oxides or to treat those materials as residues. If a reactor is selected for plutonium disposition, much of the existing MOX can be easily recycled in the process of fuel fabrication.

This report examines the possible consequences of substituting uranium oxide for plutonium oxide on thermal stabilization, specific surface area, moisture readsorption behavior, loss-on-ignition (LOI) analysis, and criticality safety of the oxide.

BACKGROUND

The MOX materials considered for inclusion in DOE-STD-3013 are compounds and/or mixtures containing both plutonium and uranium in oxide forms. These materials exist at several DOE facilities and were typically prepared for use as fuels in reactor development programs but were never irradiated. For example, Hanford has the largest MOX holdings, comprising 5.2 metric tons and containing about 0.56 metric tons of Pu. Approximately 45% of the Hanford inventory is in the form of sealed fuel pins and assemblies. The remaining material exists in forms that range from powders to unsintered (green) and finished pellets. Powders and unsintered pellets may contain organic binders and other hydrogenous materials. The uranium component may be either natural, depleted, or enriched. Plutonium concentrations vary from a few mass percent up to 25–35 mass %.

Thermal Stabilization

Thermal stabilization of plutonium oxide by firing the oxide in air is required for removing adsorbed species and organic residues. For plutonium dioxide, PuO_2 , the desorption process is complete at 950°C ² and oxidation of organic materials to volatile species undoubtedly occurs at lower temperatures. Because of the chemical similarities of plutonium and uranium, the thermal behavior of adsorbates and residues on MOX is expected to closely parallel the thermal behavior of adsorbates and residues on PuO_2 .

Different chemical properties are observed for plutonium oxide, uranium oxide, and MOX during thermal stabilization.³ Whereas the dioxide, PuO_2 , forms when plutonium oxide is fired in air, uranium dioxide oxidizes readily to U_3O_8 during heating. Oxygen to metal ratios greater than 2:1 are consistently observed when mixed oxides are fired in air, but the MOX stoichiometry varies with plutonium percentage, temperature, and type of atmosphere. Therefore, using gravimetric data from the oxidation process to define MOX composition is considered difficult.

The behavior of MOX under reducing conditions is also unpredictable.³ Uranium oxide is readily reduced to uranium dioxide, $\text{UO}_{2.00}$, when heated in a 6% H_2 –94% N_2 atmosphere at 750°C . However, similar treatment of mixed oxides does not necessarily reduce MOX to $(\text{U,Pu})\text{O}_{2.00}$.

Specific Surface Area

The specific surface area of MOX progressively decreases as the firing temperature is increased.³ Data were obtained after oxides were heated for 1.3 h under reducing (6% H₂) conditions. Surface areas for all MOX compositions in the 5–35 mass % Pu range are about 10 m²/g after firing at 650°C and consistently reach 5 m²/g as the firing temperature approaches 900°C.

The effect of MOX composition on its specific surface area is uncertain. Data for mixed oxides heated under H₂ at temperatures between 625°C and 875°C show that surface areas decrease about 30% as the Pu content is increased from 5 mass % to 35 mass %.³ However, results of measurements on coprecipitated MOX heated under similar conditions at 740°C indicate that the specific surface area increases by a factor of 2 when the Pu content is increased from 5 mass % to 20 mass %.⁴

Data on surface-area behavior of MOX during heating in air are apparently not available. Because the surface area of MOX fired under reducing conditions at 625–875°C³ exhibits temperature dependence closely parallel to the temperature dependence of PuO₂ fired over that temperature range,² the effect of atmosphere on sintering behavior is probably small.

Moisture Readsorption

A recent study shows that air-fired MOX readsorbs a small amount of moisture during exposure to the atmosphere.⁵ The mass increase of MOX (35 mass % Pu) fired at 750°C for 3 h stabilized at 0.1% after exposure to glovebox air of unspecified humidity for 9 days. Observed fluctuations in the mass are attributed to weather changes. However, data show that the mass increased steadily over the first 3 days and then became essentially constant at a value of 0.14% ± 0.01%. These results suggest that MOX adsorbs moisture relatively slowly, but additional data are needed to adequately define kinetic behavior.

The readsorption result for air-fired MOX⁵ corresponds closely with observations for air-fired PuO₂.³ Data show that the oxide with 35 mass % Pu has a surface area of approximately 7 m²/g after firing at 750°C for 3 h.⁵ If the adsorption characteristics of

MOX and PuO_2 surfaces are comparable, an equilibrium moisture loading of $0.3 \pm 0.1 \text{ mg/m}^2$ is expected for the 5–50% relative humidity range at 25°C .² On the basis of these data, the equilibrium mass increase calculated for the MOX composition used by Karraker⁵ is $0.21\% \pm 0.07\%$, a result that agrees remarkably well with the measured value of 0.14 mass %. The close correspondence of observed and calculated adsorption levels implies that: (1) firing MOX at 750°C adequately removes surface adsorbates, (2) the specific surface area of MOX after firing at 750°C is relatively low (5–10 m^2/g), (3) the equilibrium concentration of adsorbed water on MOX is similar to the equilibrium concentration of adsorbed water on PuO_2 for a broad humidity range, and (4) the maximum extent of moisture adsorption by fired MOX is small (approximately 0.1–0.2 mass %).

Loss-on-Ignition Analysis

Difficulties in reliably measuring LOI values are to be anticipated because the oxygen to metal ratio of MOX changes during firing in air. As outlined above efforts to drive mixed oxides to either a fully oxidized or fully reduced state have not been successful.³ The situation is further complicated because the oxygen to metal ratio and the rate at which the ratio changes are temperature-dependent parameters.⁶ Available equilibrium and kinetic data are insufficient for predicting MOX stoichiometries at conditions of interest.

Contrary to expectation, a successful LOI analysis of MOX is indicated by the results of measurements described by Karraker.⁵ A mixed oxide containing 35 mass % Pu was fired for 3 h in air at 750°C prior to LOI analysis by heating at 900°C for 1 h. The mass (1.468 g) of the LOI sample remained constant during analysis, suggesting that the mass loss was $<0.07\%$.

Although encouraging, this LOI result may not be valid. If the desorption behavior of MOX is similar to that of PuO_2 , an LOI value of 0.15–0.20 mass % is to be expected on the basis of a parallel test with PuO_2 .⁵ LOI analysis of the as-received mixed oxide showed a mass gain of 0.68%, a result consistent with an increase in the oxygen to metal ratio during firing in air at 750°C . This behavior is also confirmed by results of x-ray diffraction analysis showing that the single-phase mixed oxide was partially converted to a mixed valence oxide, U_3O_8 , during the firing step. Similar x-ray analysis of the product after LOI analysis showed that the relative intensities of reflections from U_3O_8 had increased. This result suggests that additional U_3O_8 formed during firing at 900°C .

Consequently, the constant mass observed during LOI analysis may have resulted from a fortuitous equality of mass loss and mass gain. Therefore, it is uncertain if LOI analysis is suitable to certify MOX for storage and additional research is needed.

Criticality Safety

DOE-STD-3013-96 limits the amount of plutonium (5.0 kg of Pu) per oxide storage package. This limit satisfies restrictions for all fissile isotopes of uranium. The respective mass limits for water-reflected metal spheres of U^{233} , U^{235} , and Pu^{239} are 6.0, 20.1, and 5.0 kg.⁷ The corresponding mass limits for oxides are substantially higher. All uranium isotopes may be treated on an equivalent basis with plutonium isotopes in criticality assessments. Use of this equivalence is highly conservative because only fissile uranium isotopes (U^{233} and U^{235}) contribute to the potential for criticality. Most of the uranium considered for storage will be natural, depleted, or of low enrichment.

CONCLUSIONS AND RECOMMENDATIONS

Evaluation of technical data suggests that substitution of uranium oxide for plutonium oxide does not detrimentally alter the thermal stabilization behavior or long-term storage behavior of those oxides. The desorption and readsorption behavior of MOX and PuO_2 are essentially equivalent and criticality safety is not compromised. Although particle-size distributions are not compared in this assessment, the risk of dispersing plutonium-containing particles should not be appreciably altered by storing mixed oxides. The suitability of MOX for storage is supported by extensive experience in the preparation and storage of MOX fuel in commercial power generation.

Modification of DOE-STD-3013 to include MOX requires that a minimum plutonium content be established for storable mixed oxides. This limit is readily established by practical considerations. Inclusion of most existing MOX fuels is desirable.

A simple gravimetric LOI analysis may be inadequate to certify that MOX meets stabilization requirements. Additional research and development work is needed before this issue can be resolved.

This assessment leads to the following recommendations:

- That uranium be considered equivalent to plutonium in DOE-STD-3013. The revised criterion in 4.1.A would require that a storable material have a minimum plutonium plus uranium content of 50 mass % and state that uranium may be considered equivalent to plutonium if the plutonium content of the mixed oxide exceeds 3 mass % and requirements for material stability are satisfied.
- That the accuracy of the LOI analysis be rigorously demonstrated. The section to be added to DOE-STD-3013 on the subject of conditions for LOI analysis should specify that a special requirement or an alternative procedure be used to certify the stability of mixed plutonium or uranium oxides containing less than 50 mass % Pu. Authorization to store MOX should require that the adequacy of the LOI analysis (or alternative procedure) be established by an independent technical review.
- That existing pelletized oxides sealed in fuel elements be stored without disassembly or oxide stabilization/certification. This variation would be allowed provided: (1) material stability can be established from documentation of conditions used in pellet fabrication, (2) the leak tightness of the sealed pin (first barrier) was demonstrated during fabrication, and (3) qualified pins or elements are sealed in a second container to satisfy the dual-barrier requirement of DOE-STD-3013. The second barrier may be a shipping container (if it meets the performance requirements of a barrier) or a new sealed and certified container. The revised DOE-STD-3013 should also specify that pellets from documented and qualified pins may be downloaded without stabilization into storage containers that comply with this standard.

REFERENCES

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," Department of Energy document DOE-STD-3013-96 (September 1996).
2. J. M. Haschke and T. E. Ricketts, "Plutonium Dioxide Storage: Conditions for Preparation and Handling," Los Alamos National Laboratory report LA-12999-MS (August 1995).
3. I. D. Thomas, "Plutonium Ceramic Fuel Preparation," in *Plutonium Handbook* (Gordon and Breach Science Publishers, New York, 1967), Chap. 19.
4. A. Biancheria, G. Ehrlich, E. E. Garcia, J. Goodman, R. A. Jaroszeski, H. Krake, and P. Rey, "Preparation and Characterization of Mixed Plutonium-Uranium Oxides," in *'Progress Report, Development of Pu Bearing Fuel Materials,'* Nuclear Materials Equipment Corporation report NUMEC P-90 (1962).
5. D. G. Karraker, "Plant PuO₂ and Mixed UO₂-PuO₂ Calcination Studies," Savannah River Technology Center letter SRTC-CTS-95-0037 (February 1995).
6. R. C. Hoyt and B. W. Rhee, "Review of the Literature for Dry Reprocessing Oxide, Metal, and Carbide Fuel—The AIROX, RAHYD and CARBOX Pyrochemical Processes," US DOE report ESG-DOE-13277 (September 1979).
7. "American National Standard for Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors," ANSI/ANS-8.1-1983 (American Nuclear Society, La Grange Park, 1983).

This report has been reproduced directly from the best available copy.

It is available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831. Prices are available from (615) 576-8401.

It is available to the public from the National Technical Information Service, US Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22616.

Los Alamos

NATIONAL LABORATORY

Los Alamos, New Mexico 87545