Gas Analyses in Support of the 3013 Destructive Evaluation Surveillance Program and Other Gas Generation Studies

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3013 Surveillance Program

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3013 Surveillance Program

- Sealed storage for containment of plutonium-bearing metals and oxides
- Alpha radiolysis of water in these materials leads to hydrogen gas generation
- A significant portion of the plutonium oxide inventory contains chloride
- Nested containers developed
3013 configurations

- Storage of surplus nuclear materials for DOE - 2002
- Ongoing small container studies (SRNL/LANL) and shelf life program (LANL)
- Mission to support 3013 Surveillance Program – 2007
- Storage shelf life 50 years
• **Pressure equation and assumptions**
  - Ideal gas law \( PV = nRT \)
  - All water undergoes radiolysis such that \( n_{H_2O} = n_{H_2} \)
  - All oxygen from radiolysis consumed (not in gas phase)

• **Mechanistic reasons this assumption is conservative**
  - Formation of surface hydroxyls
  - Recombination reactions: \( H_2 + \frac{1}{2} O_2 \rightarrow H_2O \)
  - Formation of non-volatile hydrogen containing species such as HCl, NH₄Cl, etc…

\[
P = P_F + P_{H_2} + P_{He}
\]

• **Packaging Requirements**
  - <0.5 wt % \( H_2O \)
    - Limits \( H_2 \) generation
    - Limits corrosion (no limit on Cl)
  - Stabilization at 950 °C for at least 2 h
    - Resistant to re-adsorption of water
    - Control relative humidity
9975 Shipping Package

Ceolotex®

lead shield

SCV

PCV

35-gallon stainless drum

DOE 3013 container (not shown)
3013 Containers: Outer, Inner, and Convenience Cans

- Capture gas from outer-inner (OI) and inner can (IC)
- Analyze captured gas to ensure atmosphere is not flammable
- Determine pressure
Can Puncture Device
Typical Pressure Curve

[Graph showing a typical pressure curve with time and pressure values labeled]
Leak Check

Pressure (psia)

- Vacuum pump valved off
- Pre-puncture leak check
- Inner Can Punctured
Gas Processes and Results

- Captured gas from outer-inner (OI) and inner can (IC) sent to SRNL for analysis (150 mL sample cylinders)
  - Micro-Gas Chromatography (microGC)
  - Fourier Transform-Infrared Spectroscopy (FTIR) with 10 m gas cell
  - 1-80 m/z Direct Inlet Mass Spectroscopy (DIMS)

- Verify that the captured gases are not a flammable mixture

- Use microGC gas results in combination with pressure measurement as technical justification that no leak has occurred from inner to outer container
SRNL Laboratory and Glovebox for Gas Analyses

East View of Laboratory showing FTIR, Lab Controllers, and Supply Manifold for Gas Analysis Instrumentation

FTIR Spectrometer (MIDAC I Series) and Dry Pump in Radiological Hood

Micro-GC and Gas Handling Manifold

West View of Laboratory Showing MDP, Direct Inlet Mass Spectrometer, and Radiological Gloveboxes
Micro-Gas Chromatography, Agilent CP-490

- **Typical pressures as received sample cylinders in FY17**
  - OI sample cylinders ~1.6-2.2 psia
  - IC sample cylinders ~4.2-9.2 psia
  - Further expanded: at least 1 psia sample pressure in manifold

- **Argon push gas: 18-22 psia**

- **Columns:**
  - PoraPlot Q (10 m):
    - *Carrier gas:* He
    - \( \text{CH}_4, \text{CO}_2, \text{N}_2\text{O} \)
  - Molsieve 5 Å (20 m):
    - *Carrier gas:* Ar
    - \( \text{He, H}_2, \text{O}_2, \text{N}_2, \text{(CH}_4\text{), CO} \)

- **Commonly observed gasses**
  - Helium and Nitrogen
  - Hydrogen observed in some cans; *typically* those sealed with moisture

Micro-GC with PPQ Column Removed
Micro-GC Standards

**He**

\[ y = 1.354E-17x^2 + 5.555E-08x \]

\[ R^2 = 9.992E-01 \]

**N2**

\[ y = -1.070E-16x^2 + 4.217E-07x \]

\[ R^2 = 9.998E-01 \]

**H2**

\[ y = 6.989E-18x^2 + 3.690E-08x \]

\[ R^2 = 9.997E-01 \]

**O2**

\[ y = -3.123E-16x^2 + 3.539E-07x \]

\[ R^2 = 1.000E+00 \]
FTIR and DIMS

• **Currently, microGC data collected (first priority)**

• **DI-MS collected during or after microGC data**
  – Only way to measure argon
    • Argon is found in IC samples
    • Confirm no argon from push gas (leak)

• **FTIR collected for FY2007-2010 and all FY2016-2017 and some additional backlog samples**
  – Consumes remaining sample
  – Collect FTIR data after initial data analysis (microGC/DIMS)
  – Working toward improving method for quantitative measurement
Maintenance Activities FY2010-Present

• **Procedures for each**: DI-MS, microGC, FTIR, Gas Analyses, Standards addition to GB
  – Periodic reviews
  – Changes due to equipment changes
  – Changes due to DSA revision
  – Changes due to MS&E procedure changes

• **Hazards Analyses**
  – Addition of Gas Standards to the Glovebox
  – Gas Analyses including DI-MS, microGC, FTIR

• **MicroGC replaced in 2010 and 2016**
  – Vendor changed from Varian to Agilent

• **FTIR**
  – Replacement purchased FY2010, installed FY2015 (MIDAC)

• **DI-MS (Pfeiffer Vacuum)**
  – Last maintenance in FY2010 (filaments replaced)

• **Molecular Drag Pump (Adixen/Pfeiffer)**
  – Replaced in 2011
GEST Overview

• **GEST (Gas Evaluation Software Tool) Purpose**
  – Calculate pre-puncture 3013 conditions
    • *Gas composition and pressure measured at DE are inputs*
  – Predicts composition of six gases
    • \(N_2\)
    • \(O_2\)
    • \(H_2\)
    • \(CO_2\)
    • \(CH_4\)
    • \(He\)
## FY17 Gas Composition Results-OI (Outer)

<table>
<thead>
<tr>
<th>Values (in vol% with uncertainty)</th>
<th>CH\textsubscript{4}</th>
<th>CO\textsubscript{2}</th>
<th>N\textsubscript{2}O</th>
<th>He</th>
<th>H\textsubscript{2}</th>
<th>O\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
<th>CO</th>
<th>Ar</th>
<th>Pressure (Psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE1 H001304</td>
<td>ND</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>99.2\pm3.1</td>
<td>0.7\pm0.2</td>
<td>ND</td>
<td>0.1\pm2.1</td>
<td>ND</td>
<td>ND</td>
<td>11.6</td>
</tr>
<tr>
<td>DE2 H002575</td>
<td>Trace</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>99.4\pm3.1</td>
<td>0.5\pm1.0</td>
<td>ND</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>ND</td>
<td>11.9</td>
</tr>
<tr>
<td>DE3 H003352</td>
<td>Trace</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>98.61*\pm4.1</td>
<td>0.91*\pm0.2</td>
<td>ND</td>
<td>0.48*\pm1.6</td>
<td>ND</td>
<td>ND</td>
<td>11.3</td>
</tr>
<tr>
<td>DE4 H003695</td>
<td>Trace</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>99.3*\pm2.8</td>
<td>0.7\pm2.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>11.4</td>
</tr>
<tr>
<td>DE5 H002508</td>
<td>Trace</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>99.4*\pm3.1</td>
<td>0.6*\pm1.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>11.3</td>
</tr>
<tr>
<td>DE6 R600793</td>
<td>ND</td>
<td>0.2</td>
<td>ND</td>
<td>89.7\pm4.8</td>
<td>0.3\pm0.1</td>
<td>ND</td>
<td>9.8\pm1.8</td>
<td>ND</td>
<td>ND</td>
<td>9.2</td>
</tr>
</tbody>
</table>

*Values have been normalized such that summation of compositions is 100%.*

"ND" = 0
"Trace" = 0 - 0.01
"< 0.1" = 0.01 - 0.1
### FY17 Gas Composition Results-IC (Inner)

<table>
<thead>
<tr>
<th>Values (in vol% with uncertainty)</th>
<th>CH₄</th>
<th>CO₂</th>
<th>N₂O</th>
<th>He</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂</th>
<th>CO</th>
<th>Ar</th>
<th>Pressure (Psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE1  H001304</td>
<td>ND</td>
<td>ND</td>
<td>Trace</td>
<td>47.0 ±2.9</td>
<td>2.9 ±0.2</td>
<td>ND</td>
<td>50.1 ±1.8</td>
<td>ND</td>
<td>ND</td>
<td>12.3</td>
</tr>
<tr>
<td>DE2  H002575</td>
<td>ND</td>
<td>Trace</td>
<td>Trace</td>
<td>45.2 ±2.8</td>
<td>22.0 ±0.9</td>
<td>ND</td>
<td>32.8 ±1.4</td>
<td>ND</td>
<td>ND</td>
<td>13.7</td>
</tr>
<tr>
<td>DE3  H003352</td>
<td>ND</td>
<td>Trace</td>
<td>Trace</td>
<td>75.34* ±3.8</td>
<td>2.545* ±0.2</td>
<td>ND</td>
<td>22.115* ±1.2</td>
<td>ND</td>
<td>ND</td>
<td>8.4</td>
</tr>
<tr>
<td>DE4  H003695</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>ND</td>
<td>35.2 ±2.5</td>
<td>46.6 ±2.0</td>
<td>ND</td>
<td>18.1 ±1.1</td>
<td>ND</td>
<td>ND</td>
<td>18.7</td>
</tr>
<tr>
<td>DE5  H002508</td>
<td>Trace</td>
<td>&lt; 0.1</td>
<td>Trace</td>
<td>43.8 ±2.8</td>
<td>30.7 ±1.3</td>
<td>ND</td>
<td>25.5 ±1.2</td>
<td>ND</td>
<td>ND</td>
<td>15.1</td>
</tr>
<tr>
<td>DE6  R600793</td>
<td>ND</td>
<td>ND</td>
<td>Trace</td>
<td>90.0 ±4.3</td>
<td>Trace</td>
<td>ND</td>
<td>10.0 ±1.0</td>
<td>ND</td>
<td>ND</td>
<td>13.1</td>
</tr>
</tbody>
</table>

*Values have been normalized such that summation of compositions is 100%.

"ND" = 0  
"Trace" = 0 - 0.01  
"< 0.1" = 0.01 - 0.1
Changes in the 3013 Standard Pressure Equation

\[ P = P_F + P_{H2} + P_{He} \]

\[ P = P_F + \eta_{H2}P_{H2} + \eta_{He}P_{He} \]

\( \eta_{H2} \) and \( \eta_{He} \)

1. are between 0 and 1
2. are evaluated for all materials from empirical observations

\[ \eta_{H2} = \frac{n_{H2,obs}}{n_{H2O}} \]

where \( n_{H2,obs} = \) moles of \( H_2 \) (gas)

\( n_{H2O} = \) moles of \( H_2O \) (container)

The $H_2$ fraction was determined for all 114 DEs through FY17.

Summary of 3013 Gas Analyses

- To date no flammable gas mixture has been measured

- MicroGC data analyzed for most samples in support of the 3013 destructive evaluation program accounts for >99% of the gas composition

- Commonly observed gasses
  - Helium and Nitrogen
  - Hydrogen seen *typically* in cans sealed with moisture

- MicroGC gas results have been used in combination with pressure measurement as technical justification that no leak has occurred from inner to outer container

- Gas analysis data provide technical justification for continued safe storage of PuO₂ materials
**Program Objective**
- Increase the actinide waste oxide loading in a suitable waste form
  - Microencapsulate oxide waste loading in a hydrated cement matrix such that \( H_2 \) generation rates are acceptable for processing, storage, transportation, and disposal.

**Technical Objectives**
- Identify hydrated cement matrices suitable for microencapsulation of rad waste oxide
- Demonstrate “smart processing” mixing technology for accountable oxide waste
- Demonstrate microencapsulation of waste oxide at a 1 wt. % loading
- Measure \( H_2 \) generation rates of selected waste forms
- Correlate \( H_2 \) generation rates to waste loading and form of water

**Business Goal**
- Increase waste oxide loading up to 10 wt.% based on acceptable \( H_2 \) generation rates to reduce cost and schedule
Calculated effective $\text{H}_2$ G-values for cement

Theoretical g-values for alpha radiolysis of varying amounts of water in a solid matrix based on estimated fractions of decay energy deposited in water and matrix.

Effective hydrogen g-values calculated from SRNL experimental results for alpha radiolysis of water in a solid matrix containing nitrate as a chemical scavenger for hydrogen.
Evaporable H$_2$O versus total H$_2$O

Sum of bound (in Blue) and physiosorbed water (in red): w/c = 0.2

105° C water = 2.5 % (11d), 1.5 % (25d)

Evaporable H$_2$O vs total H$_2$O.
Glovebox and RAM Mixer for Microencapsulation

Glovebox north side (left) and south side (right)

Mixing container and cement in glass jar placed in glovebox for rad sample preparation.

Sample in mixing container bagged out and mixed (2 min) in RAM mixer. Total time less than 10 min from water addition to mixed.
Sample vessel and containers for radiolysis studies

Sample container and pressure vessels for radiolysis experiments

Manifold for gas sampling and pressure measurement

Samples to be loaded in pressure vessels for radiolysis experiments
MicroGC data for 1 wt % oxide (w/c 0.2) without and with nitrate.
# Effective $H_2$ G-values

<table>
<thead>
<tr>
<th>wt % α-solids</th>
<th>wt % water</th>
<th>Effective $H_2$ G-value for cement waste forms (Molecules of $H_2/100$ eV)</th>
<th>G-Value Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Estimate</td>
<td>LDRD 2017 SRNL data</td>
</tr>
<tr>
<td>1</td>
<td>16.5</td>
<td>0.38</td>
<td>0.15 ± 0.02 (0.14, 0.16), (0.12, 0.11)</td>
</tr>
<tr>
<td></td>
<td>(water only)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15.2</td>
<td>0.36</td>
<td>0.012 ± 0.001 (0.012, 0.011) (0.012, 0.011)</td>
</tr>
<tr>
<td></td>
<td>(5 M NaNO$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.2</td>
<td>0.36</td>
<td>0.012 ± 0.001 (0.013, 0.012)</td>
</tr>
<tr>
<td></td>
<td>(5 M NaNO$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.2</td>
<td>0.36</td>
<td>0.007 (cement with more evaporable H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>(5 M NaNO$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.007</td>
<td>14.5</td>
<td>0.34</td>
<td>--</td>
</tr>
<tr>
<td>(NaNO$_3$ Soln)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.008</td>
<td>19.5</td>
<td>0.43</td>
<td>--</td>
</tr>
<tr>
<td>(NaNO$_3$ Soln)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Calculated and measured effective $\text{H}_2$ G-values for cement

Theoretical g-values for alpha radiolysis of varying amounts of water in a solid matrix based on estimated fractions of decay energy deposited in water and matrix.

Effective hydrogen g-values calculated from SRNL experimental results for alpha radiolysis of water in a solid matrix containing nitrate as a chemical scavenger for hydrogen.
Summary

- Gas analysis data can be used to provide technical justification for safe storage of alpha bearing materials

- MicroGC analysis provides quantitative results for 8 common gases including H$_2$ and O$_2$

- Results from Direct Inlet-Mass Spectroscopy and Fourier Transform Infrared Spectroscopy have not yet been used quantitatively but have provided additional supporting information on gas compositions

- Gas analysis results have been used in combination with pressure measurement as technical justification that no leak has occurred from inner to outer container in the 3013 Surveillance Program

- Gas analysis results have been used to determine effective hydrogen G values for alpha bearing waste forms

- SRNL has unique capabilities to analyze gas samples collected in contaminated environments
End of Presentation