



Standard Test Method for Determination of Uranium, Oxygen to Uranium (O/U), and Oxygen to Metal (O/M) in Sintered Uranium Dioxide and Gadolinia-Uranium Dioxide Pellets by Atmospheric Equilibration¹

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1. Scope

1.1 This test method applies to the determination of uranium, the oxygen to uranium (O/U) ratio in sintered uranium dioxide pellets, and the oxygen to metal (O/M) ratio in sintered gadolinium oxide-uranium dioxide pellets with a Gd_2O_3 concentration of up to 12 weight %. The O/M calculations assume that the gadolinium and uranium oxides are present in a metal dioxide solid solution.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards statements, see Section 8.

2. Referenced Documents

2.1 ASTM Standards:²

- C 696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets
- C 776 Specification for Sintered Uranium Dioxide Pellets
- C 922 Specification for Sintered Gadolinium Oxide-Uranium Dioxide Pellets
- C 968 Test Methods for Analysis of Sintered Gadolinium Oxide-Uranium Dioxide Pellets
- C 1287 Test Method for Determination of Impurities in Nuclear Grade Uranium Compounds by Inductively Coupled Plasma Mass Spectrometry

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3. Summary of Test Method

3.1 The uranium, and either O/U or O/M, are determined by measuring the weight change of a sintered pellet after it has been exposed to an equilibrating atmosphere to bring it to the stoichiometric condition. Sintered pellets are weighed and loaded into a sample boat. The boat is placed in a tube furnace capable of holding a temperature of $800 \pm 10^\circ C$. The furnace is purged with a moist gas flow of 4 % hydrogen and 96 % argon or nitrogen to remove all air. The temperature of the furnace is raised to $800^\circ C$ and held at this temperature with constant gas flow for 4 h. The furnace then is turned off and allowed to cool, with gas purge on, to room temperature. The samples are removed from the furnace and reweighed.

3.2 The weight change, gadolinia content, and chemical impurity content are used to calculate % uranium and the O/U or O/M.

4. Significance and Use

4.1 Uranium dioxide is used as a nuclear-reactor fuel. This test method is designed to determine whether the percent uranium and O/U or O/M content meet Specifications C 776 and C 922.

5. Interferences

5.1 Parameters for temperature, gas composition, gas flow, and moist air purge must be monitored and maintained carefully within the limits set in the procedure.

5.2 This test method assumes that chemical impurities meet Specifications C 776 and C 922 limits. Potential method interferences from higher impurity concentrations will require evaluation.

5.3 Furnace tubes or boats made from metals that oxidize under the test conditions may prevent proper equilibration by consuming available oxygen.

5.4 Precise weighing of samples is critical to the accuracy of this test method.

5.5 Loss of weight due to pellet chipping would invalidate the analysis. Handle pellets with care.

5.6 This test method assumes that pellets are sintered. It does not correct for moisture or volatile additives.

5.7 This test method assumes that $UO_2-Gd_2O_3$ pellets have formed a solid solution; however, the error from incomplete dissolution of Gd_2O_3 would be very small (see the calculation in 10.2).

6. Apparatus

6.1 *Analytical Balance*, capable of weighing to ± 0.0001 g.

6.2 *Tube Furnace*, capable of controlling temperatures at $800 \pm 10^\circ C$, that has been fitted with a fused quartz furnace tube.

6.3 *Fused Quartz Sample Boats*.

6.4 *Assorted Connectors, Tubing, Flasks, Stoppers, and Delivery Tubes*—The purge gas is passed through a humidifier, into the tube furnace. A bubbler flask is attached to the furnace outlet to monitor gas flow (see Fig. 1).

6.5 *Gas Pressure Gage and Regulator*.

6.6 *Purge Gas* (4 % hydrogen, 96 % argon or 4 % hydrogen and 96 % nitrogen. Gas purity of 99.995 % has been found to perform satisfactorily.

6.7 *Purge Gas Humidifier*, with heater and controller capable of maintaining water temperature at $35 \pm 10^\circ C$.

7. Standard Materials

7.1 *NBL³*, NBL-traceable, or equivalent, uranium dioxide pellets. Analyze at least one standard pellet per batch.

³ Available from the New Brunswick Laboratory, 9800 S. Cass Ave., Argonne, IL.

8. Hazards and Precautions

8.1 Take proper safety precautions for handling uranium.

8.2 The furnace, sample tube and sample boats are heated to $800^\circ C$. Care must be taken to avoid burns.

8.3 Exercise appropriate caution when working with compressed gasses.

9. Procedure

9.1 Analyze samples as whole pellets. No preparation is required. The nominal sample size is 5–10-g pellet. Smaller pellets may need to be composited (two pellets/test) to maintain minimum weight. Avoid using chipped or cracked pellets.

9.2 Place a small weighing tray or watch glass on the balance pan. Tare the balance and check to ensure that the balance is stable. If the balance will not stabilize, do not proceed.

NOTE 1—The extremely small weight changes that are being measured in this test method make it critical that the balance is working properly.

9.3 Weigh a check weight at least daily to confirm that the analytical balance is operating correctly.

9.4 Create a boat map to maintain sample identity.

9.5 Use a pair of tweezers and carefully weigh the pellet. Rezero the balance and repeat the pellet weighing until a consistent weight is obtained. Carefully place the pellet in the quartz sample boat. Repeat for each pellet.

9.6 Include one or two equilibrated standard control pellets with each sample batch.

9.7 Carefully place the loaded boat into the sample tube. Position the boat as close to center of the furnace tube as possible.

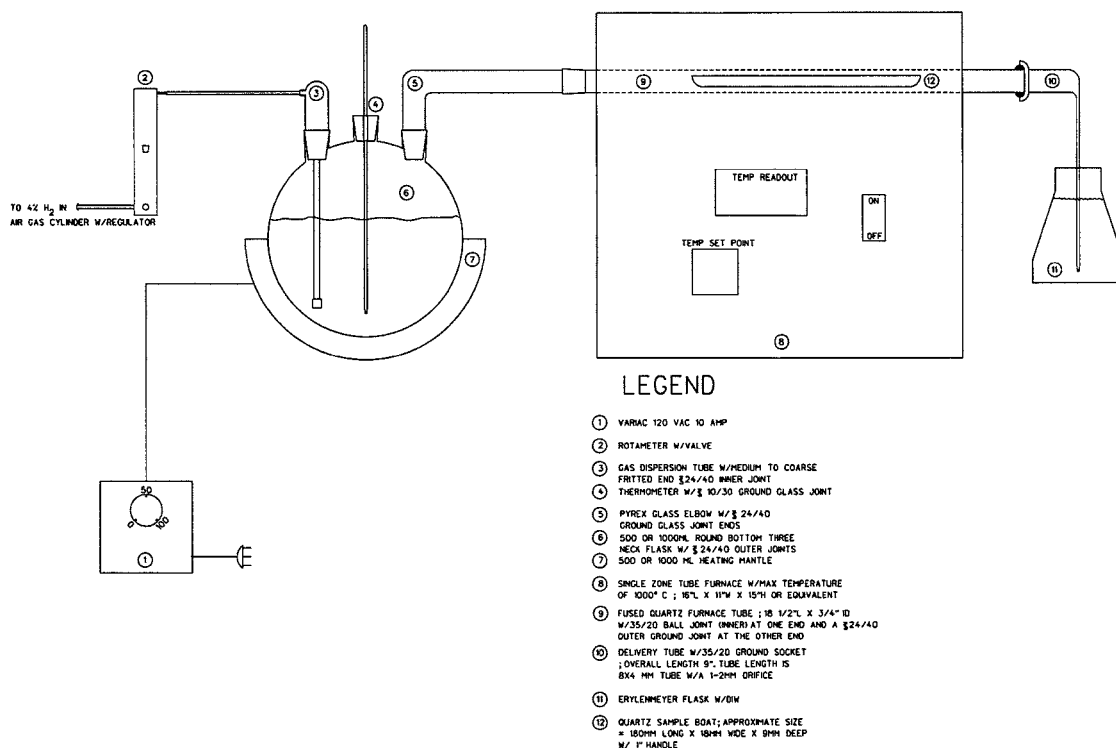


FIG. 1 Assorted Connectors, Tubing, Flasks, Stoppers, and Delivery Tubes

9.8 Fit the purge gas connection to end of tube and clamp. Make certain that the water in the humidifying flask is at $35 \pm 10^\circ\text{C}$ ($\pm 5^\circ\text{C}$ is optimal) and check the gas cylinder pressure to verify there is sufficient gas to complete the cycle.

9.9 Turn on the gas flow and allow the chamber to purge for approximately five minutes.

NOTE 2—The flow rate of the purge gas and the length of the purge cycle will vary with the size of the furnace tube. A purge of greater than or equal to three furnace volumes/minute is the recommended minimum. The flow rate must be adequate to maintain a positive pressure inside the sample chamber.

9.10 Attach a Pyrex® delivery tube with ground glass fitting to the exit end of the furnace, and place the end in a container of water to verify and monitor the gas flow.

9.11 Turn on the furnace and bring the temperature to 800°C .

9.12 After temperature is reached, allow the pellets to equilibrate for a minimum of 4 h. Monitor the system occasionally during the run to ensure constant temperature and gas flow.

9.13 At the end of the 4-h cycle, turn the furnace down to 50°C and allow the samples to cool. The purge gas flow must be maintained until the samples reach 50°C . Then, turn off the carrier gas and allow the pellets to cool to room temperature.

NOTE 3—If the samples are allowed to cool to room temperature while the purge gas is flowing, the water in the purge gas will begin to condense inside the tube and on the pellets. A temperature of 50°C is high enough to prevent condensation but low enough to prevent oxidation by room air.

9.14 Remove the sample boat and reweigh the pellets immediately. Use multiple weighings as necessary to obtain a consistent weight.

10. Calculation

10.1 O/U (UO₂ Pellets):

$$\begin{aligned} &= 2.000 - \frac{(W_2 - W_1)}{(W_2) [(AW_o)/(AW_u + 2AW_o)]} \\ &= 2.000 - \frac{(W_2 - W_1)}{(W_2) (0.0593)} \end{aligned} \quad (1)$$

where:

W_1 = Weight of sample before equilibration, g,
 W_2 = Weight of sample after equilibration, g,
 AW_o = Atomic weight of oxygen,
 AW_u = Atomic weight of uranium, and
 $0.0593 = \frac{(AW_o)}{(AW_u + 2AW_o)}$.

10.2 O/M (UO₂-Gd₂O₃ Pellets):

$$\begin{aligned} \text{Pellet O/M} &= 2.000 - \Delta \text{ O/M} \\ &= 2.000 - \frac{(W_2 - W_1)}{(W_2) [0.0593 + (\% \text{ Gd}_2\text{O}_3 \times 0.00026)]} \end{aligned} \quad (2)$$

where:

W_1 = Weight of sample before equilibration, g,
 W_2 = Weight of sample after equilibration, g,

$\% \text{ Gd}_2\text{O}_3$ = Measured Gd, expressed as stoichiometric weight $\% \text{ Gd}_2\text{O}_3$, and
 $(\% \text{ Gd}_2\text{O}_3)(0.00026)$ = Correction factor for weight gain due to formation of oxygen-rich UO₂-Gd₂O₃ solid solution during sintering. For processes that do not produce a 100 % solid solution, this factor should be evaluated to determine if modification is necessary (see Appendix X1).

10.3 Percent Uranium:

10.3.1 Percent Uranium, Based on Sample Weight:

$$\%U = \frac{\left[\frac{(100 - G - \%I)}{15.9994} \right] - \left[\frac{O/M \times G}{157.25} \right]}{\left[\frac{O/M}{AW_u} \right] + \left[\frac{1}{15.9994} \right]} \quad (3)$$

where:

G = Weight % Gd = weight % $\text{Gd}_2\text{O}_3 \times 0.86759$
 $\%I$ = Total nonvolatile impurities, expressed as weight % impurity oxides in UO₂. Add the weight % of each detected impurity oxide plus a correction factor to account for less than threshold of detection impurities. This correction factor will need to be determined for each facility. A factor of 0.01 % has been found to provide satisfactory results. See Table 1 to obtain conversion factors to convert common impurity elements to oxides.

The list of impurities to be tested for will depend upon specification requirements (see Specifications C 776 and C 922), elements obtained from multi-element methods (see Test Methods C 696, C 968, and C 1287), and fuel processing conditions. In some cases, a nominal value for impurities is adequate.

O/M = Oxygen/uranium ratio or oxygen/metal ratio calculated in 10.1 or 10.2, respectively.

AW_u = Atomic weight of uranium. Normally for U-235 enrichment of approximately 4 %, a nominal value of 237.96 may be used. For accuracy better than 0.03 %, or for U-235 enrichments > 5 %, calculate the actual atomic weight.

10.3.2 Percent Uranium, Corrected for % Gd₂O₃ Content:

$$\%U, \text{ Corrected} = \frac{\%U}{[1 - (0.01)(\% \text{ Gd}_2\text{O}_3)]} \quad (4)$$

10.4 Precision and Bias:

10.4.1 *Percent Uranium Uncertainties*—Percent uranium was determined on 29 NBL-125 UO₂ standards by five operators in one laboratory over a two month period, using a single spectrometric measurement for total impurities (%I) and a single measured value for atomic weight (AW). The certified value of the standard is 88.079 % uranium. The bias was + 0.005 % (absolute), with an average result of 88.0841 %. The precision was 0.0004 % (1 s.d.).

10.4.2 *O/U and O/M Uncertainties*—Certified NBL, or equivalent, standards for O/M and O/U are not available. The O/M ratio was determined on 27 working UO₂-Gd₂O₃ standard pellets over a two month period by five operators in one

**TABLE 1 Stoichiometric Factors to Convert Metals to Oxides
Oxide Conversion Factors for Impurity Calculation^A**

Element	Oxide	Factor
Al	Al ₂ O ₃	1.89
B	B ₂ O ₃	3.23
Ba	BaO	1.12
Be	BeO	2.78
Ca	CaO	1.40
Cd	CdO	1.14
Co	Co ₂ O ₃	1.41
Cr	Cr ₂ O ₃	1.46
Cu	CuO	1.25
Dy	Dy ₂ O ₃	1.15
Eu	Eu ₂ O ₃	1.16
Fe	Fe ₂ O ₃	1.43
Gd	Gd ₂ O ₃	1.15
Hf	HfO ₂	1.18
Li	Li ₂ O	2.15
Mg	MgO	1.66
Mn	MnO ₂	1.58
Mo	MoO ₃	1.50
Na	Na ₂ O	1.35
Ni	NiO	1.27
P	P ₂ O ₅	2.29
Pb	PbO ₂	1.15
Sb	Sb ₂ O ₄	1.26
Si	SiO ₂	2.14
Sm	Sm ₂ O ₃	1.16
Sn	SnO ₂	1.27
Ta	Ta ₂ O ₅	1.22
Th	ThO ₂	1.14
Ti	TiO ₂	1.67
V	V ₂ O ₅	1.79
W	WO ₃	1.26
Zn	ZnO	1.24
Zr	ZrO ₂	1.35

^AOxide conversion factor is defined as grams oxide per gram of element.

laboratory. The nominal value of the standard pellets which were made by equilibrating a batch of 8 % Gd₂O₃ production pellets, is 2.000. The average result of 2.0002. The precision was 0.0002 (1 s.d.). The bias from the nominal value is not statistically significant.

10.4.3 Sampling and Impurities Measurement Uncertainties—The uncertainties associated with sampling and measurement of impurities are not included in the precision and bias information in 10.4.1 and 10.4.2. Uncertainties associated with determination of values for % Gd₂O₃ and % U-235 are negligible.

10.4.4 Equilibration Procedure Uncertainties—Uncertainties associated with the equilibration procedure, such as weighing errors, furnace temperature, gas composition, gas flow, and pure gas humidity are included in the 10.4.1 and 10.4.2 data. These errors, however, will vary with equipment and the laboratory environment. Each laboratory should perform its own precision and bias evaluation.

11. Keywords

11.1 atmospheric equilibration; equilibration; oxygen to metal; oxygen to uranium; uranium

APPENDIXES

(Nonmandatory Information)

X1. MODEL FOR NONSTOICHIOMETRY OF URANIA-GADOLINIA

X1.1 A thermodynamic analysis of the published oxygen potential data for urania-lanthanide solutions gives a set of equations relating the atmospheric oxygen potential at which a solid solution specimen neither gains or loses oxygen, to the specimen composition (lanthanide content and O/M) and temperature. The oxygen potential for stoichiometry (O/M = 2.00) is defined by the intersection of curves representing the hypo and hyper stoichiometric composition ranges^{4,5,6}.

X1.2 The equations for the hypo and hyper stoichiometric regions are shown in X1.2.1-X1.2.3 and plotted in Fig. 2 for

several gadolinia contents:

X1.2.1 For hypostoichiometry, from the reaction:

$$3Gd_{4/3}O_2 + 4UO_2 + O_2 = 6U_{2/3}Gd_{2/3}O_{8/3} \quad (X1.1)$$

$$R \cdot T \cdot \ln(\rho_{O_2}) \text{ (J/mol)} = -753\,600 + 196.7 \cdot T + 6 \cdot R \cdot T \cdot \ln(1.5 \cdot z) - 3 \cdot R \cdot T \cdot \ln(X) - 3 \cdot R \cdot T \cdot \ln(1.5) - 4 \cdot R \cdot T \cdot \ln(1 - 2 \cdot z)$$

X1.2.2 For hyperstoichiometry, from the reaction:

$$4UO_2 + O_2 = 2U_2O_5 \quad (X1.2)$$

$$R \cdot T \cdot \ln(\rho_{O_2}) \text{ (J/mol)} = -336\,600 + 154.6 \cdot T + 2 \cdot R \cdot T \cdot \ln(X) - 4 \cdot R \cdot T \cdot \ln(1 - 2 \cdot z) + (41\,400 - 38.1 T) \cdot (2) \cdot (1 - 2 \cdot z)^2 + 108\,000 \cdot (2) \cdot (1 - 2 \cdot z) \cdot (2 \cdot z)$$

X1.2.3 The terms in $\ln(X)$ are eliminated by adding 0.4 times the first equations to 0.6 times the latter to give the oxygen potential for exact stoichiometry.

⁴ Lindemer and T.M. Bessman, *Journal Nuclear Materials*, Vol 130, p. 473, 1985.

⁵ Lindemer and J. Brynstad, *Journal American Ceramic Society*, Vol 69, p. 867, 1986.

⁶ Lindemer and A.L. Sutton, *Journal American Ceramic Society*, Vol 71, p. 553, 1988.

Gadolinia Stoichiometry

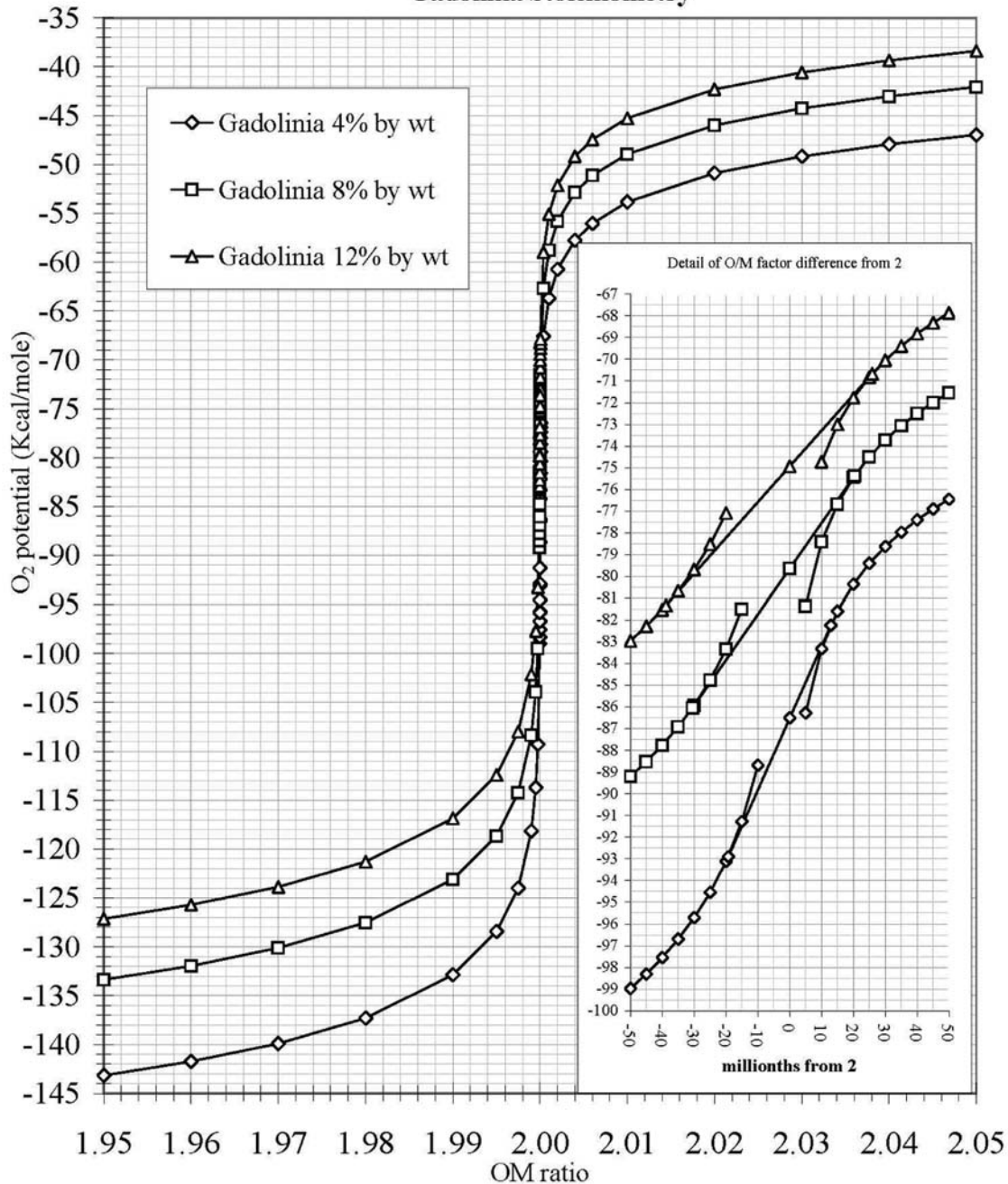


FIG. 2 Gadolinia Stoichiometry

$$R \cdot T \cdot \ln(\rho_{O_2}) \text{ (J/mol)} = -503\,400 + 167.4 \cdot T + 2.4 \cdot R \cdot T \cdot \ln(1.5 \cdot z) - 4 \cdot R \cdot T \cdot \ln(1 - 2 \cdot z) + (108\,000) \cdot (1.2) \cdot (1 - 2 \cdot z) \cdot (2 \cdot z) + (41\,400 - 38.1 \cdot T) \cdot (1.2) \cdot (1 - 2 \cdot z)^2$$

where:

- Z = the atom fraction in gadolinium,
- X = the deviation from stoichiometry,
- ρ_{O_2} = the oxygen pressure,
- R = the gas constant, and

T = the temperature, K.

X1.2.4 The equations predict that for temperatures around 800°C, and oxygen potentials near -350 KJ/mol (-85 Kcal/mol), the range of gadolinia contents of interest for burnable absorber fuel (1-12 wt % Gd₂O₃) are within ± 0.001 of exact stoichiometry. This oxygen potential can be achieved by about 1 % hydrogen in an inert gas, with a water content equivalent to a room temperature dew point.

X2. CORRECTION FACTOR FOR Gd₂O₃-UO₂ SOLID SOLUTION

X2.1 The chemistry of sintered gadolinium oxide-uranium dioxide pellets is not simply an arithmetic weighted average of the theoretical oxygen-to-uranium ratio of 2.0 and the sum of the theoretical oxygen-to-gadolinium ratio of 1.5. In fact, sintering of the mixture results in a solid solution where some of the uranium is in the plus six valence state, as compared to plus four in UO₂. The solid solution gains 0.5 mole oxygen for each mole of Gd₂O₃. With this oxidation, the oxygen-to-total metal ratio becomes nearly 2.0.

X2.2 The 0.00026 correction factor in calculation 10.1 can be derived as described in X2.2.1-X2.2.3.

X2.2.1 Consider 90 g of UO₂ and 10 g of Gd₂O₃ (no lubricant, no pore former, no moisture). This appears to be 10 wt % gadolinia. This mixture contains $90/270 = 0.3333$ moles

of UO₂ and $10/181.26 = 0.0552$ moles of GdO_{1.5}. When this mixture is sintered, each mole of gadolinia gains 0.5 moles of oxygen, so the final weight is $100 + 0.0552 * 8$, or 100.4414 g. The total moles of cations are $0.3333 + 0.0552 = 0.3885$ moles. The O/M is 2.000. If the O/M were reduced by 0.01, then 0.003885 moles of oxygen are removed, for a weight loss of $0.003885 * 16 = 0.062165$ g. The relative weight change is $0.062165/100.4414 = 6.1892E-04$.

X2.2.2 If 100 g of urania is reduced from an O/U of 2.00 to 1.99, the weight loss would be $100/270 * 0.01 * 16 = 0.059259$ g, for a relative weight loss of 5.9259E-04.

X2.2.3 The difference between these two cases is $6.1892E-04 - 5.9259E-04 = 0.2633E-04$, or 2.63E-5. The difference per weight percent gadolinia is then 2.63E-4, and the divisor should be $0.0593 + 0.00026 * \text{wt \% gadolinia}$.

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