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Title:	Re-evaluation of Moisture Controls During ARIES Oxide Processing, Packaging and Characterization
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1 Introduction

1.1 3013 Moisture Processing, Packaging and Representative Sampling Requirements

DOE-STD-3013 [1] requires limiting the relative humidity (RH) in the glovebox during processing of the oxide product for specific types of plutonium oxides. This requirement is mandated in order to limit corrosion of the stainless steel containers by deliquescence of chloride salts if present in the PuO_2.

DOE-STD-3013 also specifies the need to limit and monitor internal pressure buildup in the 3013 containers due to the potential for the generation of free H_2 and O_2 gas from the radiolysis of surface-adsorbed water.

DOE-STD-3013 requires that the oxide sample taken for moisture content verification be representative of the stabilized material in the 3013 container. This is accomplished by either limiting the time between sampling and packaging, or by control of the glovebox relative humidity (%RH). This requirement ensures that the sample is not only representative, but also conservative from the standpoint of moisture content.

1.2 Objectives of the Present Document

The ARIES program generated conservative initial controls in response to the DOE-STD-3013 requirements summarized above. These initial controls covered feed material produced by the 94-1/00-1 project which is known to contain non-impurity levels of chloride salts. These measures were simply replicated to cover high-purity materials, thus a single set of controls is operative regardless of the purity of the feed material. The more conservative control set also worked well for high-purity PuO_2 generated by the MOX Pu Polishing Program. Though they contained no Cl or admixed salts, the MOX oxides had very high (5 to 15 m^2/g) specific surface area (SSA), and were able to adsorb >0.5 Wt. % water when exposed to high humidity [2]. ARIES oxides, on the other hand, have very low SSAs, typically <0.5 m^2/g, and have much lower adsorptive capacity [2]. As a result, the conservatism of these initial controls with respect to ARIES feed material is unnecessary and overly burdensome.

The present document provides technical justification to update the controls designed to meet the 3013 moisture requirements related to processing, packaging and representative sampling of ARIES PuO_2. The proposed update would only be applicable to the high purity ARIES feed material. These updated controls would not be applicable to any other feed material. This technical justification has no impact on currently established controls, and simply provides the technical justification to make changes to the approved documents (i.e., revisions to the 20 points documents and the equivalency), or to provide technical justification to an NCR if the RH limits are exceeded.

The arguments provided in this document are based on ARIES data generated from 52 blend lots [3], and information in technical documents, including the DOE-STD-3013. The result demonstrates that high purity, low SSA ARIES oxide produced by either direct oxidation and calcination of plutonium metal in a muffle furnace (at 950ºC) or by the DMO furnaces (at 950ºC or 650ºC) poses little to no risk of pressurization or corrosion of 3013 containers. It is important to note that the metal to oxide conversion which occurs at 450ºC to 550ºC is independent of furnace, and that the resulting low SSA is a characteristic of the metal to oxide conversion process. Additionally, an argument is made showing that a representative moisture sample of this material can be achieved without the need to follow one of the three techniques initially proposed for limiting adsorption/desorption of moisture between sampling and subsequent moisture analysis if the SSA is <0.5 m^2/g.

1.3 ARIES Responses to DOE-STD-3013 Moisture Processing, Packaging and Representative Sampling Requirements

LANL's ARIES Program developed the initial responses to the 3013 requirements prior to the acquisition of substantial analytical data. While it was almost a given that Cl would be at or below trace levels in the finished product, there were no data on the SSA, particle size distribution or moisture content of the finished product. These initial responses accommodated the less pure plutonium oxide for the 94-1/00-1 project and the high SSA PuO_2 generated by the MOX Pu Polishing Program. The oxide produced by the 94-1/00-1 project is known to have chlorine contents above impurity levels, and was being processed at the time of the initial responses. Subsequently, processing of the 94-1/00-1 material and PuO_2 generated by the MOX Pu Polishing Program ceased, and ARIES material processing became predominant.

The measures adopted by DOE-STD-3013 require that the impure oxide be 'stabilized' at ≥950°C. In the ARIES paradigm, 'stabilization' consists of high-temperature calcination in an oxygen-rich atmosphere such that there is no potential for the existence of remnant Pu metal or PuO_{2-x}. Initial responses of the ARIES Program to DOE-STD-3013 pertained to ARIES oxide calcined at temperatures ≥950ºC. Subsequent to these initial responses, work was done to technically justify a lower stabilization temperature for ARIES oxide [4]. The technical justification demonstrated that calcination in air at 650ºC produces oxide that is certifiably free of Pu metal and reactive PuO_{2-x}. Therefore all of the controls imposed on the 950ºC product were also imposed on the 650ºC product [4].

1.3.1 Initial ARIES Response to %RH and Deliquescence

LANL implemented the following control for both ARIES and 94-1/00-1 oxide [5], despite the low level risk of corrosion of the 3013 container from the generation of hydrated chloride salts in the ARIES oxide,

> "If, after stabilization (defined as the time elapsed from furnace shutoff until the material is welded into the inner container), the glovebox relative humidity rises above 15% (8% for material containing calcium chloride-based salts) place the material in a sealed container until the relative humidity is brought below 15% (or 8% respectively), at which time processing can resume."

The same control carried over when the 650ºC equivalency was granted.

1.3.2 Initial ARIES Response to Pressurization

Despite the low level of risk related to the pressurization of the 3013 container as a result of the radiolysis in the ARIES oxide, the following controls were also put into place, applicable to both ARIES oxides and the impure 94-1/00-1 oxides [6],

> "LANL will be using a combination of absolute height measurements of the inner container after welding and radiographs of the package after closure. Internal pressure indication relies on the deflection of the inner container lid upon can pressurization. Baseline radiographic photographs will be taken after the 3013 package is closed. The inner container is manufactured to a height of 9 inches. We will measure the inner container height within 24 hours after welding and again within 24 hours of placing the container in the electrolytic decontamination (EDC) fixture. Each measurement is made on a different instrument that is calibrated to ± 0.001 inches. Container heights are measured at four inscribed points across the lid, and have consistently been repeatable to better than ± 0.003 inches. EDC removes an insignificant amount of stainless steel from the container (much less than 0.001 inches). Height measurements will be taken again within 24 hours after decontamination and again within 24 hours before closing the 3013 package. These measurements provide a basis for

> determining internal pressure buildup between inner container welding and just before outer container welding. The data collected is entered into the PCD."

And,

> "LANL will strive to have both the inner container height measurements and the package radiographs completed within 30 days of inner container weld completion. If radiography is completed within 30 days of inner weld completion, height measurements are not required, but will be provided if available."

And,

> "LANL will commit to having the radiograph completed within 15 days of the last micrometer reading before package closure."

The same control carried over when the 650°C equivalency was granted.

1.3.3 Initial ARIES Response to Representative Sampling

The following controls ensure compliance with the requirement to ensure representative sampling [5],

> "To prevent the possible loss of moisture before sample measurement and thus a non-conservative bias one of the following techniques will be implemented.
>
> 1. The time from when the lid is removed from the sample vial to the time each subsample is weighed may not exceed two minutes.
> 2. The relative humidity in the moisture measurement glovebox may not be more than 3% less than the relative humidity in the processing glovebox at the time of sample closure. There is no upper limit. However, to prevent false failures the humidity should be below 15%.
> 3. The ~10-gram sample will be placed in a weighing dish for fifteen minutes. The weight will be recorded when the sample is placed in the weighing dish and every five minutes thereafter. The TGA sample will then be cut and weighed. The time of the first, second, and last weight measurement will be recorded. The time the TGA sample is weighed will be recorded. If the sample has lost weight during the fifteen-minute period, the weight loss rate will be determined and further extrapolated to the time at which the TGA measurement was started. This weight loss will then be added to the final result obtained from TGA. If the sample gains weight no action is required. The weight gain may not be subtracted from the LOI result."

These controls were initiated in the absence of substantial TGA-MS moisture desorption data for the ARIES PuO_2.

The same controls carried over when the 650°C equivalency was granted.

2 Deliquescence of Chloride Salts

2.1 Background

DOE-STD-3013 states the following for managing corrosion by deliquescence of chloride salts in 3013 containers:

- Paragraph 6.1.2.4: “Oxides suspected to contain chlorides shall not be exposed after stabilization to a relative humidity greater than 15%.”
- Appendix A: “Corrosion issues, particularly those involving chlorides, have been addressed and recommendations on container materials and relative humidity controls are provided, specifically, when packaging chloride salts, a maximum relative humidity of 15% is allowed between stabilization and packaging to prevent salt deliquescence.”
- Appendix A: “…examinations have provided evidence that corrosion events occur within the 3013 Container and they could be controlled by the form and quantity of a deliquescent salt and the relative humidity in the container.”
- Paragraph A.6.1.2.1: “Because thermal stabilization does not completely convert the alkaline earth chlorides to alkaline earth oxides, control of time and relative humidity between thermal stabilization and packaging is strongly advised when handling plutonium oxides containing magnesium and calcium chloride impurities.”

2.2 Discussion - Deliquescence of Chloride Salts in ARIES Oxide Stabilized at 950°C

In addition to the background information related to deliquescence of chloride salts given above, DOE-STD-3013 also states:

> “It is the intent to require control of the relative humidity for materials that are known to contain chloride salts such as from chemical processing, e.g. electrorefining or direct oxide reduction, or for materials that have been mixed with, come into contact with, or have been processed in the same equipment as materials known to contain chloride salts. See for instance the criteria used to select containers for field surveillance due to the presence of chloride. It is not the intent to require control of the relative humidity for materials that contain impurity amounts of the element chlorine such as the oxide from direct metal oxidation.”

Therefore, it is implicitly understood by the authors of the DOE-STD-3013 that ARIES PuO_2 should contain only “impurity amounts” of chlorine, and that the deliquescence of any potentially small amounts of chloride salts does not present a corrosion concern.

Data from 52 blend lots confirm the high-purity of ARIES PuO_2 (~86 Wt. % Pu), and the assumption by the DOE-STD-3013 of only “impurity level” amounts of chlorine. Additionally, the principal elements that could generate chloride salts (Mg, Ca, K and Na) are only found at “impurity level” quantities in the ARIES oxide (Table 1).

Element	**Average Measured Content (µg/gPu)**	**Maximum Measured Content (µg/gPu)**	**Maximum Content per ICD (µg/gPu)**
Mg	2.9	60	500
Ca	9	170	500
K	6.7	13	150
Na	31.4	84	300
Cl	<23 and <35[1]	140	+F<250

Table 1 – Content of Impurities Associated with Chloride Salts in ARIES Blend Lots 1 – 52

Reference [7] provides the criteria for categorizing PuO_2 material in different risk categories. In order to be classified as a pressure or corrosion risk, the material must have a chlorine content greater than 1000 ppm. Reference [7] states,

> “The primary constituent for causing corrosion is chloride salts or possibly fluoride-containing materials. Using information from the database, containers identified as containing either chloride (greater than 1,000 ppm) or fluoride (greater than 8,000 ppm), are placed in the Pressure and Corrosion bin.”

Therefore, even the spuriously elevated chlorine content found in one ARIES blend lot (a concentration of 140 ppm) is well below this 1000 ppm limit. Indeed, the maximum allowable chlorine content for ARIES material (250 ppm) is also well below the 100 ppm limit.

Due to the extremely low content of Cl and F in ARIES oxide, there is no specific need to control relative humidity (%RH) during processing and characterization of ARIES oxide stabilized at 950°C. It is recommended that %RH should continue to be monitored for processing purposes, but there should be no processing limit on %RH to protect against deliquescence of chloride salts.

2.3 Discussion - Deliquescence of Chloride Salts in ARIES Oxide Stabilized at 650°C

Trace chemistry results from the first 52 PuO2 lots unambiguously show that ARIES oxide contains very low levels of chlorine. ARIES oxide processing consists of milling, sieving and blending the oxide to a fine powder (<200 μm) and adds few impurities, typically only stainless steel constituents [8]. The end product is sampled and analyzed for trace element contents, and consistently and verifiably contains less than the 250 ppm specification limit for chlorine. No chlorine or chlorine-bearing compounds are utilized in the ARIES process and the vapor pressure for the chloride salts are very low and not significantly different at 650°C compared to 950°C. Therefore, from a chlorine content standpoint, there is likely to be little to no difference between the chlorine content of ARIES material stabilized at 650°C and ARIES oxide stabilized at 950°C.

Due to the low content of Cl and F in ARIES oxide, there is no specific need to control humidity during processing of ARIES oxide stabilized at 650°C. It is recommended that humidity should be monitored for processing purposes, but there should be no processing limit on %RH to protect against deliquescence of chloride salts.

3 Container Pressurization

3.1 Background

DOE-STD-3013 states the following related to pressurization of 3013 containers:

> 6.4.1.3: “Initial baseline inspection for pressure indication, required for oxides but not metals, within 30 days of inner container closure.”

And,

> 6.4.2: “The following parameters shall be included in the non-destructive examination of containers:
>
> > 1) For oxide bearing material, indication of internal pressure build-up in the inner container.”

And,

> 6.5.2.2: “The database shall include, as a minimum, identification of the following 3013 container characteristics:
>
> > 9) Baseline inspection for pressure indication (e.g., lid deflection).”

And,

> A.6.2.1.4: "Pressure indication, such as a pressure deflectable lid or bellows observable by radiography, will permit early detection of inner container pressurization prior to potential failure."

And,

> A.6.3.2.7: "Radiography to observe physical changes in the stored material...and dimensional changes of the inner container from pressure generation."

And,

> A.6.4.1.3: "Since pressure inside the inner container may change after welding, the baseline non-destructive examination for pressure should be performed as soon as possible after the inner container is welded. This examination may be done either before or after the inner container is welded in the outer container. Allowing up to a maximum 30 day delay accommodates operational considerations."

3.2 Discussion – Container pressurization of ARIES Oxide Stabilized at 950°C

The main driver for pressure buildup in 3013 containers is the conversion of water adsorbed on the surface of the PuO_2 into oxygen and hydrogen gases. It is important to consider that all ARIES samples measured to date have contained < 0.015 Wt. % moisture, a quantity that is very close to the 0.011 Wt. % moisture corresponding to 1 monolayer (ML) of H_2O using B.E.T theory and an assumed SSA of 0.5 m^2/g. Another way to look at this is that all ARIES samples so far have contained less than 3% of the 0.5 Wt. % limit imposed by [1]. This limited moisture content is in large part due to the very low SSA of the ARIES oxide.

The ARIES oxide is produced by a repeatable process under conditions that consistently produce an oxide with a SSA <0.5 m^2/g[1], and in many cases a SSA much lower than 0.5 m^2/g. Reference [1] states the following for high purity oxides having an SSA ten times that of ARIES oxide,

> "High-purity oxide of less than 5 m^2/gram specific surface area will not re-adsorb sufficient water to exceed the 0.5 Wt. % limit even when allowed to equilibrate with a controlled atmosphere of about 50% relative humidity."

The report, "The Effect of Plutonium Dioxide Water Surface Coverage on the Generation of Hydrogen and Oxygen" [9] states,

> "The first two molecularly adsorbed water mono layers (ML) are not active to form hydrogen and oxygen. Thus, the water that is active in oxygen gas generation begins with the third molecularly adsorbed layer that occurs at approximately 50% RH."

This appears to be true regardless of the absolute amount of water adsorbed on the PuO_2.

Brunauer, Emmett, and Teller (BET) theory can be used to estimate the equilibrium number of ML of water on the surface of PuO_2 as a function of RH for different isotherms, see Figure 1 below [9]. The number of MLs in Figure 1 are in addition to first strongly bound (chemisorbed) ML of H_2O, so one ML in the figure is equal to two total MLs.

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[1] It should be noted that a few isolated oxide samples from the ARIES line have SSAs between 1 and 2 m^2/g. These measurements are significantly larger than the maximum SSA measured for ARIES oxide during production. Although these samples are from the ARIES DMO-2 furnace, they were produced during the demonstration and testing phase of ARIES operations (circa 2002-3) and were not calcined to 950°C. Thus, it is not appropriate to compare the oxide from the demonstration and testing phase of ARIES with those generated during full-on production as the processes and circumstances by which they were produced differ significantly. Using the data from the first 52 ARIES blend lots, it is reasonable to conclude that the largest credible SSA of PuO_2 that will result from oxide produced by the ARIES process is 0.5 m^2/g

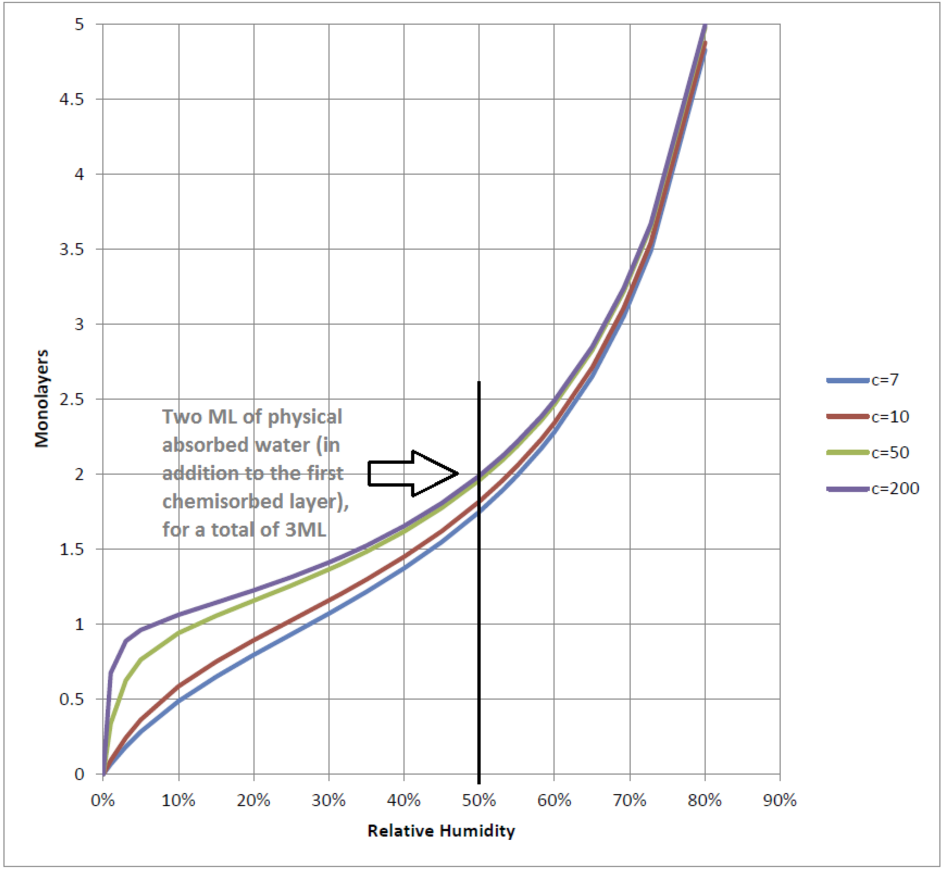

Figure 1 – Adsorption isotherms of water on PuO2 surface calculated from BET theory (adapted from [5])

The theoretical graph in Figure 1 does not assume a certain specific surface area (SSA). Obviously with increasing SSA, the weight percent of H_2O per monolayer of adsorbed H_2O increases. The SSA of plutonium oxide is a function of the process used to produce the oxide and typically decreases with increasing oxidation temperature.

Reference [9] also states,

> "…3 – 5 ML of water are necessary for hydrogen and oxygen generation."

The reason for this 3 – 5 ML threshold for hydrogen and oxygen generation is explained in more detail in [5] and is somewhat beyond the scope of this document. Nevertheless, it is important to note that up to approximately 50% RH, there are not sufficient mono-layers of water on the PuO_2 surface for oxygen and/or hydrogen gas to form in amounts that could result in a dangerous pressurization of the 3013 container.

Although the mechanism of water adsorption on the surface of PuO_2 is not well understood, experimental data supports the theoretical approximation in Figure 1. The document, "Hydration of plutonium oxide and process salts, NaCl, KCl, $CaCl_2$, $MgCl_2$: effect of calcination on residual water and rehydration," [10] states,

> "A second mono-layer of water begins to adsorb at humidity greater than 1% with complete coverage by 20% relative humidity."

This matches well with the estimation in Figure 1. At 20% RH, the B.E.T. model predicts between 0.75 and 1.25 ML in addition to the chemisorbed layer for a total of between 1.75 and 2.25 ML.

Reference [10] also states,

> "From 20 to 50% relative humidity no additional adsorption appears to take place. Over 50% relative humidity, additional water adsorbs at a faster rate."

Although the BET theory predicts a small increase in the MLs between 20 and 50% RH and is therefore not in total agreement with the experimental data presented in [10], the predicted change in number of ML in this region is small compared to the predicted number of ML below and above this region. The difference between experimental observations and theoretical predictions can be explained by either an inability to detect this small change experimentally, or by a slightly flawed theoretical model. Either way, relatively little adsorption happens between 20 and 50% RH. The theoretical model and experimental results seem to agree for RH above 50%. Both the model and the experimental results show a significantly increased number of equilibrium MLs and adsorption rate above 50% RH.

Reference [10] states,

> "For a sample with a surface area of 5 m^2/g or less (obtained by calcining at 950ºC), a two monolayer coverage corresponds to 0.18 Wt. % water. Calcining at 800ºC results in a surface area of 6-8 m^2/g and would raise the water content to 0.26 Wt. %."

As a point of reference, ARIES oxide consistently has a SSA < 0.5 m^2/g and measured water content of <0.015 Wt. %. This data (ten times less moisture and ten times smaller SSA) is consistent with a predominantly two ML adsorption for ARIES PuO_2. Based on theoretical and experimental data, this moisture content should remain relatively constant up to the 50% RH threshold at which time further molecularly adsorbed monolayers would begin to form.

In addition to the inherent limit to the amount of moisture that can adsorb onto the surface of ARIES PuO_2 due to its very low SSA, and thus the limited potential for pressure buildup in the 3013 container, the Materials Identification and Surveillance (MIS) program has observed the following in high purity oxides [1],

> "High-purity oxides with up to 0.5 Wt. % added water were observed in both large-scale and small-scale studies. At an initial water surface coverage of one monolayer water activity was observed to decrease on a time scale of days to weeks and no hydrogen gas was observed. A reasonable hypothesis is that the surface-adsorbed water is slowly consumed by formation of surface hydroxyls. At somewhat higher water surface coverage, hydrogen is observed, but at a small fraction of the maximum possible given the water content present (approximately 0.1% of the maximum calculated using the aggregate pressure equation [23] in Appendix B). After an initial hydrogen increase in the first month of about 2 kPa, the hydrogen partial pressure is observed to decrease with time. Oxygen is consumed in the presence of water vapor. [Veirs 2008] Carbon dioxide and nitrogen gas generation is observed and attributed to desorption due to competition with water or reaction of surface species with water. [Veirs et al., 2008]"

Thus, even when 0.5 Wt. % water is present on pure PuO_2 oxide (over 15 times more water than would be present on ARIES oxide exposed to 50% RH), there appears to be only a small pressure buildup. It is interesting to note that the results described by the MIS program above match with the results described in [9] (i.e. hydrogen gas was not observed at lower ML coverage).

Consequently, there is no credible pathway for significant pressure buildup in the 3013 package as long as RH is limited to 50% in all process and packaging gloveboxes after stabilization by muffle furnace or DMO furnace at 950ºC. It is therefore justifiable to simplify the method for establishing the baseline pressure of the 3013 containers containing ARIES oxide stabilized by muffle or DMO furnace at 950°C exposed to RH ≤ 50%.

The current method of performing multiple height measurements of the inner container, multiple times, followed by radiographs of the package after closure can be simplified. Performing the inner container height measurements once is sufficient for the case of ARIES oxide. The height measurements (made using an instrument that is calibrated to ± 0.001 inches at four inscribed points across the lid, and have consistently been repeatable to better than ± 0.003 inches) will provide sufficient information to determine if the lid has deflected significantly in the future. For example, a future radiograph of the 3013 containers compared to the initial height measurements of the inner containers could be used to detect a change in lid height with enough accuracy to determine if the container was dangerously pressurized. Considering that it is highly unlikely that the ARIES oxide will produce significant inner container pressurization, this methodology is technically justifiable.

3.3 Discussion - Container pressurization of ARIES Oxide Stabilized at 650°C

SSA is the primary property governing total moisture adsorption on PuO_2. SSA measurements made during thermal stabilization equivalency testing showed that the SSA of the PuO_2 after oxidation and prior to calcination in the DMO process was 0.34 m^2/g [11]. This SSA is very similar to the SSA found in the 950°C DMO stabilized oxide during the first 52 blend lots of the ARIES program. This result showed that the final SSA of the stabilized oxide is mostly dependent on the oxidation process/parameters (pressure, flow rate, flow duration of the 75% O_2, 25% He gas mixture, and temperature of oxidation). These oxidation parameters remain the same regardless of the subsequent stabilization/calcination temperature (650°C or 950°C), and thus the SSA of the stabilized oxide is not significantly changed by the stabilization/calcination conditions (i.e. temperature). In addition, in the ARIES paradigm, 'stabilization' consists of high-temperature calcination in an oxygen-rich atmosphere such that there is no potential for the existence of remnant Pu metal. Therefore the SSA of ARIES material stabilized in the DMO furnace at 650°C and ARIES material stabilized in the DMO furnace at 950°C are very similar [4].

There is significantly less SSA data available for the 650°C calcined material compared to the 950°C calcined material, but as previously stated, the determining factors for physical characteristics of the PuO_2 are primarily dependent on the oxidation parameters which are equivalent for the two processes (650°C or 950°C).

Due to the low SSA of ARIES oxide, only a very small amount of moisture can adsorb onto the surface when exposed to an atmosphere of ≤50% RH. Therefore, even if this moisture dissociates into hydrogen and oxygen, an insignificant increase in pressure would result. Additionally, the number of MLs present on the oxide surface at RH ≤50% are likely too low for any gas to form.

The argument in paragraph 3.2 above is valid for ARIES material stabilized in a DMO furnace at 650°C, and the reduction of baseline height measurements is recommended as there is no credible risk of 3013 pressurization for this material.

4 Representative Sampling

4.1 Background - Representative Sampling

DOE-STD-3013 states the following related to taking PuO_2 samples:

> Paragraph A.6.3.2.5: "Because the oxide (including contained impurities) will pick up atmospheric water, it is important that the sample taken for moisture analysis be representative of the material actually packaged into the 3013 container. This can be

> done, for example, by controlling the glovebox relative humidity and/or packaging within a very few minutes of sampling.

And,

> Paragraph 6.3.2.5: “The Oxide sample taken for stabilization verification shall be representative of the stabilized material to be sealed in the inner container at the time of packaging.”

4.2 Discussion – Representative Sampling in ARIES Oxide Stabilized at 950°C

Calculated moisture content of PuO_2 using B.E.T. theory matches well with the measured moisture content of the ARIES oxide and other measurements made of other types of PuO_2 with different SSA exposed to varying RH [9,10]. Using the B.E.T. method for calculating the theoretical moisture content of ARIES oxide at different RH, it can be shown that even if ARIES PuO_2 having the maximum possible SSA (0.5 m^2/g) is exposed to 50% RH in the processing glovebox and then to 0% RH in the TGA-MS glovebox, the loss of moisture from the oxide is negligible (0.022 Wt. %) compared to the maximum allowable by [1], see Table 2 below. This analysis uses the conversion provided in [1] for conversion of ML to Wt. % moisture (0.22 mg/m^2 for each ML).

RH Initial (%)	RH Final (%)	SSA (m2/g)	ML Initial*	ML Final	ML Lost	Initial Wt. % H_2O (%)	Final Wt. % H_2O (%)	Lost Wt. % H_2O (%)
10	0	0.5	2.1	1	1.1	0.0231	0.011	0.0121
20	0	0.5	2.25	1	1.25	0.02475	0.011	0.01375
30	0	0.5	2.4	1	1.4	0.0264	0.011	0.0154
40	0	0.5	2.7	1	1.7	0.0297	0.011	0.0187
50	**0**	**0.5**	**3**	**1**	**2**	**0.033**	**0.011**	**0.022**

*Based on B.E.T. theory and isotherm c=200

Table 2 – Calculated Moisture Loss from ARIES oxide Exposed to Varying RH and then to 0% RH

In addition, the relatively elevated uncertainty of the TGA-MS moisture measurement (1σ = 20% RSD) makes these very small theoretical changes in the moisture content of the oxide almost impossible to definitively detect and quantify. For example, if a TGA-MS analysis of a sample of ARIES PuO_2 results in a measured content of 0.033 Wt.Wt. % moisture (which corresponds to the moisture content of ARIES PuO_2 exposed to 50% RH using B.E.T. theory), the actual moisture content could be as high as 0.0462 Wt. % and as low as 0.0198 Wt. %. This also means that that if a TGA-MS analysis of a sample of ARIES PuO_2 results in a measured content of 0.011Wt. % moisture (which corresponds to the moisture content of ARIES PuO_2 exposed to 0% RH using B.E.T. theory), the actual moisture content could be as high as 0.0154 Wt. % and as low as 0.0066 Wt. %. The difference between the lowest measured moisture content at 50% RH including measurement uncertainty (0.0198 Wt. %) and the highest measured moisture content at 0% RH including measurement uncertainty (0.0154 Wt. %) is only 0.0044 Wt. %, see Figure 2 below.

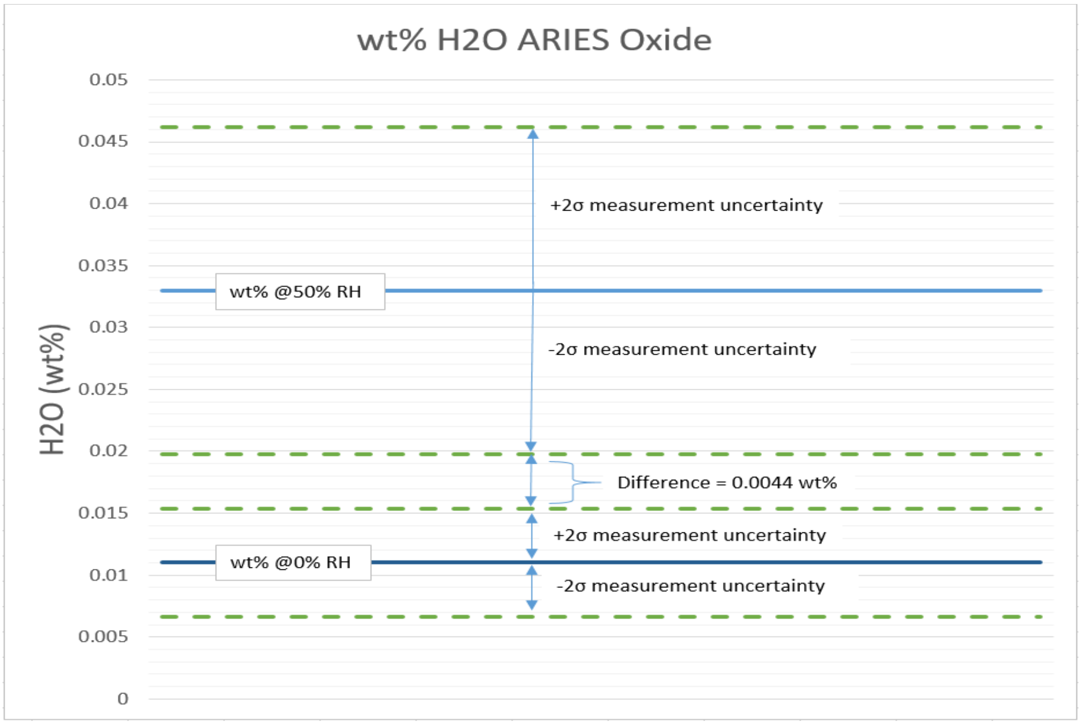

Figure 2 – Comparison of Moisture Content in ARIES PuO2 at 50% RH and 0% RH including TGA-MS Measurement Uncertainty

As long as the processing glovebox remains ≤ 50% RH, even in the extreme case where the processing glovebox is 50% RH and the TGA-MS glovebox is 0% RH, small and barely detectable/quantifiable amount of moisture could desorb from the PuO_2 sample if the SSA of the sample is ≤ 0.5 m^2/g.

There is considerable margin to increase the acceptable amount of time the sample can be exposed to the TGA-MS glovebox atmosphere before a measurement is made. There is also margin to increase the acceptable difference between the processing glovebox RH and the TGA-MS glovebox RH. Therefore it is recommended that there be no limit to the difference between the processing glovebox RH and the TGA-MS glovebox RH, as long as both remain below 50% RH. For the purposes of simplicity, it is recommended that a time limit of one 8 hour shift be implemented between when the TGA-MS sample is exposed to the TGA-MS glovebox atmosphere and when the analysis begins. In reality, if the analysis proceeds as expected, the sample should not be exposed to the glovebox atmosphere for more than 30 minutes. If for some reason there is a delay caused by an unexpected event such as an evacuation of the process room, the 8 hour time limit could be useful. Additionally, if the sample is re-sealed in the airtight conflat after being exposed to the glovebox atmosphere, the 8 hour time clock is stopped and the countdown only restarts after the conflat is once again re-opened.

Although all ARIES PuO_2 produced to date has been shown to have a SSA ≤ 0.5 m^2/g, it is conceivable, however unlikely that an undetectable process upset could result in a PuO_2 with a SSA ≥ 0.5 m^2/g. In order to guard against this case the above 8 hour time limit is only acceptable if a measurement has shown that the specific blend lot of PuO_2 has a SSA ≤ 0.5 m^2/g.

4.3 Discussion – Representative Sampling in ARIES Oxide Stabilized at 650°C

As previously established (paragraph 3.2), SSA is the primary property governing total moisture adsorption on PuO_2. Also, the SSA of ARIES material stabilized in the DMO furnace at 650°C and ARIES material stabilized in the DMO furnace at 950°C are very similar [4]. Therefore, even if much of the adsorbed moisture on the PuO_2 desorbs in the TGA-MS glovebox prior to the measurement, the end result will not be significantly different compared to the initial moisture content. This is all the more true when considering the relatively large measurement uncertainty associated with the TGA-MS method which renders definitive detection and quantification of small moisture changes on the scale described above difficult.

The argument in paragraph 4.2 above is valid for ARIES material stabilized in a DMO furnace at 650°C, and it is recommended that the same controls are implemented (50% RH limit, and 8 hour time limit) if SSA is measured and is ≤ 0.5 m^2/g,.

5 Conclusions / Recommendations

5.1 RH and Representative Sampling

The new proposed controls, based on significant ARIES oxide production data and supported by literature sources, are as follows:

1. If RH exceeds 50% in any processing or measurement glovebox, production will be stopped and the First Line Manager (FLM) will be contacted.
2. The TGA-MS moisture sample will not be exposed to the measurement glovebox atmosphere for greater than 8 hours before a measurement is executed. The 8 hour allowable time duration is only acceptable if the SSA of the sample is known. If it is not, the original controls are still applicable.

These proposed changes are conservative as significant margin exists above 50% RH and 8 hours, while still providing enough flexibility to enable oxide production and characterization to proceed under most atmospheric conditions experienced in PF-4 processing and characterization gloveboxes. The moisture content of ARIES oxide will continue to be measured using TGA-MS and the result of this measurement alone will be used to judge passing or failing product properties.

The technical arguments presented for these proposed changes are valid for ARIES oxide produced at 950°C in a muffle furnace or DMO furnace, and for ARIES oxide produced at 650°C in a DMO furnace. However, there are differences with respect to how these changes could be implemented.

For ARIES oxide produced at 950°C in a muffle furnace or DMO furnace, the proposed changes could only be implemented after the current authority approved a revision to reference [5] by official memorandum; this is similar to how the original controls were approved [12].

For ARIES oxide produced at 650°C in a DMO furnace, the proposed changes could only be implemented after the current MIS Working Group reviewed a revision to reference [4] and the current authority approved the revision by official memorandum; this is similar to how the original equivalency was approved [13].

If the proposed changes to references [5] and [4] are not made, ARIES could proceed as follows:

- If the RH is between 15 and 50%, processing has to be stopped, an NCR has to be developed and dispositioned.
- For RH > 50%, processing should be halted and material should be containerized.

5.2 Pressurization

Radiographs of the 3013 package after closure are deemed to be technically unnecessary as there is no credible risk of 3013 pressurization for AREIS oxide. Height measurements of the inner container are sufficient as a baseline internal pressure indicator and should continue to be performed as a defense in depth.

This proposed change is technically valid for all types of ARIES oxide, but in all cases implementation would require modification of [1] as the radiograph baseline measurement is an explicit requirement of all materials stabilized and packaged in accordance with the DOE-STD-3013.

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