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Author(s):

P. Gary Eller
Jerry L. Stakebake
Thruman D. Cooper

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REDOX BIAS IN LOSS ON IGNITION MOISTURE MEASUREMENT FOR RELATIVELY PURE PLUTONIUM-BEARING OXIDE MATERIALS

P. Gary Eller
Los Alamos National Laboratory
Los Alamos, New Mexico 87544

Jerry L. Stakebake
U. S. Department of Energy
Rocky Flats Environmental Technology Site
Golden, Colorado 80030

Thurman D. Cooper
Fluor Hanford Company
Richland, Washington 99352

Abstract. This paper evaluates potential analytical bias in application of the Loss on Ignition (LOI) technique for moisture measurement to relatively pure (plutonium assay of 80 wt.% or higher) oxides containing uranium that have been stabilized according to stabilization and storage standard DOE-STD-3013-2000 (STD-3013). An immediate application is to Rocky Flats (RF) materials derived from high-grade metal hydriding separations subsequently treated by multiple calcination cycles. Specifically evaluated are weight changes due to oxidation/reduction of multivalent impurity oxides that could mask true moisture equivalent content measurement. Process knowledge and characterization of materials representing complex-wide materials to be stabilized and packaged according to STD-3013, and particularly for the immediate RF target stream, indicate that oxides of uranium, iron and gallium are the only potential multivalent constituents expected to be present above 0.5 wt.%. The evaluation shows that of these constituents, with few exceptions, only uranium oxides can be present at a sufficient level to produce weight gain biases significant with respect to the LOI stability test. In general, these formerly high-value, high-actinide content materials are reliably identifiable by process knowledge and measurement. Significant bias also requires that UO_2 components remain largely unoxidized after calcination and are largely converted to U_3O_8 during LOI testing at only slightly higher temperatures. Based on well-established literature, it is judged unlikely that this set of conditions will be realized in practice. We conclude that it is very likely that LOI weight gain bias will be small for the immediate target RF oxide materials containing greater than 80 wt.% plutonium plus a much smaller uranium content. Recommended tests are in progress to confirm these expectations and to provide a more authoritative basis for bounding LOI oxidation/reduction biases. LOI bias evaluation is more difficult for lower purity materials and for fuel-type uranium-plutonium oxides. However, even in these cases testing may show that bias effects are manageable.

INTRODUCTION AND BACKGROUND

This paper evaluates potential oxidation-reduction (redox) bias when Loss on Ignition (LOI) measurement of moisture equivalent content is applied to relatively pure plutonium oxides. A Los Alamos report on this topic recently has been issued. (1)

The Department of Energy (DOE) stabilization and storage standard DOE-STD-3013-2000 (referred to herein as STD-3013) refers to materials with greater than 85 wt.% plutonium content as relatively pure. (2) This paper also has relevance to the DOE standard for uranium-233 storage. (3) For operational purposes at various sites, the definition of "relatively pure" oxide sometimes is extended downward to 80 wt.% actinide content. The latter definition is used for the purposes of this discussion. In general, oxides with such high plutonium content resulted from separations processes designed to minimize impurities.

Calcined oxide material with plutonium content of 80 wt.% contains about 11 wt.% oxide ion associated with the plutonium. The remaining 9 wt.% of the mass balance generally will be present as inorganic oxides. When the oxygen associated with inorganic cations is taken into account, the actual maximum metal element content always will be less than about 7-8 wt.% and will vary with cation mass and valence, as indicated in Table 1.

Table 1. Limiting plutonium, oxygen key metal element bounding impurity levels for >80 wt.% representative STD-3013 items. Assumes plutonium and uranium are present as isotopes Pu-239 and U-238. The composition of pure PuO_2 is 88.2 wt. % plutonium and 11.8 wt.% oxygen. * Calculation based on metal content. Pure PuO_2 contains 88.2% Pu, 11.8% O_2. For limiting Pu content of 80% the oxygen content = 80/88.2 x 11.8 = 10.7% O_2.

compound	formula wt. per metal element	limiting wt. % of metal element	limiting wt.% of oxygen associated with metal element
PuO_2	271	80.0	10.7*
U_3O_8	281	7.6	1.4
Fe_2O_3	79.9	6.3	2.7
CuO	79.5	7.2	1.8
Ga_2O_3	93.7	6.7	2.3

This report specifically addresses the effect (referred to herein as redox or LOI bias) on LOI results of variable valence metal oxide impurities for relatively pure plutonium oxides that have been calcined to 950°C or higher in an oxidizing atmosphere, in accordance with STD-3013. This standard applies more broadly to plutonium metal and to oxides with a combined uranium and plutonium content of 30 wt.% or higher. In the STD-3013 LOI test for oxide materials, the weight of the analytical sample is measured before and after heating to 1000°C for one hour, after bulk calcination in an oxidizing atmosphere for two hours or more at 950°C or higher. Strictly speaking, the LOI test is intended to demonstrate acceptable chemical stability of packaged material during storage, where instabilities theoretically could be due to excessive residual species such as oxyanions, organics, or moisture equivalent content (various forms of molecular water and hydroxide). In practice, the 0.5 wt.% criterion often is interpreted less strictly as a test for moisture equivalent content since the most plausible container failure mechanisms for calcined and packaged STD-3013 materials are connected with excessive residual moisture equivalent. The ensuing discussion will assume the less precise residual moisture equivalent interpretation of the 0.5 wt.% criterion.

If a residual oxide impurity or co-constituent such as UO_2 is present after calcination that can be converted to a higher oxide such as U_3O_8 during the LOI test, the weight gain due to the oxidation could mask weight loss due to water. Conversely, if oxygen evolution occurs during LOI testing, for example residual UO_3 decomposing to U_3O_8, the moisture equivalent content could be overestimated.

Table 2 lists the highest inorganic impurity assays above 0.5 wt.% that have been observed in STD-3013 representative items, either as received from the sites or after calcination at Los Alamos. Elemental composition data, together with scientific literature on the known behavior of oxides that could be significant impurities in STD-3013 materials, provide the basis for evaluating the significance of oxide-based weight gain/loss (redox bias) on LOI measurements. From Table 2, it can be seen that only a limited number of impurities above 0.5 wt.% have been reported for representative STD-3013 items, consistent with the relatively limited number of processes that generated the materials. Also, it can be seen from Table 2 (and the ensuing discussion) that elements that potentially could exist as oxides in more than one oxidation state under STD-3013 conditions are limited to uranium, iron and gallium. Uranium is the only major co-constituent detected for oxide materials with greater than 70 wt.% plutonium content.

Another potential LOI analytical bias source for oxide materials is moisture adsorption after calcination and before packaging. (E.g., see Refs. 4,5) This issue is addressed later in this report in the context of potentially offsetting biases.

For convenience, the following discussion is organized by primary categories of impurity oxides: uranium, other actinide, transition metal, alkali/alkaline earth and main group elements. Possible effects of oxide mixtures, non-metallic impurities, unoxidized metal residuals and oxide volatility also are discussed briefly.

Table 2. Maximum wt.% metal element impurities observed at 0.5 wt.% or higher in STD-3013 representative items after calcination.[a,b]

	max. observed metal impurity wt.%	wt. % Pu
U	**78**	6
Mg	41	8
Ca	11	34
Cu	**9.0 (0.4)**	49 (60)
Na	7.4	71
Zn	6.1 (1.5)	49 (60)
K	10.6	66
Fe	**5.4**	29
Ni	4.3	65
Ga	**2.4**	63
Al	1.9	64
Cr	1.5	60
Si	1.4	66
Am	6.2	90
Ta	0.6	68
Np	0.6[c]	78
Be	0.5	63

a) Data are taken from the STD-3013 representative item database as of 9/10/01. (Ref. 19) Impurity entries indicate the maximum observed value for calcined or as received materials. Plutonium values are for calcined materials where available and for as received materials otherwise. Impurity elements with potential for multiple valence oxides under STD-3013 calcination conditions are emboldened. For materials with > 70 wt.% plutonium, only gallium was observed as an impurity above 0.5 wt. %. For copper and zinc, the higher number listed is for a single unique material; numbers in parentheses are the highest observed values for all other representative STD-3013 items. As indicated in the discussion, limited subsets of materials may contain percent levels of neptunium.

b) After calcination, the only non-metal impurities observed above 0.5 wt.% were Cl (7.7 wt.%, plutonium content 29 and 37 wt.%, two items) and F (3.2 wt.%, plutonium content 68 wt.%, one item).)

URANIUM OXIDES

Table 2 and extensive process knowledge for STD-3013 materials indicates that uranium is the most important variable oxidation state oxide to consider in the context of LOI measurements. The uranium-oxide system is not only the most complex actinide oxide system, but also one of the most complex of all oxide systems. (E.g., see Ref 6) This complexity, plus the presence of uranium up to about 70 wt.% in some representative items, makes uranium oxides the most significant by far of the possible actinide oxide constituents in the universe of STD-3013 materials with respect to possible redox weight gain.

Many decades of literature exist which provide an authoritative technical basis on the behavior of uranium oxide systems. Many excellent summaries specifically pertinent to the present evaluation have been published. (E.g, see Refs. 7-12) A recent Rocky Flats report evaluates the effects of variable uranium oxidation states in terms of STD-3013 LOI measurements. (13) The DOE standard on uranium-233 stabilization and storage contains additional pertinent information. (3) A recent Los Alamos report addresses the suitability of mixed uranium oxides in the context of plutonium oxide stabilization and storage. (14). A comprehensive review of uranium dioxide oxidation at 400°C and lower, with an excellent bibliography applicable to higher temperatures, was published in 1998. (15)

The extensive scientific literature indicates that, for the purpose of the present discussion, it is sufficient to focus on two end members, UO_2 and UO_3, and the intermediate U_3O_8. The literature strongly indicates that U_3O_8 should be the dominant, perhaps exclusive, uranium oxide phase after STD-3013 calcination at 950°C in the required oxidizing atmosphere for all uranium-containing STD-3013 materials except mixed uranium-plutonium oxides (as discussed below). All three of these uranium oxides are considered appropriate for long-term storage by the uranium-233 standard. (3,12) As stated in the uranium-233 standard:

> "U_3O_8 is the most attractive storage form because it is the most stable uranium oxide (the others convert to U_3O_8 upon heating)."

The principal uranium oxide reactions to consider are indicated in Equations 1, 2, and 3.

1. $UO_2 + 1/2O_2 \rightarrow UO_3$

2. $3\ UO_2 + O_2 \rightarrow U_3O_8$

3. $U_3O_8 + 1/2O_2 \rightarrow 3\ UO_3$

Reaction 3 does not occur in practice. Instead, UO_3 typically is prepared by thermal decomposition of uranyl salts around 400C. The reverse of Reaction 3 occurs around 700C.

The preponderance of scientific literature indicates that under conditions relevant to STD-3013, the primary weight loss mechanism for UO_3 should be loss of oxygen, not volatilization. The uranium-233 standard indirectly contains a single primary reference to "gaseous UO_3" when U_3O_8 is heated in the temperature range of interest (1000°C or below). (16) This reference, which describes calorimetric heat capacity measurements on U_3O_8, is cited indirectly via general scientific encyclopedia references in the uranium-233 standard. (3,17,18). Actually, the primary reference does not mention UO_3 volatility specifically. The most reasonable possible inference to volatility from this work probably derives from the observation that "...in the neighborhood of 1100°C (2012°F), the mean heat capacity appeared to rise." Interpretations other than UO_3 volatility can explain this observation.

In the suite of representative STD-3013 items, U_3O_8 and PuO_2-UO_2 solid solutions (in the cubic MO_2 structure) are the only uranium-containing phases that have been detected by x-ray diffraction after calcination at 950°C. (19) This result is consistent with related studies on fuel-type uranium-plutonium oxides (solid solutions) over various temperature ranges. (E.g., see Refs. 10, 20-22)

Effects of relative humidity on oxidation of UO_2 and uranium-plutonium oxides recently have been summarized. (15). These authors concluded that for both categories of materials, relative humidity effects are small.

Oxide materials containing high plutonium plus uranium content that are subject to STD-3013 exist in two predominant categories. (23) The first category, which constitutes a significant category of the plutonium/uranium oxide material at Rocky Flats (RF), consists of physical mixtures of uranium compounds and plutonium compounds. Typically, these RF materials are relatively pure and have uranium content ranging from low percent to tens of percent levels. As discussed in a later section of this report, an important subset has low uranium content (often 1 wt.% or lower) and plutonium content of 80 wt.% or higher. The available technical literature strongly indicates that separate uranium and plutonium phases in this category of materials should behave independently, and that the uranium oxide chemistry will be as described in preceding sections. As discussed in a subsequent section, UO_2 is the only plutonium oxide expected to be of significance under STD-3013 conditions.

The second major category of STD-3013 materials, located largely at Hanford and Savannah River, consists of PuO_2-UO_2 solid solutions. Such materials mostly resulted from nuclear fuel fabrication but also may have arisen to some extent from plutonium alloy oxidation. All known STD-3013 mixed oxides of this type have plutonium content much lower than 80 wt.% and therefore do not apply to the specific RF application discussed later in this report. However, for completeness the oxidative behavior of this category of materials is discussed briefly below.

It has been observed repeatedly that it is difficult to fully oxidize the uranium constituent in mixed uranium-plutonium oxides. (E.g., see Refs. 10,13,14,20-22) Available equilibrium and kinetic data appear to be insufficient to globally and accurately predict PuO_2-UO_2 stoichiometries after calcination. Thus, Haschke et al. (14) state that it is "uncertain if LOI analysis is suitable to certify MOX storage" and that more research and review is needed to clarify the issue. Stakebake (13) came to a similar conclusion on applicability of LOI to these materials. These reports also recognize that, while a recent study (with mixed oxides containing 35 wt.% plutonium) led to stable weights during LOI tests at 900°C, possible offsetting affects of moisture readsorption were not considered fully. (14) None the less, available literature suggests the possibility that further analysis and testing might define processing regimes relevant to STD-3013 where sufficient weight stability can be achieved for LOI to be a viable test method for water determination.

Table 3 lists maximum weight gains and losses possible in Reactions 1-3. For >80 wt.% plutonium oxide material, if 7 wt.% uranium impurity is assumed, then the maximum redox biases are 0.31 wt.% for Reaction 2 (conversion of UO_2 to U_3O_8), 0.16 wt.% for Reaction 3 (conversion of U_3O_8 to UO_3) and 0.47 wt.% for the combination of the two reactions (Reaction 1). Because Reaction 2 is very likely the dominant uranium oxide reaction to consider with respect to LOI under STD-3013 conditions, and because both the scientific literature and STD-3013 item characterization indicate this reaction should be driven partially or totally to completion by calcination, the actual uranium oxide weight gain bias under practical conditions for oxide materials with plutonium assay of 80 wt.% or higher is expected to be minimal.

Table 4. Effect of uranium oxide impurity on LOI. Assumes uranium as isotope U-238 and Reactions 2 and 3 as described above. The maximum uranium assay for representative STD-3013 items was 78 wt.%.

compound	formula wt. per U	% wt. change for pure U oxide	% wt. change for 7 wt. % U
UO_2	270		
U_3O_8	281	4.1	+0.31
UO_3	286	1.8	+0.16

This conclusion is subject to confirmation by straightforward testing. For RF target materials discussed later in this report, it is recommended that STD-3013 oxide materials and carefully selected surrogates with a relevant range of uranium and plutonium content be subjected to thermogravimetric analysis, possibly supplemented by identification and quantification of evolved gases under conditions directly related to actual bulk stabilization and LOI conditions. These tests should allow direct quantification of actual extents and rates of redox processes under conditions directly relevant to STD-3013 processing. The solid products from these tests should be subjected to x-ray diffraction and uranium oxidation state testing to confirm the chemical nature of the uranium oxide constituent. These methods should authoritatively test the conclusion, based on the analysis above, that redox bias should be minimal for the target RF materials, and most likely for other relatively pure STD-3013 oxides, even if they contain uranium impurities. On this basis, defensible bias corrections (if any are needed at all) can be derived for uranium oxide co-constituents.

OTHER ACTINIDE OXIDES

The only neptunium oxide expected to be significant under STD-3013 conditions is the dioxide. (24) A limited subset of STD-3013 materials is known to contain percent levels of neptunium. Process knowledge strongly indicates that although neptunium is an identifiable impurity, it should not have a significant negative impact on STD-3013 materials processing. (19,23). Other than NpO_2, the only other known well-defined neptunium oxide, Np_2O_5, is not expected to exist under typical processing conditions. (24) It has been shown that a discrete neptunium analogue to U_3O_8 does not exist. Oxide weight change bias therefore is not an issue for neptunium.

Plutonium dioxide is the only significant plutonium oxide phase expected under STD-3013 conditions. (21,25) This compound typically occurs with a slight oxygen deficiency that is small in the context of the present discussion. The value of x=0.05 for PuO_{2-x} bounds the lowest plausible substoichiometry for STD-3013 conditions. This value corresponds to a weight difference of about 0.30 wt.% relative to exact dioxide stoichiometry.

Dependent upon time since purification and isotopic composition of the plutonium, percent levels of americium can be present in STD-3013 materials. Most americium assays are below 0.8 wt.%, but some Hanford materials have americium content approaching 7 wt.%. Both a sesquioxide and dioxide are known for americium. (26) Because the sesquioxide readily oxidizes in air, even at room temperature under some circumstances, only the dioxide (typically slightly substoichiometric) should be significant with respect to 3013 stabilization. For this reason, and because the americium content is generally anticipated to be low except for some easily identified material subsets, LOI biases due to oxide weight change should be insignificant for americium impurities.

TRANSITION METAL OXIDES

Table 2 shows that the only transition metal oxides detected to date above 0.6 wt.% content in representative STD-3013 items are copper, iron, nickel, chromium and zinc. Oxides of nickel, chromium and zinc should be limited to NiO, Cr_2O_3 and ZnO under STD-3013 conditions and need not be considered further with respect to redox weight changes. (27,28)

As Table 2 indicates, characterization of STD-3013 items indicated a copper impurity level of 9 wt.% in one sample, but all other measured copper levels were under 0.5 wt.%. The high copper sample was a Los Alamos research material that also had a uniquely high level of zinc (6.1 wt.%). All other measured zinc concentrations were 1.5 wt.% or less and also possessed a relatively low plutonium content (40-60 wt.%). Process knowledge, together with the characterization data, strongly indicates that this sample is a unique material and that similar Los Alamos items with strongly elevated copper and zinc levels should be easy to anticipate during STD-3013 processing.

Two copper oxides are reasonable to consider with respect to STD-3013 processing, Cu_2O and CuO. Cuprous oxide can be oxidized to cupric oxide as indicated in Reaction 4.

4) $Cu_2O + 1/2\ O_2 \rightarrow 2\ CuO$

According to the literature, CuO is unstable with respect to Cu_2O at elevated temperatures. (27). However the free energy change for Reaction 4 remains negative up to 1400K. This shows that 950°C calcination should effectively convert Cu_2O to CuO.

If one assumes the maximum possible copper content and that Reaction 4 is ineffective during the stabilization process but efficient in LOI testing, Table 4 indicates that the maximum possible redox bias is about 0.88 wt.%. As discussed above, copper assays will be much less than 7 wt.% for almost all STD-3013 materials. In practice, from the known chemistry of copper oxides, levels of Cu_2O are not expected to be significant relative to CuO. Therefore, LOI redox bias is expected to be negligible for copper oxides.

Table 4. Effect of copper oxide impurity on LOI. Assumes Reaction 4 as the bounding oxide reaction. The maximum copper assay for STD-3013 representative items was 9.0 wt.%.

compound	formula wt. per Cu	% wt. change for pure Cu oxide	% wt. change for 7 wt. % Cu
Cu_2O	71.5		
CuO	79.5	+11.2	+0.88

Characterization shows that several percent levels of iron impurity are common in STD-3013 materials and a maximum level of 5.4 wt.% has been detected. (Table 2) However, levels above 0.5 wt.% have not been detected for materials with plutonium assay above 70 wt.%. Three oxides of iron (FeO, Fe_2O_3 and Fe_3O_4) are considered with respect to STD-3013 processing, as indicated in Reactions 5 and 6.

5) $3\ FeO + 1/2\ O_2 \rightarrow Fe_3O_4$

6) $2\ Fe_3O_4 + 1/2\ O_2 \rightarrow 3\ Fe_2O_3$

Ferrous oxide, FeO, disproportionates into Fe and Fe_3O_4 when it is cooled slowly from high temperature. (27) The monoxide can be a reactive (even pyrophoric) material, with respect to oxidation but can exist in less reactive forms as well. The literature strongly indicates that FeO will not be significant in the STD-3013 system. The intermediate oxide Fe_3O_4 can be prepared by ignition of Fe_2O_3 above 1400°C or by heating Fe_2O_3 to 250°C in vacuum. Thus, the literature indicates that the intermediate oxide also should not be a major constituent in STD-3013 processing. Ferric oxide, Fe_2O_3, is expected to be the dominant (probably exclusive) iron oxide under STD-3013 conditions. X-ray diffraction studies have detected no iron compounds in the representative materials, perhaps due to the relatively low iron concentrations that are present.

Table 5 indicates that, assuming the presence of about 7 wt.% iron impurity, the maximum possible oxide weight changes due to Reactions 4 and 5 are about 0.67 and 0.33 wt.%, respectively. Since iron assays generally are expected to be much less than 7 wt.% in actual practice and because Fe_2O_3 should be the dominant iron oxide in STD-3013 materials based on well established iron oxide chemistry, actual LOI redox biases should be negligible.

Table 5. Effect of iron oxide impurity on LOI. Assumes Reactions 5 and 6 as bounding oxide reactions. The maximum iron assay for STD-3013 representative items was 5.4 wt.%.

compound	formula wt. per Fe	% wt. change for pure Fe oxide	% wt. change for 7 wt. % Fe
FeO	71.9		
Fe_3O_4	77.2	+7.4	+0.67
Fe_2O_3	79.9	+3.5	+0.33

While levels of manganese have not been detected above 0.5 wt.% for the representative STD-3013 items, they are considered in the present discussion since manganese compounds have been used in some plutonium solution processes. (29) The oxide chemistry of manganese, as is the case for iron, is quite complex. (27) Reaction 7 indicates inter-conversion of the two most important manganese oxides to consider for STD-3013 conditions.

7) $Mn_2O_3 + 1/2\ O_2 \rightarrow 2\ MnO_2$

The sesquioxide can be prepared by heating MnO_2 in air at temperatures of about 550-900°C and therefore is likely to be the dominant (perhaps exclusive) oxide of manganese under STD-3013 conditions. As Table 6 indicates, the maximum bias from Reaction 7 (assuming about 7 wt.% manganese) is about 1.0 wt.%. Because of the expected dominance of Mn_2O_3 after calcinations and the expectation that manganese levels will be much lower than 7 wt.% in STD-3013 materials, even for materials that were generated by chemical processes involving manganese, LOI biases due to manganese oxide weight changes should be negligible.

Table 6. Effect of manganese impurity on LOI. Assumes Reaction 7 as the bounding oxide reaction. The maximum manganese assay for STD-3013 representative items was 0.44 wt.%.

Compound	**Formula wt. per Mn**	**% wt. change for pure Mn oxide**	**% wt. change for 7 wt. % Mn**
Mn_2O_3	78.9		
MnO_2	86.9	+10.1	+1.0

ALKALI AND ALKALINE EARTH OXIDES

Table 2 indicates that alkaline earth and alkali metal compounds can be major impurities in STD-3013 materials. However, process knowledge and characterization data suggest the alkali and alkaline earth compounds largely will be present as chlorides, not oxides (or hydroxides). The literature indicates that alkali and alkaline earth oxides, if they are present at all under STD-3013 conditions, should exist in only one well-defined oxide composition. While peroxides are known, in general they decompose far below the calcination and LOI test temperatures and are not expected to form on cooling. Therefore, alkali and alkaline earth impurities should cause no LOI analytical bias problems due to oxide weight change.

Alkali and alkaline earth oxides do have some potential under STD-3013 conditions for oxidation reactions involving oxygen and actinide oxides to form higher valent compounds such as Na_3UO_6 and Ca_3PuO_6. Thus, Keller (30) states:

> "The best way to prepare these (hexavalent) transuranium compounds is to heat the appropriate mixtures of alkaline earth oxide and actinide dioxides at 1000-1200°C in an oxygen flow."

To date, such compounds have not been observed in the STD-3013 materials characterization program, either because they did not form or were present in such low concentrations that x-ray diffraction could not detect them. In general, if ternary oxides were to form, these products would intrinsically be more thermodynamically stable than the reacting components. From process knowledge, the likelihood that appreciable quantities of alkali metal oxides are present in STD-3013 materials is judged to be low. For the materials with plutonium content greater than 80 wt.% primarily addressed in this report, the likelihood is extremely small.

Additional discussion of alkali earth oxides is given in a subsequent section on oxide volatility.

MAIN GROUP OXIDES

Characterization data, in combination with process knowledge, strongly indicates that the only appreciable main group element impurities anticipated in STD-3013 materials are gallium, aluminum and silicon (Table 2). The latter two elements are virtually certain to exist under STD-3013 conditions in only one oxide stoichiometry each (Al_2O_3 and SiO_2), while gallium could exist as Ga_2O and/or Ga_2O_3. (27) The sesquioxide is slightly more stable under ordinary conditions than Ga_2O. (31) Reaction 8 indicates the conversion between these two oxides.

8) $Ga_2O + O_2 \rightarrow Ga_2O_3$

The maximum gallium assay for all representative items was about 2.4 wt.%. Process knowledge indicates this may be a bounding value for STD-3013 materials. (23). The sesquioxide is the form that usually results when gallium compounds are heated in air and thus is expected to be dominant for STD-3013 processing. (27,32) Table 7 shows that if gallium (7 wt.%) was present as Ga_2O in calcined 80 wt.% plutonium materials and Reaction 8 occurred fully during an LOI test, the maximum possible bias due to oxide weight change would be about 1.6 wt.%. In practice, the actual bias should be negligible since the bounding gallium concentration will be much less than 7 wt.% and negligible Ga_2O is expected to be present.

Table 7. Effect of gallium oxide impurity on LOI. Assumes Reaction 8 as the bounding oxide reaction. The maximum gallium assay for STD-3013 representative items was 2.4 wt.%.

Compound	**Formula wt. per Ga**	**% wt. change for pure Ga oxide**	**% wt. change for 7 wt. % Ga**
Ga_2O	77.7		
Ga_2O_3	93.7	+20.6	+1.6

OXIDE MIXTURES

The preceding sections each assumed that the entire impurity content in >80 wt.% plutonium oxide material involve a single metal element. The discussions should bound oxide impurity effects for physical impurity mixtures because the effects should be additive. No non-additive impurity effects are known or have been suggested to the authors that would lead to behavior involving significantly enhanced oxide weight gain.

UNOXIDIZED METAL

Residual unoxidized metal after STD-3013 calcination represents another potential source of LOI weight gain. Weight gains from such reactions theoretically can be substantial, for example 12 wt.% for Reaction 9 and 30 wt.% for Reaction 10. Based on current knowledge, these two reactions are the most important to consider in the context of the present discussion.

9) $Pu\ (metal) + O_2 \rightarrow PuO_2$

10) $2Fe\ (metal) + 3/2\ O_2 \rightarrow Fe_2O_3$

Despite the high reactivity (even pyrophoricity) of plutonium metal under some conditions, cases exist where plutonium metal, apparently protected by an impervious oxide coating, has partially survived calcination. For example, it has been observed at Hanford and Savannah River that after one calcination cycle in large furnace boats (950°C, 2 hrs) subsequent LOI measurements frequently show a gain on ignition, most likely due to incomplete metal oxidation during calcination. (33-35) After sieving, mixing and re-firing such material, Hanford and Los Alamos found that a second LOI test usually shows a weight loss, indicating that oxidation is complete in the second calcination cycle. (33,35) Alloys can show even greater resistance to oxidation, as indicated by Pu-Al-Mo alloys that show gains on ignition even after 950°C calcination for up to thirty hours. (33) Because of this experience, oxide materials directly derived from metal oxidation merit special consideration since in some cases multiple calcination cycles may be required to complete the oxidation.

Metallic iron likewise is capable of surviving calcination conditions, as illustrated by its use in many elevated temperature applications.

Pyrochemical materials comprise the second significant category of STD-3013 materials that can contain residual plutonium metal after calcination. (23) These items typically contain significant amounts of chloride salts of sodium, potassium, calcium and/or magnesium. Because the plutonium content for pyrochemical materials almost always is well below 80 wt.%, these materials are not pertinent to the immediate discussion on redox bias. However, it is well recognized that percent levels of chloride impurities can cause weight losses of many percent due to sublimation of sodium, potassium or magnesium chloride, or very significant weight gains due to moisture uptake on calcium and magnesium chloride. (2,4,19,36) Thus, STD-3013 items with these impurities may be highly problematic with respect to LOI testing.

For Reactions 9) and 10) to be significant in actual STD-3013 stabilization and LOI testing, two conditions must be met:

a) Substantial wt.% levels of elemental metal must survive calcinations, and

b) A substantial fraction of the surviving metal must be converted to oxide during the LOI test.

For plutonium and uranium metal, condition a) is very unlikely for most processing schemes, and categorically excluded for aqueous processing products.

Metallic iron will only be present as "tramp" material and has been seen in only a few representative items. Section 6.3.3.1 of STD-3013 addresses the problem of tramp material by stating:

> "Obvious, readily-removed tramp materials such as metal fasteners and other debris shall be removed from the material prior to packaging."

This requirement greatly diminishes the importance of Reaction 9) and related reactions in STD-3013 processing. The requirement also should ensure that large pieces of metallic uranium and plutonium are detected prior to packaging, and thus minimizes (but does not completely eliminate) the possibility that small metallic pieces from pyrochemical salts survive calcination.

NON-METAL IMPURITIES

As indicated in Table 2, chloride and fluoride are the only non-metal impurities that have been detected above 0.5 wt.% in calcined representative STD-3013 items (silicon is considered a metallic element in previous discussion). Volatilization of certain chloride salts, notably sodium, potassium and magnesium chlorides, can occur during calcination and thus can cause LOI analysis to overestimate apparent moisture content. (19) Testing shows that for certain STD-3013 representative items, the magnitude of this effect can be many percent. However, except for moisture uptake after calcination, no mechanism is known for these impurities to cause a non-conservative LOI estimate of apparent moisture content.

LOI RESULTS FROM REPRESENTATIVE STD-3013 ITEM CHARACTERIZATION

The STD-3013 representative item characterization program includes two items (5505179 and CAN 92) with plutonium contents of 85 and 82 wt.% and uranium contents of 1 and 3 wt.% respectively. These items were calcined at 950°C and LOI determinations indicated 0.07 and 0.02 wt.%, respectively.

To date, LOI measurements after calcination have been made on twelve representative plutonium oxide items with plutonium content of 80 wt.% or higher and no appreciable quantities of uranium. LOI measurements for eleven items indicated a weight loss of less than 0.5 wt.%. One item had an LOI of 0.81 wt.%, but there is no ready explanation for this high result. Measurements by alternative methods indicated that moisture contents were less than 0.5 wt.% and no significant impurities were found.

OXIDE VOLATILITY

Certain metal oxides pertinent to the present discussion potentially can volatilize, sublime, or decompose during LOI testing and cause moisture equivalent content to be overestimated. Based on process knowledge and characterization, as discussed in preceding sections, only the oxides of hydrogen, sodium and potassium need to be considered further with respect to weight change bias.

Water is present because it occurs ubiquitously in the processing and storage environment unless extraordinary measures are taken and because of the general propensity of oxides to take up moisture. For oxides with plutonium content greater than 80 wt.%, process knowledge indicates that sodium and potassium concentrations should be negligible. Separations processes that are highly exclusive of such constituents generally were used to prepare these high plutonium assay items. Characterization bears out this expectation, since impurity levels above 0.5 wt.% have not been detected in representative STD-3013 items (Table 2). Therefore no appreciable LOI effects are expected due to sodium and potassium oxides for relatively pure STD-3013 materials.

An additional point of relevance is that, unlike magnesium chloride, the chlorides of calcium, sodium and potassium are not expected to hydrolyze during STD-3013 calcination to form oxides. (4)

MOISTURE ABSORPTION

While the issue of moisture uptake is not the primary theme of this evaluation, it is treated here briefly because residual moisture equivalent content is the parameter of greatest interest that is potentially masked by redox bias during LOI measurements. This subject has been discussed in detail elsewhere. (4) Various definitions are commonly used for the terms physisorption, chemisorption, absorption, absorption and sorption. In the following discussion, the term sorption is used to encompass the various processes implied by these terms.

Moisture contents of calcined plutonium oxides are expected to be due largely or entirely to sorption from the glovebox atmosphere in the time between calcination and packaging. (2,4) A number of independent studies show that for plutonium dioxide, the amount of uptake is limited by the oxide surface area, relative humidity and exposure time. The kinetics of moisture uptake is highly transport limited and as such varying moisture contents are anticipated unless precautions are taken to ensure that identical conditions are used for all studies.

Recently, moisture uptake measurements were made at Oak Ridge National Laboratory on UO_2, U_3O_8 and UO_3, in support of the technical basis for the uranium-233 stabilization and storage standard. (37) Weight gains were measured at ambient temperature using relative humidities of 70 and 97 wt.%. In a period of three days at 70 % relative humidity, water uptake of about 14 wt.% was observed, corresponding to slightly more than the stoichiometric amount for the well known UO_3 monohydrate that is more accurately represented as $UO_2(OH)_2$. For U_3O_8, exposure at 70 % relative humidity for one day led to weight gains under 0.5 wt.%. For a very long U_3O_8 exposure of forty three days at this humidity level, an uptake of 2.8 wt.% was observed. Uranium dioxide showed "no weight gain on exposure to the humidification apparatus – even at 97.5 % relative humidity." In addition, Icenhour et al. reported that surface adsorbed moisture on these uranium oxides was relatively inert to radiolysis and that the uranium oxide surface areas used in these studies were generally below 1 m^2/gm. The general thrust of the Oak Ridge work is that the interaction of moisture with UO_2 and U_3O_8 is qualitatively similar to that with PuO_2.

In general, all published studies surveyed in this report on PuO_2, UO_2 and U_3O_8 that address surface specificity and molecular scale information are consistent with rapid formation at ambient temperature of a chemisorbed surface hydroxide layer plus a less strongly adsorbed molecular water, to relative humidities at least as high as 60 wt.%. (E.g., see refs 4, 38-41) These studies indicate that for surface areas below 5m^2/g, the corresponding moisture equivalent content is about 0.1-0.2 wt.%. Characterization shows that after calcination, with the exception of one material with elevated magnesium content, the specific surface area of representative STD-3013 items is always below 5 m^2/g. This observation is consistent with similar surface area investigations of plutonium dioxide. Therefore, in STD-3013 practice, this moisture range generally should be bounding for relatively pure plutonium oxides including those containing uranium.

As indicated in the preceding discussion and Table 2, for representative items with plutonium content of 80 wt.% or greater, the overwhelmingly dominant non-plutonium oxide constituent is uranium oxide. The extensive scientific and technologic literature referenced above indicates that the nature of water interaction with uranium oxide is comparable to that of plutonium oxides. (42-46) With reasonable confidence, similar moisture equivalent content per unit surface area from readsorption can be assumed for uranium and plutonium oxides. In this regard, it is pertinent to consider the following statements in the uranium-233 stabilization and storage standard (3):

> "...since chemisorption is a surface phenomenon it will have little impact on the 0.5 wt.% (moisture) limit for ^{233}U oxides."; and
>
> "Moisture does not tend to readsorb in significant quantities on stabilized U_3O_8."

The uranium-233 standard further states:

> "If the volatiles content cannot be shown to be less than 0.5 wt.%, this Standard specifies that oxide material will be placed in a continuously oxidizing atmosphere at a material temperature of greater than 750°C (1382°F) for a minimum of one hour."

Thus, a specific test for residual moisture or chemical stability is not required absolutely by this standard.

Table 2 shows that no significant constituents other than uranium were detected in >80 wt.% plutonium content representative items. Extensive scientific literature exists for the interaction of moisture with a wide range of oxides that could be present at low levels in these materials. (E.g., see Refs. 39, 42- 44) The literature indicates that thermodynamics, kinetics and chemical transformations involved with water interactions with typical transition metal and lanthanide oxides are comparable to those with plutonium oxide. Therefore, it is not anticipated that minor impurities of this type will appreciably affect overall moisture adsorption on calcined plutonium oxides. The authors are not aware of any literature or other reliable information that seriously challenges this generalization.

Certain compounds containing chloride, magnesium and calcium are capable of absorbing significant amounts of moisture equivalent as either hydroxides or hydrates, even when present at only percent levels. (4) However, none of these elements were detected above 0.5 wt.% in the STD-3013 representative items where plutonium content was about 80 wt.%. This result is consistent with process knowledge for these materials, which indicates that levels of such impurities should be minimal. (23)

NATURE OF ROCKY FLATS (RF) MATERIALS BEING ADDRESSED

A significant fraction of the current Rocky Flats inventory of oxide materials contains uranium oxide and greater than 80 wt.% plutonium content that is scheduled for stabilization and packaging in STD-3013 containers. The discussion in this section is specific to this feed stream and is intended to elucidate possible problems in the use of LOI to infer moisture content after stabilization.

Key to this discussion is an understanding of the origins of the materials and the processes that generated the current material forms. Two processing operations at Rocky Flats involved the removal (separation) of plutonium contamination from uranium. Both separation processes may have contributed to the generation of oxide materials containing both plutonium and uranium. Brief discussions of these two processes follow.

<u>RF process 1:</u> Metal Hydriding

Both plutonium and uranium react with hydrogen to form the respective metal hydrides according to the following reactions:

$$\text{Pu (metal)} + 3/2\ H_2 \rightarrow PuH_3$$

$$\text{U (metal)} + 3/2\ H_2 \rightarrow UH_3$$

Because plutonium reacts much faster than uranium with hydrogen, the differing kinetics of these two reactions makes the separation of Pu and U feasible. The key to success is to control the process so the plutonium reaction proceeds effectively to completion, but to stop before appreciable uranium react occurs. In practice, the reactions overlap to some extent and the resultant plutonium hydride product contains some uranium impurity. The hydride product was subsequently converted to the oxide by burning in air (spontaneous), followed by a second burn in oxygen.

$$PuH_3 + O_2 \rightarrow PuO_2 + 3/2H_2$$

Some uranium oxide from the uranium impurity also results from this reaction.

This hyride operation also was used to convert significant quantities of pure uranium metal to oxide, using the same process equipment and gloveboxes that were used for plutonium materials. As a result, cross contamination of plutonium oxide products with low uranium concentrations occurred to some degree.

Because of high temperatures generated by the oxidation of hydrides, uranium oxide constituents are expected to consist largely, if not completely, of U_3O_8. The demonstrated effectiveness of the hydriding reaction and the two stages of oxidation makes the possibility for residual actinide metal or hydride content in the products extremely remote. Finally, because the hydriding process was designed to produce high purity, high value products, the likelihood that impure materials may have been incorrectly included in hydride product IDCs is considered very small.

RF process 2: Uranium Acid Leach

Nitric acid leaching was used at RF to remove plutonium from uranium metal. The leachate then was processed via solvent extraction (PUREX) and the separated plutonium solution subjected to ion exchange, oxalate precipitation, calcination and finally conversion to metal. This process resulted in a very clean Pu/U separation.

The uranium solution from the separation was precipitated with ammonia to form ammonium diuranate, which was then calcined initially at about 450°C. The focus of the initial calcination was to dry the uranium oxide and to convert the ammonium diuranate to oxide. The final oxide composition could be anywhere from UO_2 to UO_3, with a strong possibility that the UO_3 was converted effectively to U_3O_8.

Batch LOI measurements performed at 450°C on the uranium oxide product prior to offsite shipment generally showed a weight gain (failed LOI test), suggesting that some UO_2 was present initially and was converted to U_3O_8 during the test. A second LOI test was almost universally successful, with of observation of no significant weight gain or weight loss less than 1 %. It cannot be ascertained with certainty that the LOI results are not complicated by a combination of "oxidation", "reduction" and "water desorption". However, LOI did produce consistent results which led to a procedure change that called for all material to be calcined twice at 450°C.

In considering the two RF processes described above, it can reasonably be concluded that the oxide materials addressed in this paper (greater than 80 wt.% plutonium) were largely or entirely generated by the hydriding process. Metal was only involved as a source material, and there is no reason to expect metal residuals to have survived the processing and to complicate STD-3013 processing and packaging operations. In order to be present, metal residuals would have to survive both hydriding and the double burning at high temperature. Metal residuals also would have to survive the 3013 stabilization and LOI process. Similarly, the likelihood is judged to be small that significant amounts of UO_2 or UO_3 would not have been converted to U_3O_8 during the multiple stages of processing. Indeed, these hydride-derived materials may very well have undergone more thermal processing than any other material in the RF inventory.

SUMMARY, RECOMMENDATIONS AND CONCLUSIONS

The technical evaluation presented in the preceding discussion strongly indicates that, with the possible exception of uranium oxides and unoxidized metals, LOI bias due to inter-conversion of multivalent oxide constituents in STD-3013 materials with plutonium assay above 80 wt.% should be minimal with respect to the 0.5 wt.% moisture threshold. This conclusion is based on several lines of evidence: process knowledge on potential impurities for this category of materials, confirmation of the process knowledge by analysis of representative samples and evaluation of extensive chemical literature in the context of STD-3013 stabilization and LOI conditions.

The possible exception to the above conclusion is when an appreciable fraction of the maximum theoretical impurity consists largely of uranium oxide. Even in this case, it is necessary for a substantial fraction of the uranium oxide to survive calcination as UO_2 and then to be converted efficiently to U_3O_8 in the LOI test at slightly higher temperature. Based on the chemical literature, the importance of this scenario is judged to be highly unlikely.

The behavior of mixed uranium-plutonium oxides, occurring most often as fuels-type solid solutions, is more complicated. In this case, oxidation of the UO_2 component indeed can be incomplete under STD-3013 calcination conditions. However, oxidation in the standard LOI test likewise is expected to be sluggish so the 0.5 wt.% criterion could be met for some materials of this type. In any case, because little or no STD-3013 mixed oxide material exists where the plutonium assay is high, it is not pertinent to the present evaluation. The literature does suggest that further analysis and testing may show that STD-3013 operating conditions are such that bias effects may be manageable even for fuels-type materials.

To further substantiate the evaluation presented above, it is recommended that TGA tests be conducted on carefully selected STD-3013 representative items and surrogate materials containing uranium. In addition, direct measurements of uranium valence state should be made before and after STD-3013 calcination and LOI testing using techniques such as reflectance or x-ray photoelectron spectroscopy on solids or characterization following dissolution in non-oxidizing media. Starting and ending materials also should be characterized by x-ray diffraction. Minimal testing to confirm expectations of minimal moisture uptake on post-calcination cool down under conditions relevant to STD-3013 also is recommended. All of these tests should be done in a way such that any small scale tests can clearly be related to batch processing conditions.

Well designed tests as suggested above should authoritatively bound the maximum possible LOI weight gain bias from possible oxide valence state changes. This work also would lay the basis for evaluating the redox bias issue for materials containing higher levels of uranium and metal element impurities, including fuels-type materials.

In concluding, it is noted again that the immediate application of the present evaluation is on uranium-containing STD-3013 materials with 80 wt.% or greater plutonium content. However, the evaluation also indicates there is promise for successfully extending similar analyses to a greater range of materials on a case-by-case basis.

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