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Pressure Development in Sealed Containers with Plutonium-Bearing Materials

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Abstract

Gas generation by plutonium-bearing materials in sealed containers has been studied. The gas composition and pressure are determined over periods from months to years. The Pu-bearing materials studied represent those produced by all of the major processes used by DOE in the processing of plutonium and include the maximum amount of water (0.5% by weight) allowed by DOE's 3013 Standard. Hydrogen generation is of high interest and the Pu-bearing materials can be classed according to how much hydrogen is generated. Hydrogen generation by high-purity plutonium oxides packaged under conditions typical for actual 3013 materials is minimal, with very low generation rates and low equilibrium pressures. Materials with chloride salt impurities have much higher hydrogen gas generation rates and result in the highest observed equilibrium hydrogen pressures. Other materials such as those with high metal oxide impurities generate hydrogen at rates in between these extremes. The fraction of water that is converted to hydrogen gas as equilibrium is approached ranges from 0% to 25% under conditions typical of materials packaged to the 3013 Standard. Generation of both hydrogen and oxygen occurs when liquid water is present. The material and moisture conditions that result in hydrogen and oxygen generation for high-purity plutonium oxide and chloride salt-bearing plutonium oxide materials have been characterized. Other gases that are observed include nitrous oxide, carbon dioxide, carbon monoxide, and methane.

Introduction

Since the end of the Cold War, the disposition of surplus plutonium-bearing materials that are no longer needed for nuclear weapons production has become an increasing mission for the U.S. Department of Energy (DOE). The safe packaging, transportation, and storage of surplus plutonium materials are required until disposition processes are implemented. Since disposition of weapons grade plutonium involves complex international agreements, storage times for material awaiting disposition may be many decades.

Nuclear materials are typically packaged in sealed containers for transportation and storage to prevent the spread of radioactive contamination. The sealing of the storage containers also provides a potential for pressurization that might lead to loss of containment of the contents. Thus, pressure development during storage has been an important consideration. Pressure buildup in sealed containers of plutonium-bearing materials may result from several causes including: (1) temperature increase of the container and contents after sealing (minor effect), (2) helium production from alpha decay of the packaged material (minor effect), and (3) gases evolved due to desorption from the contained materials, radiolysis of water or other decomposable compounds, or chemical reactions that may produce one or more gaseous species (potentially major effect).

The DOE-STD-3013 contains requirements for the stabilization, packaging and safe storage of plutonium-bearing metals and oxides containing 30 wt % or more of plutonium plus uranium.[1] This Standard requires stabilized plutonium-bearing materials to be packaged in two individually welded, nested containers where the minimum design pressure of the outer container is 4920 kPa. According to DOE-STD-3013, "The only evolved gas of significance anticipated during extended storage is hydrogen from decomposition of adsorbed water." The standard assumes that oxygen is not produced in any significant quantity by radiolysis or chemical reaction, and that oxygen present at the time of packaging is consumed by recombination with hydrogen or reaction with the packaged contents. Because DOE-STD-3013 conservatively assumes that all the adsorbed water associated with the packaged material is either desorbed or converted to hydrogen gas, the water content of materials packaged in the 3013 storage container is limited to 0.5 wt % or less to ensure the container does not exceed an internal pressure of 4920 kPa.

Existing literature appears to suggest that gas generation from high-purity plutonium oxide packaged in accordance with the 3013 Standard could range from minimal hydrogen steady-state pressures[2—5] to explosive high-pressure mixtures of hydrogen and oxygen.[6] Although there is minimal literature information concerning gas generation for plutonium oxide materials with chloride salt impurities, hydrogen production is observed in the gamma and helium ion radiolysis of magnesium and calcium chlorides[7] and in the gamma irradiation of NaCl and $MgCl_2 \cdot 6H_2O$.[8] In order to clarify the gas generation behavior of materials packaged according to the 3013 Standard, the Standard recommends establishment of an experimental program tasked with determining the gas generation behavior of representative materials.[9] This paper presents the results of the gas generation studies on a range of materials specifically chosen to be representative of the full range of materials actually stored in 3013 containers to date. Additional studies using prepared materials are included when needed to clarify important observations such as the conditions required to generate both hydrogen and oxygen.

Experimental

Savannah River National Laboratory (SRNL) and Los Alamos National Laboratory (LANL) have been collaborating in studies of gas generation by samples of plutonium oxide material representative of material to be stored in 3013 containers, or known to be intended for storage. Each Laboratory has prepared samples of pure and impure PuO_2, added moisture to them, sealed the material into test containers, and monitored gases for periods of months to years. Because these studies are conducted differently at the two sites, they are described separately below.

MIS Shelf-Life Studies

In the Materials Identification and Surveillance (MIS) Shelf-Life Studies conducted at LANL, gas pressures and compositions are monitored over periods of months to years for Pu-bearing materials stored in full-scale (i.e., 3013 size) and small-scale (1:500 scale) test containers. The full-scale test container is a 316L stainless steel cylinder 4 inches in diameter and approximately 9 inches tall with internal volume of 2.3 liters. This container reproduces size, shape, and materials of construction of a typical production 3013 inner container. The container is instrumented with thermocouples, a pressure transducer, a Raman chamber, and a gas manifold. The gas manifold is used to extract 5-mL gas samples for gas chromatography (GC) analysis with a thermal conductivity detector (Agilent 6890). The Raman chamber allows measurement of all gases except He without extracting a gas sample. The sensitivity for both methods was approximately 0.1 kPa. The GC was calibrated for He, H_2, N_2, O_2, CO_2, CO, and N_2O.

The MIS small-scale test container is a 316L stainless steel container approximately 0.5 inches in diameter and 2.5 inches tall with internal volume of 5 mL. The small-scale container is approximately a 1:500 scale version of the inner 3013 container. Fifty-microliter gas samples are extracted through a gas manifold and analyzed using a GC (Agilent 5890) calibrated for the same gases evaluated in the large scale sample studies. Each container is instrumented with a pressure transducer. Nine small-scale containers are placed in a heated aluminum block and five aluminum blocks are held in an insulated tray to form the small-scale array with a total capacity of 45 simultaneous experiments. Each aluminum block is temperature regulated at 55 °C.

The small-scale containers are loaded with samples having a range of impurity compositions and processing histories representative of the full diversity of oxide material stored in 3013 containers. The distinguishing emphasis is on understanding the material-dependent aspects of gas generation, so other parameters such as moisture content, temperature, free gas volume, etc. are varied as little as possible. Each experiment is designed to have an equal total moisture content of 0.5 wt % when the test begins. The initial moisture content of each material is measured by mass loss of a sample heated to 200 °C and adding 0.07 wt % for residual water not lost at 200 °C. Then the moisture content of the material is adjusted up to 0.5 wt % by exposing the material to humid air and monitoring the weight gain until it reaches the target value. The uncertainty in the moisture content is estimated to be 0.05 wt %.

Small-scale Corrosion Studies with Gas Analysis

Laboratory-scale studies conducted at SRNL were designed to investigate the corrosivity of moist plutonium oxide/chloride salt (PuO_2/Cl^-) mixtures on 304L and 316L stainless steel coupons.[10,11] They are relevant to this paper because internal test container pressures and final gas compositions were measured as part of these tests. These experiments were conducted with PuO_2 obtained by anion exchange and oxalate precipitation of Pu from nitric acid solutions followed by calcination in air to 950 °C for two hours to convert to the oxide. PuO_2 prepared in this way was of two different isotopic compositions – a “weapons grade” composition with a specific decay heat of 2.3 W/kg Pu and a “high-alpha” composition, consisting of “fuel grade” material doped with ^{238}Pu and ^{241}Am, with a specific decay heat of 5.1 W/kg Pu (Table 1).

Mixtures of NaCl, KCl, $MgCl_2$, and $CaCl_2$ were prepared by combining the desired amounts of each salt in a dry argon glove box. The dry salt mixtures were heated in a static air atmosphere to between 820 °C and 850 °C for two hours, then ground and pre-weighed into screw-cap glass vials in the dry argon glove box. The salt mixtures were combined with pre-weighed amounts of PuO_2, heated in a static air atmosphere at 850 °C for two hours, and stored in screw-lid glass jars inside sealed plastic bags until ready for use.

PuO_2/salt mixtures and corrosion test coupons were loaded into test containers in a He-purged glove bag deployed inside a radiological glove box. The glove bag was purged with dry He until the relative humidity was below 10%. PuO_2/salt mixtures (20 to 30 g) were then weighed into glass inserts containing the corrosion test coupons and placed in small stainless steel pans for ease of handling during moisture uptake. The relative humidity in the glove bag was gradually increased by bubbling He through distilled water. Sample sets were weighed periodically until the weight gain corresponded to a water uptake of approximately 0.3 wt % for the sample of pure PuO_2 and from 0.5 to 0.6 wt % for salt-containing materials. The maximum relative humidity required for samples to reach the target moisture loading in an eight-hour period ranged from 50% to 94%. Test materials were packaged in He at ambient pressure in stainless steel test containers equipped with a pressure transducer and a micro-valve for gas sampling. Each container with the oxide/salt mixtures and coupons in place had a free volume of 100 ± 5 mL.

The sealed containers were stored at ambient temperature for extended times while their pressures were monitored. At the end of each test, the container headspace was diluted with He, sampled, and analyzed by GC (Varian CP 4900) or by mass spectrometry (MS) using a residual gas analyzer (Pfeiffer Prisma QME 200). After exposure, the test coupons were removed for visual and metallographic examination, and thermogravimetric analysis with mass spectrometric detection (TGA-MS) was performed on each PuO_2/salt mixture to determine the post-exposure H_2O content.[10,11]

Results

MIS Shelf-Life Studies

Reports documenting material characterization and gas pressure and composition data for the MIS represented materials are available on the Internet. The MIS material designation, source site, actinide content, presence of chloride, and references to the relevant reports are given in Table 2.[12]

MIS Shelf-Life Studies: High-purity oxides

The MIS representative materials with plutonium content greater than 85% are considered high-purity oxides for this discussion. The batch designations of the high-purity plutonium oxides included in this study are listed in Table 3 along with the source and process, the calcination and loading dates, the wattage, and the specific surface area. The gas generation from TS707001 illustrates the gas composition behavior typical of high-purity oxides packaged with 0.5 wt % water observed in the MIS Shelf-life Studies, Figure 1. The gas generation is dominated by N_2 and CO_2 with H_2 being a minor component. The hydrogen generation for all of the high-purity oxides identified in Table 3 shows a maximum hydrogen pressure of 6 kPa, Figure 2.

One high-purity oxide, PEOF1, has been studied using the full-scale container. After exposure to humid gas, the oxide mass had increased by 0.9 g, corresponding to adding approximately 0.72 monolayers of water. No hydrogen gas was observed.[13]

MIS Shelf-Life Studies: Chloride containing materials

The MIS representative materials with greater than 1% chloride are listed in Table 4. The pressure and composition of gases from the material that has generated the most hydrogen, C06032A, is given in Figure 3. The hydrogen partial pressure for this material has reached 425 kPa in about 4.5 years. All chloride containing materials exhibit qualitatively similar behavior: the hydrogen pressure asymptotically approaching a maximum after an initial increase. Other gases such as CO_2 and N_2 are also seen. When CO_2 is present with high partial pressures of hydrogen, such as with chloride containing materials, CO and CH_4 are also seen at maximum pressures of less than 25 kPa with CO always exceeding CH_4. The observed increases in hydrogen pressure are reasonably fit to single exponential functions of time.[14] These functions extrapolate to sample-specific steady-state H_2 pressures that are all less than 25% of the amount of hydrogen expected if alpha radiolysis converts all of the water to hydrogen gas, Table 5.

One MIS chloride-bearing material, 011589A, generated oxygen in nearly stoichiometric ratio to hydrogen. The three conditions common to previously observed cases of generation of both hydrogen and oxygen by chloride-containing materials are:[15] (1) an alkaline earth chloride such as $MgCl_2$ or $CaCl_2$ is present, (2) the molar ratio of water to alkaline earth chloride is at least 4, and (3) the absolute water content exceeds 0.3 wt %. Calcium chloride deliquesces and forms a liquid with slightly more than four waters of hydration while magnesium chloride requires about nine waters to form a liquid.[16]

MIS Shelf-Life Studies: Other materials

The results for all other materials, those with <85% Pu and <1% chloride, show much less hydrogen gas generation than observed in chloride-containing materials. For example, materials formed from magnesium hydroxide precipitation which contain significant amounts of magnesium oxide, R441 and R438, generate hydrogen with a maximum observed partial pressure of 50 kPa. Additionally, many materials generate CO_2 and N_2, although not as much as the high-purity oxides.

Small-Scale Corrosion Studies with Gas Analysis

Temperature corrected pressure traces for selected small-scale corrosion test samples are shown in Figure 4. Chemical compositions of the small-scale corrosion test materials are given in Table 6. Pressure and temperature signals were not recorded for the first 60 to 80 days after the test containers were sealed. The total headspace gas pressure and partial pressures of hydrogen, oxygen, and nitrogen just prior to opening each container are shown in Table 7. The presence of nitrogen is assumed to be due to residual air remaining at the time the container was sealed. Only trace amounts of gases other than He, H_2, N_2, and O_2 were detected.

The rates of hydrogen and oxygen generation (in excess of the amount of oxygen from trace air remaining at the time the container was sealed in helium) are presented as radiolytic G-values (i.e., G_{H2} and G_{O2}), where G is equal to the number of molecules of gas produced per 100 eV of absorbed radiation dose either by the material plus water or by the water. The *G*-values were calculated from the initial rates of hydrogen or oxygen production during the first 60 days using the total alpha radiation dose and the fraction of alpha decay energy absorbed by the electrons from water contained in the sample. The fraction of alpha decay energy absorbed was corrected for the decreasing dose to water over time due to consumption of water by radiolysis (Table 8). The amount of water consumed by radiolysis was determined from the initial G-value. Because gas compositions were only measured at the end of each test, the ratio of hydrogen to oxygen generation at 60 days was assumed to be equal to the ratio of hydrogen and oxygen generated over the entire test period.

Discussion

The hydrogen gas generation by high-purity oxides in the MIS Shelf-Life studies differs markedly from that in the Small-Scale Corrosion Studies as well as from that in results reported by Duffey and Livingston[4,5] and Vladimirova and Kuilikov.[6] The differences probably stem from large differences in the number of monolayers of water on the plutonium oxide surfaces. The differences in surface water coverage are due to differences in test container designs and thermal gradients rather than differences in plutonium oxide material properties. The adsorption of 0.5 wt % water onto the surfaces of typical PuO_2 of moderate surface area (i.e., 1 to 2 m^2/g) corresponds to an average surface coverage of approximately 10 to 20 monolayers of water. Such high coverage can only be achieved and maintained under conditions of extremely high relative humidity (>80%).[13] Multilayer water coverage will be maintained during storage only as long as the relative humidity of the gas in contact with the material within the container remains high. Any reduction in relative humidity to more moderate levels will cause rapid evaporation of this liquid layer and reduction in surface coverage to approximately one monolayer. In the Small-Scale Corrosion Studies and experiments by Duffey and Livingston and Vladimirova and Kuilikov, the experimental apparatus is isothermal, meaning that the multiple layers of adsorbed water will remain in place on the surface until depleted by radiolysis during the experiments. In the LANL MIS Shelf-Life experimental apparatus the test container and the material within are held at 55 °C, but the gas sampling manifold, which extends some distance away from the heated block, is as cool as 35 °C. These cooler locations provide a sink for water to condense as it evaporates from the warmer material. The dew point of water at 35 °C corresponds to about 35% relative humidity at 55 °C. Since multiple layers of water on PuO_2 surfaces are not stable at 35% RH, water will evaporate from the surface of the material as soon as the container is placed in the heated block, condensing in the cooler tubing until the dew point of the gas in the container is reduced to $\leq$35 °C. The surface coverage at 35% RH is approximately one monolayer.[17] Therefore, the LANL MIS shelf-life results should be interpreted as showing that the single monolayer of water expected on high-purity PuO_2 material under storage conditions is not converted to hydrogen or oxygen gas at a significant rate. In contrast, the Small-Scale Corrosion Studies and the results of Duffey and Livingston[4,5] and Vladimirova and Kuilikov[6] show that if multiple layers of water are forced onto the oxide surface at high RH and conditions are maintained so that those layers persist, hydrogen and oxygen are generated in significant quantity.

These results can be applied to the 3013 storage inventory in order to understand the hydrogen and oxygen gas generation behavior of packaged high-purity oxides because the relative humidity conditions during packaging are known. The relative humidity was/is controlled per procedure to 3.5% or less at RFETS and 25% or less at SRS. At LANL and LLNL, facility operations control the relative humidity to less than 1%. At Hanford, the relative humidity of the dry packaging line (SPE line) was controlled to below 1% by facility operations, and the relative humidity of the wet packaging line (C line) was controlled per procedure to less than 60%. Thus, the >80% RH required to form multiple layers of water from adsorption of water vapor onto PuO_2 surfaces did not occur during packaging of the existing inventory. In addition, the thermal gradients within a 3013 container stored in a 9975 transportation package result in the material being approximately five degrees Centigrade higher in temperature than the coolest part of the inner container,[18] so the condensation on the container surface would limit the RH at the material in similar manner to the condensation in the tubing of the MIS Shelf-Life experimental conditions discussed above. Therefore, the production of hydrogen and oxygen by high-purity oxides in the existing 3013 inventory is extremely unlikely.

The situation is different when alkaline earth chloride salts are present as impurities. Alkaline earth salts deliquesce to form aqueous solution when exposed to much lower relative humidity than is required to condense multiple layers of water on oxide surfaces. Liquids almost certainly formed in the Small-Scale Corrosion Studies series 4a, 4b, and 5a and probably formed in the MIS shelf-life study on sample 011589A. The gas generation results are consistent with the hypothesis that the generation of oxygen is strongly correlated with the existence of liquid water within the material bed, whether on high-purity oxides that exist at very high relative humidity or through the deliquescence of chloride salts, which can occur down to 16% RH.[19] The possibility of having a persistent aqueous phase inside a container packaged in accordance with the 3013

Standard depends on additional factors including thermal gradients within the containers, and is still being addressed.[18]

For the small-scale corrosion tests at SRNL, the solid lines in Figure 5 show extrapolated H_2, or H_2 plus O_2, partial pressures calculated from the initial G-values given in Table 8 and assuming that the reactions producing H_2 and O_2 are pseudo first-order in total remaining H_2O in the system, and that the gases produced undergo no other reactions. These model curves approach asymptotic pressure values dictated by the total initial water, the container's free volume and the temperature. While the measured and extrapolated pressures are in good agreement up to a point which varies somewhat between materials, the measured pressures consistently fall below the extrapolations, indicating that the kinetics are actually more complicated and that the ultimate pressures are limited by factors in addition to the initial water content. The deviations from the first-order model are quantified in Fig. 5 by listing the consumed fraction of the initial H_2O required to produce the observed and the predicted (parentheses) pressures at the time of the last experimental data point available for each sample.

The fraction of water converted to H_2 in the small-scale corrosion tests in less than two years ranged from 8 to 63% (Table 8). The larger values are significantly higher than the fraction of water consumed in the MIS shelf-life studies, which range from 0 to 24% of the total water content after five years. The corrosion test results are consistent, however, with literature reporting complete conversion of water to hydrogen at steady state for PuO_2 samples with varying amounts of added water.[6]

One possible explanation for these discrepancies is that the H_2 gas may undergo additional reactions that deplete it from the headspace, and the ultimate H_2 pressure is reached when the consumption rate equals the generation rate. The Small-Scale Corrosion Studies have significantly greater free volume relative to the mass of contained material than do either the MIS shelf-life experiments or actual 3013 containers. Therefore, under this hypothesis the corrosion studies would not reach the equilibrium-condition H_2 pressure until much more of the initial water had been converted to H_2. Although there is not sufficient information in reference (6) to determine the volume-to-mass ratios, this line of reasoning would lead one to speculate that the free gas volumes were relatively large.

The MIS Shelf-Life Studies were undertaken to obtain gas generation information from a diverse set of samples representing the full range of stored materials, and containing the maximum fraction of moisture allowed by the 3013 Standard. The results of the MIS Shelf-Life Studies are compared qualitatively in Table 9 with the headspace gases found inside containers selected from the storage inventory for destructive evaluation (DE) as reported by Almond et al.[20] The major trends observed in the MIS Shelf-Life Studies are also observed in the 3013 DE observations. The most significant difference is the observation of a flammable mixture of hydrogen and oxygen within the 0.5 wt % water limit in the MIS Shelf-Life Studies for one chloride bearing material whereas no oxygen is observed when hydrogen is present in the 3013 DE observations.

Conclusions

Both small and full-scale experiments with sealed containers of pure and impure PuO_2 containing moisture demonstrate that maximum steady state pressures are well below the minimum design pressure for the 3013 containers in which stabilized Pu-bearing materials are stored. Contrary to assumptions in the 3013 standard, both hydrogen and oxygen generation are observed for materials with 0.5 wt % water when liquid water is present. Test results from containers with different free volume-to-sample mass ratios suggest that the small volume-to-mass ratios in the 3013 container configuration contribute to the relatively small amounts of moisture (typically less than 10%) converted to H_2 gas after up to five years of storage because hydrogen consumption reactions, with rates governed by the hydrogen partial pressure, reach equilibrium with regard to hydrogen generation sooner. These results along with data from actual 3013 containers examined after approximately five years of storage provide confidence that the maximum pressure within the 3013 storage inventory will remain nearly an order of magnitude below the allowed container pressure of 4920 kPa. The achievement of steady-state hydrogen partial pressures long before all moisture is consumed suggests that a balance is achieved between hydrogen production and consumption reactions. The factors leading to this balance, particularly the mechanisms of consumption, remain an area for future study.

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Table 1. Isotopic Composition of PuO_2 Used in SRNL Corrosion Tests

Material	**Isotope (wt %)**						**Decay Power**
	Pu-238	**Pu-239**	**Pu-240**	**Pu-241**	**Pu-242**	**Am-241**	**(W/kg Pu)**
Weapons Grade	0.013	93.6	6.2	0.15	0.02	–	2.3
Increased α-dose	0.38	83.3	15.2	0.80	0.02	0.32	5.1

Table 2. MIS Represented material with report references. NA – reports not available.

MIS SAMPLE ITEM	Pu/U (%)	Cl	Source Site	Characterization report	Pressure and composition report
SCP711-56	17/69		LANL	LA-UR-09-07099	LA-UR-09-07149
TS707013	69.7/0	Y	RFETS	LA-UR-09-07100	LA-UR-09-07167
63-88-06-121	35/0		Hanford	LA-UR-09-07101	NA
64-85-12-1858	32.7/0		HANFORD	LA-UR-09-07102	LA-UR-09-07171
011589A	77.7/0	Y	RFETS	LA-UR-09-07103	LA-UR-09-07151[a] LA-UR-09-07152[a]
053038	62.6/0	Y	RFETS	LA-UR-09-07104	LA-UR-09-07153[a]
669194	13.8/69		RFETS	LA-UR-09-07105	LA-UR-09-07138
1000089	84.6/0		RFETS	LA-UR-09-07106	LA-UR-09-07150[a]
5501407	65.7/11		RFETS	LA-UR-09-07107	LA-UR-09-07141
5501579	88.1/0		RFETS	LA-UR-09-07108	LA-UR-09-07136
07032282A	69.4/0	Y	RFETS	LA-UR-09-07109	LA-UR-09-07169
07161856	84/0		RFETS	LA-UR-09-07110	LA-UR-09-07134
07242141A	69.7/0		RFETS	LA-UR-09-07111	LA-UR-09-07156[a]
07242165A	34/0		RFETS	LA-UR-09-07112	LA-UR-09-07155
07242201A	63.5/0		RFETS	LA-UR-09-07113	LA-UR-09-07140
520610020	33.7/0	Y	RFETS	LA-UR-09-07114	LA-UR-09-07154[a]
ARF-102-85-114-1	86.3/0		HANFORD	LA-UR-09-07115	LA-UR-09-07173
ARF-102-85-223	67/0	Y	HANFORD	LA-UR-09-07116	LA-UR-09-07144
ARF-102-85-295	28-40/0	Y	HANFORD	LA-UR-09-07117	LA-UR-09-07174 LA-UR-09-07175
ARF-102-85-355	69.5/0		HANFORD	LA-UR-09-07118	LA-UR-09-07158
BLO-39-11-14-004	87.5/0		HANFORD	LA-UR-09-07119	LA-UR-09-07146
ARF-102-85-365	65.9/0	Y	HANFORD	LA-UR-09-07120	LA-UR-09-07159
C00024A	73.4/0	Y	RFETS	LA-UR-09-07121	LA-UR-09-07163
C00695	73.9/0	Y	RFETS	LA-UR-09-07122	LA-UR-09-07166
CAN92	82.6/2.8		RFETS	LA-UR-09-07123	LA-UR-09-07162
C06032A	74/0	Y	RFETS	LA-UR-09-07124	LA-UR-09-07143
CLLANL025	77.7/0	Y	RFETS	LA-UR-09-07125	LA-UR-09-07139
MISSTD-1A	85/0		LANL	LA-UR-09-07126	LA-UR-09-07180
MT-1490	78/0		RFETS	LA-UR-09-07127	LA-UR-09-07137
PBO-47-09-012-023	88/0		HANFORD	LA-UR-09-07128	LA-UR-09-07157
PMAXBS	68/0	Y	LANL	LA-UR-09-07129	LA-UR-09-07177
PEOF1	86/0		LANL	LA-UR-09-07130	LA-UR-09-07178
PSU-84-06-05	14.4/65.1		HANFORD	LA-UR-09-07131	LA-UR-09-07147
TS707001	87/0		RFETS	LA-UR-09-07132	LA-UR-09-07135
PuF4-1	72/0		LANL	LA-UR-09-07133	LA-UR-09-07176
R441	67/0		HANFORD	NA	LA-UR-09-07148
R438	28.1/0		HANFORD	NA	LA-UR-09-07161[a]
41-85-08-1379B	41/0		Hanford	NA	LA-UR-09-07170

[a] These samples experienced a temperature excursion from Dec. 3, 2007 to Dec. 10, 2007 to between 146 °C and 154 °C.

Table 3. MIS represented materials with plutonium content greater than 85% studied in the MIS Small-Scale Tests.

Sample	Pu	Source	Process	Calcine date	Load date	Remove date	Wattage W/kg	SSA m^2/gm
TS707001	87%	RFETS	Metal Oxidation	1/21/1998	12/16/2003	---	2.20	2.35
5501579	88%	RFETS	Hydride oxidation	7/17/1997	12/17/2003	---	2.21	0.58
PBO-47-09-012-023	88%	HANFORD	Oxalate precipitation and calcination	8/20/1997	4/7/2004	6/18/2007	3.20	1.2
ARF-102-85-114-1	86%	HANFORD	Peroxide precipitation and calcination	6/30/2004	2/2/2005	11/6/2007	2.18	1.02
PEOF1 at 0.08% H_2O	86%	LANL	Oxalate precipitation and calcination	10/17/2001	8/22/2005	---	2.10	1
BLO-39-11-14-004	88%	HANFORD	Oxalate precipitation and calcination	6/19/1997	1/8/2004	---	14.70	3.48
MISSTD1	85%	LANL	Oxalate precipitation and calcination	1/1/1997	8/22/2005	---	2.09	31

Table 4. MIS Represented materials with chloride.

Sample	**Pu**	**Source**	**Process**	**Wattage W/kg**
CLLANL025	78%	RFETS	Pyrochemical	1.96
C06032A	74%	RFETS	Screenings from pyrochemical	1.85
ARF-102-85-223	67%	HANFORD	Scrap from pyrochemical	1.67
11589	78%	RFETS	Metal oxidation	1.99
53038	63%	RFETS	Hydroxide precipitation	2.28
520610020	34%	RFETS	Pyrochemical	0.95
ARF-102-85-365	66%	HANFORD	Scrap from pyrochemical	1.6
C00024A	73%	RFETS	Pyrochemical	1.89
C00695	74%	RFETS	Pyrochemical	1.86
TS707013	70%	RFETS	Metal oxidation	1.71
ARF-102-85-295	40%	HANFORD	Scrap from pyrochemical	0.98
PMAXBS	68%	LANL	ER salt	1.69
07032282A	69%	RFETS	Foundry scrap oxide	1.73

Table 5. The results of fitting the hydrogen partial pressure to a single exponential formation. The fitting parameters are expressed as the maximum pressure and time to reach half of the maximum pressure. The fitting parameters can be used to calculate how complete the reaction will be at five years. The 3σ error in P_{max} is estimated as between 5% and 10% of the value and in $t_{1/2}$ is estimated as between 15% and 30% of the value.

Material	P_{max} (kPa)	$t_{1/2}$ (yr)	Fraction complete at 5 years	$P_{H2}$from 3013 pressure equation (kPa)	Ratio of hydrogen partial pressures
CLLANL025	171	0.65	99.5%	1490	11%
C06032A	425	0.70	99.3%	1780	24%
ARF-102-85-223	137	0.51	99.9%	1870	7%
011589A	103	--	--	2070	5%
53038	112	0.32	100.0%	2200	5%
520610020	101	0.80	98.7%	970	10%
ARF-102-85-365	144	0.86	98.2%	1680	9%
C00024A	7	0.09	100.0%	1820	0%
TS707013	32	0.55	99.8%	1910	2%
ARF-102-85-295	379	1.03	96.5%	1660	23%
ARF-102-85-295 HT	178	0.59	99.7%	2200	8%
PMAXBS	87	0.38	100.0%	1350	6%

Table 6. Chemical Compositions of Corrosion Test Mixtures

Test Mixture ID	**Chemical Composition (wt %)**				
	PuO_2	**NaCl**	**KCl**	**$MgCl_2$**	**$CaCl_2$**
1a	100	-	-	-	-
1b	72	11.7	14.8	1.1	0.4
4a	98	0.90	0.90	-	0.20
4b	98	0.54	0.54	-	0.92
5a	95	2.25	2.25	0.5	-

Table 7. Headspace Gas Composition at End of Exposure

Sample ID	Days Until Sampled	Pressure (kPa)					
		P_{final}	P_{H2}	P_{O2}	P_{N2}	P_{H2corr}	P_{O2corr}
1a-1	324	147	31.5	0.8	2.4	45.6	0.21
1b-1	486	162	61.3	0.5	1.9	61.1	-0.04
1b-2	149	134	32.3	0.0	1.4	33.8	-0.36
4a-1	496	175	61.8	9.6	1.0	64.2	9.7
4a-2	334	165	52.5	11.3	0.0	52.6	11.4
4b-1	192	142	26.5	7.0	0.3	32.8	8.6
4b-2	340	147	38.3	12.4	-0.1	34.4	11.2
4b-3	487	161	50.9	6.5	0.5	53.0	6.7
5a-1[a]	352	221[b]	73.2	27.3	0.0	95.4	35.6
5a-2[a]	168	506[b]	63.0	30.5	0.0	143	69.3
5a-3[a]	459	217[b]	56.8	19.3	0.2	88.9	30.2

[a] Containers 5a-1, 5a-2, and 5a-3 were diluted with helium and sampled prior to opening due to higher than expected rate of pressure increase for 5a-2 and preliminary gas analysis indicating a nearly stoichiometric ratio of H_2 and O_2 generated.

[b] Total pressure increases from gas generation were 131 kPa for 5a-1, 212 kPa for 5a-2, and 119 kPa for 5a-3.

Table 8. H_2 and O_2 Yields and H_2O Consumption during Small-Scale Corrosion Studies

Exp ID	**Initial H_2O content**[a]	**Yield per total absorbed dose (molecules/100 eV)**		**Yield per dose absorbed by H_2O (molecules/100 eV)**		**H_2O consumed during exposure (%)**	
	wt %	G_{H2}	G_{O2}	G_{H2}	G_{O2}	Measured	Predicted
1a-1	0.38	0.019	0.00009	3.8	0.02	41	42
1b-1	1.00	0.021	-0.00001	1.7	0.00	14	21
1b-2	0.94	0.027	-0.00028	2.2	-0.02	8.3	9.4
4a-1	0.58	0.022	0.0034	3.0	0.44	38	47
4a-2	0.63	0.023	0.0049	2.8	0.60	30	31
4b-1	0.66	0.022	0.0057	2.5	0.66	17	18
4b-2	0.61	0.020	0.0065	2.5	0.81	21	30
5a-1	0.49	0.023	0.0085	3.7	1.4	63	71
5a-2	1.24	0.057	0.028	3.7	1.8	43	45
5a-3	0.45	0.018	0.0061	3.2	1.1	58	75

[a] The initial moisture content of each sample was calculated from the measured post-exposure H_2O content plus the amount of H_2O converted to H_2 during test period.

Table 9. Qualitative comparison of the MIS Shelf-Life results to the destructive evaluation gas analysis.

	MIS Shelf-Life	**3013 DE gas analysis**
Gases observed	He, H_2, O_2, N_2, CO_2, CO, CH_4, N_2O	He, H_2, O_2, N_2, CO_2, CO, CH_4, N_2O
High-Purity Oxide		
Hydrogen	Little to none	None
Oxygen	None	None
Chloride impurities		
Hydrogen	Yes, 0% to 24% of avail. H_2O	Yes, 0% to ~10% of avail. H_2O
Oxygen	No, unless liquid water present	None

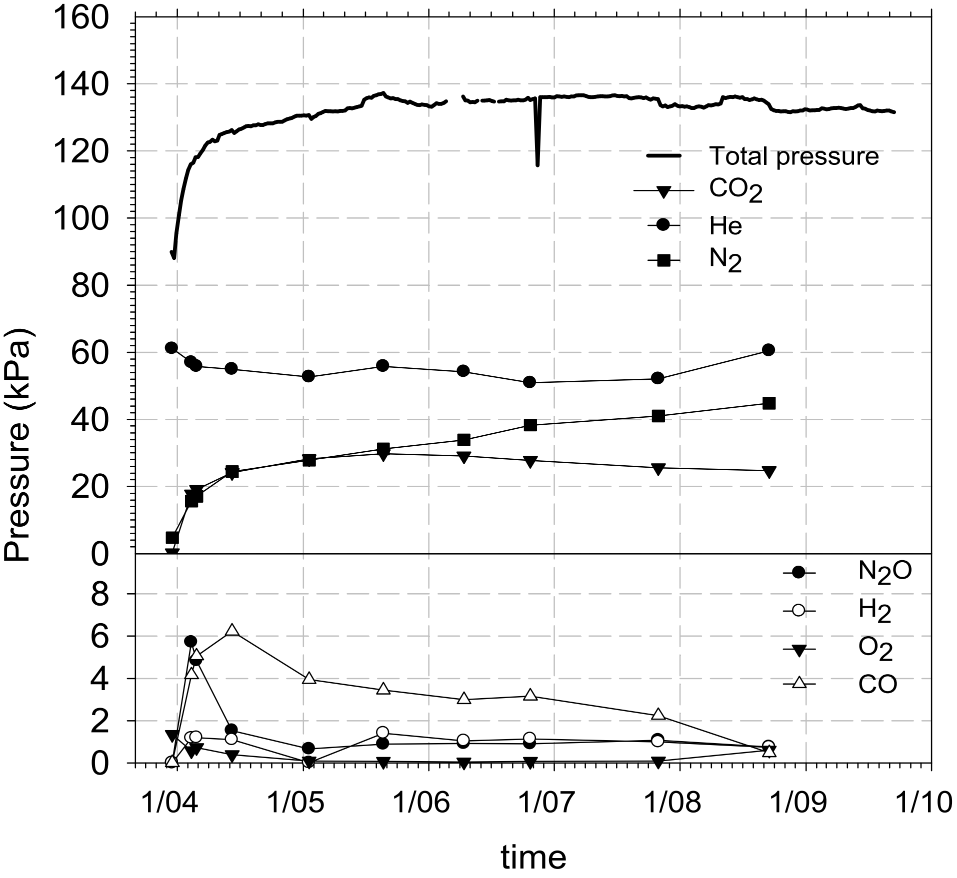

Figure 1. The gas pressure and composition observed for MIS represented material TS707001. The major gases are show in the top graph and the minor gases in the lower graph.

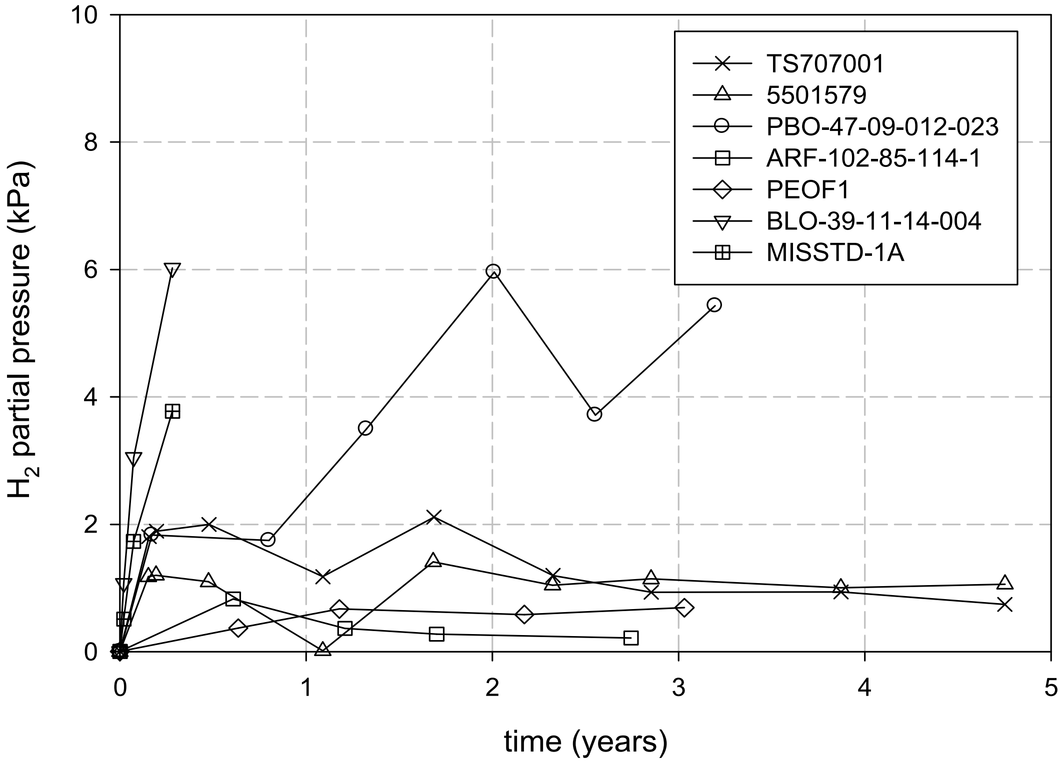

Figure 2. Hydrogen partial pressure gas generation for all high-purity oxide MIS Represented materials in the MIS Small-Scale Studies. The maximum hydrogen gas pressure observed is 6 kPa. All materials are loaded with 0.5 wt % water except PEOF1 which contains 0.08 wt % water. The hydrogen partial pressures for BLO-39-11-14-004 and MISSTD-1A may be close to the maximum these materials produce because the hydrogen generation for high-purity plutonium oxides level off after the first three months and the pressure curves for these materials also level off after three months.

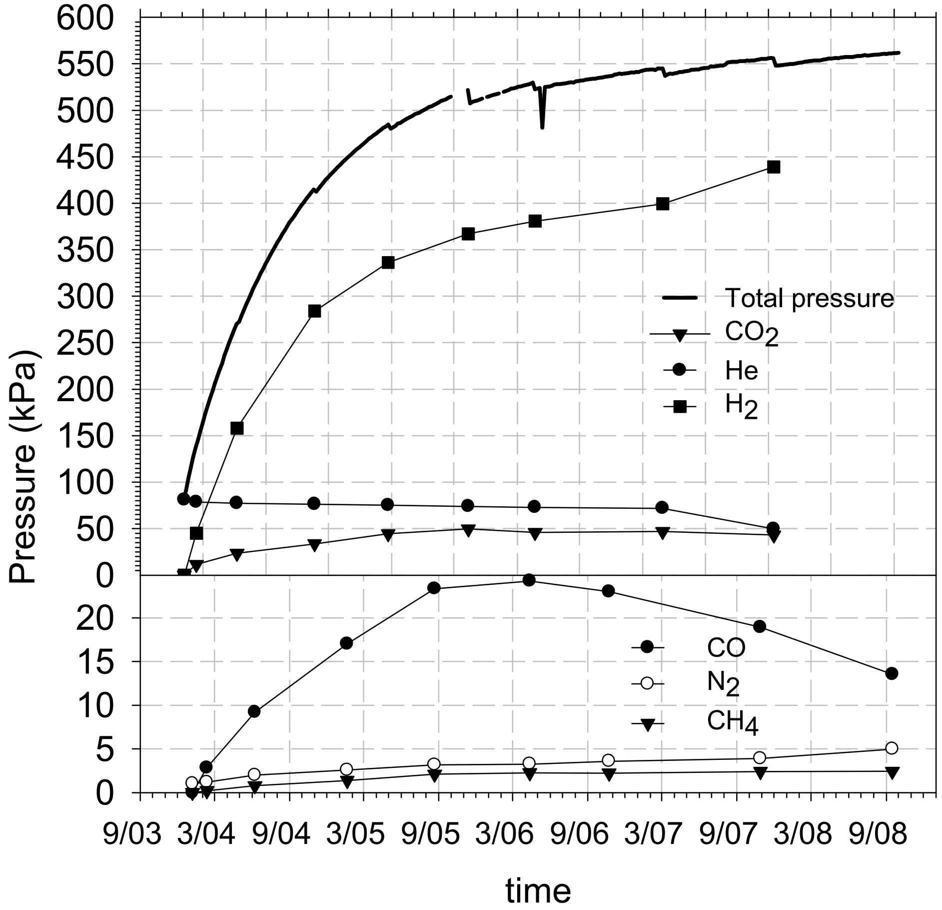

Figure 3. Gas pressure and composition for MIS represented material C06032A.

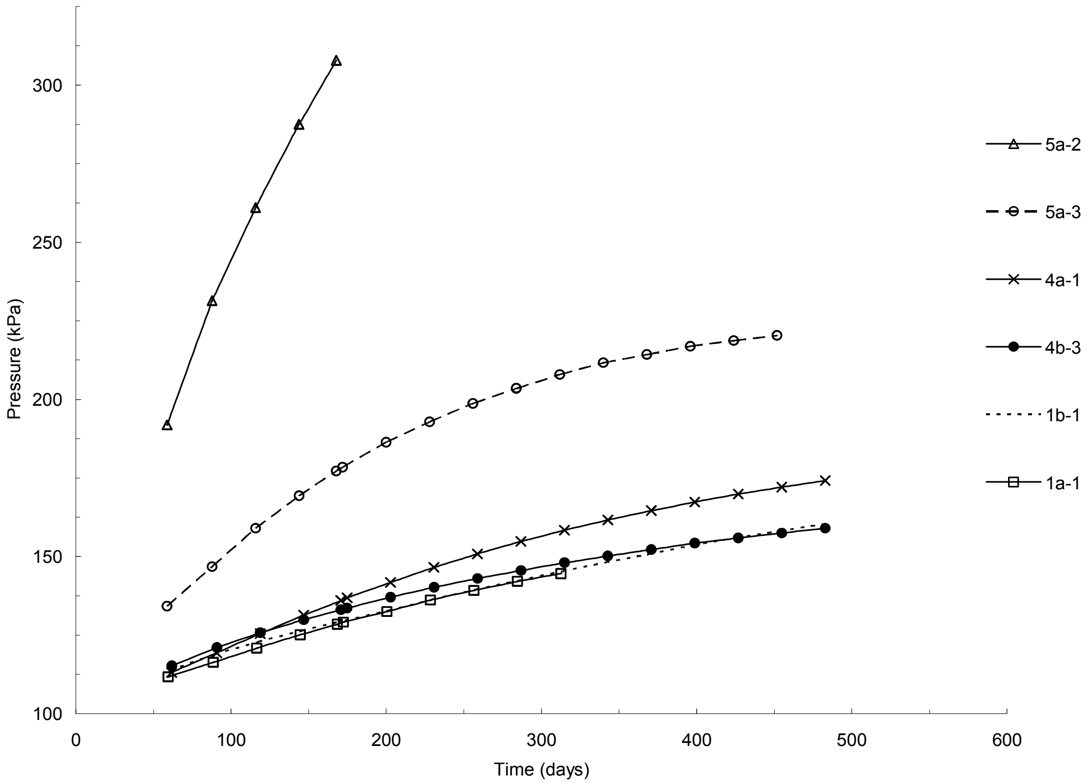

Figure 4. Pressure vs. time curves for selected corrosion test compositions with initial water contents (wt %) as follows: 5a-2 (1.2%); 5a-3 (0.45%); 4a-1 (0.58%); 4b-3 (0.61%); 1b-1 (1.0%); and 1a-1 (0.38%). All pressures are corrected to 25 °C. Pressures for 5a-2 and 5a-3 were corrected for pressure changes due to dilution with He and sampling prior to opening the container.

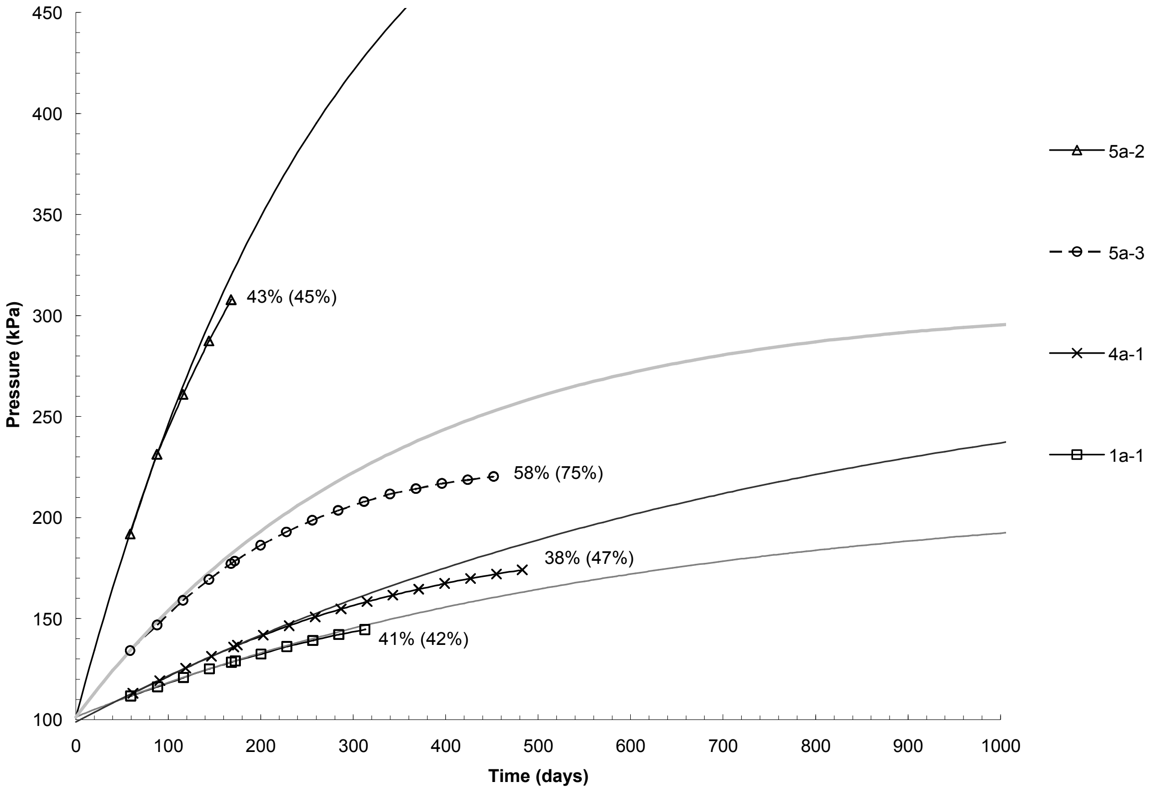

Figure 5. Measured and extrapolated pressure vs. time curves for selected corrosion test compositions. Extrapolated pressure curves were calculated from *G*-values for initial H_2 and O_2 generation rates and initial sample water contents, correcting for water consumed by radiolysis. Percentages are fractions of initial water consumed at test end; values in parentheses are calculated values for the same time period.