LA-UR- 11-02118

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Title:	3013 Surveillance and Monitoring Program Review, January 25 to 27, 2011
Author(s):	See attached list Laura Worl, IPM-2
Intended for:	Submission to Allen Gunter, Department of Energy, Savannah River

Los Alamos NATIONAL LABORATORY EST. 1943

3013 Surveillance and Monitoring Program Review
January 25 to 27, 2011

Abstract
A DOE packaging and storage standard (DOE-STD-3013) is being used for long-term storage of excess weapons-grade materials. The DOE-STD-3013 requires a surveillance program to validate technical assumptions used to develop the Standard, and assure the long-term safety of plutonium storage in DOE-STD-3013 compliant containers. Close to five thousand 3013 storage containers remain in long term storage at the Savannah River Site (SRS). An Integrated Surveillance Program based at SRS assures the safe long-term storage of these materials that were processed at Rocky Flats Environmental Technology Site (RFETS), Fluor Hanford Site, and SRS, Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL). The effort includes a site wide integration of the surveillance and consolidation activities at SRS, Hanford Site, LANL, and LLNL. These presentations review the annual progress and results for the ISP and shelf life surveillance work across the DOE complex. The review also considers nuclear material storage in the M441.1-1 and 9975 containers. The current focus of the surveillance work is to demonstrate and validate safe storage of DOE-STD-3013 containers until the material is converted to mixed-oxide fuel or otherwise dispositioned.

3013 Surveillance and Monitoring Program Review Savannah River Site, Building 766-H, Room 2138 January 25-27, 2011			
Tuesday			
8:00 AM	0:10	Welcome/ Introductions	C. McClard
		DE, NDE Results and Update	
8:10 AM	0:40	K Area FY10 and FY11 status	A. Reedy, B. Hackney
8:50 AM	0:30	DE Gas Analysis and Pressures in 3013 containers	N. Bridges
9:20 AM	0:20	GEST results	J. Elkourie
9:40 AM	0:30	Pressures and Gas Analysis of LARIPOs and MIS-STD1	K. Veirs
10:10 AM	0:15	**Break**	
10:25 AM	0:40	Gradients of Thermal conductivity, Relative Humidity and Moisture in 3013 Containers	B. Nguyen, K. Veirs
11:05 AM	0:40	3013 Can analysis from DE	J. Ziska
11:45 AM	1:00	**LUNCH**	
12:45 PM	0:40	Oxide Analysis in DE	G. Kessinger, D. Missimer
1:25 PM	0:30	DE of H003328, LANL and SRNL results	L. Worl
		Shelf Life Surveillance Results	
1:55 PM	0:30	SRNL Corrosion Shelf Life Studies Update	J. Duffey, J.Mickalonis
2:25 PM	0:15	**Break**	
2:40 PM	0:30	Status of Large Scale Corrosion Containers	J. Narlesky
3:10 PM	0:20	Summary Corrosion Test Results and FY11 plans	S. Lillard
3:30 PM	1:00	Corrosion Working Group Meeting	
Wednesday			
		Represented Material, Material Characterization and 3013 Selection	
8:00 AM	0:30	Shelf Life Surveillance Gas Generation Results and Future Recommendations	K. Veirs
8:30 AM	0:20	DE Analysis reduction	G. Kessinger
8:50 AM	0:30	Prompt Gamma Analysis	J. Narlesky
9:20 AM	0:20	Engineering Judgment, FY11	T. Venetz, Berg
9:40 AM	0:30	**Break**	
10:10 AM	0:20	Database Updates and Queries	G. Friday, B. Cheadle
10:30 AM	0:30	Selection of 3013 Containers for Field Surveillance - outline	E. Kelly
11:00 AM	0:30	Pu Metal Eutectic	R. Mason
11:30 AM	1:00	**LUNCH**	
		Site Updates	
12:30 PM	0:30	LLNL Deinventory: packaging and shipping	D. Riley
1:00 PM	0:30	LANL 3013 packaging for 00-1 materials and AFS demonstration project	J. Rubin
1:30 PM	0:15	LANL 3013 packaging for ARIES materials	S. McKee
1:45 PM	0:30	3013 Equivalency /Low Temp Stabilization for Metal Oxidation Material	J.Berg
2:15 PM	0:15	3013 Standard X	GD Roberson, A. Gunter
2:30 PM	0:30	**Break**	
3:00 PM	0:30	Status of LANL's M441.1- 1 container	K. Veirs
		9975 Surveillance Program	
3:30 PM	0:30	O-ring surveillance	E. Skidmore
4:00 PM	0:30	9975 recent surveillance results	B. Daugherty
4:30 PM	0:30	Engineering Review of 14 Hanford Items	Engineering Review Team
Thursday			
8:30 AM	3:00	**MIS-Working Group Meeting (Meeting Action Items, SRNL and LANL AOPs)**	MIS-WG
11:30 AM	0:00	Meeting End	

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NDE of 9975s

Beth Hackney
Material Storage Lead Engineer
Jan 25, 2011

MIS Presentation

9975

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Overview

- 9975 NDE Process
- Example Findings
- Axial Gap Indications
- Actions Taken
- Conclusions

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Elements of the 9975 NDE

- Perform post load Leak Check of PCV and SCV
- Measure dimensions of Celotex and weigh upper assembly
- Measure thickness of lead shielding
- Record temperatures of lead shield, SCV and 3013
- Measure O-rings before and after removal from plug
- Photograph and record any other unusual conditions

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9975 Findings

- Damage to the Celotex

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Findings

- Mildew

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Findings

Lead Carbonate Flakes

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Findings

Excessive Lead Carbonate

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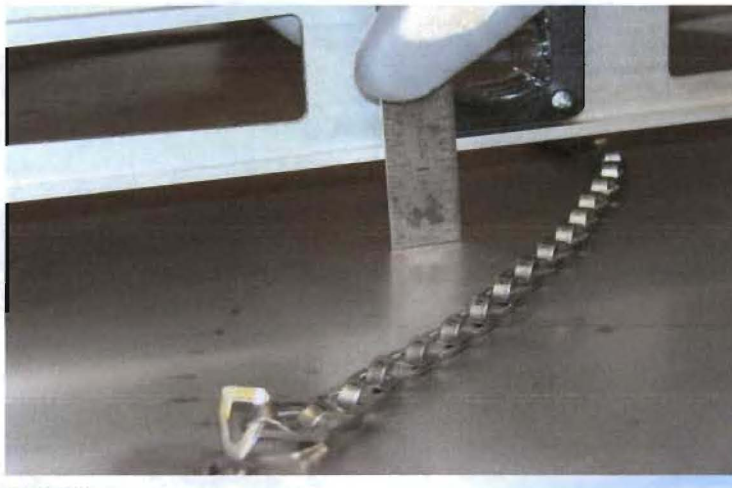
Findings

Axial Gap > 1"



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Axial Gap Findings

- **FY'09 a total of 6 NCRs written for failed axial gap.**
  - <1" is the SARP Criteria
  - 0.8" nominal
- **Two of these were found by the surveillance program**
- **Four were found during annual maintenance**
- **Items affected (01729, 01818, 01819, 01836, 01879, and 02287)**
  - 01818 had the largest axial gap (1.43") and greatest degradation
  - 01819 very similar

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9975-01818 Examination

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9975-01818 Cont'd

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9975-02287 Examination

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9975-02287 Cont'd

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Results

- Axial gap issues found in RFETS drums only
- Drums affected were packaged within a 3 month timeframe
- 1818 and 1819 had significantly higher levels of moisture than other drums (estimated to be 2.5 l)
- Completed a Thermal Analysis for a KAMS fire to show that the increased moisture and axial gap was still safe for storage in KAMS
- Completed a statistical analysis that concluded that 8% of the RFETS packaged during that period are expected to exceed the 1" axial gap.
- No correlation between axial gap and heat load.

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Actions Taken

- Added the measurement of the humidity in the headspace of the drum prior to opening.
- Added measurement of the fiberboard moisture WME.
- Revised the 9975-96 SARP to include the axial gap measurement during annual maintenance.

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FY'10 Findings

- **NDE31 / DE-15 9975-02130 failed the axial gap criteria**
  - Closer inspection found Small spots of mold
  - Moisture 14-23% WME range which is higher than a compliant package but not as high as other axial gap drums.
  - No apparent degradation of the fiberboard
- **9975-01968 was found during verification measurements**
  - No mold found
  - Moisture levels (10-14% WME) just slightly above average
  - No apparent degradation of the fiberboard

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2130 Inspection

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Conclusions

- Axial Gap can be an indicator for degradation of the fiberboard due to migration of moisture within fiberboard assembly.
- Proper Storage of 9975s is critical to the integrity of the fiberboard (based on field surveillance & lab studies)

- (Don't send us your wet ones)

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Overview of the FY10 and FY11 KIS Non-Destructive Examination (NDE) and Destructive Examination (DE) Runs

Amanda Reedy

Manager for the KIS Processing Group
January 25, 2011

MIS Working Group Meeting

766-H

Outline

- FY10 / FY11 KIS NDE and DE Processing Overview
- Process Improvements
- Future Surveillance Changes – Digital Radiography
- Summary

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DE / NDE Overall Performance

YEAR	NDE	DE
2005	27	N/A
2006	24	N/A
2007	14	7
2008	27	17
2009	26	19
2010	16	18
2011	N/A	18 (7 of 18 field complete)

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FY10 - FY11 DE / NDE Summary

- 16 NDE and 18 DEs were performed in KIS in FY10
  - 29 containers from Hanford, 4 containers from RFETS, and 1 container from SRS
  - 16 NDEs and 2 DEs were performed for a foreign material evaluation.
- 18 DEs are scheduled in FY11
  - 9 from Hanford, 5 from RFETS, 2 from SRS and 2 from LLNL
  - No NDEs are scheduled
  - 13 Prompt Gamma measurements were performed due to questionable baseline measurements on these containers at Hanford
- Two SPA Evaluations were completed in FY10
  - DE10: Valving Error
  - DE15: 9975 Celotex
  - No 3013 conditions identified requiring SPA evaluation

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FY10 Surveillance Summary

	Pressure	Pressure and Corrosion	Innocuous	Facility	Total
Random (NDE)	0	0	0		0
Random (DE)	0	13	0	8 Hanford, 4 RFETS 1 SRS	13
Engineering Judgment (NDE)	8	6	2	Hanford	16
Engineering Judgment (DE)	0	5	0	Hanford	5
Total	8	24	2		34

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FY11 Surveillance Summary

	Pressure	Pressure and Corrosion	Innocuous	Facility	Total
Random (NDE)	0	0	0		0
Random (DE)	0	13	0	6 Hanford, 5 RFETS 2 LLNL	13
Engineering Judgment (NDE)	0	0	0		0
Engineering Judgment (DE)	0	5	0	3 Hanford, 2 SRS	5
Total	0	18	0		18

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3013 Surveillance Process - NDE

- Receptor 9975 container undergoes inspection.
- 9975 Containers transported from storage room to KIS Vault.
- 3013 removed from donor 9975 and Surveillance performed on both donor 9975 and 3013 (only one 3013 container allowed at a time).
- 3013 placed into receiver 9975 or prepared for Destructive Evaluation.
- Surveillance Program Authority (SPA) reviews Surveillance Data.

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3013 Surveillance Criteria - NDE

- **Contamination:**
  - <20 dpm/100 cm2 Alpha transferable contamination
- **3013 Mass:**
  - < 1.0 gram difference between Buoyancy Corrected Baseline Mass and Surveillance Mass
- **Visual Inspection:**
  - Cracking of Container Surface
  - Pitting Corrosion on Container Surface
  - Generalized Corrosion
  - Bulging or Buckling
  - Metal discoloration or staining

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3013 Surveillance Criteria – NDE (cont.)

- Lid Deflection:
  - Pressure must be less than 100 psig @ 95% confidence interval temperature corrected to 412°F.
- Prompt Gamma:
  - No criteria (data used by SPA to validate the 3013 is binned correctly)

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Full Can Radiography – FY10

- Full can radiography was specified for foreign material in FY10 due to instances of tramp / foreign material being found in FY09.
  - Hanford containers
  - 16 NDE, 2 DE
- Radiographs taken at 0 and 90 degrees
  - Initial radiographs taken
  - Material agitated by rolling container
  - Radiographs taken again
  - At least three evolutions
- No foreign material found.

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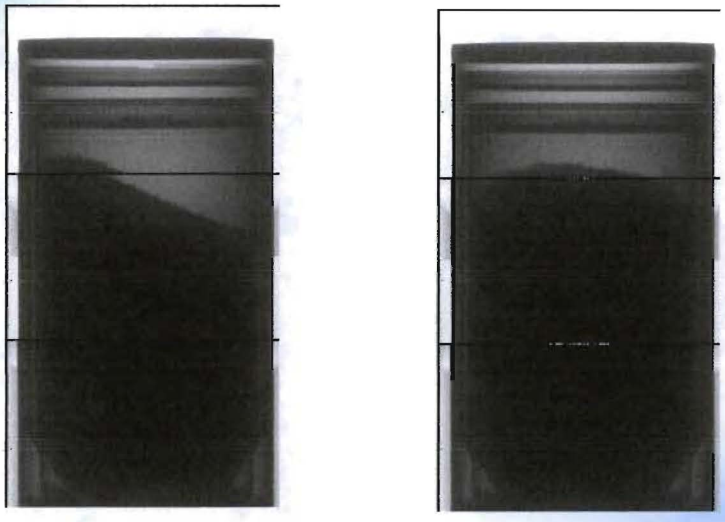
Typical Full Can Radiography Images



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Prompt Gamma – FY11

- **Used to measure impurities within the oxide material**
  - The impurity data is used to confirm that the material is in the correct bin (innocuous, pressure or pressure & corrosion)
- **13 prompt gamma measurements were performed in FY11**
  - A small group of containers from Hanford did not have a prompt gamma baseline
- **Prompt Gamma Process**
  - 60 minute live time count for each 3013
  - Field Surveillance Engineer obtained spectra.
  - Spectra then forwarded to Joshua Narlesky at LANL for verification of analysis.

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3013 Surveillance Process – DE

- The 3013 container is transported to the glovebox by hand and introduced to the glovebox.
- After verifying that the relative humidity is below the operational setpoint, the 3013 container is loaded into the Can Puncture Device (CPD).
- Once gas sampling is completed, the punctured 3013 container is removed from the CPD and transferred to the can cutter and both outer and inner cans are opened.
- The convenience can containing plutonium oxide material is removed from the inner container, and the lid is removed.
- The plutonium oxide material is poured into a pan and weighed.

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CPD Operations

- Equipment arrangement – see next slide
- System evacuation and nitrogen backfill performed three times to ensure air is removed.
- 10-minute leak check performed prior to puncture. Acceptance criteria is 0.004 psia/min. Most leak rates (50 of 58) have been ≤ 0.001 psia/min.
- CPD Pressure prior to puncture must be ≤ 1.0 psia
- 4-minute soak time required after puncture to allow for mixing and diffusion
- Purge cylinder used to eliminate "dead" space
- Gas sample error for DE#10 will be discussed later

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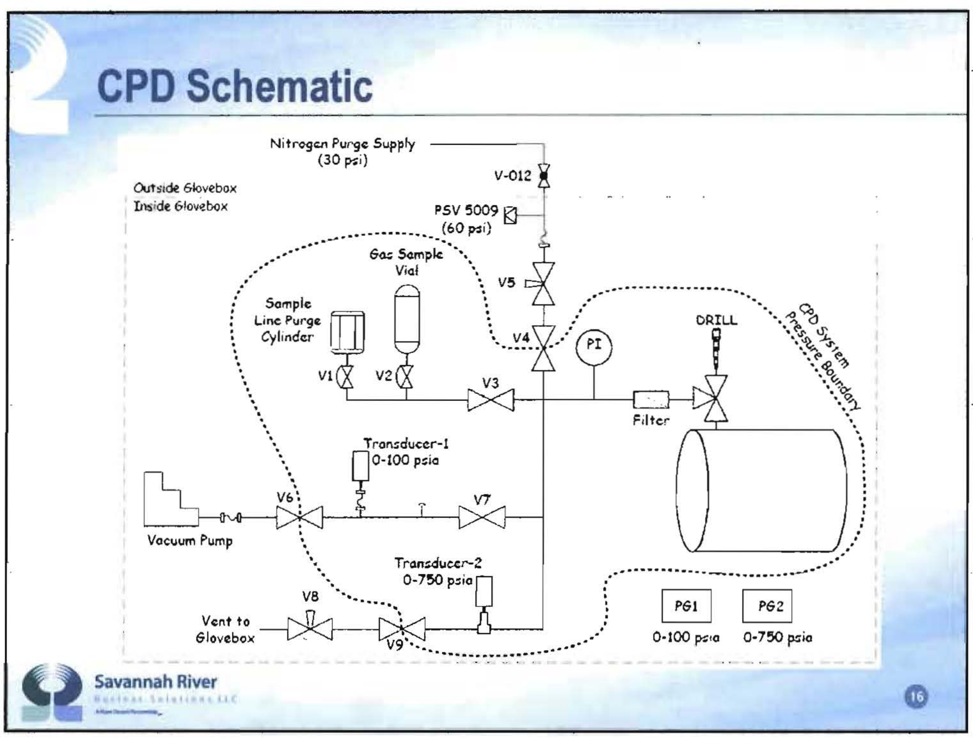
SHOP FOX


CPD Schematic
Nitrogen Purge Supply (30 psi)
V-012
Outside Glovebox
Inside Glovebox
PSV 5009 (60 psi)
Gas Sample Vial
V5
Sample Line Purge Cylinder
V4
PI
DRILL
CPD System Pressure Boundary
V1
V2
V3
Filter
Transducer-1 0-100 psia
V6
V7
Vacuum Pump
Transducer-2 0-750 psia
V8
Vent to Glovebox
V9
PG1
PG2
0-100 psia
0-750 psia
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Can Cutter Operations

- **Equipment arrangement – see next slide**
- **Cut location is the key**
  - Cut location changed after DE Run FY07-04. No problems since.
- **All convenience cans have been opened by hand.**
- **One point of concern:**
  - LANL can design will be problematic
  - NMS needs "test cans" to resolve this issue and determine how the cans will be sampled and opened.

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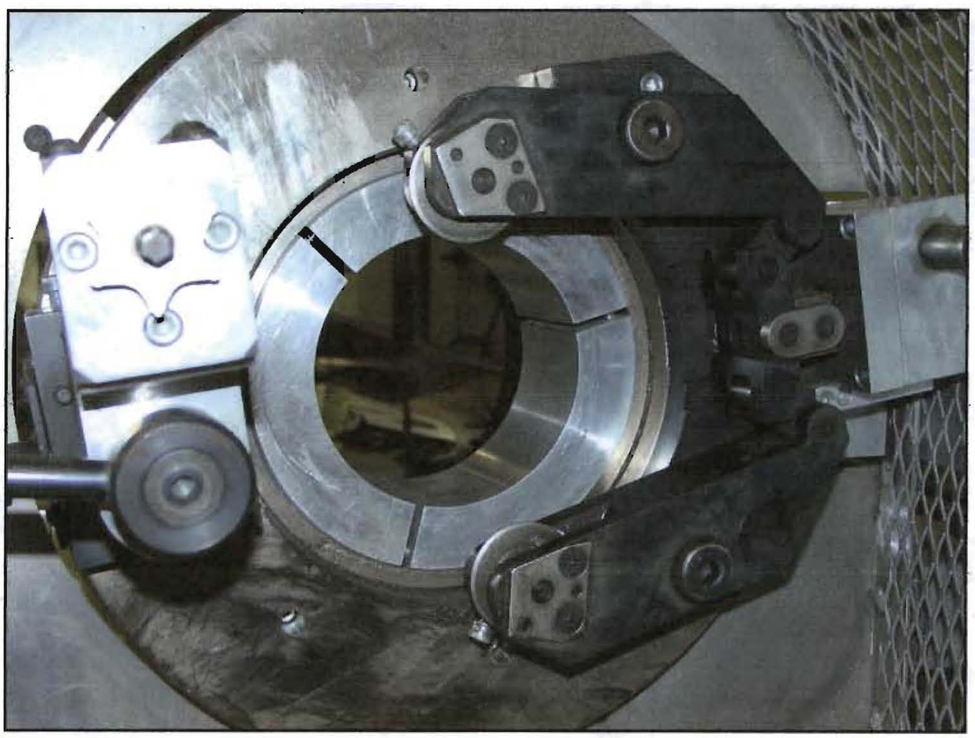

Oxide Sampling and Repackaging Operations

- Samples include "initial moisture", "final moisture" "sample of interest", and "representative sample"
- A "sample of interest" was taken for 5 of 18 DE Runs
  - DE #1, 2, 13, 15, and 16
  - Additional chemical analysis will be performed and the results will be evaluated in the Annual SPA Report.
- Most containers look "clean" and "shiny". A few cases in which we have seen surface staining.
  - DE# 3, 8 and 13
- Two or three daughter cans produced per run.
- Daughter cans stored in 910-B Storage Vault with hydrogen getters.

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Sample of Interest – FY10

Oxide Material – DE 16

Oxide Material – DE 15

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Sample of Interest – FY10

Oxide Material – DE 13

Oxide Material – DE 2

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Oxide Material – FY10

Oxide Material – DE 6

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Inner Can Staining – FY10

DE 3

Inner Can Staining – FY10

DE 13

Future Surveillance Changes - Digital Radiography

- The ADRIS Software in the DR unit on KIS currently does not have an analysis module for LLNL or LANL ARIES 3013s. The first LLNL can will be process this year.
- Software modifications to provide the capability for the KIS DR Unit to analyze Lid Deflection in LLNL 3013s is currently underway.
- Software modifications to provide the capability for the KIS DR Unit to analyze Lid Deflection in LANL 3013s will be scheduled. First can expected in FY2014, but could be as early as FY2012.

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Future Surveillance Changes – Digital Radiography

- Software Modifications for LANL include the following:
  - Create ADRIS Software Modifications to measure lid response and calculate pressure.
  - Develop standards to verify proper performance of the DR system.
  - Perform acceptance testing at SRNL.
  - Load modifications on DR system in the KIS vault and conduct startup testing
- Software modifications for LLNL do not require the development of standards

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Process Improvements

- LEAN Initiative
  - Temperature and humidity data collection time reduced from 12 hours to 6 hours – Implemented September 2010
  - Eliminated blank gas sample – Implemented August 2010
  - Additional Initiatives are working (automated humidity data transfer process)
- Sample Analysis Reductions
  - Based on SPA evaluation, sample reductions were made resulting in a cost savings of approximately $500K
- Californium Shuffler
  - Provides capability to assay Pu and EU in Pu/EU oxide mixtures

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Summary

- Overall performance of DE and NDE equipment is good.
- Process is working well and supporting 3013 surveillance schedule and commitments.
- No foreign material found during FY10 NDE / DE
- The 13 Prompt Gamma measurements scheduled for 2011 have been completed.

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Update on the 3013 Gas Analysis at SRNL

Nicholas J. Bridges
Savannah River National Laboratory

MIS meeting

25Jan11

Gas Processes and Results

- **Captured gas from outer-inner (OI) and inner can (IC) sent to SRNL for analysis**
  - Micro-Gas Chromatography
  - 10 m Fourier-Transition Infrared Red Spectroscopy
  - 1-80 m/z Direct Inlet Mass Spectroscopy
- **Confirmation of non-flammable head space**
  - Common observed gasses
    - Helium and Nitrogen
    - Hydrogen seen in cans; sealed with moisture
- **To date, no flammable mixture has been measured**

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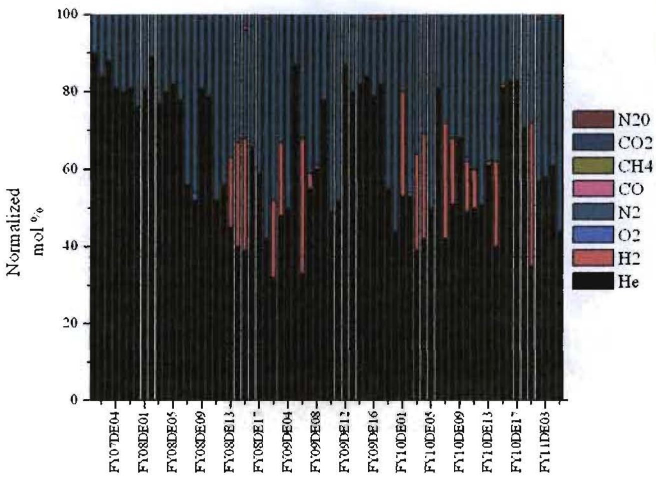
Gas Results Through FY11-DE05



- **Mostly He & N_2**
- **Some H_2**
- **Two cans had measurable O_2**
  - FY10-DE10 valving error
  - Neither can had a flammable mixture

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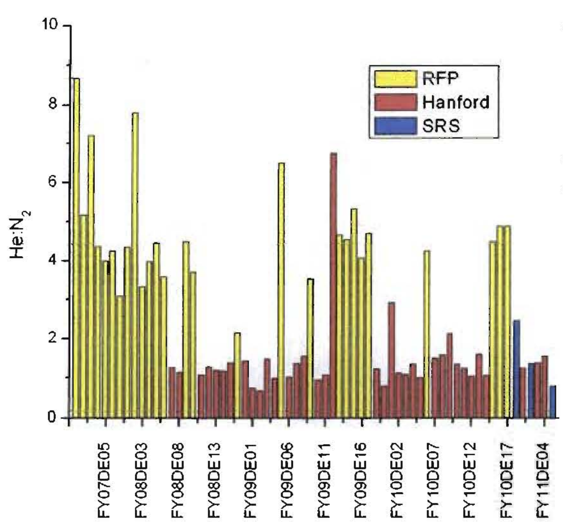
He:N_2 Concentration



- **Hanford cans generally have higher N_2 concentration**
- **SRS cans indicating the same trend as Hanford, low He:N_2**

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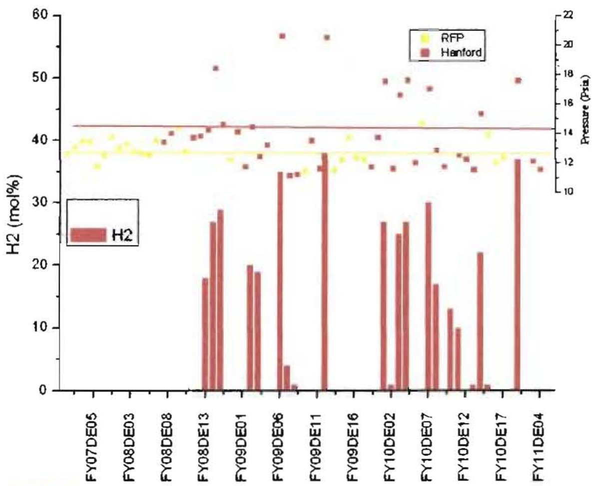
Correlation of H_2 to Pressure



- **Assumption that all can packaged at ambient pressure**
  - No pressure lost over time
- **Any H_2 generation would increase the pressure**
  - Some of the cans follow expected trend, but not all.

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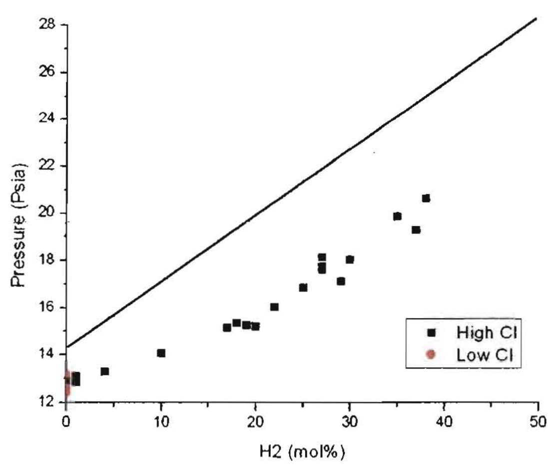
Observed Lower Pressure than Predicted



- **Hanford cans have produced H_2**
  - Total pressure build-up less than predicted.
  - O_2 consumption would add about 1.3 psia.
    - Deviation still about -2 psia

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Assumed atmospheric pressure of 14.35 psia

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FY10-DE10 (H002728) Mis-Valving at Sampling

- **After puncturing inner can, an error in valving occurred.**
  - 18 s of ambient glovebox air introduced into the CPD.
- **SRNL analysis of head space gas observed elevated O_2 and N_2 (7.4 and 50 mol% respectively).**
- **SRNL modeled the system and provided three different scenarios:**

	He	H_2	O_2	N_2	CO_2	N_2O
Partial Mixing	52	14	0.0	34	<0.1	<0.1
Diffusion Mixing	49	13	1.2	37	<0.1	<0.1
Complete Mixing	47	13	2.0	38	<0.1	<0.1

- **SRNL could not discount the possible presence of O_2 in the inner can of FY10-DE10 (H002728).**
  - Based on the history of all other containers, it is unlikely that O_2 was present at the time of sampling

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Equipment Status

- **Four year continuously operating FTIR, DI-MS, and microGC**
- **Failure of all three systems within a three week span**
  - FTIR inoperable power supple and laser
    - Failure due to lighting strike
    - Direct replacement purchased and received
  - DI-MS filaments burned out
    - Lost of power due to lighting strike exposed hot filament to air
  - microGC secondary pump failure
    - Installation of back-up, failure within 30min of installation
    - Cannibalized between two microGC to yield operational system
    - New back-up ordered
- **As part of the DE Reduction of Analysis**
  - MicroGC and FTIR will be reported for each can
  - DI-MS will be collected on each can, and only reported if FTIR is inoperable, or for clarification of results

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GEST Results

Jessica Elkourie

KIS Process Engineering
Savannah River Nuclear Solutions, LLC
January 25, 2011

3013 Surveillance and Monitoring Program Review
766-H Room 2138

Agenda

- GEST Purpose
- GEST Input
- GEST Results for FY10 and FY11(preliminary)

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GEST Overview

- **GEST (Gas Evaluation Software Tool) Purpose**
  - Calculate pre-puncture 3013 conditions
    - Gas composition and pressure
  - Predicts composition of six gases
    - N_2
    - O_2
    - H_2
    - CO_2
    - CH_4
    - He

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CPD (Can Puncture Device) Operation

- **Gas samples obtained during 3013 puncture**
  - Used as input into GEST
- **Pressures and times recorded during CPD operation**
  - Used to make graphs to determine if CPD in-leakage occurred

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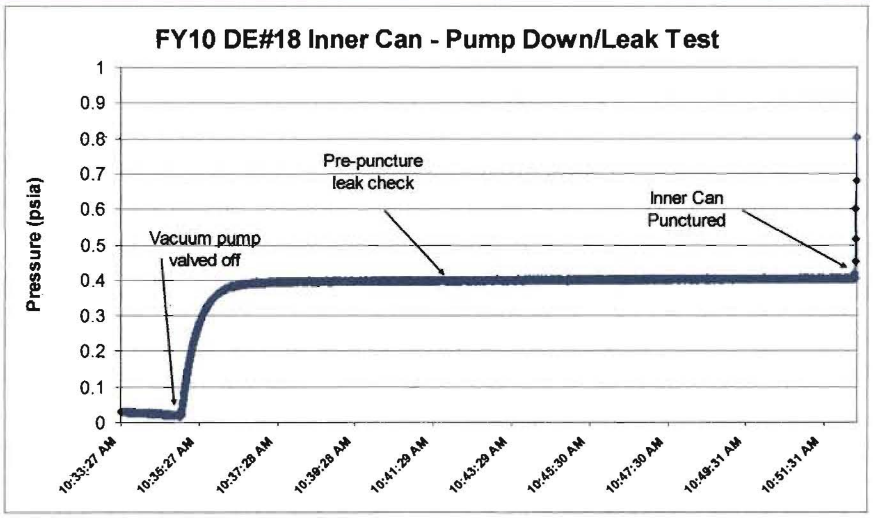
Leakage Graphs



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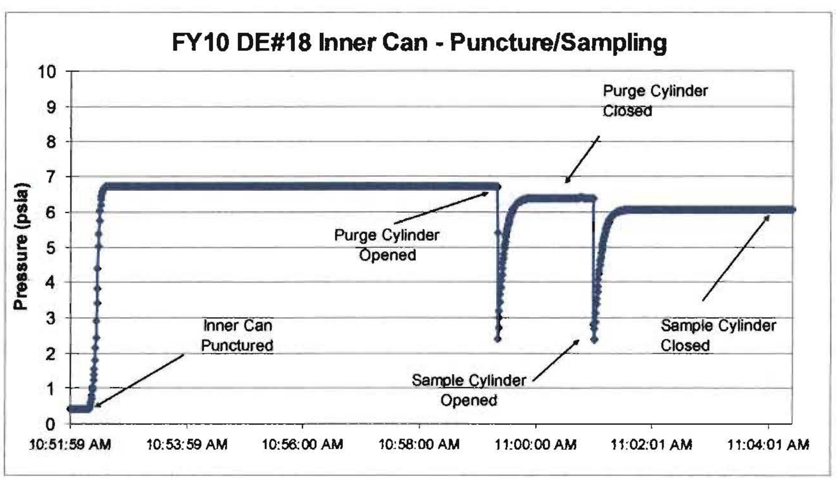
Leakage Graphs



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GEST Output

Post-Puncture 3013 Gas Compositions (FY10 DE#18)

Gas	CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO
Composition (Volume %)	0.000	0.001	0.109	71.288	0.000	0.046	28.556	0.000

GEST Calculated Pre-Puncture 3013 Gas Compositions (FY10 DE#18)

Gas	CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO
Inner Can Composition (Volume %)	ND	Trace	0.1	73.6	Trace	< 0.1	26.2	ND
Uncertainty (±)	N/A	N/A	0.0	2.6	N/A	N/A	1.3	N/A

Note: ND = No peak is present

Trace = 0.01 vol % or less

<0.1 = greater than 0.01 vol%, but less than 0.1 vol%

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FY10 GEST Results – First Quarter

DE # Can #		CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Pressure (Psia)
FY10 #1 H004251	IC Comp (Vol%)	Trace	< 0.1	Trace	0.5	0.3	Trace	0.2	Trace	17.5
	Uncertainty (±)	N/A	N/A	N/A	0.0	0.0	N/A	0.0	N/A	0.5
FY10 #2 H002496	IC Comp (Vol%)	ND	ND	Trace	0.5	< 0.1	Trace	0.4	ND	11.6
	Uncertainty (±)	N/A	N/A	N/A	0.0	N/A	N/A	0.0	N/A	0.4
FY10 #3 H003710	IC Comp (Vol%)	Trace	Trace	Trace	0.4	0.3	Trace	0.3	Trace	16.6
	Uncertainty (±)	N/A	N/A	N/A	0.0	0.0	N/A	0.0	N/A	0.4
FY10 #4 H003655	IC Comp (Vol%)	Trace	Trace	Trace	0.4	0.3	Trace	0.3	Trace	17.6
	Uncertainty (±)	N/A	N/A	N/A	0.0	0.0	N/A	0.0	N/A	0.5
FY10 #5 H002447	IC Comp (Vol%)	ND	ND	Trace	0.5	Trace	Trace	0.5	Trace	12.0
	Uncertainty (±)	N/A	N/A	N/A	0.0	N/A	N/A	0.0	N/A	0.4

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FY 10 GEST Results – Second Quarter

DE # Can #		CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Pressure (Psia)
FY10 #6 R610627	IC Comp (Vol%)	ND	Trace	ND	0.9	Trace	Trace	0.1	Trace	14.7
	Uncertainty (±)	N/A	N/A	N/A	0.0	N/A	N/A	0.0	N/A	0.6
FY10 #7 H003900	IC Comp (Vol%)	Trace	Trace	ND	0.4	0.3	ND	0.3	ND	17.0
	Uncertainty (±)	N/A	N/A	N/A	0.0	0.0	N/A	0.0	N/A	0.5
FY10 #8 H003650	IC Comp (Vol%)	ND	ND	<0.1	52.2	16.9	<0.1	30.9	ND	12.8
	Uncertainty (±)	N/A	N/A	N/A	2.3	0.3	N/A	1.3	N/A	0.4
FY10 #9 H002567	IC Comp (Vol%)	ND	ND	<0.1	57.9	<0.1	<0.1	42.1	ND	11.7
	Uncertainty (±)	N/A	N/A	N/A	2.4	N/A	N/A	1.6	N/A	0.4
FY10 #10 H002728	Partial Mixing Model	ND	<0.1	<0.1	54.0	14.7	-0.1	31.3	ND	11.4
	Complete Mixing Model	ND	<0.1	<0.1	48.9	13.3	2.0	35.7	ND	11.4

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FY 10 GEST Results – Third Quarter

DE # Can #		CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Pressure (Psia)
FY10 #11 H002786	IC Comp (Vol%)	ND	<0.1	<0.1	51.7	10.5	<0.1	37.7	<0.1	12.5
	Uncertainty (±)	N/A	N/A	N/A	2.3	0.2	N/A	1.5	N/A	0.4
FY10 #12 H003077	IC Comp (Vol%)	ND	ND	1.0	52.3	<0.1	<0.1	46.7	ND	12.2
	Uncertainty (±)	N/A	N/A	0.1	2.4	N/A	N/A	1.7	N/A	0.4
FY10 #13 H003367	IC Comp (Vol%)	ND	<0.1	<0.1	61.2	0.8	<0.1	38.0	<0.1	11.5
	Uncertainty (±)	N/A	N/A	N/A	2.5	0.1	N/A	1.5	N/A	0.4
FY10 #14 H003704	IC Comp (Vol%)	<0.1	<0.1	<0.1	41.3	22.5	<0.1	36.0	<0.1	15.3
	Uncertainty (±)	N/A	N/A	N/A	2.2	0.4	N/A	1.5	N/A	0.4
FY10 #15 R610785	IC Comp (Vol%)	ND	Trace	ND	84.8	0.7	< 0.1	14.5	< 0.1	13.9
	Uncertainty (±)	N/A	N/A	N/A	2.7	0.1	N/A	1.1	N/A	0.5

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FY 10 GEST Results – Fourth Quarter

DE # Can #		CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Pressure (Psia)
FY10 #16 R610826	IC Comp (Vol%)	ND	< 0.1	ND	88.5	ND	< 0.1	11.5	ND	12.0
	Uncertainty (±)	N/A	N/A	N/A	2.8	N/A	N/A	1.1	N/A	0.5
FY10 #17 R610853	IC Comp (Vol%)	ND	Trace	ND	86.8	ND	< 0.1	13.2	ND	12.3
	Uncertainty (±)	N/A	N/A	N/A	2.8	N/A	N/A	1.1	N/A	0.5
FY10 #18 S001721	IC Comp (Vol%)	ND	Trace	0.1	73.6	Trace	< 0.1	26.2	ND	12.0
	Uncertainty (±)	N/A	N/A	0.0	2.6	N/A	N/A	1.3	N/A	0.4

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FY 11 GEST Results – Preliminary

DE # Can #		CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Pressure (Psia)
FY11 #1 H003443	IC Comp (Vol%)	ND	<0.1	<0.1	35.1	37.5	Trace	27.3	ND	18.1
	Uncertainty (±)	N/A	N/A	N/A	2.2	0.5	N/A	1.2	N/A	0.5
FY11 #2 S002129	IC Comp (Vol%)	ND	Trace	0.4	60.0	Trace	Trace	39.7	ND	12.4
	Uncertainty (±)	N/A	N/A	0.0	2.4	N/A	N/A	1.6	N/A	0.4
FY11 #3 H002592	IC Comp (Vol%)	ND	ND	< 0.1	60.0	Trace	Trace	39.9	ND	11.8
	Uncertainty (±)	N/A	N/A	N/A	2.4	N/A	N/A	1.6	N/A	0.4
FY11 #4 H003337	IC Comp (Vol%)	ND	Trace	Trace	62.8	Trace	< 0.1	37.2	ND	12.3
	Uncertainty (±)	N/A	N/A	N/A	2.5	N/A	N/A	1.5	N/A	0.4
FY11 #5 S001105	IC Comp (Vol%)	ND	Trace	0.9	45.0	Trace	Trace	54.1	ND	12.0
	Uncertainty (±)	N/A	N/A	0.0	2.3	N/A	N/A	1.9	N/A	0.4
FY11 #6 H003343	IC Comp (Vol%)	ND	ND	0.5	55.2	Trace	< 0.1	44.2	ND	11.6
	Uncertainty (±)	N/A	N/A	0.0	2.4	N/A	N/A	1.6	N/A	0.4

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End of Presentation

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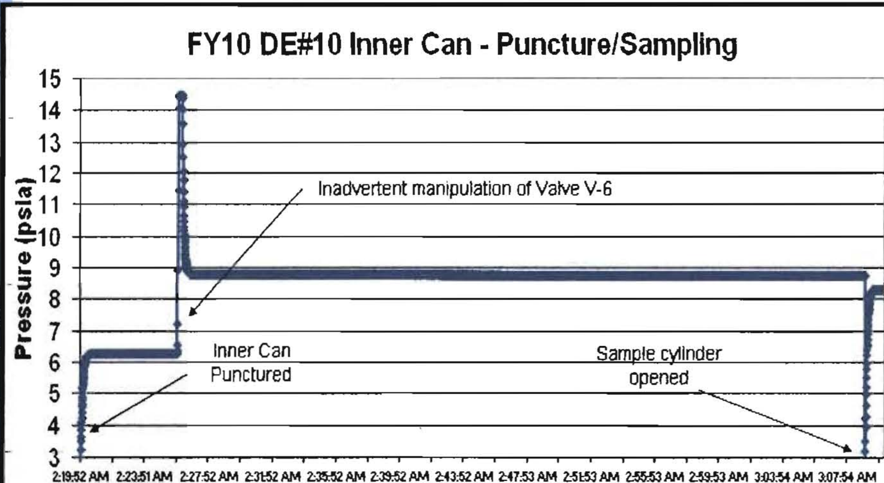
FY10 DE#10 Results



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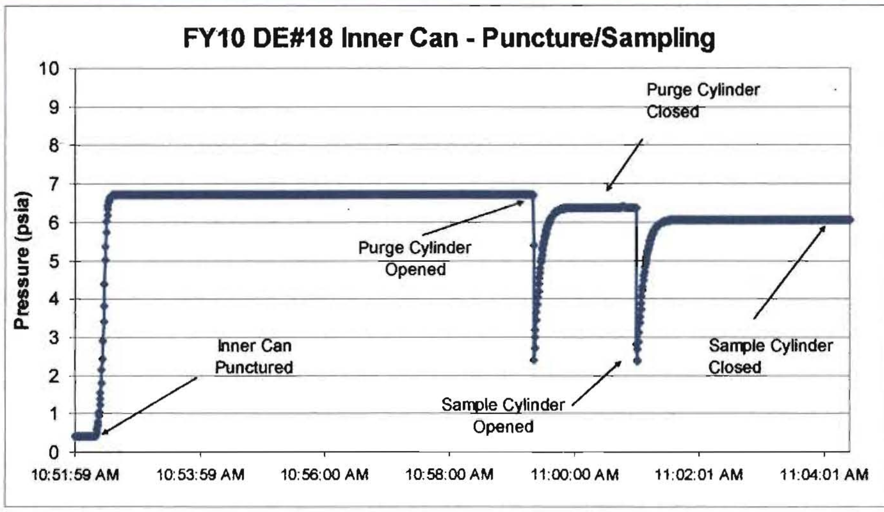
Normal Leakage Graph



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CPD (Can Puncture Device)

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Pressures and Gas Analysis of LARI-Pos and MISSTD-1

D.K. Veirs, Josh Narlesky, Leonard Trujillo, Max Martinez, Alex Carillo, Laura Worl, Larry Peppers, and John Berg

3013 Surveillance and Monitoring Program Review
Jan. 25-27, 2011
Savannah River Site

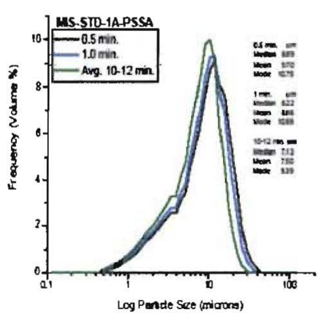
Introduction

- Six packages have been opened using the Can Punch system at Los Alamos. Measurements included internal pressure, gas composition, relative humidity, and temperatures. Material samples were collected for TGA/MS and specific surface area.
- MISSTD-1 was chosen as a test package to demonstrate the Can Punch system was working properly.
- The LARI-PO series of containers were being opened by ARIES to use the material. Four of these containers went through the LANL opening process in order to provide preliminary information on the behavior of material from the ARIES process that had undergone low-temperature calcination.

MISSTD-1

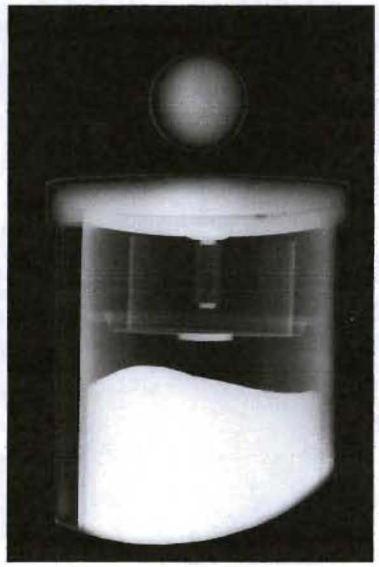
- MISSTD-1 was blended from five batches of oxalate precipitation from nitrate solution after anion exchange. The date of original production ranged from Dec. 1988 to Mar. 1992. The Pu content of the batches ranged from 87.8% (4) to 82.2% (1).
- The material was blended on 3/27/97 and packaged in a special container in early May of 1997. The package consisted of a welded outer container, an inner container with a protected bellows for pressure measurement, and a vented aluminum innermost container which held the material.
- The pressure was been measured for over a decade. Pressure rise occurred in the first year followed by a stable pressure.
- Measurements of the specific surface area range from 32 m^2/g to 19 m^2/g.
- Moisture measurements range from 0.03wt% and 0.21wt% (Supercritical Fluid Extraction) to 1.1wt% (inferred from hydrogen).

Particle size distribution



- MISSTD-1 heated to 200 °C for 2 hours: mass loss 0.43%.

Radiograph of MISSTD-1



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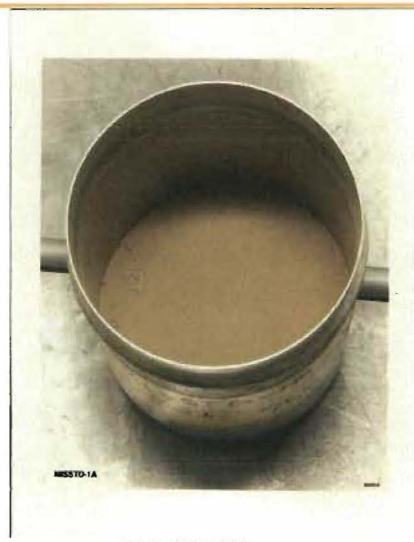
MISSTD-1



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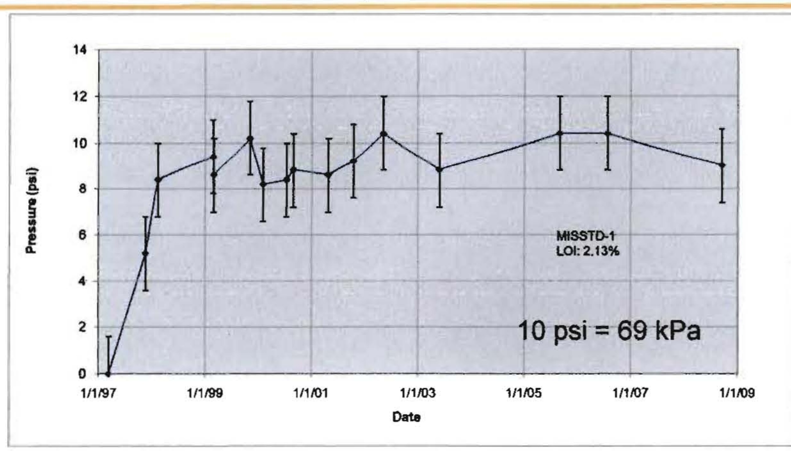
MISSTD-1 Pressure from radiographs of bellows



- PuO_2; oxalate ppt; 2.85 kg; $32 m^2/g$; moisture 0.2 wt% water

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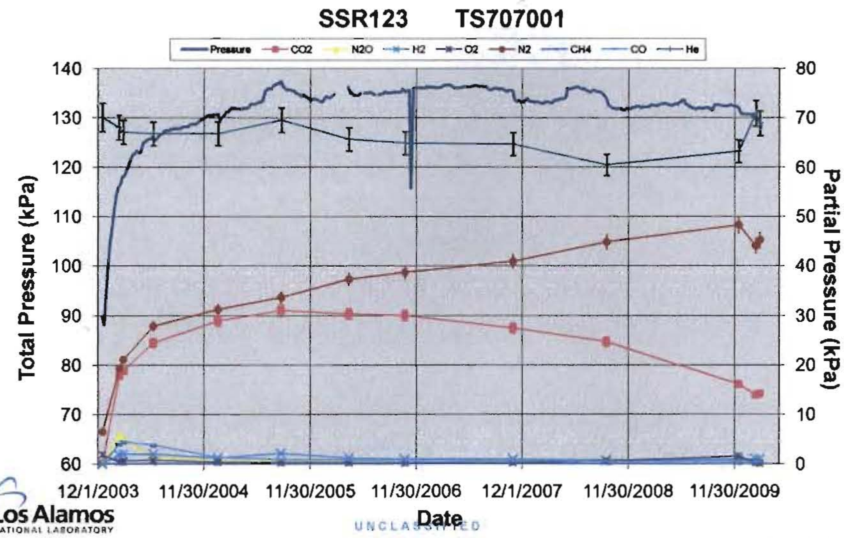
Similarity to high purity oxide gas generation



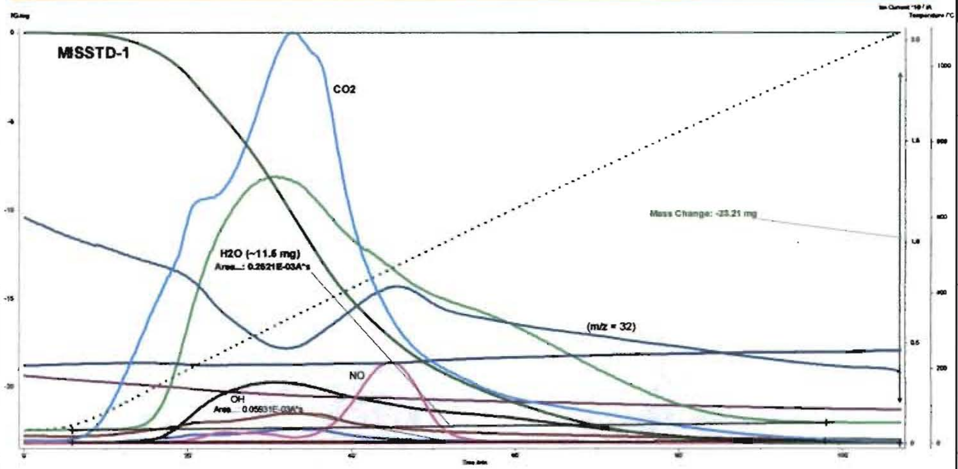
Gas observations

	Pressure (kPa)	Uncertainty (kPa)
MISSTD-1 O	78.8	5.5
MISSTD-1 I	156.6	16.0

- Dew point -68C or less than 1% RH .

	MISSTD-1		MISSTD-1 P
	Outer	Inner	Inner (kPa)
CO_2	0.00%	0.01%	0.02
N_2O	0.00%	0.58%	0.91
He	99.79%	49.91%	78.15
H_2	0.07%	0.01%	0.02
O_2	0.01%	0.01%	0.02
N_2	0.13%	49.48%	77.49
CH_4	0.01%	0.00%	0.00%
CO	0.00%	0.00%	0.00%

TGA-MS: loss ~2.3%, H_2O ~1.1%, CO_2 ~1.2%



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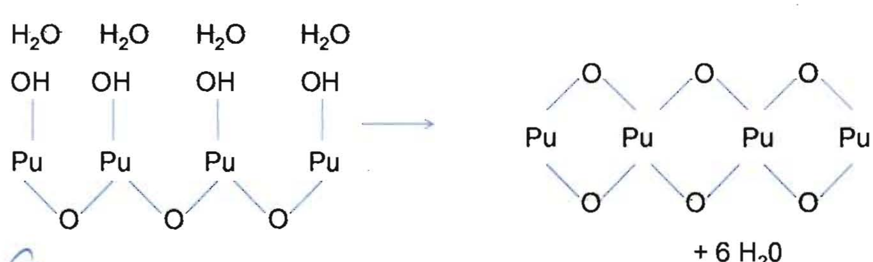
Water

- 1 monolayer (ML) of water weight 0.00022 g/m²
- 1 ML water on 32 m²/gram material = 0.007 g/gram material = 0.7wt%
- Loss of 1 ML water and OH termination = 1.5 ML = 1.15wt%.



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Comments on CO_2 and N_2

•Source of CO_2:

•Residual $C_2O_4^{2-}$; survive 12 years of radiation?

•Surface adsorbed: material was exposed to air for up to 10 years before packaging, CO_2 from air can adsorb and radiolysis of air can form nitrogen oxides which can adsorb.

•Carbon oxidized by H_2O?

•Why N_2 and no CO_2 in gas phase? Is carbon oxidized by nitrogen oxides on the surface forming N_2 and CO_2 which subsequently adsorbs.

Comments on H_2 and H_2O

•No H_2 in gas phase from monolayer concentrations of H_2O is consistent with observations of other high purity plutonium oxides.

•ML of H_2O on surface generally associated with RH of greater than 20%. What might be the role of CO_2, which desorbs first as the temperature is increased, in reducing the water vapor pressure?

LARI-POs

- From ARIES DMO furnace – captured as batches. Batches calcined at low temperatures – documentation of the temperature is being sought.
- Packaged in 2002.
- Behavior may be useful to developing the argument for lowering the calcination temperature for the 3013 Standard.
- Three items processed: LARI-PO Low T1, LARI-PO Low T2, LARI-PO Low T3, and LARI-PO Low T4.

Internal pressure from Can Punch gas expansion

	Pressure (kPa)	Uncertainty (kPa)
LARI-PO Low T1	77.1	5.4
LARI-PO Low T2	71.0	5.0
LARI-PO Low T3	72.0	5.0
LARI-PO Low T4	72.5	5.1

	LARI-PO Low T1	LARI-PO Low T2	LARI-PO Low T3	LARI-PO Low T4
	Inner	Inner	Inner	Inner
CO_2	0.00%	0.00%	0.00%	0.00%
N_2O	0.00%	0.00%	0.00%	0.00%
He	98.52%	99.77%	99.84%	99.34%
H_2	0.00%	0.00%	0.00%	0.00%
O_2	0.01%	0.06%	0.04%	0.13%
N_2	1.47%	0.17%	0.13%	0.52%
CH_4	0.00%	0.00%	0.00%	0.00%
CO	0.00%	0.00%	0.00%	0.00%

Comments on LARI-PO gas composition

- A high purity oxide with no CO_2 and little N_2
  - Perhaps this reflects that they were packaged relatively soon after production and there was little time to form nitrogen oxides or adsorb small gas phase molecules.
  - If true, the shelf-life studies will see more N_2 and CO_2 than DE; future studies with representative materials would begin studies immediately after calcination.

Condition of containers is good.

Temperatures and RH

	Material Height	Center Line °C[1]	Container Wall (inside) °C[1,2]	Glovebox °C[3]	Container Wall (outside) °C[3]	Container Bottom (outside) °C[3]	Container Headspace °C[3]	Headspace Dew Point °C[3]	Headspace RH % (calc)	GB Dew Point °C[4]
MISSTD-1	Filled	62.9	59.0	25.1	42.5	34.4	27.0	-68	0.02	-69
LARI-PO Low T1	Half-Filled	70.4	43.7	25.5	51.2	43.2	27.8	-68	0.02	-68
LARI-PO Low T2	Half-Filled	66.4	52.1	25.4	48.0	42.0	27.7	-68	0.02	-69
LARI-PO Low T3	Half-Filled	65.5	49.0	24.8	48.7	42.2	26.8	-68	0.02	-69
LARI-PO Low T4	Half-Filled	67.9	56.1	24.9	47.5	41.6	28.2	-67	0.02	-69
LARI-PO Avg		67.6	50.2	25.1	48.9	42.3	27.6	-68	0.02	

1. Temperature measured prior to taking container off-line
2. Temperature measured midway between surface of material and bottom of can
3. Temperature monitored as a function of time; values above taken at 4 hours
4. GB Dew point measured prior to placing RH probe inside container

Conclusions

- High SSA oxide with moisture
  - pressurized to ~78 kPa with N_2 after 12 years.
  - Adsorbed water did not radiolyse to H_2.
  - Corrosion mainly consisted of discoloration.
- Material from the DMO furnace and batch calcined after 8 years
  - Very low RH
  - No signicant gases produced.
  - Some discoloration of metal.

The DMO and calcined oxalate precipitation methods of producing high-purity oxides at low temperatures resulted in very little gas pressure, no flammable gases, and no significant corrosion after 8 to 12 years.

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Relative Humidity, Moisture & Thermal Gradient Part 1: Data Collection

Binh V. Nguyen

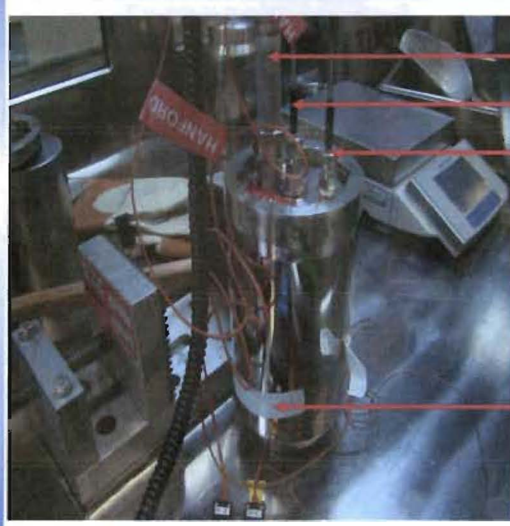
K-Area Complex Process Engineer
Savannah River Nuclear Solutions, LLC

January 25th, 2011

3013 Surveillance and Monitoring Program Review

766-H Room 2138

Temperature & Relative Humidity



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Instruments

Relative Humidity

Vaisala Model HMI41 / HMP45

Accuracy: ± 2% RH

Temperature

Omega Model HH147 / J / K

Accuracy: ± 4°F or 0.4% of reading, whichever greater

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3013 Containers Collected To Date (FY09 to present)

- **One Rocky Can** (R610806)
- **Three SRS Cans** (S001721, S002129, S001105)
- **20 Hanford Cans** (H003119, H002195, H004251, H002496, H003710, H003655, H002447, H00390, H003650, H002567, H002728, H002786, H003077, H003367, H003704, H003443, H002592, H003337, H003343, H003371)
- **Seven more to go in FY11** (5 Hanford, 1 Rocky and 1 LLNL)

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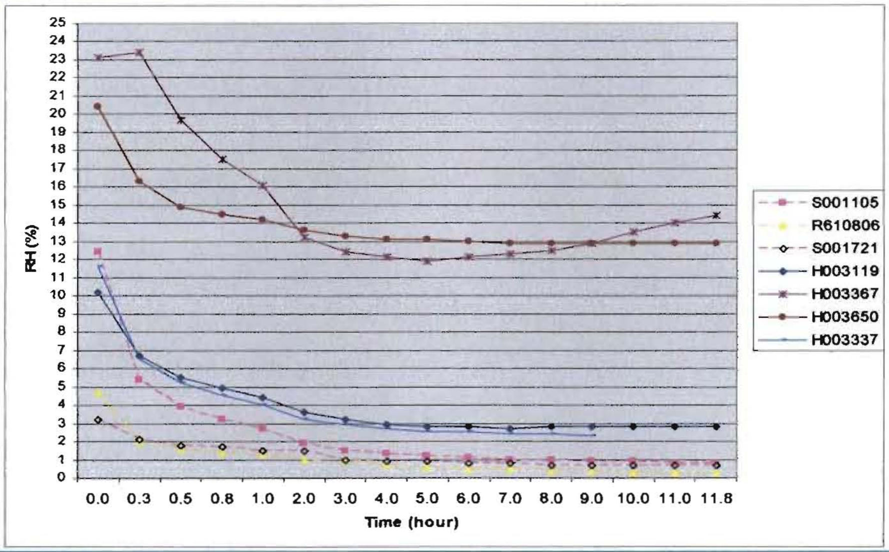
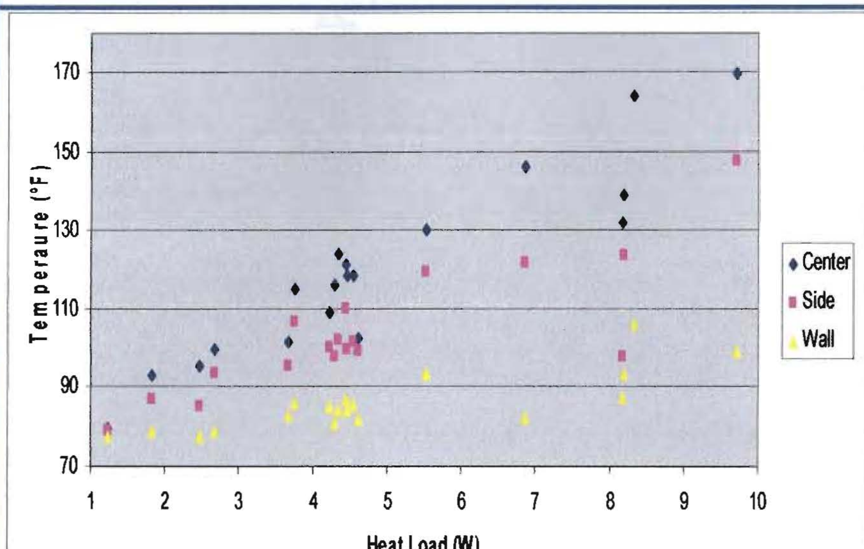
Relative Humidity Over Time



Temperatures vs. Heat Load



Data (1 of 2)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
R610806	8.2	0.3	138.6	123.4	93.6
S001721	8.3	0.7	164.2	n/a	106.1
S002129 (6)	9.6	1.0	154.3	136.2	98.1
S001105	9.7	0.8	169.9	147.7	99.1
H003119	5.5	2.8	129.8	119.1	93.6
H002195	8.2	n/a	131.8	97.8	87.2
H004251	3.8	3.7	115.1	106.5	86.0
H002496	2.5	12.1	95.2	85.1	77.4
H003710	4.5	5.3	118.0	99.5	84.2
H003655	4.5	3.1	118.4	101.3	85.5
H002447	4.8	5.3	n/a	n/a	n/a
H00390	3.7	5.7	101.4	95.2	82.6
H003650	4.6	12.9	102.5	99.1	81.8

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Data (2 of 2)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H002567	1.2	11.8	79.2	78.8	77.5
H002728	4.4	4.2	123.8	102.0	84.1
H002786	4.3	3.2	115.7	97.4	80.9
H003077	6.9	4.1	146.4	121.7	82.4
H003367	2.7	14.4	99.5	93.6	78.8
H003704	4.4	3.1	120.8	109.9	86.9
H003443	4.2	8.0	108.8	100.1	84.9
H002592	1.8	11.6	93.1	87.0	79.0
H003337(9)	3.3	2.3	108.1	98.6	81.2
H003343	3.7	1.2	112.4	85.6	76.5

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Gradients of Thermal Conductivity, Relative Humidity, and Moisture in 3013 Containers

D.K. Veirs and F. Coyne Prenger

3013 Surveillance and Monitoring Program Review
Jan. 25-27, 2011
Savannah River Site

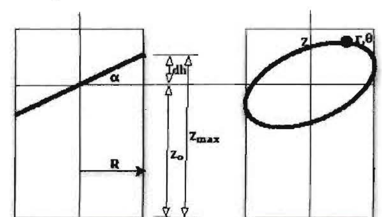
Introduction

- Goal is to map the temperature and relative humidity within 3013 containers when stored in 9975s and to relate the conditions to salt phases and liquid formation.
  - The temperature and water vapor pressure at which salts form liquids has been mapped out (see talk last year and INMM articles).
  - Need the thermal conductivity of the material/fill gas system and the water vapor pressure.
  - The thermal conductivity of the material/fill gas can be estimated using models: Eian-Deissler or Bielenberg. They result in significant differences.
  - Measure the thermal profile and RH of materials before they are removed from their Convenience Containers. This provides the required information for a small group of containers.
  - Derive the effective thermal conductivity from the temperature measurements, compare to models, and evaluate which model can be used when measurements are not available.

Model input

- In order to estimate the effective thermal conductivity of a material/fill gas system, the models require the gas composition and the void space.
  - The gas composition is assumed to be air for the DE temperature measurements.
  - The void space can be calculated from the bulk density and the pycnometer density.
  - The bulk density is determined from radiographs and the mass of the contents.
  - The pycnometer density is calculated from the actinide percentage assuming theoretical density of the PuO_2 and an average salt density.

Fill Height Prediction using Disk Model for Material Surface



a. Special Case, $r=R$; $\theta=0$; $Z=Z_o$ b. General Case; r,θ,Z

Method: Meassure Z_{max}, Z_1, Z_2, r_1, r_2 and D from radiograph. Calculate Z_o, α and dh assuming a sin θ curve fit. Check results using $Z_{max} = Z_o + dh$, shown as "error" in Parametric Table below. Adjust results using scale factor, $f_{scale} = D_o/D$.

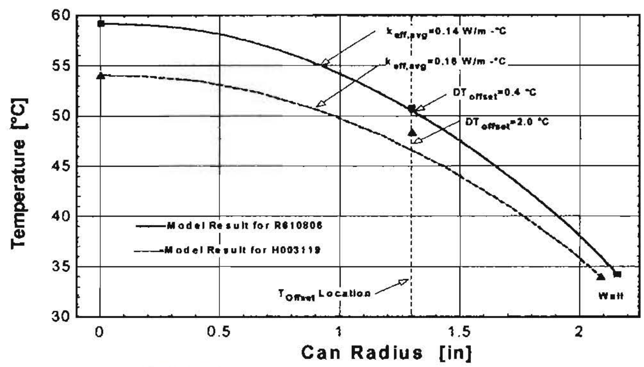
$Z_{o\,act} = f_{scale} * Z_o$

Parametric Table [illegible]

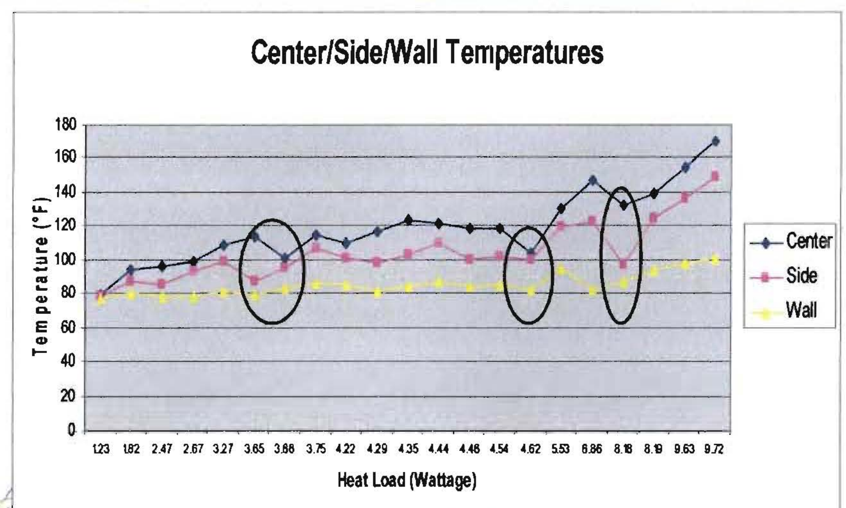
	ID#	Z_{max}	Z_1	Z_2	r_1	r_2	D	Z_o	dh	error	θ_1	θ_2	[illegible]	α	D_o	f_{scale}	$Z_{o\,act}$
Run 1	H003119	3.460	3.312	3.125	0.750	1.032	2.780	2.687	0.4754	[illegible]	57.35	-40.15	97.5	19.9	4.175	1.502	[illegible]
Run 2	[illegible]	[illegible]	2.969	4.063	1.063	[illegible]	3.000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	8.1	4.175	1.282	[illegible]
Run 3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Run 4	H002728	4.800	3.484	3.969	1.375	-0.375	3.000	2.573	[illegible]	[illegible]	23.56	[illegible]	[illegible]	15.9	4.175	1.282	[illegible]
Run 5	H002785	3.750	3.747	3.563	-0.188	-1.212	3.000	[illegible]	0.1817	[illegible]	97.18	[illegible]	[illegible]	[illegible]	4.175	1.282	[illegible]
Run 6	[illegible]	4.260	[illegible]	[illegible]	0.125	-1.400	3.000	[illegible]	0.0422	[illegible]	85.22	[illegible]	[illegible]	[illegible]	4.175	1.282	[illegible]
Run 7	[illegible]	4.255	4.125	4.180	-1.000	0.750	3.000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4.175	1.282	[illegible]
Run 8	H003794	4.835	[illegible]	3.986	-0.625	-1.125	3.000	2.841	[illegible]	[illegible]	114.6	[illegible]	[illegible]	7.2	4.175	1.282	[illegible]

Thermal profile

•The shape of the thermal profile is constant assuming the material is homogenous, the temperature measurements are made well below the surface of the material, and the placement of the temperature sensors is accurate.



Some measurements do not appear to meet the assumptions



Results

Results for k_eff and Prediction of T_offset

ID$	T_head	T_center	T_offset	T_w	T_GB	D_bed	L_bed	V_bed	m_bed	rho_bulk	rho_pyc	void	Q_bed	k_eff	k_dim
	[C]	[C]	[C]	[C]	[C]	[in]	[in]	[cm3]	[g]	[g/cm3]	[g/cm3]		[W]	[W/m-C]	
H003119	29.4	54.3	48.4	34.2	25.0	4.175	4.49	959	2429	2.53	7.47	0.661	5.53	0.165	0.943
H004251	28.9	46.2	41.4	30.0	24.1	4.175	7.07	1538	2578	1.68	4.92	0.659	3.75	0.096	0.964
H002496	24.4	35.1	29.5	25.2	23.8	4.175	5.71	1235	1887	1.53	6.06	0.748	2.47	0.127	0.958
H003710	29.4	47.8	37.5	29.0	24.7	4.175	4.88	1047	2499	2.39	6.84	0.651	4.46	0.137	0.948
H003655	32.2	48.0	38.5	29.7	23.6	4.175	6.00	1299	2589	1.99	6.61	0.698	4.54	0.120	0.960
H003900	26.7	38.6	35.1	28.1	24.3	4.175	5.40	1164	2480	2.13	5.43	0.608	3.66	0.184	0.958
H003650	25.0	39.2	37.3	27.7	23.0	4.175	4.79	1027	2483	2.42	7.77	0.689	4.62	0.234	0.953
H002728	27.2	51.0	38.9	28.9	24.7	4.175	4.97	1067	2475	2.32	6.64	0.651	4.35	0.111	0.947
H002786	26.1	46.5	36.3	27.2	23.0	4.175	4.97	1066	2505	2.35	6.65	0.647	4.29	0.126	0.949
H003077	27.2	63.6	49.8	28.0	23.4	4.175	5.86	1266	3333	2.63	10.18	0.741	6.86	0.095	0.955
H003367	24.4	37.5	34.2	26.0	23.4	4.175	5.56	1200	2052	1.71	6.04	0.717	2.67	0.119	0.956
H003704	27.2	49.3	43.0	30.5	24.4	4.175	5.35	1153	2489	2.16	6.34	0.660	4.44	0.124	0.953

Denotes input to analysis

Conclusions

- Have made progress analyzing observed temperatures to obtain thermal conductivity.
- Some of the data produced unusual results that may arise from measurements not meeting the assumptions.
- Work to do includes:
  - Compare measured effective thermal conductivity to models.
  - Develop a detailed description of the temperatures and local material RH for the DEs completed to date.

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SRNL DE – Can Analysis

Josh Ziska, Zane Nelson, Kerry Dunn, Robbie Garritano,
Thaddeus Reown, Vickie Timmerman

January 25-26, 2011

3013 Surveillance & Monitoring Program Review

Annual Meeting

EM Office of Environmental Management

Summary of Can Visual Analysis FY10

N/A = No Additional

Run	3013 ID	Analyze	Inner	Convenience
FY10DE1	H004251	N	N/A	N/A
FY10DE2	H002496	Y	N/A	Lid, Body
FY10DE3	H003710	Y	Body Near Lid	N/A
FY10DE4	H003655	N	N/A	N/A
FY10DE5	H002447	N	N/A	N/A
FY10DE6	R610627	N	N/A	N/A
FY10DE7	H003900	N	N/A	N/A
FY10DE8	H003650	Y	N/A	Lid, Body
FY10DE9	H002567	N	N/A	N/A
FY10DE10	H002728	N	N/A	N/A
FY10DE11	H002786	N	N/A	N/A
FY10DE12	H003077	N	N/A	N/A
FY10DE13	H003367	Y	N/A	Lid, Body
FY10DE14	H003704	N	N/A	N/A
FY10DE15	R610785	N	N/A	N/A
FY10DE16	R610826	N	N/A	N/A
FY10DE17	R610853	N	N/A	N/A
FY10DE18	S001721	N	N/A	N/A

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MATERIALS SCIENCE AND TECHNOLOGY DIRECTORATE 2

FY10DE2 H002496 Information

Package Information	
Bin	Pressure & Corrosion
Type	Engineering Judgment Foreign Material
TGA	0.252wt%
Total Actinides	51.80%
Prompt Gamma	Chlorides Not Detected

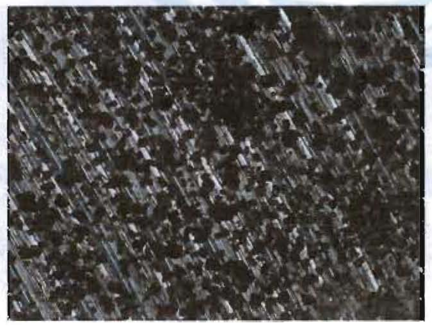
DE Data	
Gas Analysis (GEST) (Vol%)	He-54.3 N_2-44.4 H_2-1.3 O_2-<0.1 CO_2-ND CH_4-ND
Gas Pressure (GEST) (psia)	11.6
TGA/MS	TGA(0.34%) MS (0.17%)
IC (µg/mL) (Leach)	F-75 Cl-3465 NO_3-960 PO_4-<30 SO_4-1305
ICP/ES (µg/mL) (Leach)	Ca-5690 K-538 Mg-<8.6 Na-587

SRNL 3

FY10DE2 H002496 - 6866C Inside Top

SRNL 4

FY10DE2 H002496 - 6866C Inside Top



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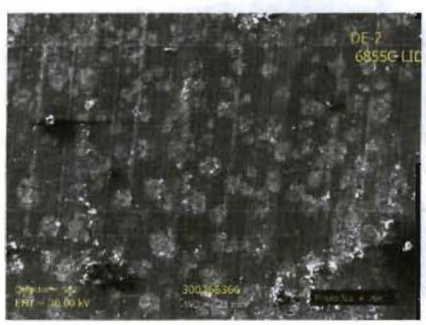
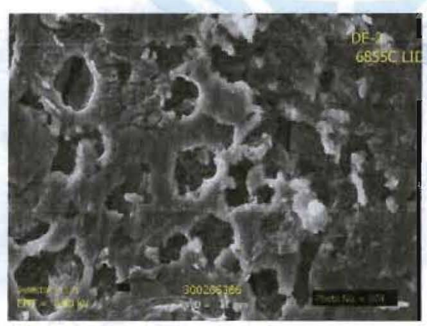
FY10DE2 H002496 - 6866C Inside Top





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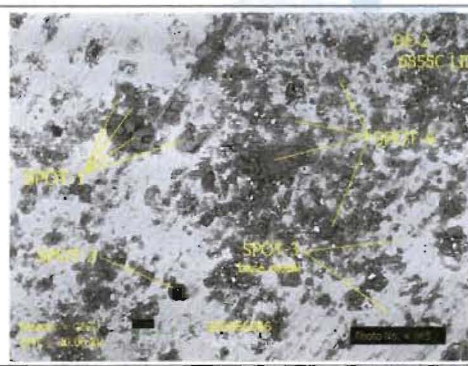
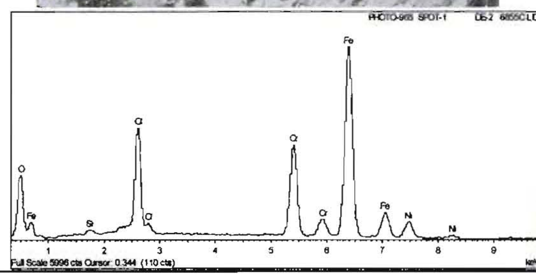
FY10DE2 H002496 - 6866C Inside Top





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FY10DE2 H002496 - 6866C Inside Body

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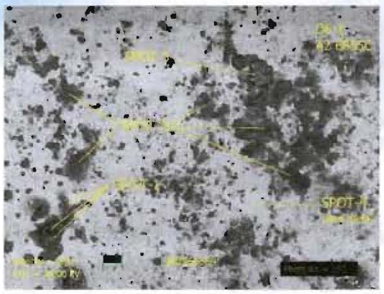
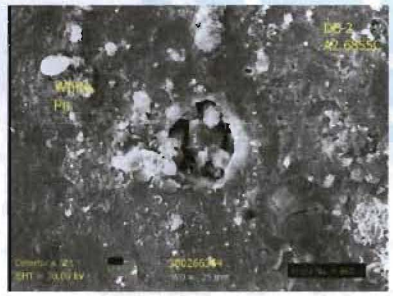
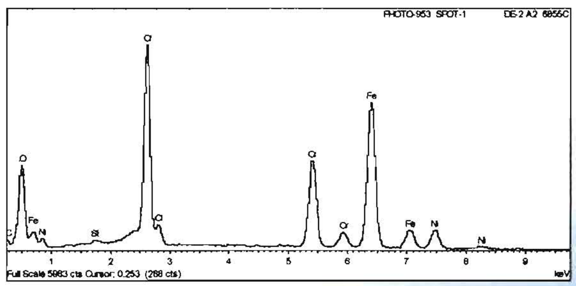
FY10DE2 H002496 - 6866C Inside Body







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FY10DE3 H003710 Information

Package Information		DE Data	
Bin	Pressure & Corrosion	Gas Analysis (GEST) (Vol%)	He-39.8 N_2-34 H_2-25.7 O_2-<0.1 CO_2-0.4 CH_4- <0.1
Type	Random ARF - Highest Water by Mass Spec	Gas Pressure (GEST) (psia)	16.6
TGA	0.34wt%	TGA/MS	TGA(0.55%) MS (0.30%)
Total Actinides	72.45%	IC (μg/mL) (Leach)	F-<164 Cl-63350 NO_3-374 PO_4-<150 SO_4-479
Prompt Gamma	8.6% Chlorides	ICP/ES (μg/mL) (Leach)	Ca-12 K-33200 Mg-1745 Na-19850

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FY10DE3 H003710 8011B Inner Can

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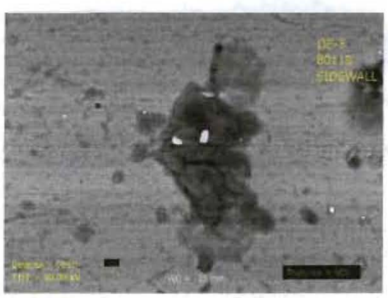
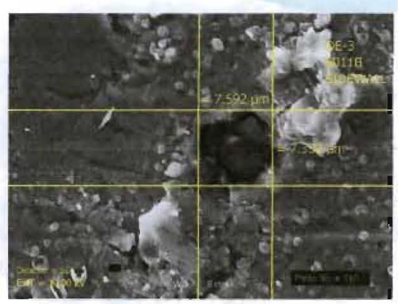
FY10DE3 H003710 8011B Inner Can





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FY10DE8 H003650 Information

Package Information	
Bin	Pressure & Corrosion
Type	Engineering Judgment High Moisture-Storage Wt. Gain (IAEA swap)
TGA	0.34wt%
Total Actinides	75.63%
Prompt Gamma	4.4% Chlorides

DE Data	
Gas Analysis (GEST) (Vol%)	He-52.2 N_2-30.9 H_2-16.9 O_2-<0.1 CO_2-ND CH_4-ND
Gas Pressure (GEST) (psia)	12.8
TGA/MS	TGA(0.38%) MS (0.16%)
IC (µg/mL) (Leach)	F-75 Cl-37400 NO_3-<150 PO_4-<150 SO_4-331
ICP/ES (µg/mL) (Leach)	Ca-265 K-20450 Mg-654 Na-12200

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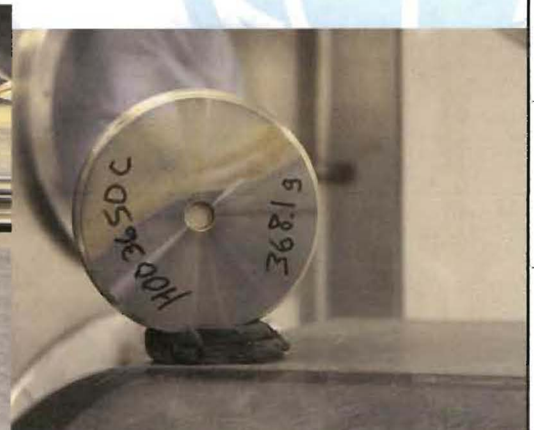
FY10DE8 H003650 6870C Convenience Can



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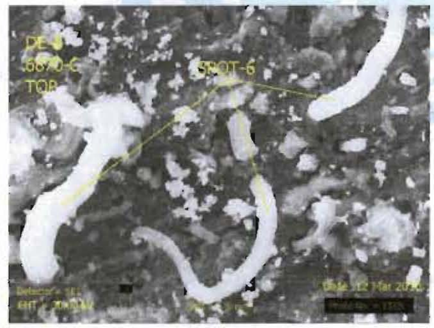
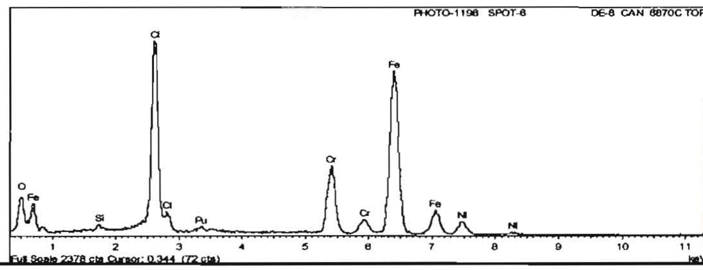
FY10DE8 H003650 6870C Convenience Can





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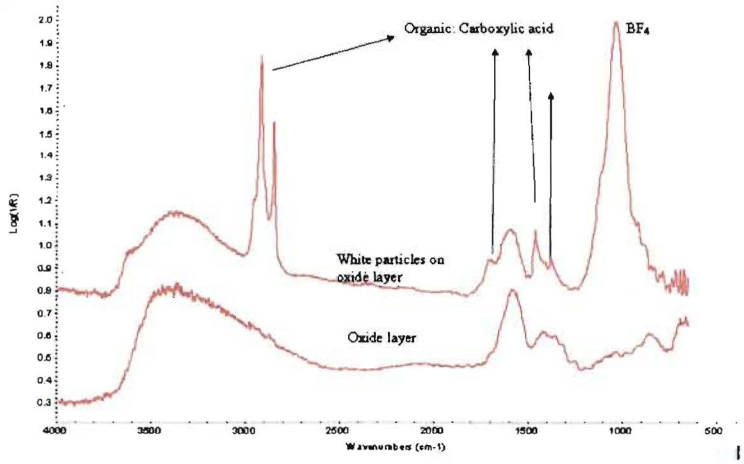
FY10DE8 H003650 FTIR 6870C Convenience Can



The area of the sample that had the "white" rods contains fluoride (like BF4) and organic material (like oxidized paraffin). There are possible amines in this sample. A phosphate could not fit the 1039 cm-1 peak.

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FY10DE13 H003367 Information

Package Information	
Bin	Pressure & Corrosion
Type	Random
TGA	0.26wt%
Total Actinides	52.47%
Prompt Gamma	0.52% Chlorides

DE Data	
Gas Analysis (GEST) (Vol%)	He-61.2 N_2-38 H_2-0.78 O_2-<0.1 CO_2- <0.1 CH_4-ND
Gas Pressure (GEST) (psia)	11.5
TGA/MS	TGA(0.46%) MS (0.22%)
IC (μg/mL) (Leach)	F-<88.5 Cl-8355 NO_3-222 PO_4-<30 SO_4-2500
ICP/ES (μg/mL) (Leach)	Ca-7915 K-3090 Mg-<12.3 Na-2240

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New Capabilities Borescope

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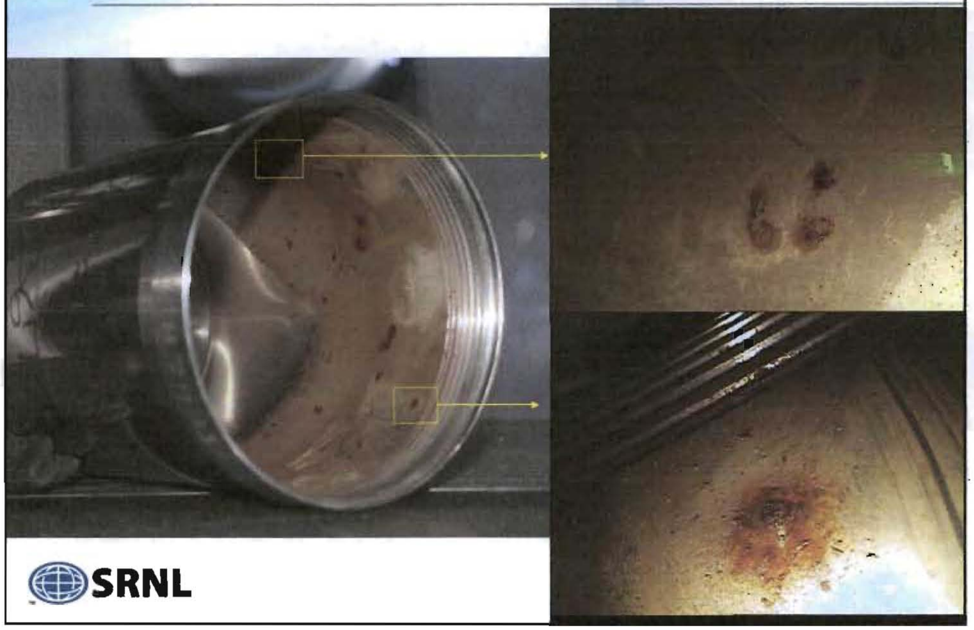
FY10DE13 H003367 7431C New Capabilities



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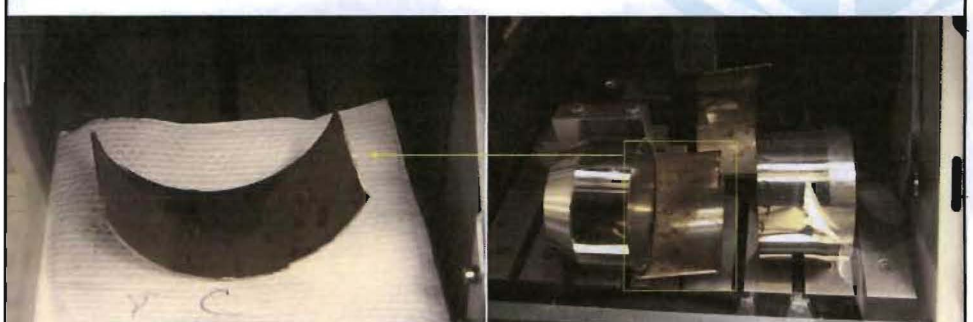
FY10DE13 H003367 7431C Convenience Can



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Summary of Can Visual Analysis for FY10

- Analyses performed with Zero Incidents and No Contamination Cases
- Total of 18 Cans examined in FY10
- No evidence of stress corrosion cracking seen
- No corrosion on any outer can
- No reason to doubt 50 year life for package

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Analytical Tests Summary

D. M. Missimer
Principal Engineer
January 2011

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Analytical Tests

Powder

- Scanning Electron Microscopy with X- ray Fluorescence (SEM/EDS)
- X-ray Diffraction (XRD)

Leachate Solutions

- Inductively Coupled Plasma Emission Spectroscopy (ICP-ES)
- Ion Chromatography (IC)

Acid Digestion Solutions

- Inductively Coupled Plasma Emission Spectroscopy (ICP-ES)
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- Radiochemistry

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SEM/EDS

Particle Size Distribution

- Very heterogeneous materials

	Particle Size		Particle Size
H004251	1-570µm	H002728	1-249µm
H002496	1-520µm	H002786	1-264µm
H003710	1-223µm	H003077	1-218µm
H003655	1-204µm	H003367	1-340µm
H002447	<1-110µm	H003704	1-209µm
R610627	1-657µm	R610785	1mm-1.3mm
H003900	1-535µm	R610826	1-512µm
H003650	1-888µm	R610853	1-216µm
H002567	1-604µm	S001721	<1-927µm

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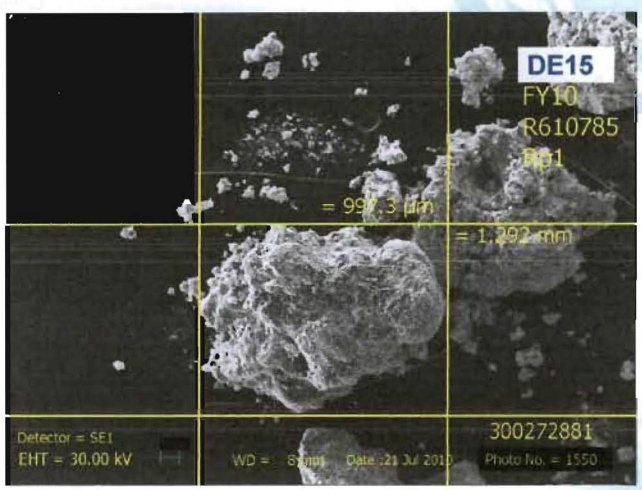
SEM/EDS



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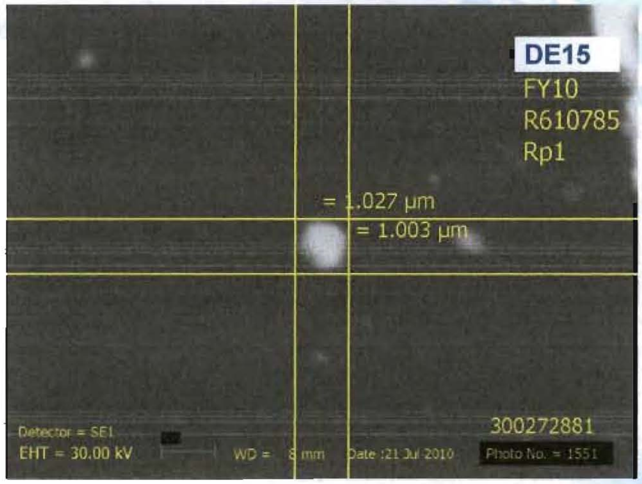
SEM/EDS



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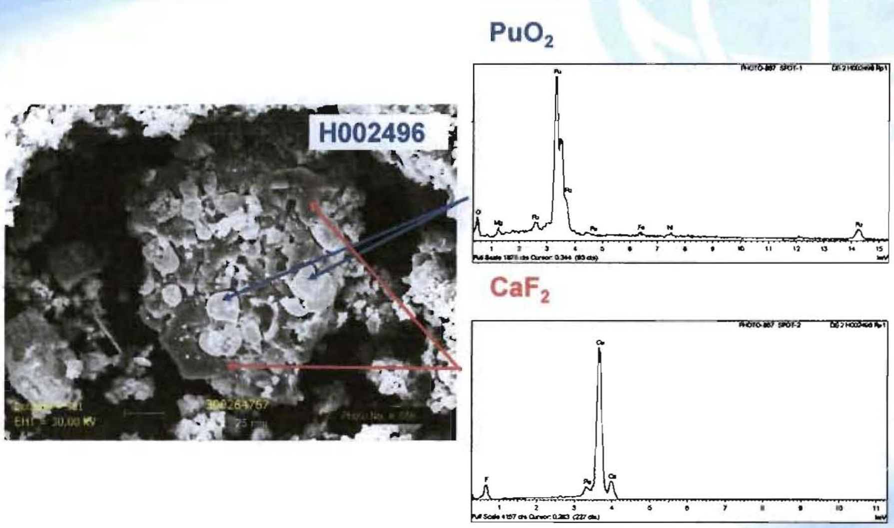

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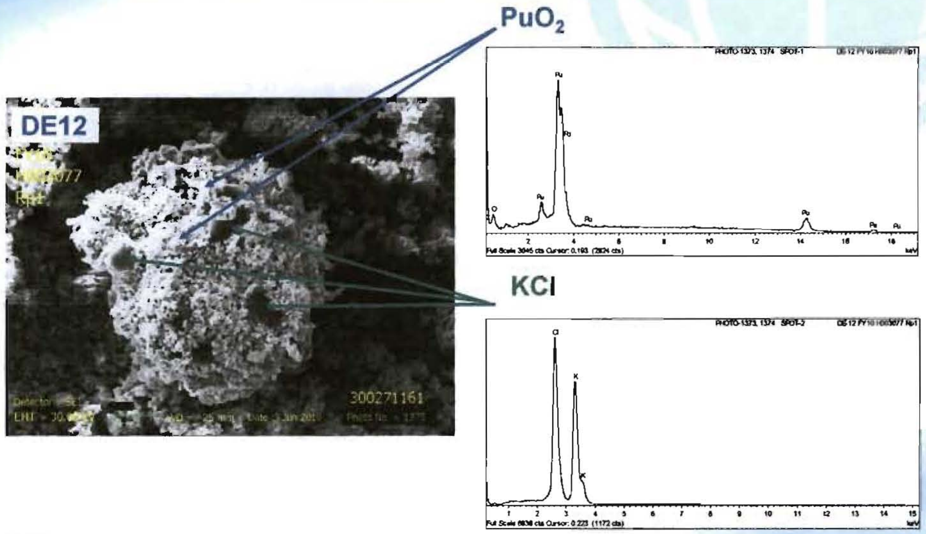
SEM/EDS



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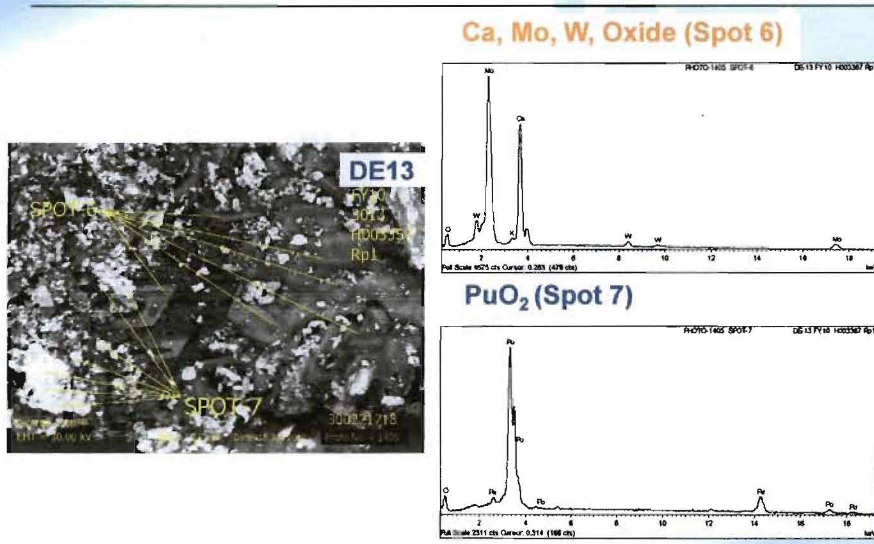
SEM/EDS



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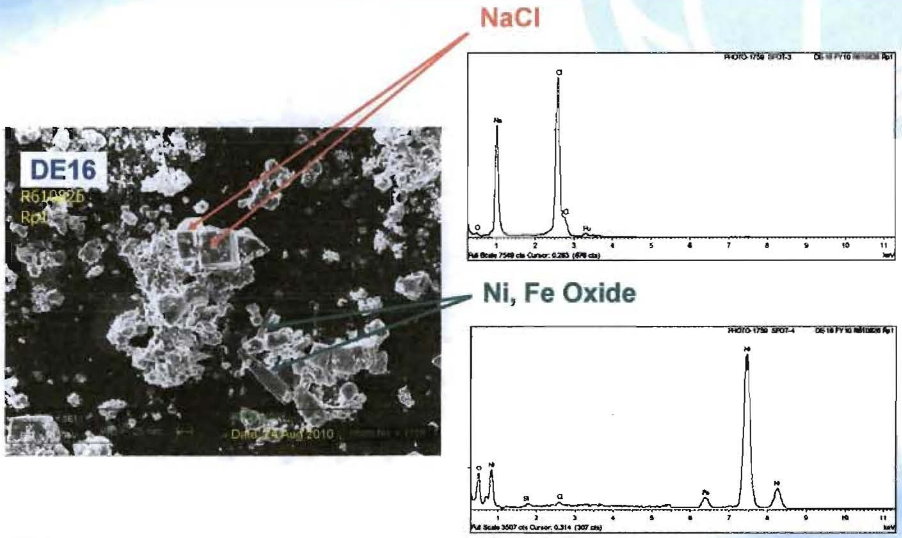

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X-ray Diffraction

Oxide Powder

- **XRD LOD: ~0.2wt%**
  - Depends on mass absorption coefficient & symmetry
- **Actinides**
  - PuO_2
- **Salts**
  - NaCl – DE1, DE3 – DE9, DE12, DE13, & DE18
  - KCl – DE1, DE3 – DE9, DE12, DE13, & DE18
  - CaF_2 – DE2 and DE13
- **Corrosion/Oxidation Products**
  - NiO, $NiCr_2O_4$, & Fe_3O_4 – 10 cans
- **Misc**
  - Tungstates – DE13
  - $Ca_2Ta_2O_7$ – DE9
  - MgO – DE1- 2, DE4 -7, DE10, DE13, DE16
  - $Ca_4Si_2O_7F_2$ – DE2

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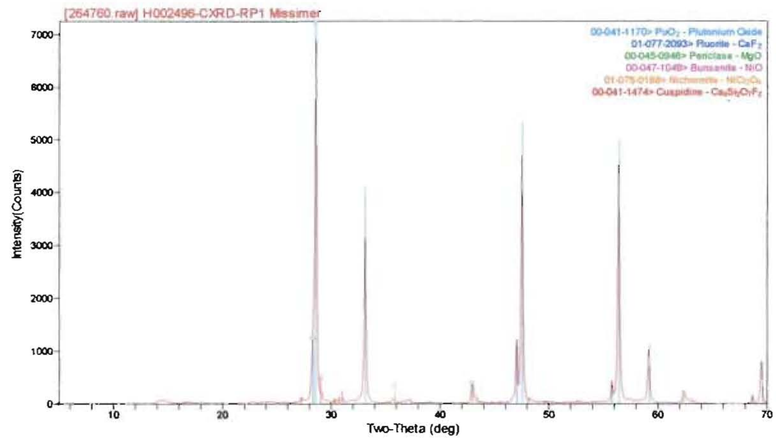
X-ray Diffraction

H002496



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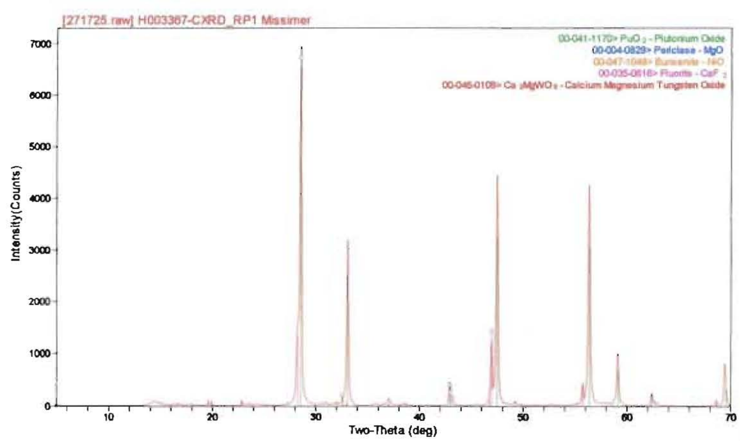
X-ray Diffraction

H003367



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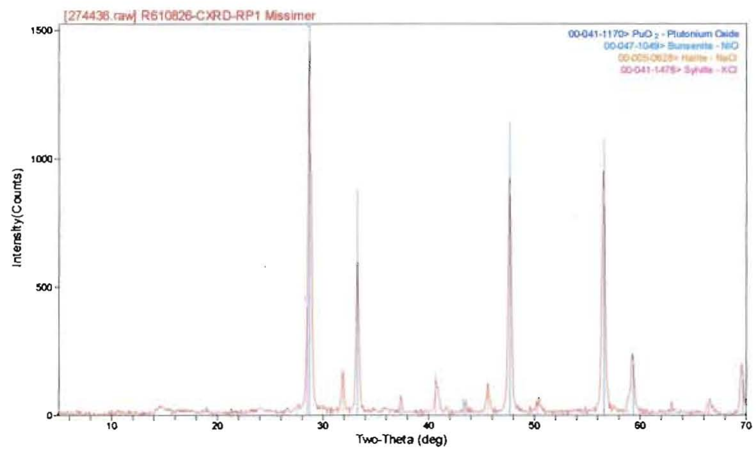
X-ray Diffraction

R610826



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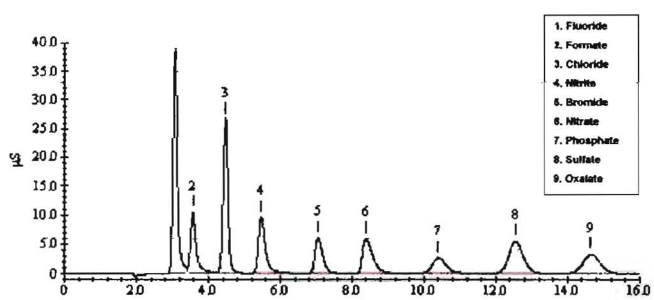
Ion Chromatography

Leachate Solution

Oxide leached for 3-hr at 90 °C in deionized water

- F^-, Cl^-, NO_3^-, PO_4^{-3}, & SO_4^{-2} were reported
- $COOH^-$, Br^-, NO_2^-, & $C_2O_4^{-2}$ were also analyzed, but not detected



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Ion Chromatography

- **Fluoride**
  - Water soluble only
  - <~150 (LOD)
  - The limit of detection is dependent on the Chloride concentration.
  - 164-µg/g (H00371)
- **Chloride**
  - <~150-µg/g (LOD)
  - 211-µg/g H002567 – 17.6 wt% R610627
- **Nitrate**
  - <~150 (LOD)
  - 80-µg/g R610826 - 2690-µg/g H003900
- **Phosphate**
  - < ~150-µg/g (LOD)
  - 240-µg/g in H004251
- **Sulfate**
  - All cans had detectable sulfate: 60 – 2500-µg/g H003367
  - Many sulfates don't decompose until 900 – 1000 °C

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ICP-ES

Although 25 elements were analyzed only the following were checked & reported for the DE program:

- **Salts**
  - **Ca, Mg, K, & Na**
- **Corrosion/Oxidation Products**
  - **Al, Cr, Fe, & Ni**
- **RCRA**
  - **Ag, Ba, Cd, & Pb**

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ICP-ES

	H002496		H003367		R610826		
	Leach µg/g	Dissolution µg/g	Leach µg/g	Dissolution µg/g	Leach µg/g	Dissolution µg/g	
Ag	<12.0	<160	<2.22	<68.6	3.56	<120	
Al		2530		2265		364	
Ba	4.835	45.85	2.17	100	50.55	<95	
Be	<0.994	66.45	<0.0832	76.8	<1.32	1305	
Ca	5690	89900	7915	75050	4340	5865	CaF_2
Cd	<0.731	<80.0	<0.994	<134	<1.00	<134	
Cr	1297	8190	3720	7205	<1.26	870	$NiCr_2O_4$
Fe	<0.760	12700	<1.25	6550	<2.52	3685	Fe_2O_3
K	538	<198	3090	2830	72450	65250	KCl
Mg	<8.56	19900	<12.3	24550	3855	12800	MgO
Na	588	1030	2240	3990	42200	42400	NaCl
Ni	<4.99	18850	<2.80	30150	1300	8960	NiO
Pb	<42.4	<640	<8.69	848	<8.77	<470	

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ICP-MS

- **Limitations**
  - 1-amu resolution for quadrupole mass spectrometer
  - Can't separate Pu^{238} from U^{238}, Pu^{241} from Am^{241}, etc
  - Isobaric interferences from gas species, doubly charged ions, oxides, chlorides, etc.
  - Only masses >80 and above routinely measured
- **Strengths**
  - Excellent sensitivity, especially for heavy masses (Ag, Ba, & Pb)
  - Isotopes with half lives >200,000-yr half life (Th^{232}, U^{235}, U^{238}, Np^{237}, & Pu^{242})
- **Masses 80 – 243 were analyzed and are available.**
- **Masses from 230 – 243 (actinides) were quality checked and reported for the DE program.**

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ICP-MS

	H002496	H003367	R610826
Mass	µg/g	µg/g	µg/g
230	<3.99	<4.01	<6.03
232	15.85	<16.0	9.11
233	<3.99	<8.02	<4.02
234	23.3	41.8	36
235	1505	3165	2620
236	114	130	100
237	61.8	58.0	54.2
238	646	548	158
239	437500	328000	456000
240	29500	21750	30350
241	1725	1235	1680
242	136	96.35	156
243	<3.99	<4.01	<6.03
244	<5.99	<4.01	<4.02

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Radiochemistry

		H002496	H003367	R610826
Gross Alpha		7.25E+10 dpm/g	7.12E+10 dpm/g	8.42E+10 dpm/g
Alpha PHA				
	Pu^{238} + Am^{241}	13.5%	12.5%	12%
	Pu^{239} + Pu^{240}	86.5%	87.5%	88%
Gamma Scan				
	Pu^{238}	0.008%	0.009%	0.010%
	Pu^{239}	94%	94.2%	94.1%
	Pu^{240}	5.86%	5.71%	5.82%
	Pu^{241}	0.086%	0.072%	0.088%
	Am^{241}	1380-µg/g	1135-µg/g	1330-µg/g

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Comparing Radiochemistry and ICP-MS

	RadChem Total Pu wt%	ICP-MS wt%
DE1	58.27	53.68
DE2	41.80	46.70
DE3	52.90	60.13
DE4	43.85	51.79
DE5	66.73	60.30
DE6	49.40	47.18
DE7	39.20	39.79
DE8	53.42	52.42
DE9	48.87	52.68
DE10	58.80	58.87
DE11	53.23	49.27
DE12	72.83	73.06
DE13	41.59	44.20
DE14	60.99	58.13
DE15	61.96	60.38
DE16	49.39	48.64
DE17	74.35	74.75

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Acknowledgements

IC: Tom White, Boyd Wiedenman, Jackie Rourk, Joyce Cartledge, Steve Moody

ICP-ES: Mark Jones, Loretta Farrow, Steve Moody

ICP-MS: Curtis Johnson & Steve Moody

Radiochemistry: Ceci Diprete, Dave Diprete, Mira Malek, Surjeet Bhutani, Sandee Wells, Viet Nguyen, Beverly Birch, Gina Robbins, Kathy Smith, Amanda Daniels, Dean Nowak, Amanda Sadler, Dan Walker

Sample Management: Leigh Brown

SEM/EDS: Mike Summer, Henry Ajo, & Jack Durden

XRD: Ronny Rutherford

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3013 - Destructive Examination Oxide Analyses

G. F. Kessinger
Separations & Actinide Science Programs
SRNL
January 2011

3013 Surveillance and Monitoring Program Review

S&ASP FY10 Destructive Examination Activities

- **Received 18 DE Oxide Samples**
- **Performed suite of analyses**
  - Pycnometry
  - Bulk & Tapped Density
  - Surface Area Analysis
  - Carbon/Sulfur Analysis
  - Thermogravimetric Analysis-Mass Spectrometry
  - Acid Dissolution
  - Aqueous Leaching

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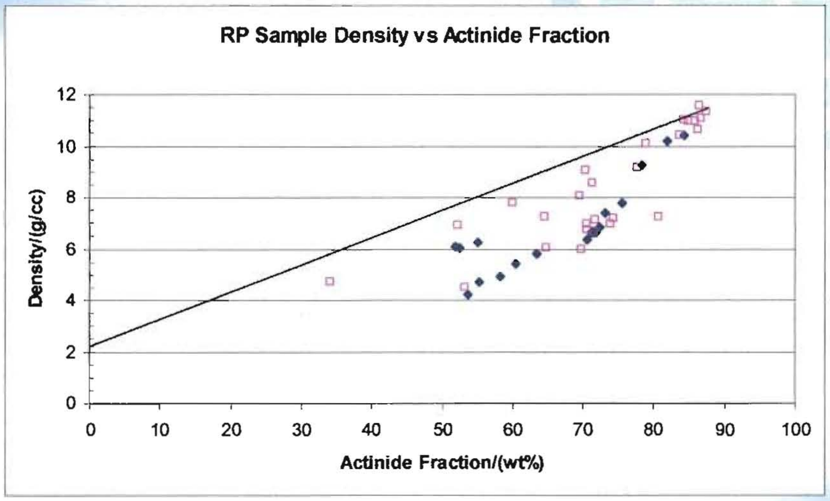
Pycnometry



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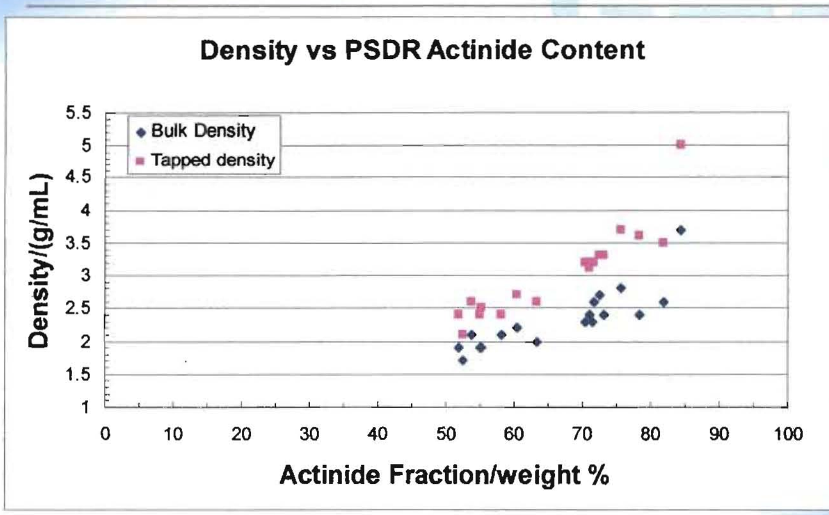
Bulk & Tapped Density



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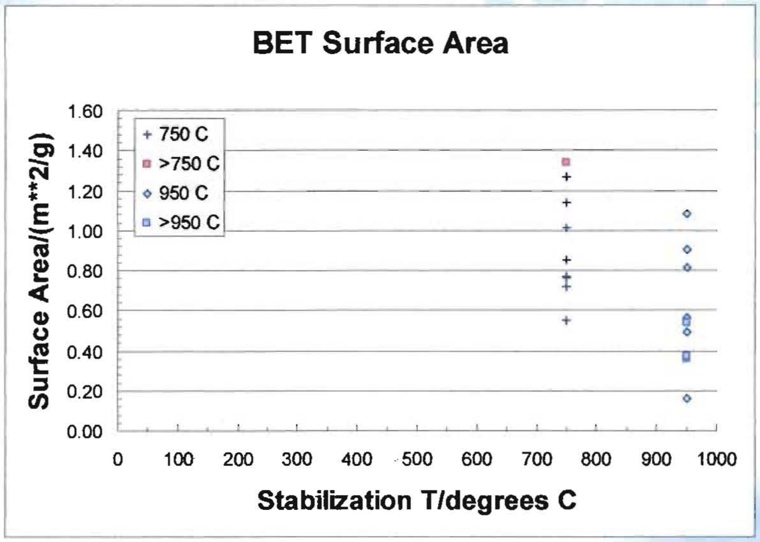
Surface Area Analyses



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Carbon-Sulfur Analyses

- **[C] > 400 µg/g**
  - H004251 (RF oxide) – 540 µg/g
  - H002496 (PFP scrap<80%) – 1200 µg/g
  - R610627 (screenings from Pu oxidation) – 970 µg/g
  - H002567 (RF oxide) – 8100 µg/g
    - SiC in XRD
  - R610826 (screenings from Pu oxidation) – 2300 µg/g
- **[S] > 400 µg/g**
  - H002496 (PFP scrap<80%) – 1400 µg/g
    - sulfate in leachate
  - H003367 (RF oxide) – 2100 µg/g
    - sulfate in leachate

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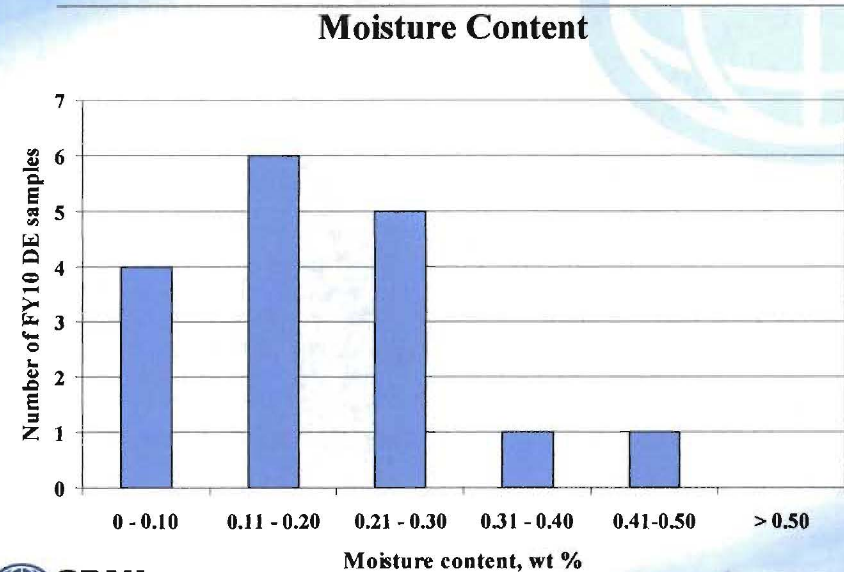
3013 Surveillance and Monitoring Program Review 6

TGA-MS Moisture Measurements



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TGA-MS Moisture Measurements

- **IM measurements of all items below 0.50 wt% H_2O**
  - One item (H003704 , RF oxide) in 0.41 – 0.50 wt% range
    - 0.41% H_2O
    - 9% Cl^-
  - One item (H003655, RF oxide) in 0.31 – 0.40 wt% range
    - 0.31% H_2O
    - 7% Cl^-

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Dissolution Flowsheet

- **No changes to dissolution flowsheet in FY10**
  - Two duplicate dissolutions
  - 12 M HNO_3-0.2 M HF dissolution media
  - Heated for 3 hours at ~95 °C
  - H_3BO_3 added near end of heating cycle (~165 min.)
- **Analyses**
  - Aqueous fraction: ICP-ES, ICP-MS, Radiochemistry
  - Insoluble fraction: XRD, SEM (sometimes)

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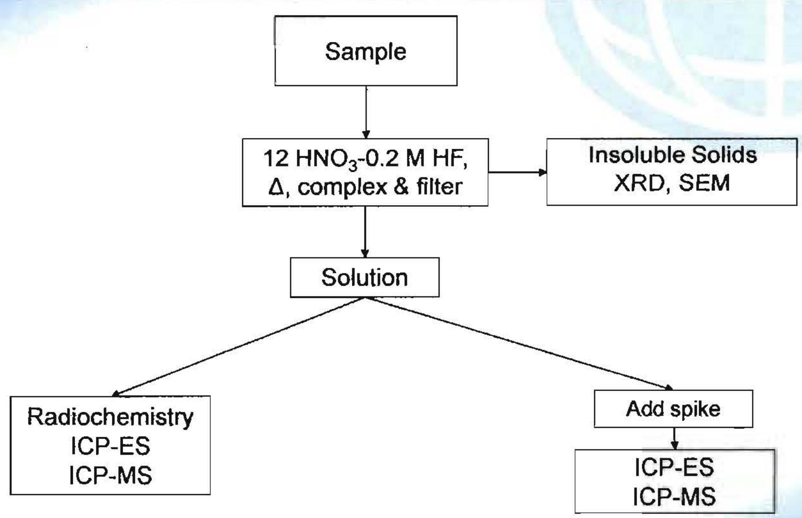
Complexed Dissolution



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Aqueous Leach Flowsheet

- **No changes to leaching flowsheet in FY10**
  - Two duplicate leaches
  - DI-H_2O dissolution media
    - ~18 MΩ H_2O
  - Heated for 3 hours at ~90 °C
- **Analyses**
  - Aqueous fraction: IC, ICP-ES
  - Insoluble fraction: no analysis
    - solids are retained until aqueous results are reviewed

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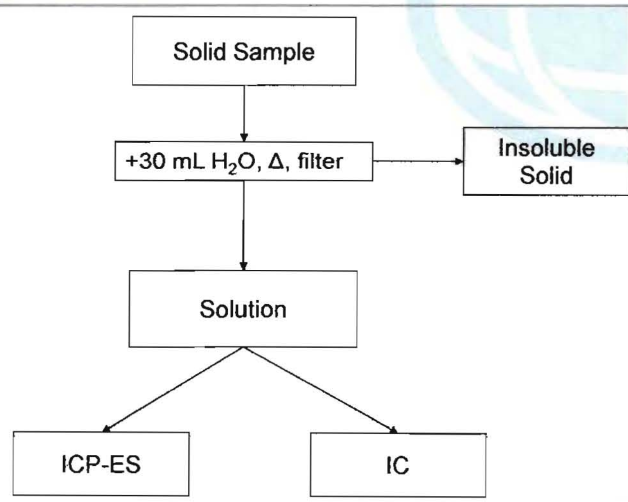
Leaching Flowsheet



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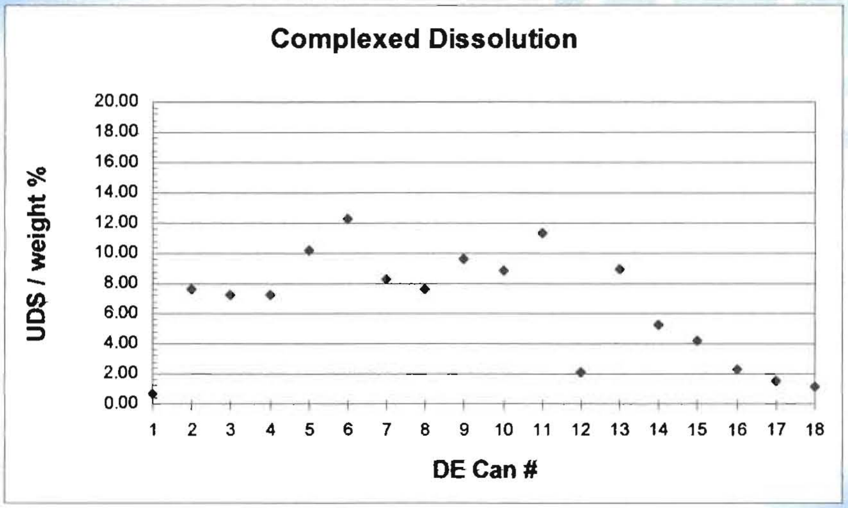
Dissolution Results



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Dissolution Results

- **Three dissolutions resulted insoluble fraction of 10% or more of initial sample mass**
  - H002447 (RF oxide) – 10% insoluble
    - PuO_2 and $Pu_3F_{12}{\bullet}H_2O$
    - ~1 wt% H_2O-soluble Cl^-
  - R610627 (screenings from Pu oxidation) – 12% insoluble
    - $Pu_3F_{12}{\bullet}H_2O$ in XRD
    - ~17 wt% H_2O-soluble Cl^-
  - H002786 (RF oxide) – 11% insoluble
    - PuO_2 and $Pu_3F_{12}{\bullet}H_2O$
    - ~7 wt% H_2O-soluble Cl^-

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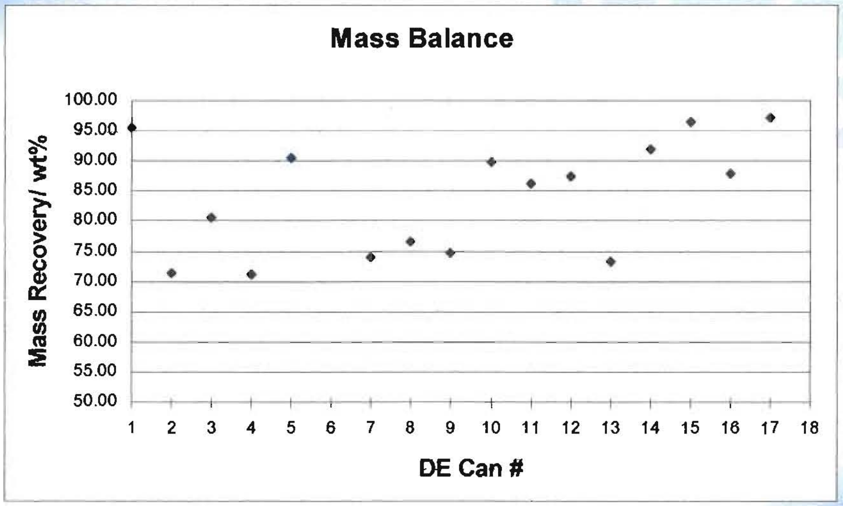
Mass Balances



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Mass Balances

- **Five below 75 wt%**
  - H002496 (PFP scrap<80%)
    - 52% actinide, 9% Ca, 1%> Cl
  - H003655 (RF oxide)
    - 71% actinide, 7% Cl
  - R610627 (screenings from Pu oxidation)
    - 54% actinide, 17.5% Cl
  - H002567 (RF oxide)
    - 55% actinide, 2% Fe, 2% Na, 1% C, 0.02% Cl
  - H003367 (RF oxide)
    - 52% actinide, 8% Ca, 2% Mg, 1% Cl

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Conclusions

- Densities fall in the expected range and measurements appear to be internally consistent
- Surface areas appear to be a function of stabilization temperature
- High carbon content is not always traceable
- IM results for all items below 0.50 wt% H_2O
- Complexed dissolution appears adequate
- Mass balances generally good
- Based on these (and previous 3 years of results), some analyses were slated for reduction or elimination (to be discussed during upcoming presentation).

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Collaborators

Technical Assistants:

Mike Lee	Wanda Matthews	Betty Mealer
Dianne Scott	Shirley McCollum	Mona Blume

Scientists/Engineers:

Mike Bronikowski	Mark Crowder	Fernando Fondeur
John Scogin	Kim Crapse	Nick Bridges

Specialists:

Angela Bowser	Patrick Westover	Sabrina Emory

Manager:

Sam Fink (Separations & Actinide Science Programs)

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Initial DE of H003328
Hanford High Water Can

Laura Worl, Kirk Veirs, Josh Narlesky, John Berg, Matt Jackson, Dennis Padilla, Lynn Foster, Leonardo Trujillo, Alex Carrillo
Plutonium Science and Manufacturing (PSM) Directorate

Ted Venetz, Hanford Site
Suzanne Clarke, DOE-RL

3013 Surveillance and Monitoring Program Review
Savannah River Site,
January 24-25, 2011

Hanford Can H003328

Material:	Rocky Flats Oxide, C-Line, ARF, 750°C	
Stabilization End Date:	9/25/2003	
Packaging RH	33%	
Duration in boat (A)	64 hrs	
Duration of storage wt gain (B)	51 hrs	
Wt. Gain	0g	
Convenience Can		
Package Date:	9/28/2003	
Inner Can Weld Date:	9/30/2003	
Assay:	Pu	74.9%
	Am	0.22%
Moisture (Hanford TGA):	0.48-0.53%	
Prompt Gamma: Hanford% (LANL %):	Cl	4.38 (3.26)
	Mg	0.56 (0.29)
	Na	0.89 (0.67)
	K	nd (1.84)

Venetz, T.J.; Berg, J.M.; Narleksy, J.E; Veirs, D.K., McClard, J.W., "Evaluation of Hanford Item Potentially Packaged in Excess of DOE-STD-3013 limit for Moisture A review by Subject Matter Experts, Sept. 2008, HNF-39080

Processing Flow Diagram

H003328 → NDE → Gas Sampling → Open Outer Container → Open Inner Container → Material Evaluation

Open Outer Container → Visual Inspection and Photograph → Ship to SRS

Open Inner Container → Visual Inspection and Photograph → Ship to SRS

Hanford Assembly

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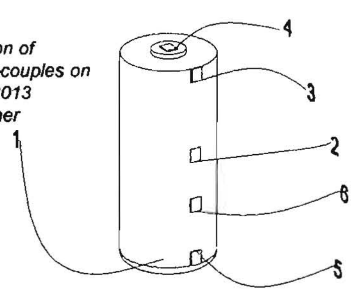
NDE: *Temperature of 3013 container in a 9975*

H003328 in 9975. Lids of PVC, SCV, and 9975 set in place allowing egress of TC wire.

Position	48 hours	Thermal model
Center top	33	
Center bottom	39	
Side wall top	34	38
Side wall midpoint	36	40
Side wall bottom	36	38
Side wall between midpoint and bottom	37	
9975 outside wall	20	
9975 outside lid	20	

Mass	2.4 kg
Total thermal output	5.0 W
Material specific wattage	2.7 W kg^{-1}
Pu content	76%
PuO2 content	86%
Salt content	14%
Density (estimated)	3 gcm^{-3}

Location of thermocouples on outer 3013 container



Berg, J.M., N. K. Gupta, B. Nguyen, J. E. Narlesky, F. C. Prenger, L.E. Traver, and D.K. Veirs. 2010. Thermal Gradients and the Potential to Form Liquids in 3013 Containers. *Journal of Nuclear Material Management 37.*

Analytical equations yield conservative wall temperatures in this test.

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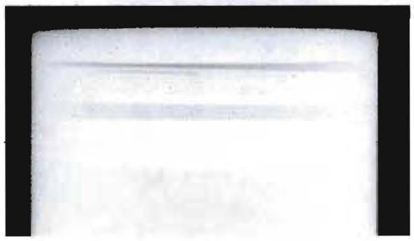
NDE: *Radiography*



Kenn Gibbs and Lynn Foster developed a method at LANL to collect lid deflection information such that the baseline radiograph and LANL radiograph could be compared to estimate an internal pressure (± 20 psig or ± 2 mils)

Variations Hanford vs. LANL include:

- 400 kV xray vs. 225 kV
- Source to can: 50 in vs. 25 in
- Frequency of images and averages of values

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Gas Sample

- Completed practice test with empty Hanford assembly (H003282) welded at SRS on 9/7/10
  - Inner and outer containers had ~10% He, detectable H_2 (0.01 and 0.06%) and balance of air
- H003328 gas sample of inner and outer 3013 on 9/13/10

	CP-H003382-I1	CP-H003382-I2	CP-H003382- O1
CO2	0.00%	0.00%	0.00%
He	14.18%	14.23%	91.87%
H2	74.34%	74.42%	0.10%
O2	0.13%	0.02%	0.15%
N2	11.35%	11.33%	0.80%
CH4	0.0%	0.0%	0.0%
Can Pressure	43.4 psia		13.4 psia

MIS Prediction… "The most likely total pressure within the inner container is between 29-65 psig …. The most likely estimate of the hydrogen pressure is between 60 and 24 psia."

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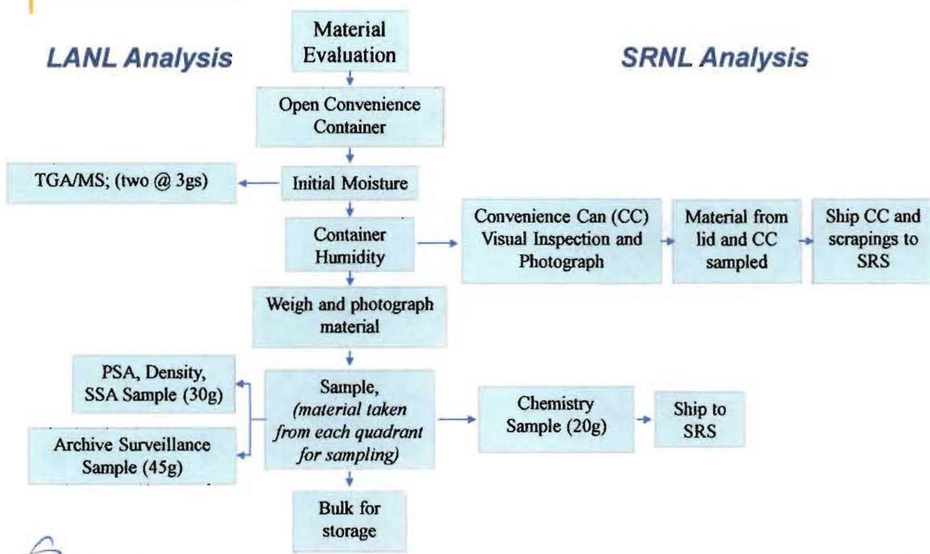
Material Evaluation



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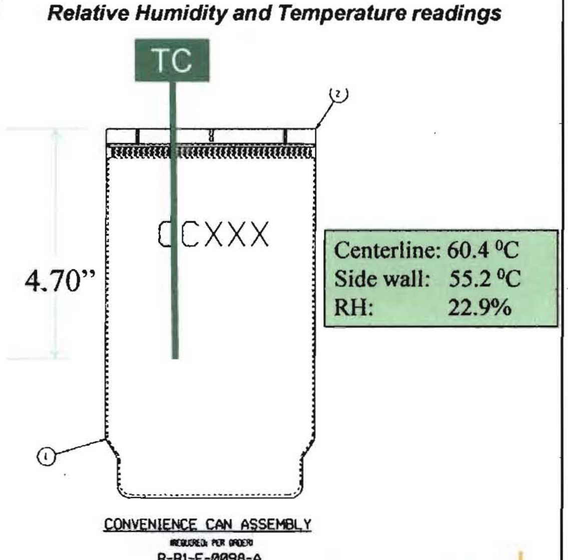
Cutting the outer and inner 3013 container and initial measurements were time sensitive.

3013 Container Cutting Equipment

Relative Humidity and Temperature readings



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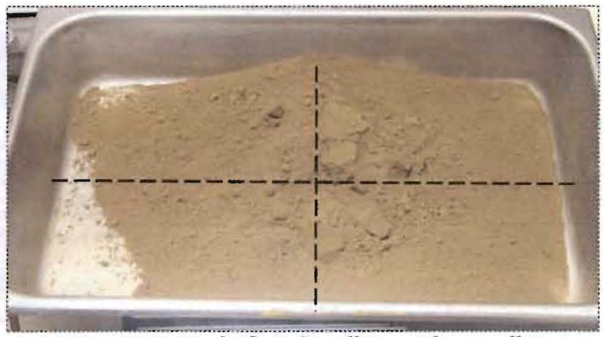
H003328 Material Images and Sampling

- **Initial moisture samples: 4 grams collected quickly from middle and side locations, stored in gas tight containers**
- **Representative samples collected from four quadrants of material spread into pan, stored in gas tight containers**

Oxide in Hanford CC



Oxide in pan before leveling and sampling

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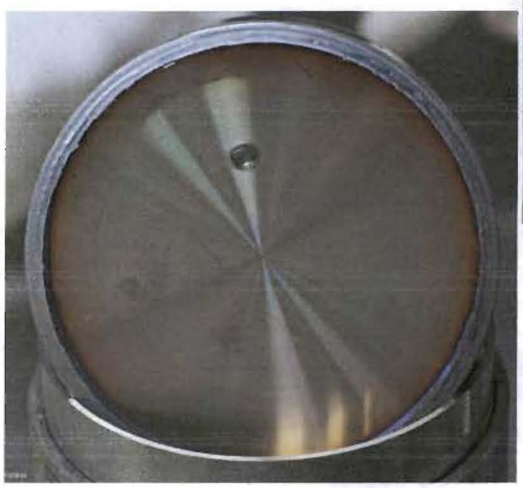
Outer 3013 Images



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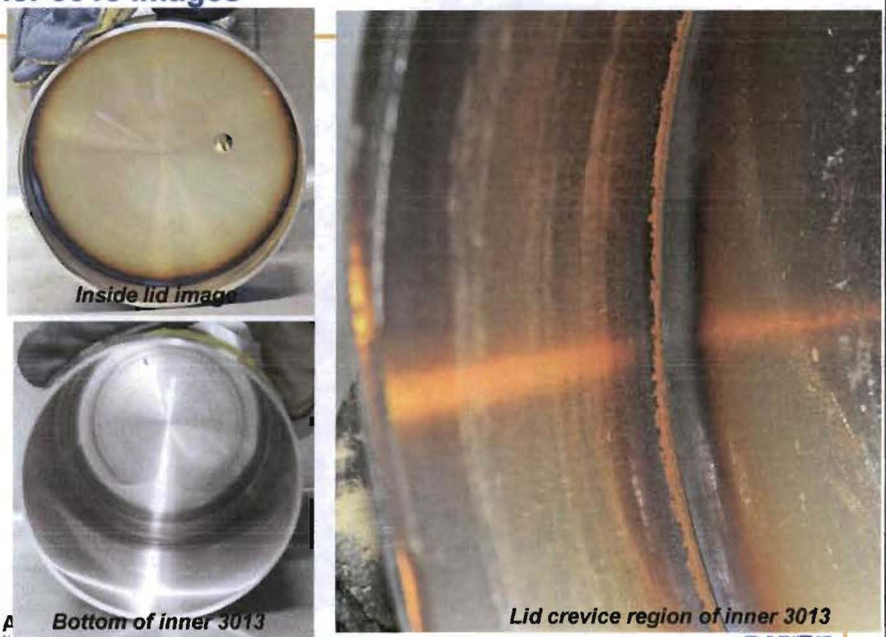
Inner 3013 Images



Convenience Can Images: outside lid showing filter

Filter region where tape was used at LANL to seal container before RH measurement, Residue was removed with tape

Convenience Can: inner images

Lid thread region

Bottom of CC lid

Convenience Can

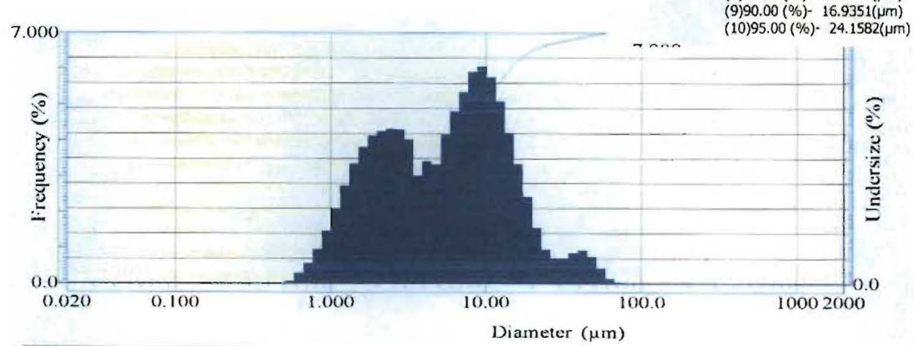
- Inside bottom image with Pu oxide removed
- 0.3 g Pu measured with long neutron multiplicity count

Particle Size Analysis

Form of Distribution :Manual
Distribution Base :Volume
Sampling Times(Li
Median : 5.8305(μm)
Mean : 8.2840(μm)
Mode : 9.4197(μm)
Span : 2.6605

Diameter on % :(1)5.000 (%)- 1.1232(μm)
(2)10.00 (%)- 1.4232(μm)
(3)20.00 (%)- 2.0190(μm)
(4)30.00 (%)- 2.7704(μm)
(5)40.00 (%)- 4.0138(μm)
(6)60.00 (%)- 7.6326(μm)
(7)70.00 (%)- 9.5958(μm)
(8)80.00 (%)- 12.1935(μm)
(9)90.00 (%)- 16.9351(μm)
(10)95.00 (%)- 24.1582(μm)

Multi-modal distribution with higher particle size changing with time.



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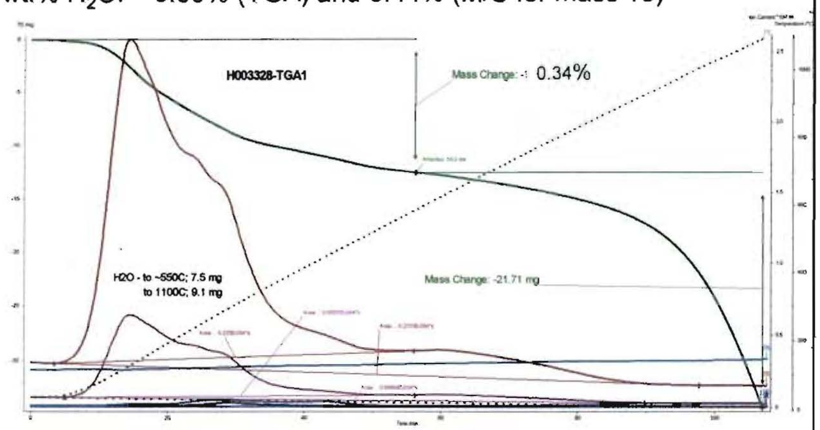
H003328 TGA-MS

Two Samples: one taken along wall (H003328-TGA2) and one from top center of material (H003328-TGA1)

TGA1, wt.% H_2O: 0.34% (TGA) and 0.24% (M/S for mass 18)

TGA2, wt.% H_2O: 0.50% (TGA) and 0.44% (M/S for mass 18)



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Summary

- Significant Hanford, LANL, SRNL efforts were critical for success;
- Results from Shelf-Life Surveillance materials allowed successful prediction of the total pressure and the hydrogen pressure;
- Successful demonstration of LANL's 3013 can punch equipment

- Highest RH and pressure observed in packaged 3013s
- Large amount of general corrosion observations in convenience can (CC)
- Evidence of corrosion seen outside of CC on filter and inner can lid crevice region

- Pending at LANL: specific surface area, pycnometer density, small scale surveillance loading, MIS-WG determination for loading in large scale or 3013 for SRS shipment; report on LANL results.
- Received OC, IC, CC and 20g oxide at SRNL last week.

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SRNL Corrosion Shelf Life Studies Update

Jon Duffey and John Mickalonis
January 25, 2011

3013 Surveillance and Monitoring Program Review
January 25-27, 2011

EM Office of Environmental Management

SRNL Radioactive Test Matrix

Test	H_2O Loading (wt %)	Loading RH (%)	Target Initial Container RH (%)	Temp (°C)	Storage Time (days)
1	0.55 – 0.60	75 max	N/A	25 – 30	75
2	0.55 – 0.60	75 max	N/A	25 – 30	<150
3	0.55 – 0.60	75 max	N/A	25 – 30	<225
4	0.10 – 0.11	20 - 45	15	25 – 30	TBD
5	0.18 – 0.19	20 - 45	20	25 – 30	TBD
6	0.22 – 0.25	20 - 45	25	25 – 30	TBD
7	TBD	TBD	TBD	TBD	TBD
8	TBD	TBD	TBD	TBD	TBD
9	TBD	TBD	TBD	TBD	TBD

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2

New Test Configuration

Use existing test container dimensions for existing heater slots

- Lid modified for RH probe
  - SS probe 0.25" o.d. by 3" long
  - 5% to 95% RH, -20 °C to 115 °C
- Probes modified to disconnect probe from electronics
- Most probes leaked around wires
  - Improved by sealing with epoxy

Limited volume for tear drop coupons only; no flat coupons

Solid contact and headspace

Glass container for visualization only

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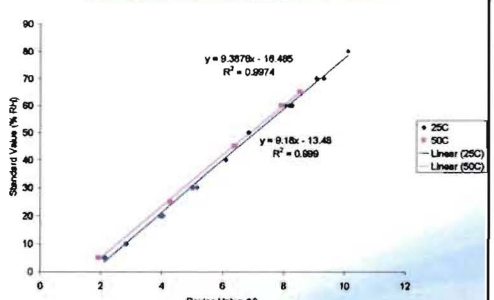
3

Sensor Calibrations

Pressure sensor and thermocouple response verified against calibrated M&TE instrumentation

RH probes calibrated using a programmable RH calibrator with chilled mirror moisture sensor

Additional calibration checks planned using saturated salt solutions



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4

Material Preparation for First Rad Test Series

PuO_2 heated to >300 °C

Cooled to ~125 °C

Added salt mixture and mixed

Heated oxide-salt mixture to ~825 °C and held for 15 min

Cooled to ~125 °C, transferred to screw-lid glass jar, placed jar in plastic jar with 4Å mol sieve

SRNL 5

Status of SRNL Radioactive Test Matrix

Ready to load first test series in early December, but delayed by lab contamination issues

- Equipment ready for first six tests
- Material ready for first three tests
- Humidity control system and glove bag in place and ready for use

Lab just returned to active status this week

Plan to load first three test containers week of Jan 31

SRNL 6

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SRNL Corrosion Shelf Life Studies Update

John Mickalonis
Jon Duffey
Savannah River National Laboratory
January 25, 2011

3013 Surveillance and Monitoring Program Review

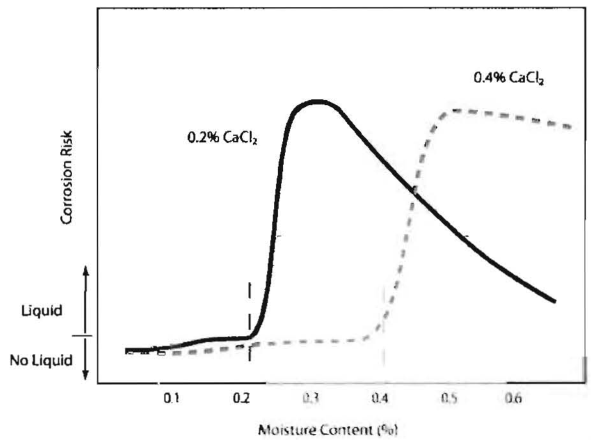
January 25-27, 2011

Integrated Stress Corrosion Cracking Test Plan

- **Goal is to resolve stress corrosion cracking (SCC) issues within 3013 storage containers**
- **SRNL Corrosion Shelf Life Studies involve:**
  - Measuring relative humidity (RH) for conditions that caused SCC in previous SRNL small scale tests with oxide/salt mixture of 98% PuO_2 – 0.85% NaCl, 0.85% KCl, 0.3% $CaCl_2$
  - Evaluating threshold RH conditions required to cause SCC for same oxide/salt mixture

SRNL 2

Integrated Stress Corrosion Cracking Test Plan



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Integrated Stress Corrosion Cracking Test Plan

Table A-1. Deliquescent relative humidity of chloride salts at 25°C (unless otherwise indicated).

Compound	RH	Compound	RH
KCl[a]	84	$MgCl_2 \cdot 6H_2O$ (70°C)[b]	27
NH_4Cl[a]	79	$KCaCl_3$ (70°C)[b]	21
$NaCl$[a]	75	$CaCl_2 \cdot 4H_2O$[b]	20
$SrCl_2 \cdot 6H_2O$[a]	71	$CaCl_2 \cdot 2H_2O$ (70°C)[b]	17
$KMgCl_3 \cdot 6H_2O$[b]	57	$KCaCl_3$[b]	16
$MgCl_2 \cdot 6H_2O$[a]	33	$LiCl \cdot H_2O$[a]	11
$CaCl_2 \cdot 6H_2O$[a]	29		

a. Lide 2000 page 15-25 add to ref, Table Constant Humidity Solutions

b. Joyce in press add to ref., Table 1. Data for magnesium chloride also in Garcia *et al* 2007.

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Integrated Stress Corrosion Cracking Test Plan

- **Goal is to resolve stress corrosion cracking (SCC) issues within 3013 storage containers**
- **SRNL Corrosion Shelf Life Studies involve:**
  - Measuring relative humidity (RH) for conditions that caused SCC in previous SRNL small scale tests with oxide/salt mixture of 98% PuO_2 – 0.85% NaCl, 0.85% KCl, 0.3% $CaCl_2$
  - Evaluating threshold RH conditions required to cause SCC for same oxide/salt mixture
    - Conducting non-radioactive, short-term tests to determine water loading conditions to achieve target RH in radioactive test containers (Non-rad humidity tests)

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Non-Rad Humidity Testing

- **Test Plan Scope**
- **Oxide/Salt Preparation**
- **Test Cell Configuration**
- **Loading Procedure**
- **Test Findings**
- **Conclusions**

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Non-Rad Humidity Testing – Defined Scope

- **Specified non-radioactive salt/oxide – 98 wt % CeO_2, 0.85 wt % NaCl, 0.85 wt % KCl, and 0.3 wt % $CaCl_2$**
- **Test cells similar to SRNL radioactive small scale tests**
- **Test protocol :**
  - Load test cells to different water contents at constant RH or to constant water content at different RH
  - Monitor closed cells with RH probes and thermocouple
  - Conduct test at both room temperature and elevated temperatures

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Non-Rad Humidity Testing – Oxide/Salt Preparation

- **Multi-step process for preparing salt mixture then combined oxide/salt mixture**
  - Salt mixture prepared in dry argon atmosphere glovebox and furnace using anhydrous salts
  - Salt mixture was prepared for both rad and non-rad testing
  - Chloride salts fused (825 °C) prior to combining with CeO_2 and heating
  - 500 g of cerium oxide/2% chloride salt mixture prepared (2-4% loss on heating)
- **Chemical analysis of leached (ICPES, ICA) and dissolved solution (ICPES)**

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Non-Rad Humidity Testing – Oxide/Salt Preparation

- Leached Sample of fused salt mixture – ICPES and IC
- Good agreement between calculated (assuming all salts dissolved) and measured

Sample	Cl*	Ca*	Na*	K*
Fused Cl- salts	26500	2960	8730	11500
Calculated	27787	2709	8360	11145

* Units in mg/L

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Non-Rad Humidity Testing – Oxide/Salt Preparation

- Leached and dissolved sample of oxide/salt mixture

Cell	Ca*	Ce*	Na*	K*	Cl-IC**
1-1	1050	712000	1720	ND	4547
1-2	1240	703000	2070	ND	12055
1-3	1090	711000	ND	ND	11844
3-1	1100	715000	ND	ND	11501
3-2	1070	739000	ND	ND	11858
3-3	1210	783000	2060	ND	11898
6-1	1040	696000	1510	2280	11770
6-2	1070	758000	ND	ND	11662
6-3	1140	747000	ND	ND	11535
Expected	1080	798000	3340	4460	11100

* ICPES data (µg/g) from dissolved sample in sulfuric acid and hydrogen peroxide
** IC data (µg/g) from leached sample; calculated from measurement (mg/L) using total weight of sample

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Non-Rad Humidity Testing – Test Cell Configuration

- **Similar in dimensions to the test cells used in the small scale hot test**
- **Cell components were tested for leak tightness by a helium leak check**
  - Body – 10^{-9} cc/He-s @ 1 atm
  - Probe – 10^{-3} to 10^{-9} cc/He–s @ 1 atm
- **Attempts were made to seal humidity probes with epoxy – limited success**

Cell consist of stainless steel body and top with a flanged fitting, o-ring and chain clamp for sealing, humidity probe, thermocouple, and glass dish for oxide/salt mixture

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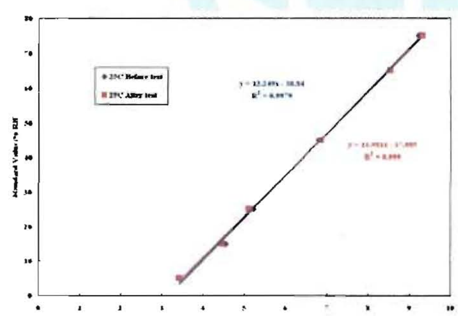
Non-Rad Humidity Testing – Calibrations

- **Thermocouples response verified against M&TE dry-well calibrator over the temperature range of 10-90 °C**
  - 0.3-0.6 °C variation in range of 20-30 °C



- **Humidity probes were calibrated using a programmable chilled mirror chamber with a RH accuracy of 5% over the RH range of 5-95%**
  - Probes were checked both before and after testing

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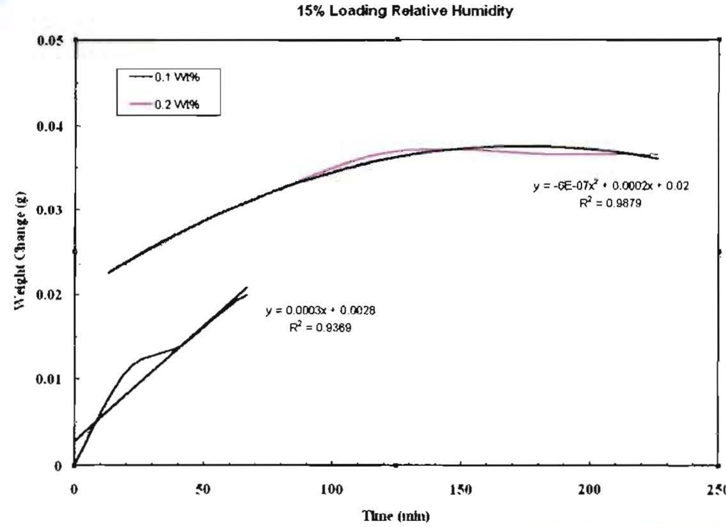
Non-Rad Humidity Testing – Loading Procedure

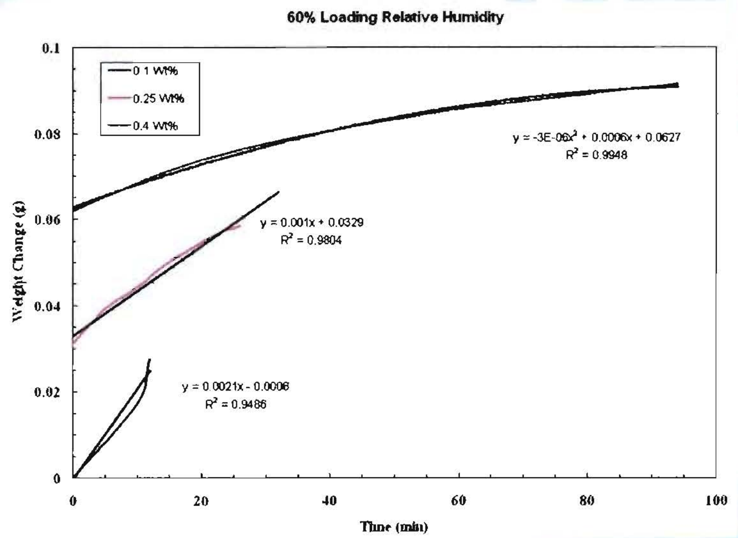
- **Mixture was weighed (20 g) into glass dishes in an argon-inert glovebox and transported to helium-inert glove bag for water loading**
- **Weights checked in dry glove bag prior to water loading**
- **Humidity in the glove bag controlled by independently adjusting the flow rate of a moist and dry helium stream**
- **Humidity of stream and glove bag monitored independently**
- **Maximum number of cells loaded was four; same cells/probes were used for all testing**
- **Control cells (no mixture) used during some tests**
- **Weight changes of mixture monitored at loading relative humidity (15-60%) until desired weight change obtained (0.1-0.5%), cells immediately sealed**

Non-Rad Humidity Testing – Test Findings

15% Loading Relative Humidity



Non-Rad Humidity Testing – Test Findings



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Non-Rad Humidity Testing – Test Findings

- **Time for water loading depended on humidity and water loading.**
- **Variability in loading characteristics for "identical cells".**

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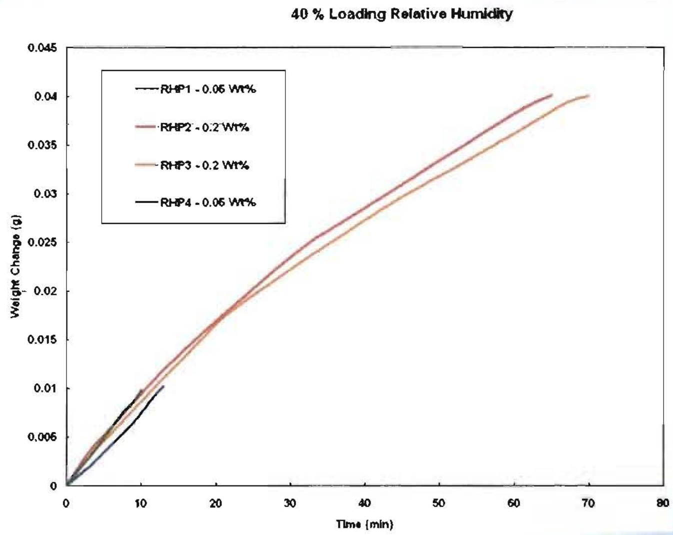
Non-Rad Humidity Testing – Test Findings



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Non-Rad Humidity Testing – Test Findings

- Time for water loading depended on humidity and water loading.
- Variability in loading characteristics for "identical cells".
- For a given test condition (humidity, water loading), variation occurred among cells in the resulting humidity

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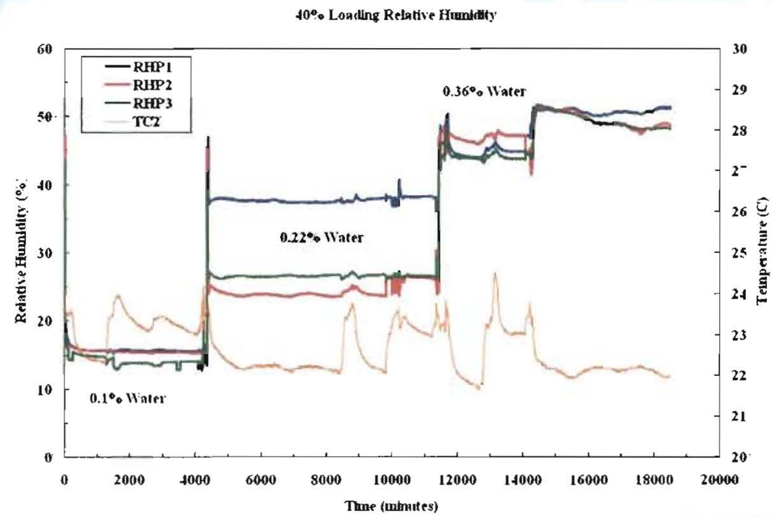
Non-Rad Humidity Testing – Test Findings



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Non-Rad Humidity Testing – Test Findings

- **Time for water loading depended on humidity and water loading.**
- **Variability in loading characteristics for "identical cells".**
- **For a given test condition (humidity, water loading), variation occurred among cells in the resulting humidity**
- **Humidity in the cells reached a plateau in approximately 30 minutes**
- **Control cells showed no change in humidity over course of test – indicating good seal**

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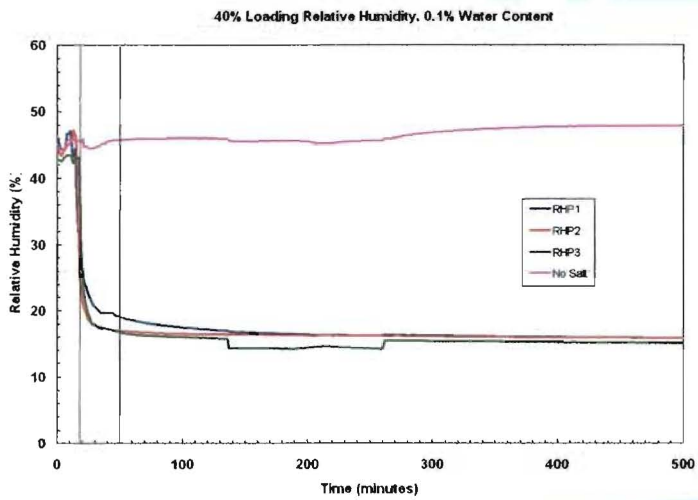
Non-Rad Humidity Testing – Test Findings



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Non-Rad Humidity Testing – Test Findings

- **Time for water loading depended on humidity and water loading.**
- **Variability in loading characteristics for "identical cells".**
- **For a given test condition (humidity, water loading), variation occurred among cells in the resulting humidity**
- **Humidity in the cells reached a plateau in approximately 30 minutes**
- **Control cells showed no change in humidity over course of test – indicating good seal**
- **Increasing temperature lead to an increase in the relative humidity**

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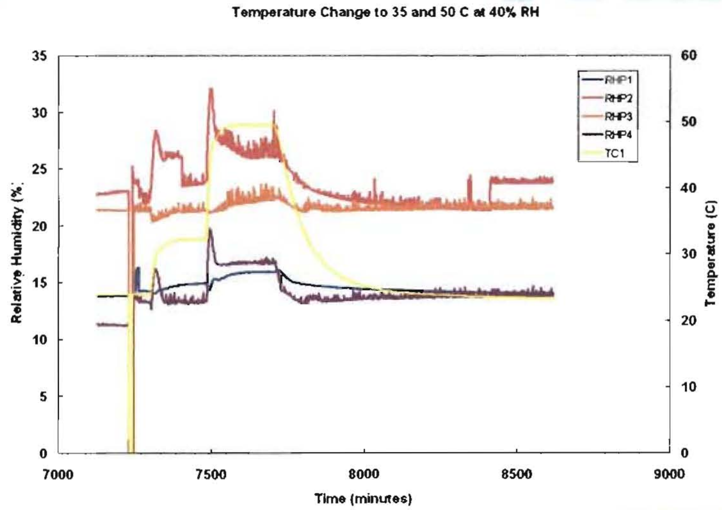
Non-Rad Humidity Testing – Test Findings



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Non-Rad Humidity Testing – Test Findings

H2O Load	Load Time	Init RH	30-min RH	Diff
0.05	12	45.8	16.2	29.6
0.10	62	23.6	17.2	6.4
0.10	26	30.0	17.2	12.8
0.11	16	44.6	17.5	27.1
0.15	14	50	18.2	31.8
0.19	289	21.7	20.6	1.1
0.20	68	43.8	24.1	19.7
0.22	48	42.9	26.1	16.8
0.25	154	28.1	27.4	0.7
0.25	46	47	28.2	18.8
0.28	499	32.5	31.3	1.2
0.28	10	60.7	33.6	27.1
0.31	47	51.5	36.8	14.7
0.38	278	47.2	45	2.2
0.34	306	46.6	45.6	1.0
0.39	32	65.1	47.7	17.4
0.45	139	58.9	50.4	6.5

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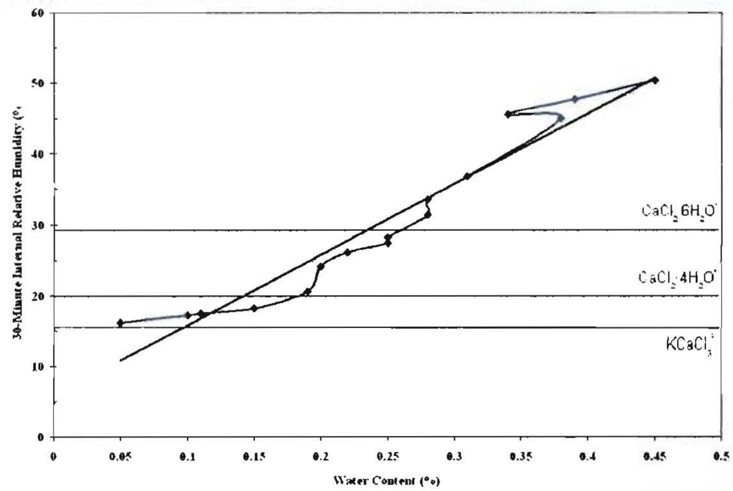
Non-Rad Humidity Testing – Test Findings



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Non-Rad Humidity Testing – Conclusions & Future Work

- **Humidity in the small scale test cells reaches an quasi-steady state value in a short time period**
- **Small scale humidity values bracket the deliquescence relative humidity values of calcium and magnesium chloride salts**
- **Determine the error associate with measured relative humidity**
- **Need to perform non-rad humidity test at same loading conditions as used in the rad test**

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Non-Rad Humidity Testing – Acknowledgements

For Experimental Assistance:

Vickie Timmerman

Gregg Creech

Wanda Matthews

Diane Scott

For Technical Assistance:

Chuck Coleman

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Status of SRNL Radioactive Test Matrix

Ready to load first test series in early December, but delayed by lab contamination issues

- Equipment ready for first six tests
- Material ready for first three tests
- Humidity control system and glove bag in place and ready for use

Lab just returned to active status this week

Plan to load first three test containers week of Jan 31

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Status of Large-Scale Corrosion Containers

Joshua Narlesky, John Berg, Alex Carrillo, Dave Harradine, Dallas Hill, Scott Lillard, Max Martinez, Rhonda McInroy, Leonard Trujillo, Charles Williams, Laura Worl, Kirk Veirs

Los Alamos National Laboratory

January 25, 2011

Outline

- Active Containers
- Review of Moisture Absorption Behavior
- Packaging Conditions:
  - Relative Humidity
  - Moisture Absorption
- Storage Conditions:
  - Relative Humidity
  - Gas Composition
  - Oxygen Generation

Pressure units:

psi · 7 → kPa

kPa · 7 → Torr

Status

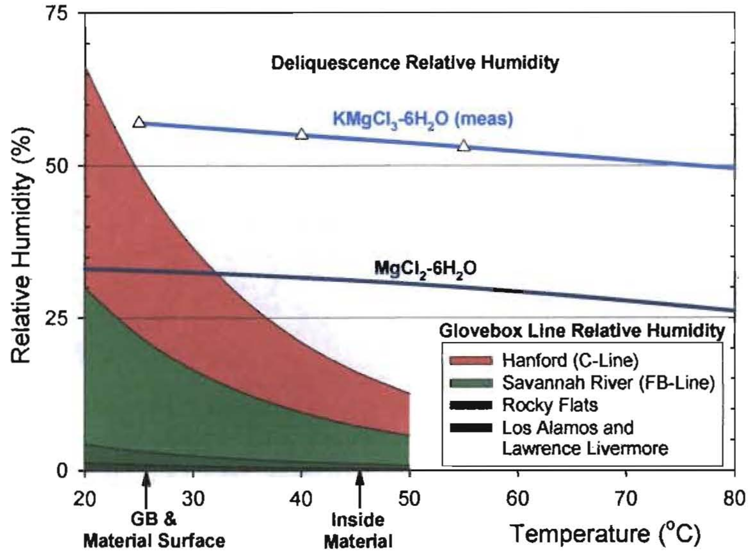
- 6 containers loaded; 2 available slots

Material	Material Description	Load Date
PMAXBS	12-14% Na/K Cl with 0.09 wt% added moisture 0.016% soluble Mg and 0.006% soluble Ca Known to cause corrosion; (5th reload)	August 2009
Base material	Scrap oxide from electrorefining process: ~14% Na/K Cl calcined in moist air (Does not have alkaline earth chloride)	September 2009
Low Ca	Base material + 0.34 wt% $KCaCl_3$ (0.28 wt% added moisture)	November 2009
Low Mg	Base material + 0.34 wt% $KMgCl_3$ (0.28 wt% added moisture)	March 2010
High Ca	Base material + 3.4 wt% $KCaCl_3$ (0.39 wt% added moisture)	August 2010
High Mg	Base material + 3.4 wt% $KMgCl_3$ (0.55 wt% added moisture)	September 2010

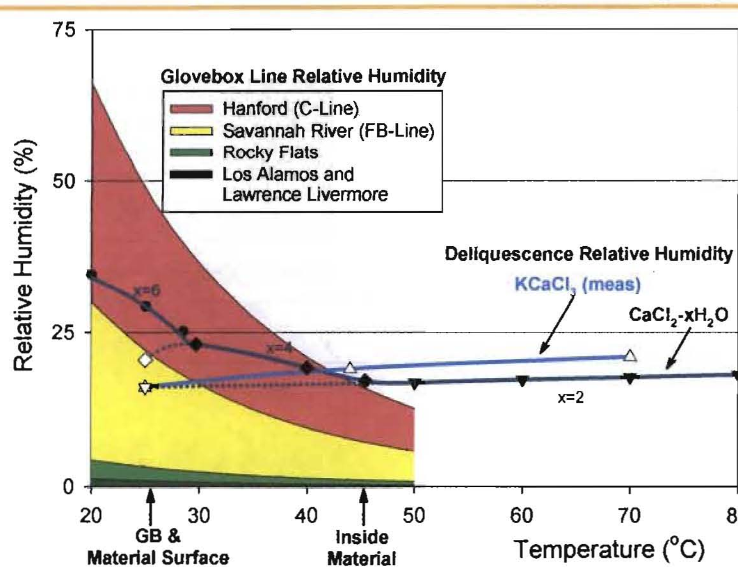
Stress Corrosion Cracking Test Plan

- SCC can occur under conditions allowed by DOE-STD-3013.
- SCC is influenced by various factors including: salt content, salt composition, absorbed moisture, packaging RH, container RH, and material temperature throughout the container.
- Want to establish means of estimating upper bounds for RH inside containers in storage from available data and determine likelihood of SCC from internal environment at bounding conditions.
- Specifically, the large scale SCC experiments address the following:
  1. *What is the RH and how does it change inside the container given its process/loading history?* HAVE DATA!!
  2. *What is the threshold RH that will support SCC?* TBD FY11-12
  3. *What containers have the residual stress exceeding* K_{SCC}? TBD FY11-12

Magnesium Chloride Salt Behavior During Packaging



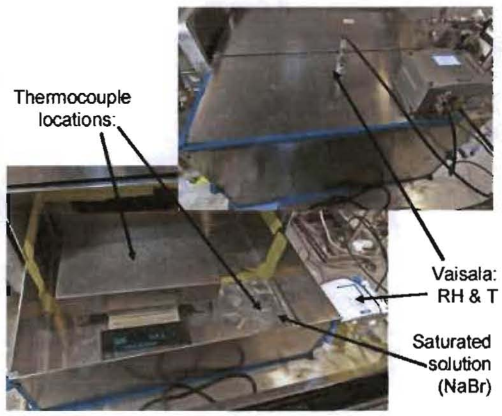
Calcium Chloride Salt Behavior During Packaging



Simulating the Worst-Case Packaging Conditions

- **Dry material placed in metal pan and exposed to high RH (~50% RH) inside an environmentally controlled enclosure**
- **RH controlled with saturated solution of NaBr (DRH = 58%)**
- **Instrumentation: T, RH, weight**
- **Material removed when**
  - Absorption reaches 0.5 wt%

    OR
  - Absorption stops



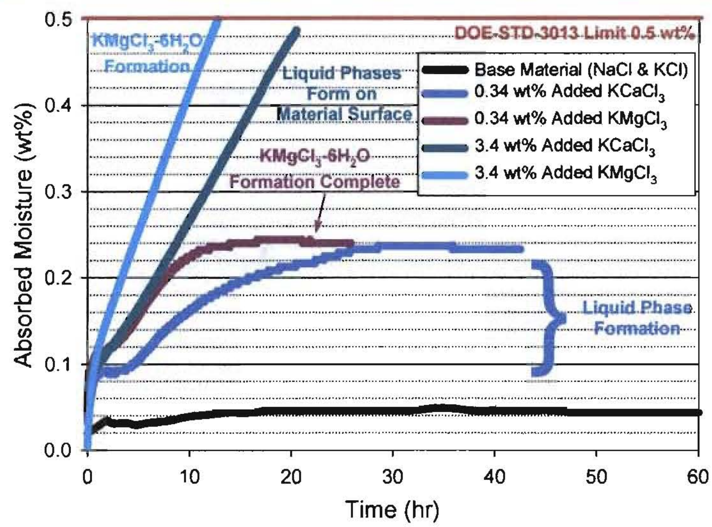
Moisture Absorption Observations

- **Magnesium-based salts**
  - Absorb moisture at very low RH (~2% RH)
  - Absorb moisture at a faster rate than Ca-based salts
- **Calcium-based salts**
  - Absorption requires higher RH (~15-20% RH)
  - Moisture absorption below 15% RH suggests that $CaCl_2$ is present in the salt

Material	wt% Moisture	Exposure Time (h)	Enclosure Temp °C	Enclosure RH%	Material Temp C	RH% in Material (calc.)
PMAXBS	0.09	100[a]	27	53	40	26
Base Material	0.05	138[a]	26	56	39	27
Low Ca	0.28	42[a]	26	53	42	22
Low Mg	0.28	26[a]	26	52	48	16
High Ca	0.39	21[b]	25	30[c]	47	9
High Mg	0.55	17[b]	24	8[c]	43	3

Notes: a. At equilibrium, b. Removed material from enclosure, c. Enclosure did not reach equilibrium RH due to high rate of absorption

Moisture Absorption—Exposure Time

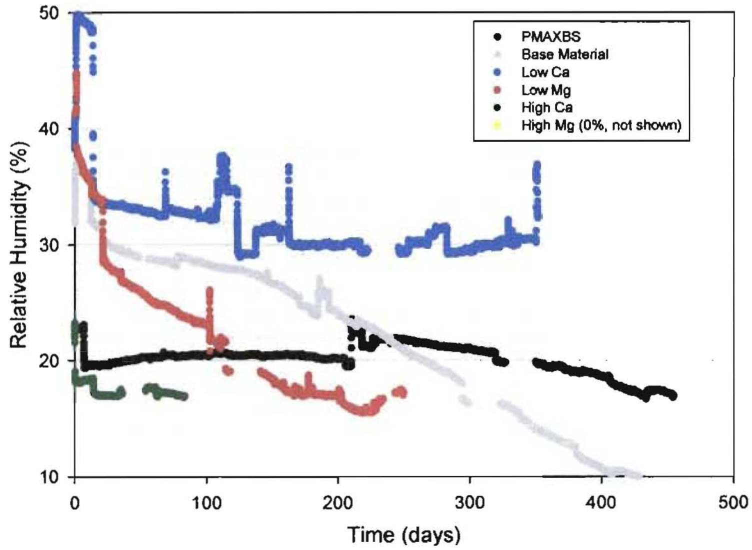


Storage Conditions (first 30 days)

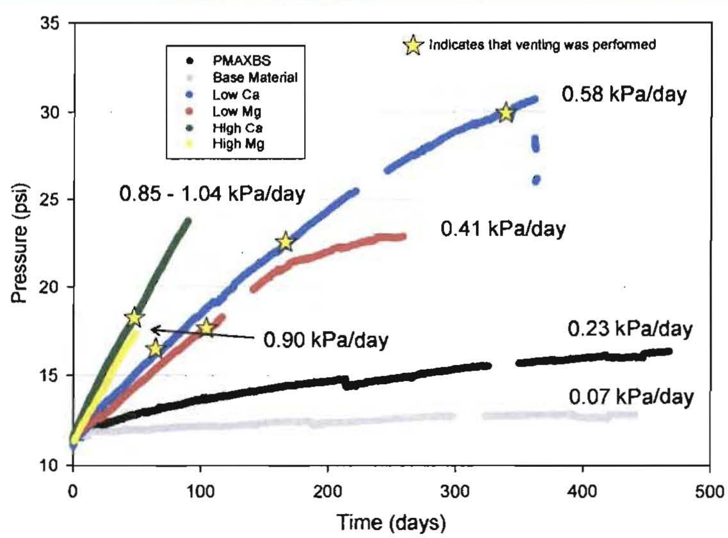
Material	wt% Moisture	Condition	Headspace Temp °C	Headspace RH (%)	Sidewall Temp °C	Sidewall RH (%) (calc.)
PMAXBS	0.09	Bare 3013	36	23	41	18
		Insulated	49	20	47	22
Base Material	0.05	Bare 3013	30	35	29	37
		Insulated	36	31	33	37
Low Ca	0.28	Bare 3013	30	49	32	44
		Insulated	39	34	35	42
Low Mg	0.28	Bare 3013	37	37	35	41
		Insulated	45	28	37	37
High Ca	0.39	Bare 3013	41	18	43	17
		Insulated	43	17	45	16
High Mg	0.55	Bare 3013	33	0	35	0
		Insulated	38	0	41	0

The measured material temperature for insulated containers ranged from 40 to 55°C

Relative Humidity



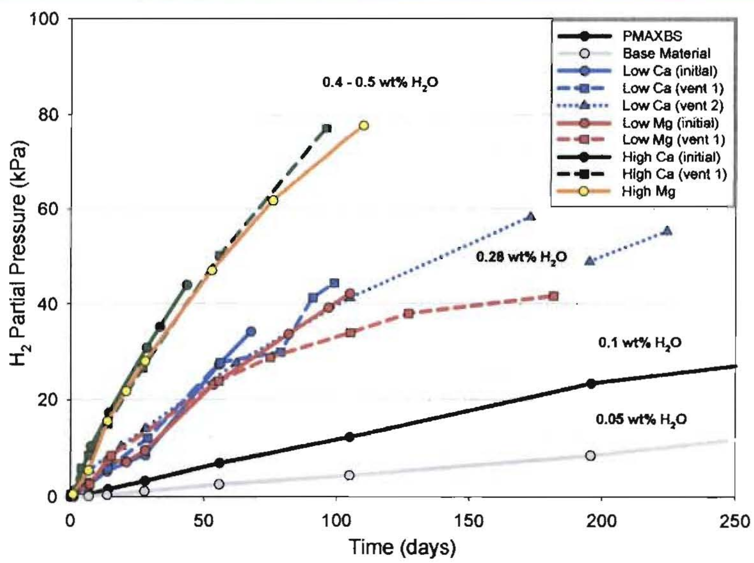
Total Pressure



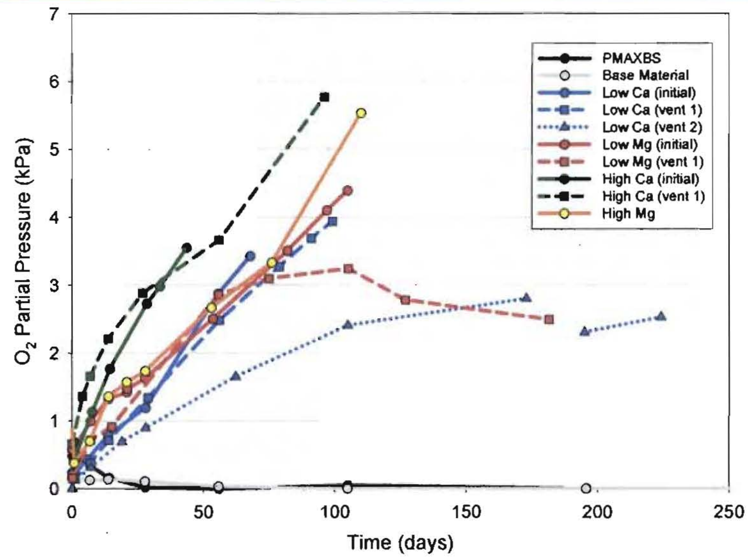
Gas Composition

- **ER scrap oxide materials: (PMAXBS and Base Material)**
  - Both generate H_2
  - O_2 is depleted in both container in the first 30 to 60 days
  - Minor gas species: CO_2 and N_2O (PMAXBS)
- **ER scrap oxide materials with added AEC salts**
  - Generate H_2 and O_2 and require venting
    - Low Ca: 2 vents
    - Low Mg: 1 vent
    - High Ca: 2 vents
    - High Mg: 1 vent
  - Minor gas species
    - Low Ca & Low Mg generate CO_2 and N_2O simultaneously
    - High Ca generates CO_2 initially. N_2O grows in after about 2 weeks and the CO_2 becomes depleted
    - High Mg generates CO_2

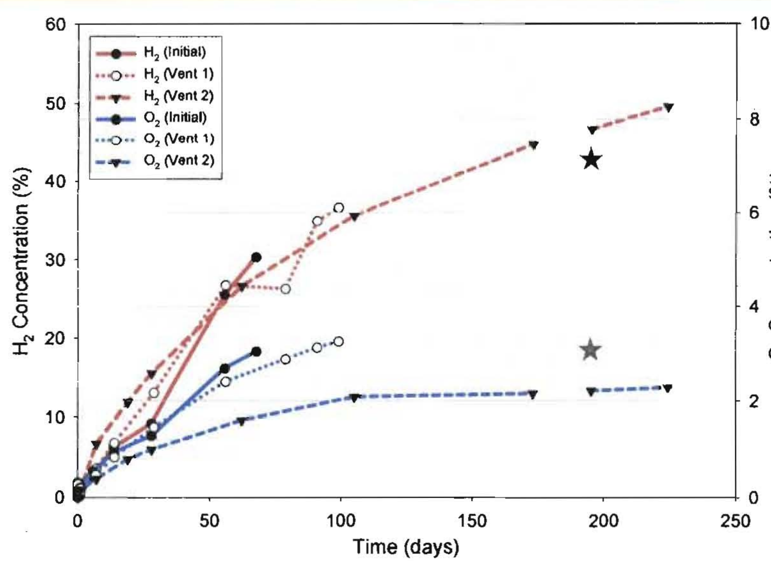
Hydrogen Generation



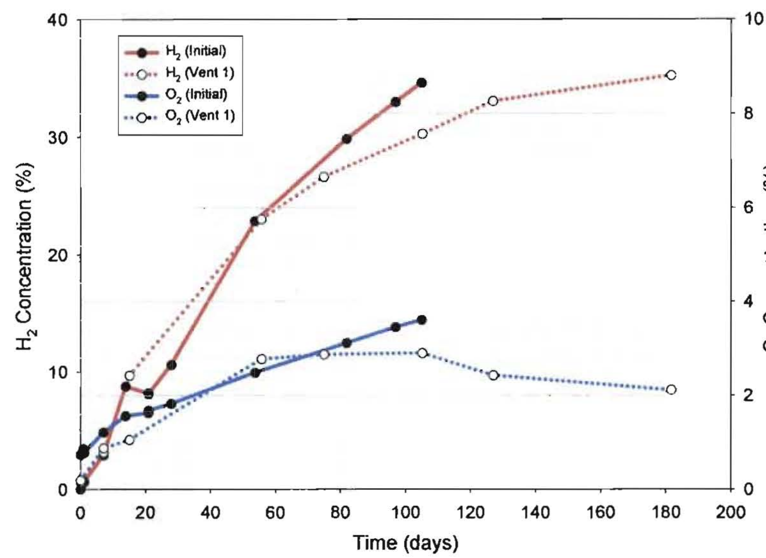
Oxygen Generation



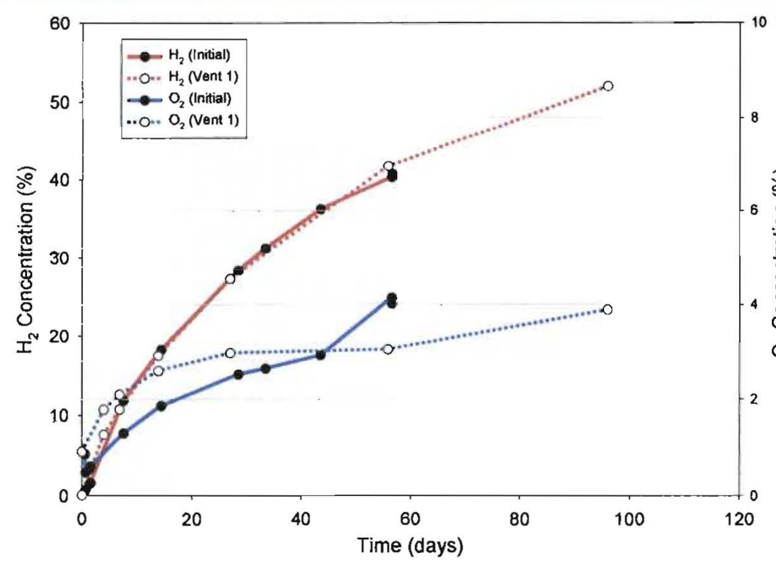
Low Ca: H_2 and O_2 Concentrations (%)



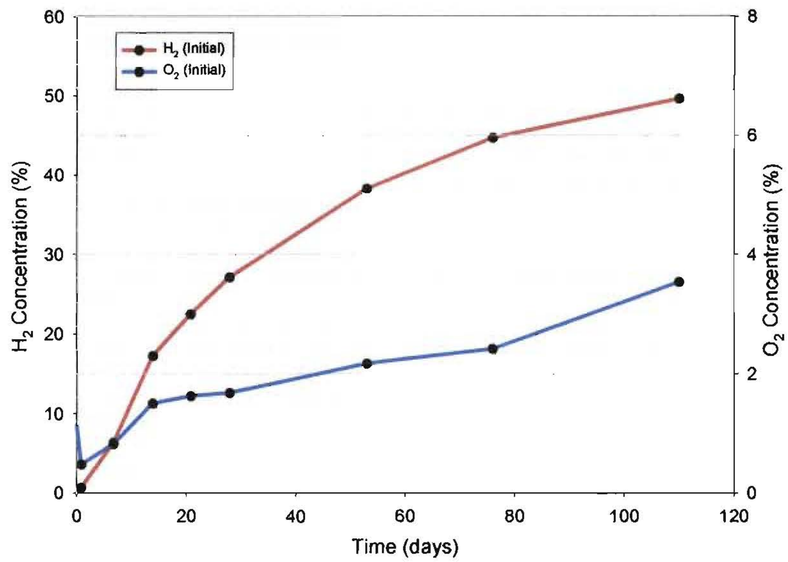
Low Mg: H_2 and O_2 Concentrations (%)



High Ca: H_2 and O_2 Concentrations (%)



High Mg: H_2 and O_2 Concentrations (%)



Conclusion

- Corrosion is possible where liquid phases are present
- Where do we expect liquid phases?

Material	Packaging Conditions	Storage Conditions
Low Ca	Yes	Yes
Low Mg	Possible (on $MgCl_2$)	Possible (on $MgCl_2$)
High Ca	Yes	Yes
High Mg	No	No

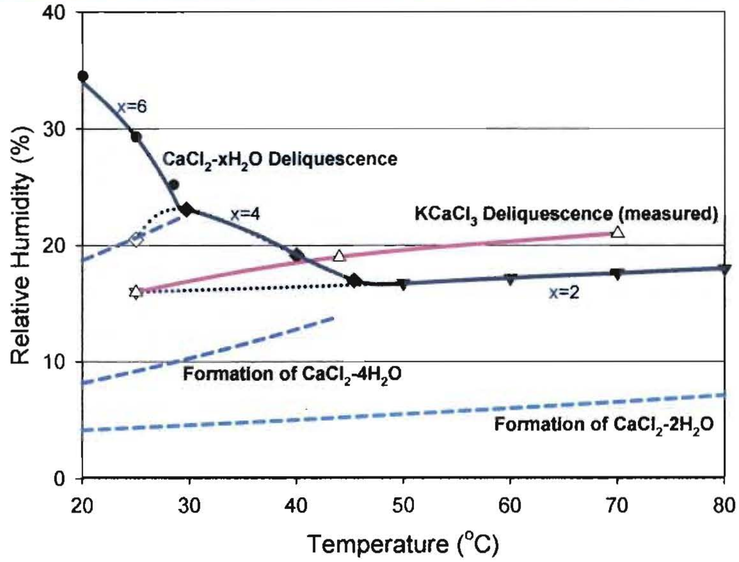
- Liquids phases possible even for short exposure to high RH
- Gas generation: O_2 being generated in all materials with AEC added

FY11 Activites

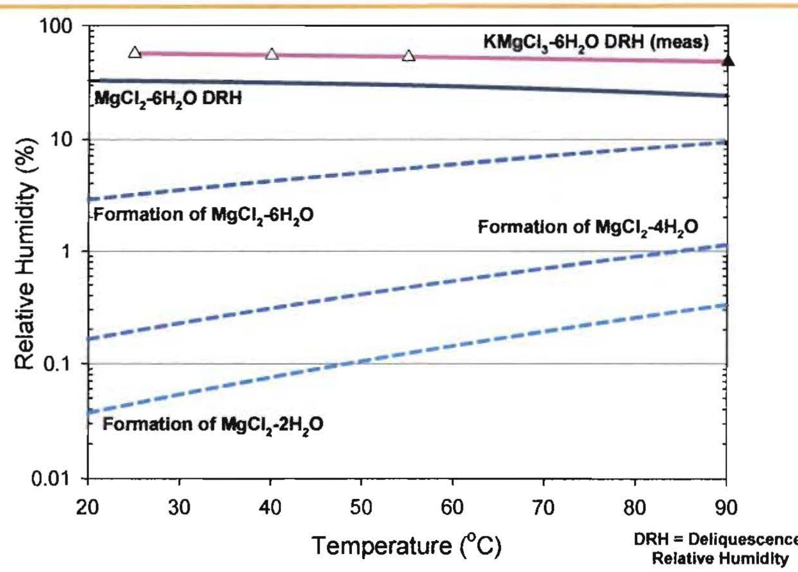
- **Maintenance:**
  - Repair of Peter-Paul valves that control solenoid valves on manifold
  - Calibration of Heise Pressure Transducers (March 2011)
- **GC fractionation issue**
- **Removal / DE of containers that are 2-years old?**
  - PMAXBS (August)
  - Base Material (September)
- **Reports**
  - Moisture absorption

Additional Information

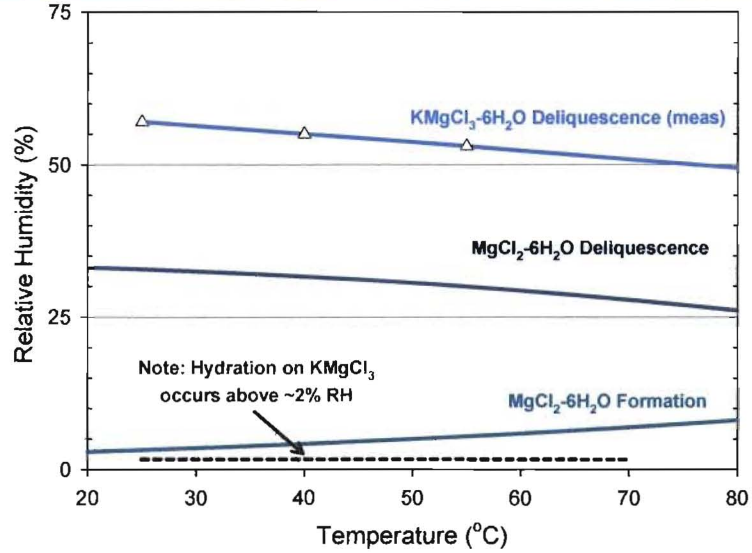
Hydration behavior of calcium chloride salts



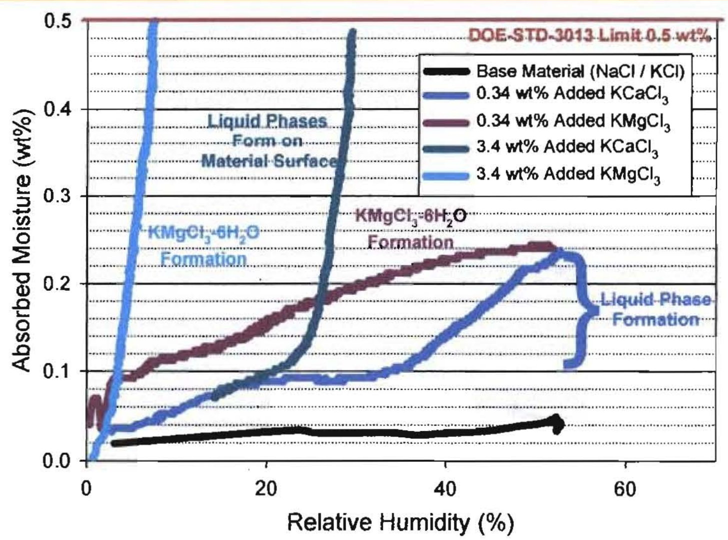
Hydration behavior of magnesium chloride salts



Hydration behavior of magnesium chloride salts



Moisture Absorption—Effect of Relative Humidity



Insulation

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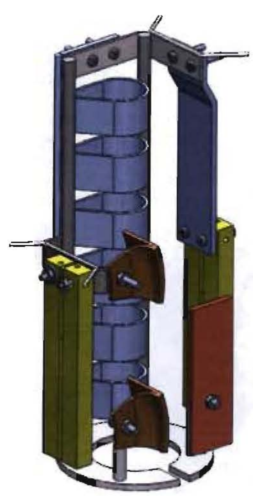
NNSA

Corrosion Specimens



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NNSA

Thermocouple Locations

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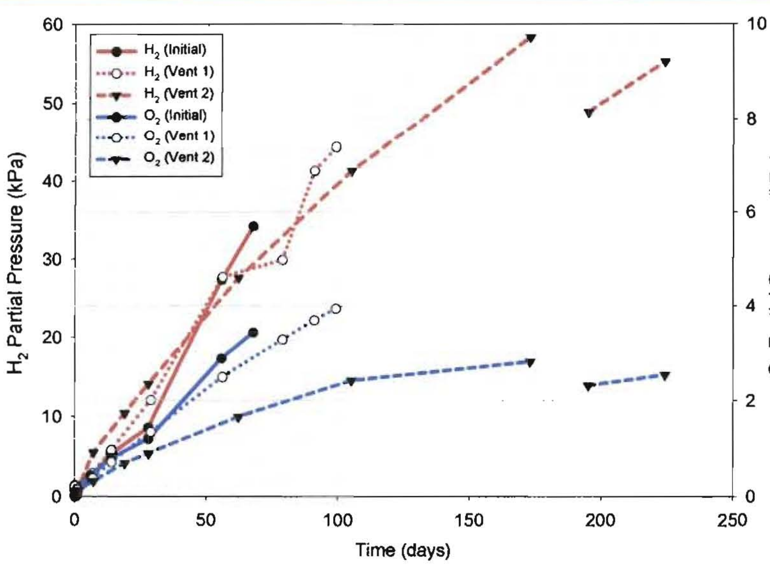
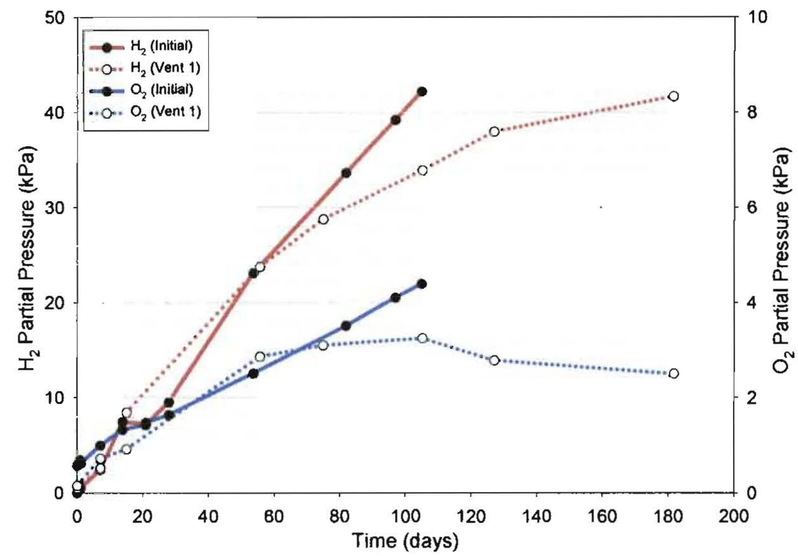
Operated by Los Alamos National Security, LLC for NNSA

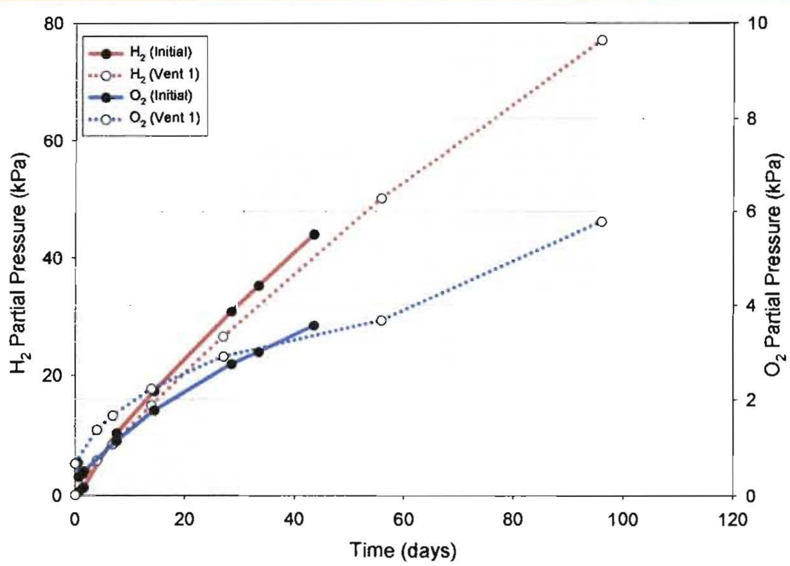
Low Ca: H_2 and O_2 Partial Pressures



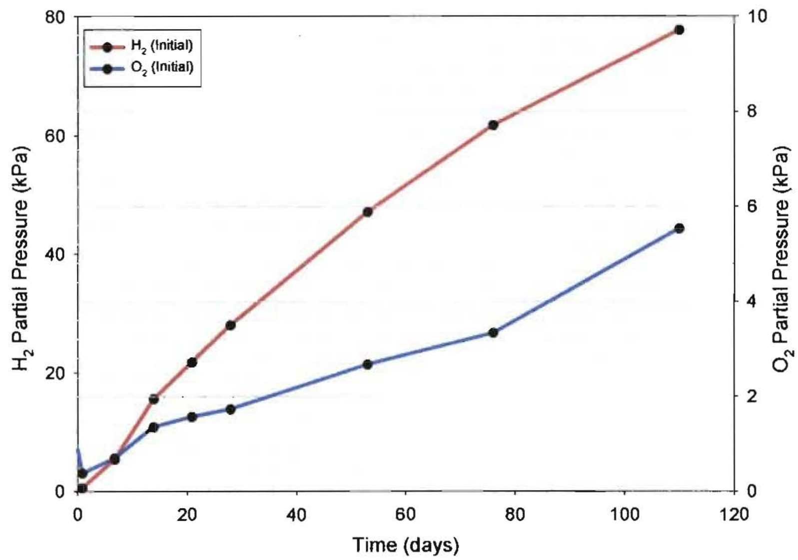
Low Mg: H_2 and O_2 Partial Pressures



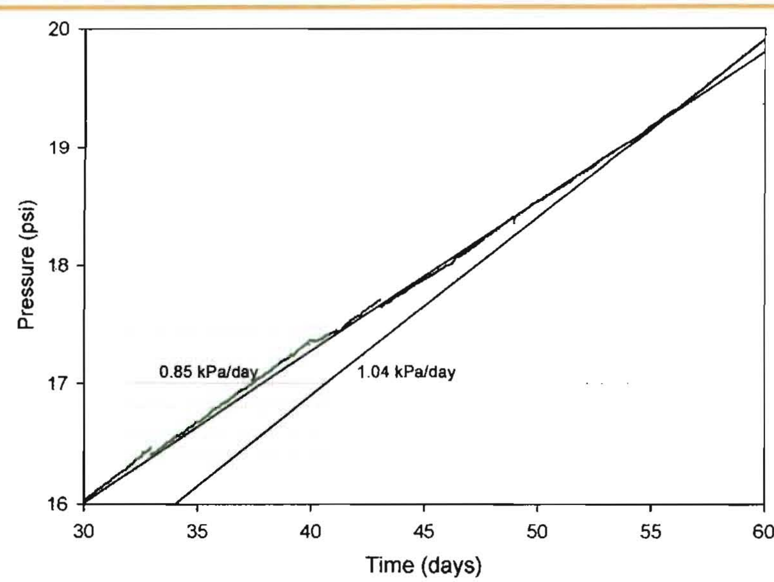
High Ca: H_2 and O_2 Partial Pressures



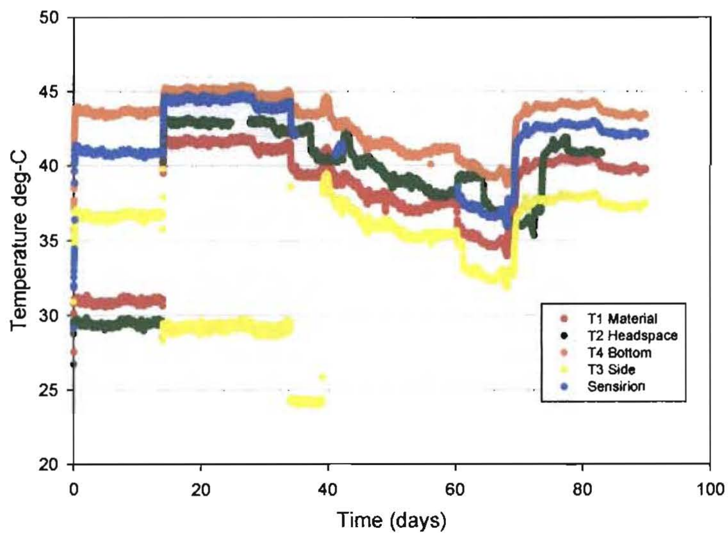
High Mg: H_2 and O_2 Partial Pressures



High Ca: Increase in Pressure Rate



High Ca: Temperatures



Stresses in Teardrop Specimens

Michael B. Prime, W-13

Hunter Swenson, MST-6

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Los Alamos
NATIONAL LABORATORY
EST. 1943

SCC Test Plan Milestone

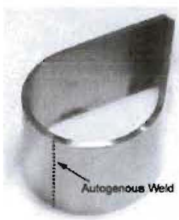
III. What containers have the highest residual stress?

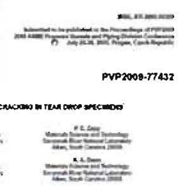
B. Residual Stress

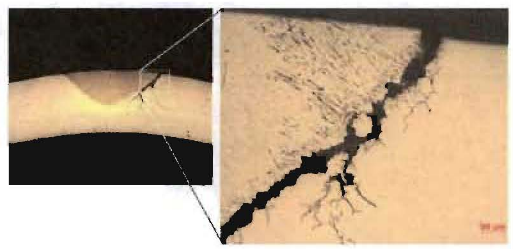
UNCLASSIFIED

Introduction

- Teardrop specimens used in SCC testing
- Stress levels apparently only quantified by FEM analysis
- Based on cracking, we care about hoop stress in weld region







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Previous stress estimate

- FE model including plasticity
- Assumes no initial welding residual stress
  - Actually OK since large plasticity during bending will wipe out most welding stress
- Peak hoop stress at apex estimated at 106 ksi (= 730 MPa)

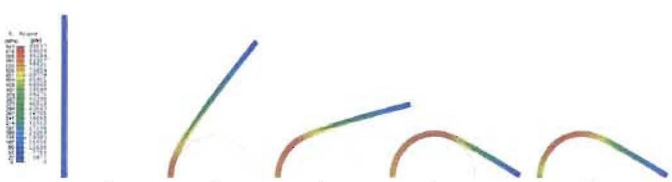

Figure 10 The Mises stress distribution during the fabrication of the tear drop specimen: (a) Undeformed state, (b) Maximum stress at the apex, (c) Maximum stress deviating from the apex when the strip continues to deform, (d) Specimen forming completed, and (e) Stress re-equilibrium upon completion of specimen fabrication.

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Slide 4

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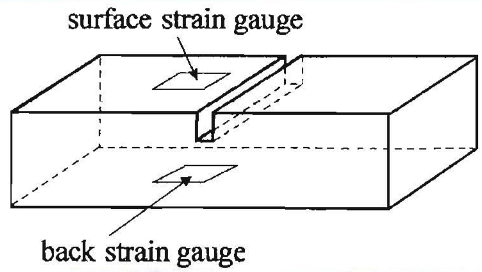
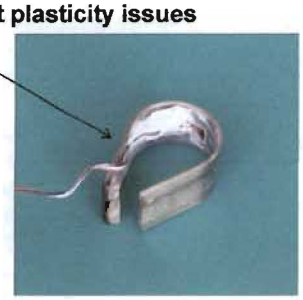
Selected Method: Incremental Slitting

- **Also known as crack compliance**
- **Mount one or more strain gauges**
- **Incrementally cut a slit**
  - Prefer wire EDM cutting for metals
- **Back-calculate stress profile**
  - All the way through-thickness
- **Why?**
  - This slit approximated the SCC cracks, so measures right stresses
  - Good resolution
  - Gives K_I – so good for SCC



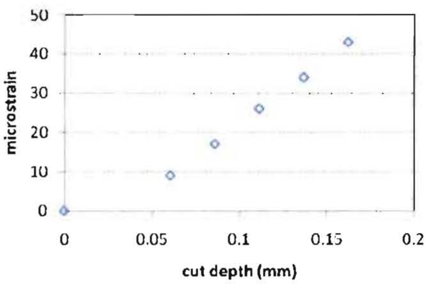
Testing plan – two pronged

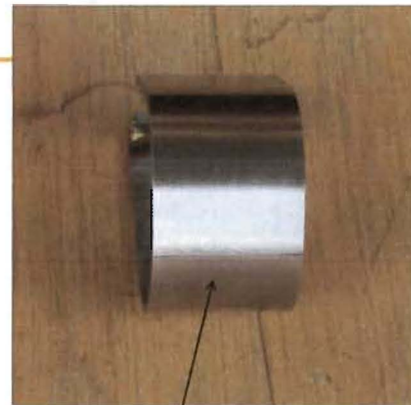
- **1: Get accurate stress measurements without plasticity issues**
  - Step 1: split ring and release bending moment
    - Measure deformation
    - Calculate bending stress
  - Step 2: slitting
    - Measure remaining stresses
      - Now low enough for no plasticity
  - Superimpose these two stress contributions
- **2: Slitting tests with full stress**
  - See if we can interpret what we get
    - There are plasticity corrections available
- **Try to repeat each test at least once**



Split then slit, 304LW-02

- **Strain gauge on inner surface**
- **Sprung open**
  - $\varepsilon = 4490\ \mu\varepsilon$
- **Incremental slitting from OD inward**
  - Unfortunately, waterproof coating failed at cut depth 0.16 mm (0.006")
  - About 12% of the way through-thickness





- **Note: significant uncertainty on slit depths because surface is curved**
  - Anti-clastic bending

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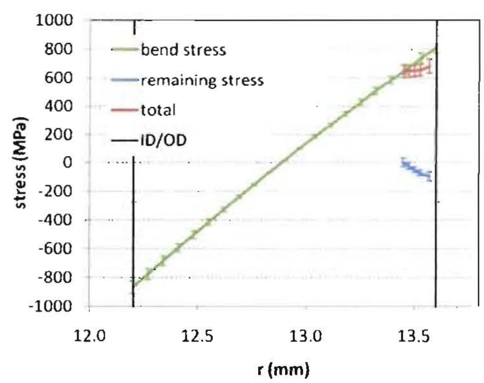
Stress, 304LW-02

- **Data analysis**
  - Bending stresses from elastic curved beam formula and measured 4490 $\mu\varepsilon$
  - Standard slitting analysis, Curvature ignored since R/t = 9.7

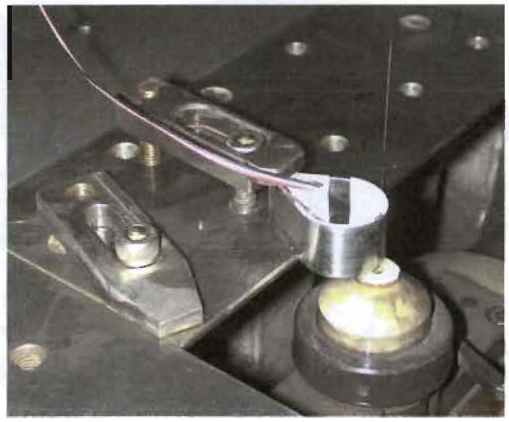
Results:

- **Large bending σ, as expected**
- **Smaller σ remaining after teardrop was sprung open**
- **Total stress on outer surface**
  - 680 ± 50 MPa (= 99 ± 7 ksi)
- **Higher than FEM at apex**
  - FEM ignored welding stress and used just a handbook σ–ε curve



Slit without splitting open, 304LW-11

- EDM cut without springing open first
- Expect large stresses/strains

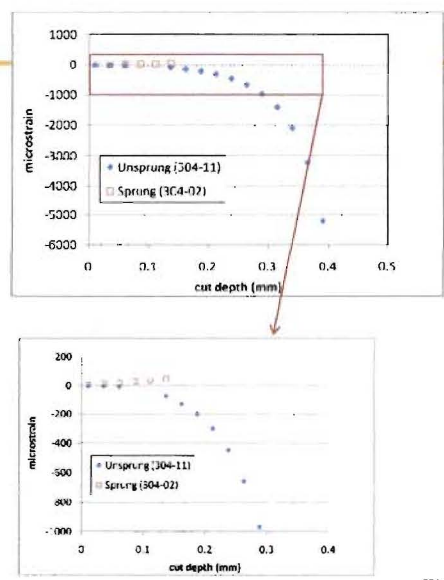


Strain data

- For unsprung specimen, strains rapidly diverge to very large magnitudes

<u>For two reasons, cannot analyze with usual analysis:</u>

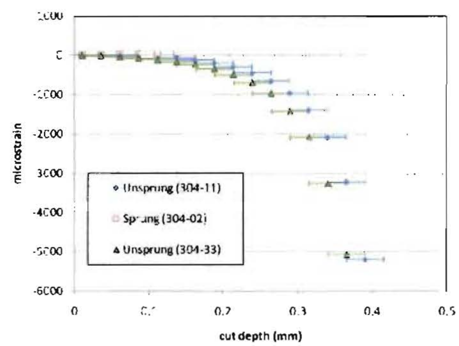
- Need custom coefficients
  - Usually use flat plate coeffs
  - For a connected loop, reinforcement gives extra stiffness
- This stress level will have cut tip plasticity
  - Nonlinear



Repeat slitting test, unsprung teardrop, 304LW-33

First look at repeatability of strain vs. cut depth data

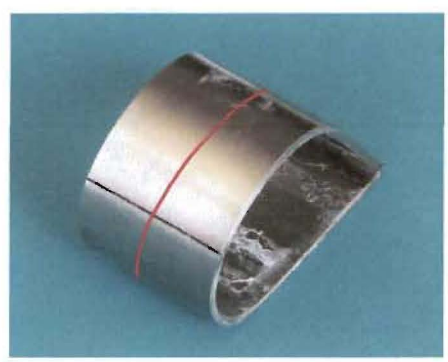
- **Agrees within uncertainty**
  - Because of curved surface of teardop, cut depth is ± 0.001"



Metallography

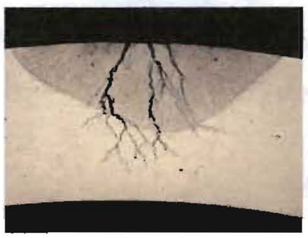
Cross-section in half to examine

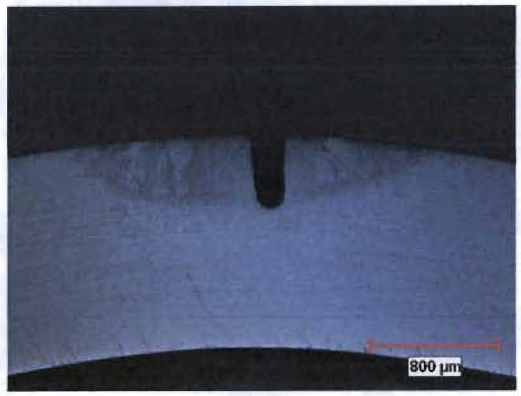
- **Location and depth of cut**
- **Profile of weld**
- **Any indication of cut tip phenomena**
  - Cracking
  - Rupture
  - Plasticity
  - ?



304LW-11

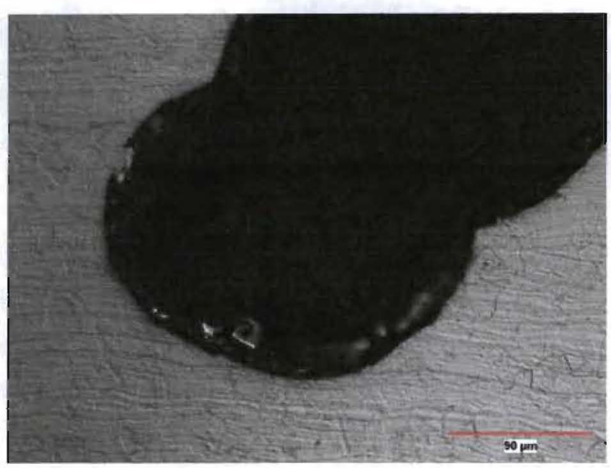
- Slot is well centered in weld
- Weld profile is much different than published results from SCC testing





304LW-11 – cut tip high mag

- No obvious clues of phenomena at cut tip



304LW-33

- **Still no evidence of much going on at cut tip**

Conclusions

- **Spring then slit gives good measurement of stresses**
  - 680 MPa (99 ksi) on outer surface at apex
- **Slitting unsprung specimen gives intriguing data**
  - Time dependent strains
  - No proven explanation

Studies of Ca-Rich Surrogate Material Using Teardrop Specimens

Scott Lillard, MST-6

Josh Narlesky, Kirk Veirs MET-1

Laura Worl IMP-2

SCC Test Plan Milestone

- *II. What is the threshold RH that will support SCC, that is, what is RH_{SCC}?*
- **II B 2. Baseline surrogate-oxide experiments to determine threshold RH_{SCC}**
- *IV. What configuration is needed for SCC initiation and propagation?*

- **SRS Material in 4-series cans**

Table 1. Test Series Solid Mixture Compositions

Series	Description	No. of Containers	Composition (wt %)				
			PuO_2	NaCl	KCl	$MgCl_2$	$CaCl_2$
1a	0% Salt	1	100	–	–	–	–
1b	LANL master blend	2	72	11.7	14.8	1.1	0.4
2a	10% NaCl/KCl	3	90	5.0	5.0	–	–
3a	10% ER Salt	3	90	4.5	4.5	1.0	–
3b	5% ER Salt	3	95	2.25	2.25	0.50	–
3c	2% ER Salt	3	98	0.90	0.90	0.20	–
4a	2% Ca Salt	3	98	0.90	0.90	–	0.20
4b	2% 11589 Salt	3	98	0.54	0.54	–	0.92
5a	5% ER Salt	3	95	2.25	2.25	0.5	–

Surrogate Composition

- $CaCl_2$ – 3.33 g, 0.3%wt%
- KCl – 9.42 g, 0.94 wt%
- NaCl – 9.42 g, 0.94
- CeO_2 – 980 g, 97.8 wt%

Surrogate Preparation – Chloride salt mixture (Narlesky)

- **1) Mixed salts (NaCl, KCl, $CaCl_2$ (anhyd) in inert Ar atmosphere glove box**
- **2) Removed mixture from Glove Box and placed in hot furnace in Lab. Calcined at 820 C for 2 hours.**
- **3) Allowed to cool to 350 C in furnace .**
- **4) Placed mixture back in inert glove box to cool.**
- **5) Ground salt mixture.**
- **6) Store in conflat.**

Surrogate Prep – CeO_2 salt mixtures

- **Seven 140g batches... limiting factor was the size of the boat that would fit in our furnace.**
- **1) Combined CeO2 and required amount of salt in inert Ar atmosphere GB, placed in a shaker bottle, and shook vigorously for 1 minute.**
- **2) Poured CeO2-salt mixture in crucible.**
- **3) Removed mixture from GB and placed in hot furnace in lab.**
- **4) Heated mixture at 850C for 2 hours.**
- **5) Allow mixture to cool in furnace.**
- **6) Returned mixture to inert Ar atmosphere GB.**
- **Once all of the batches were prepared, they were mixed together and poured into the conflats**

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Estimation of RH in SRS 4a Containers (Veirs)

- Estimation of the relative humidity in SRS 4a Series Corrosion containers
- 4a Series containers was 0.90 wt% NaCl, 0.90 wt% KCl, and 0.20 wt% CaCl2. SRS best estimate of the water content for the three containers was 0.58 wt%, 0.63 wt%, and 0.55 wt% for containers 4a-1, 4a-2, and 4a-3 respectively.
- Steve Joyce Graphs ..... Used EQ3/6 of the chloride molality and water mass in the resulting solution as a function of humidity started with 0.4 moles of CaCl2, 2 moles of NaCl, and 2 moles of KCl
- Assume CaCl2 is dissolved, the graphs can be scaled to any actual amount of $CaCl_2$

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Temperature of Exposure

- Measure "near" containers?

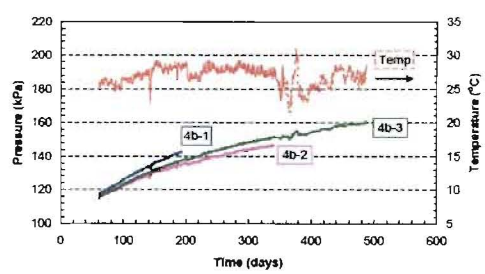

Figure A1-4. Container pressure and ambient temperature trends for Series 4b corrosion samples.

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Duration of SRS Exposure

Table 7. Summary of Corrosion Observations

Test Container	Salt Content	Days Sealed	Corrosion Observations		Maximum Pit Depth in μm
			Flat Coupons	Tear Drop Coupons	
1a-1	None	325	slight stain	slight stain	
1b-1	28% salt	489	slight stain	slight stain	
1b-2		150	slight stain	slight stain	
3c-1	2% ER Salt	274	stain, local corrosion at bottom edge	stain in 304L in solid contact region	
4a-1	2% Salt with 0.2% $CaCl_2$	506	pitting mostly in solid contact region, stain	pitting, no cracking in 316L in solid contact region	to be evaluated
4a-2		335	pitting in headspace region, edge attack in solid contact	pitting and cracking in 304L in solid contact region	to be evaluated
4a-3		166	pitting mostly in headspace region, edge attack in solid contact	pitting and cracking in 304L in solid contact region	100
4b-1	2% Salt with 0.9% $CaCl_2$	193	pitting only in solid contact region	pitting in 304L in solid contact	60
4b-2		340	pitting only in solid contact region	pitting in 304L in solid contact	to be evaluated
4b-3		496	pitting only in solid contact region	pitting, no cracking in 304L solid contact region	to be evaluated

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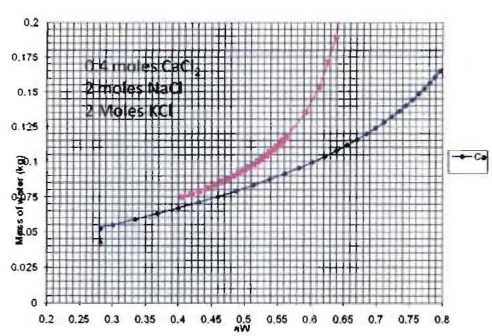
Estimation of RH – cont.

- For the three containers the mass of water is
- 4a = 128.7
- 4b = 139.8
- 4c = 122.1.
- From the graph of mass of water the relative humidities of the solutions range from 57% to 58% RH. The range for pure CaCl2 for comparison is 69% to 71% RH.



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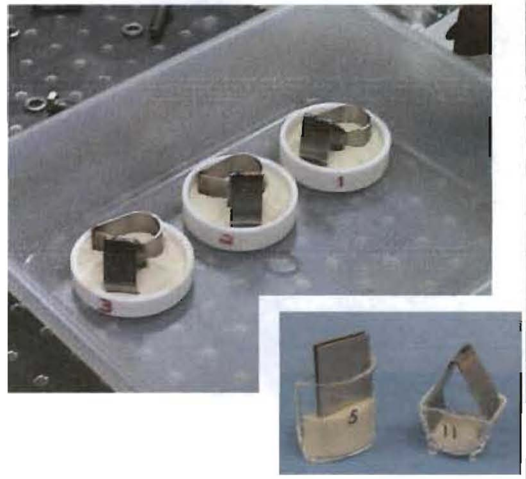
Surrogate / Teardrop Experiments

- SS 304L weld & SS 316L weld tear drops (autogenous)
- 25 grams surrogate in alumina boats, 5 mm deep?
- two orientations
- 30 C, 57.5% RH
- planned 30, 60, 90 days



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Experimental – cont.

Shelf Life Surveillance Gas Generation Results and Future Recommendations

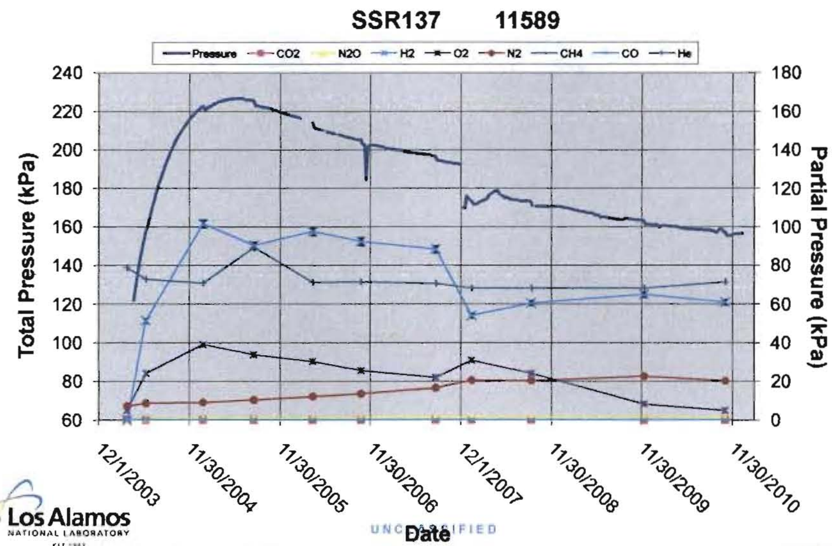
D.K. Veirs, Max Martinez, Leonard Trujillo, Josh Narlesky, Alex Carillo, John Berg, and Laura Worl

3013 Surveillance and Monitoring Program Review
Jan. 25-27, 2011
Savannah River Site

Introduction

- Trends in oxygen partial pressure from MIS material 011589A.
- The high hydrogen gas producing materials.
- MIS represented materials removed from Small-Scale Surveillance.
- MIS represented materials added to Small-Scale Surveillance.
- RH sensor added to Small-Scale Surveillance container lid to investigate the RH for various materials, for example the RH at which ARF-85-223 causes corrosion.

MIS Represented Sample 011589A



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Oxygen trends in 011589A

- Prior to a temperature controller failure, two models were fit to the data. One in which the oxygen plateaus and one in which the oxygen is consumed.
- Since the temperature excursion, the total pressure and the hydrogen and oxygen partial pressures appear to have recovered their original trajectory.
- The oxygen now appears to be on a path to be completely consumed.

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The high hydrogen producing MIS represented materials

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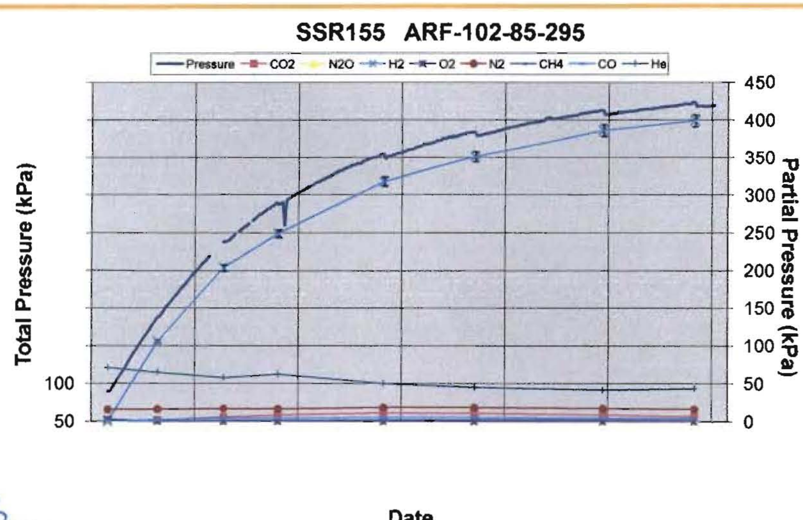

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High hydrogen partial pressure producing materials

- Both high hydrogen producing materials show continued increase in hydrogen partial pressure.
- Hydrogen partial pressure is approaching 5 atmospheres.
- Previous observations of small amounts of oxygen likely due to incomplete pumpout of capillary tubing prior to sampling.

Materials removed from Small-Scale Surveillance

- Seven MIS represented materials were removed from Small-Scale Surveillance:
  - TS707001 RFETS High-purity oxide
  - 5501579 RFETS High-purity oxide
  - 7242141 RFETS 63% Pu
  - ARF-102-85-355 Hanford 70% Pu
  - CAN92 RFETS Mixed oxide 85.4% actinides
  - C00024A RFETS 73.4% Pu
  - PuF4-1 LANL 72% Pu
- Removal procedure includes RH measurement, moisture loss to 200 C, and pictures of inner buckets.

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Material measurements

Container	Material	Date removed	RH	T	Loss on heating
SSR123	TS707001	3-2-2010/ 7 yrs	25%	24 °C	0.10%
SSR124	5501579	3-2-2010/ 7 yrs	24%	24 °C	0.06%
SSR141	7242141	5-19-2010/ 6 yrs	25%	25 °C	0.04%
SSR143	ARF-102-85-355	3-2-2010/ 6 yrs	12%	24 °C	0.42%
SSR147	CAN92	5-19-2010/ 5 yrs	75%	24 °C	0.09%
SSR148	C00024A	5-19-2010/ 5 yrs	32%	25 °C	0.28%
SSR156	PuF4-1	5-19-2010/ 5 yrs	11%	25 °C	0.25%

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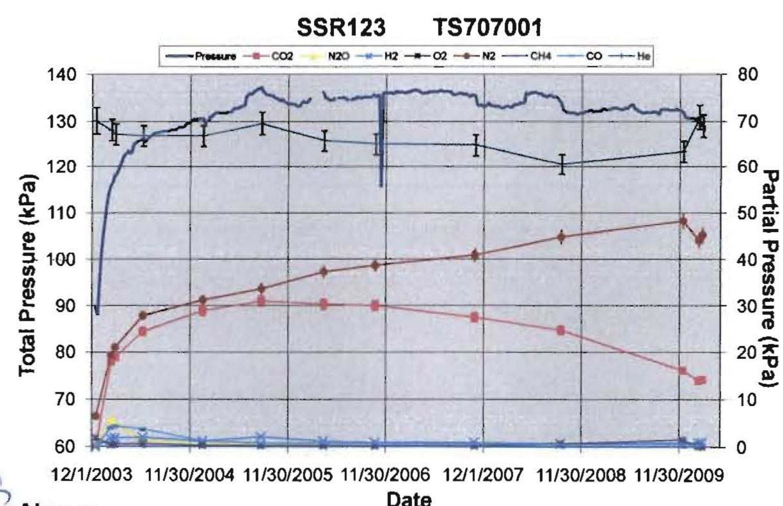
RFETS High purity oxide



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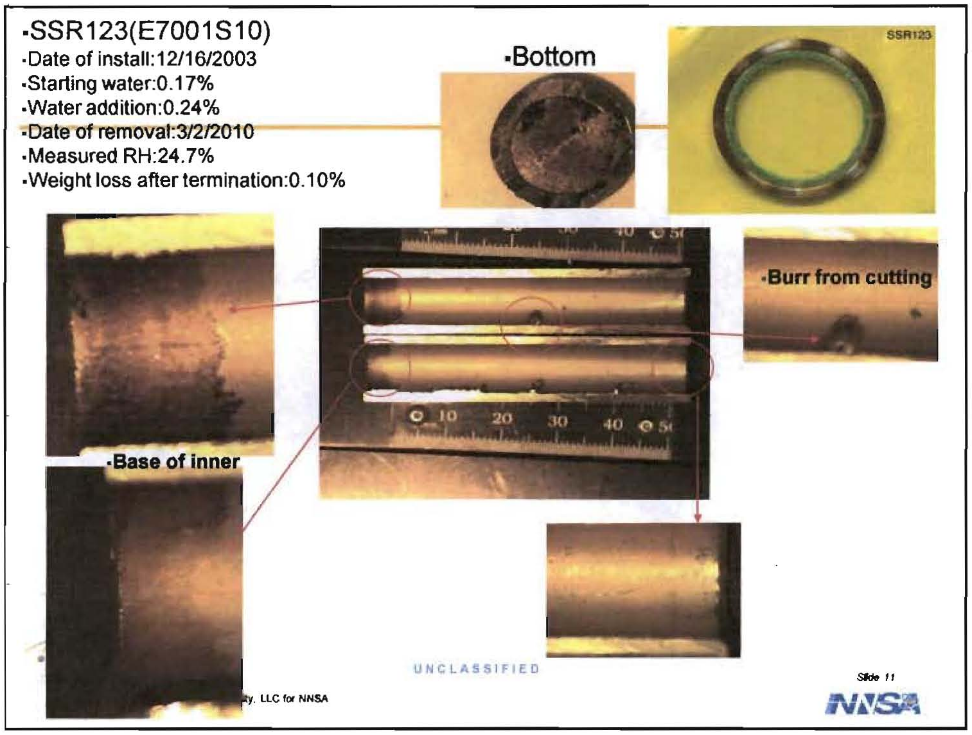
•SSR123(E7001S10)
•Date of install:12/16/2003
•Starting water:0.17%
•Water addition:0.24%
•Date of removal:3/2/2010
•Measured RH:24.7%
•Weight loss after termination:0.10%
•Bottom
SSR123
•Burr from cutting
•Base of inner
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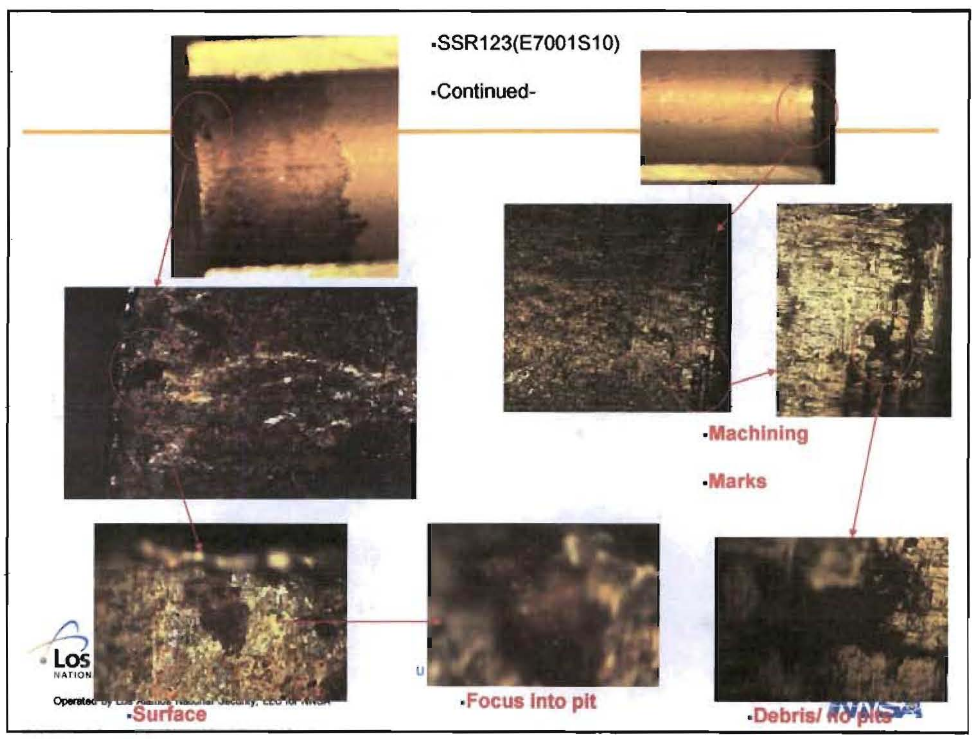
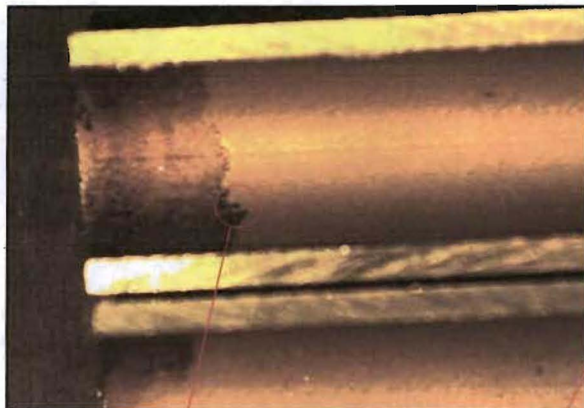

•SSR123(E7001S10)
•Continued-
•Machining
•Marks
•Surface
•Focus into pit
•Debris/



•SSR123(E7001S10) Continued....

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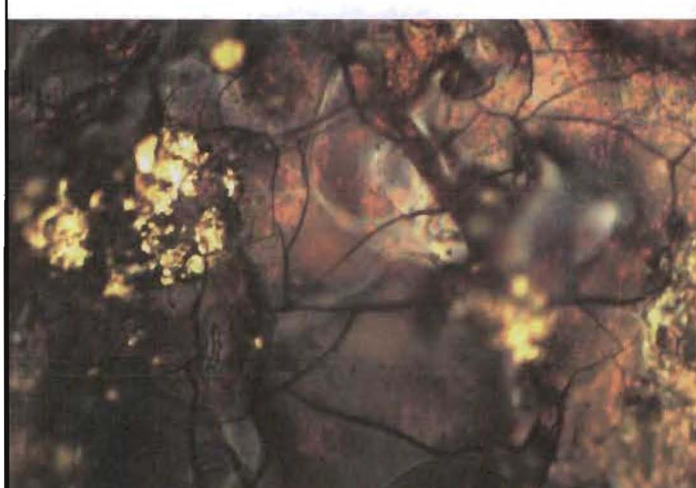
•SSR123(E7001S10) Continued



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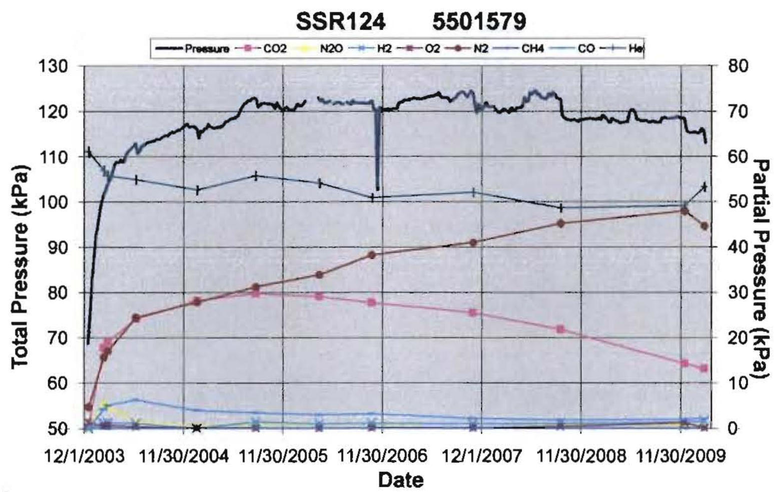
RFETS High purity oxide



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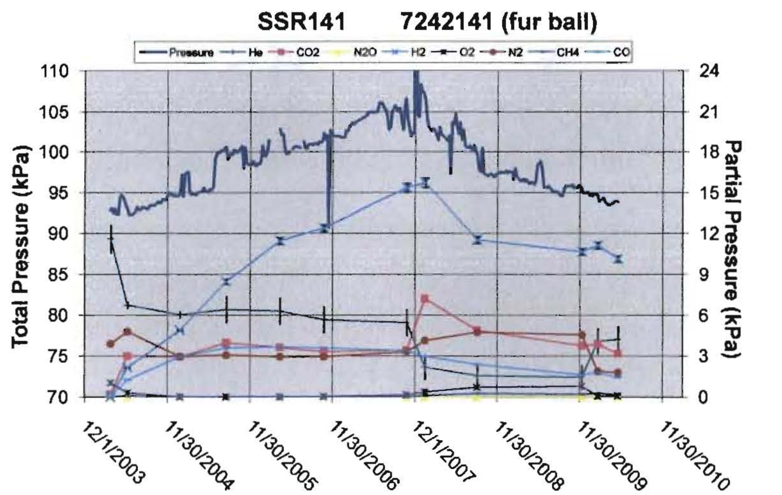
RFETS 63% Pu



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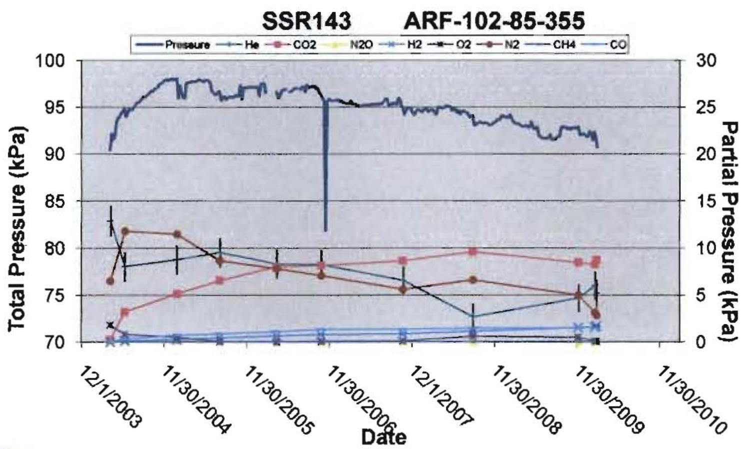
Hanford 70% Pu



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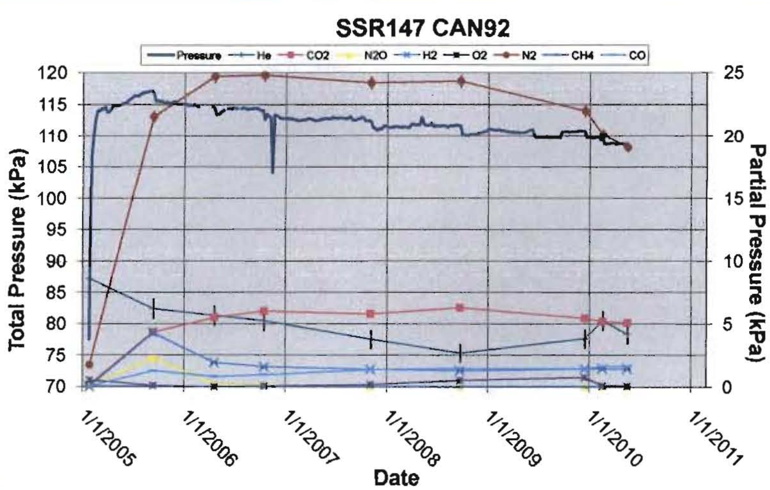
RFETS Mixed oxide 85.4% actinides



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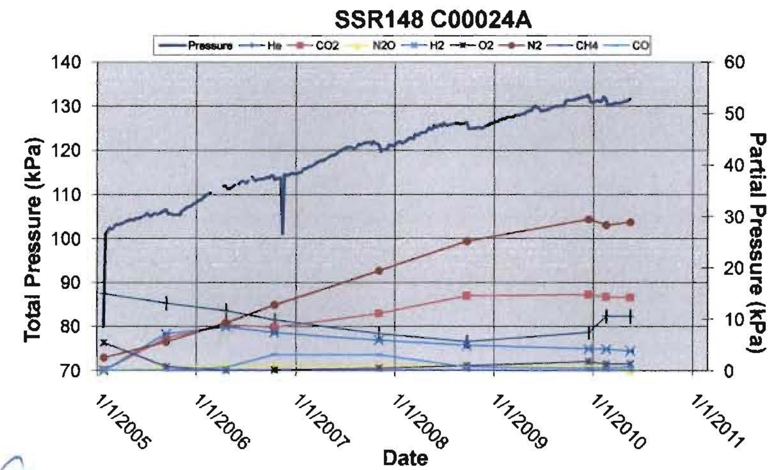
RFETS 73.4% Pu



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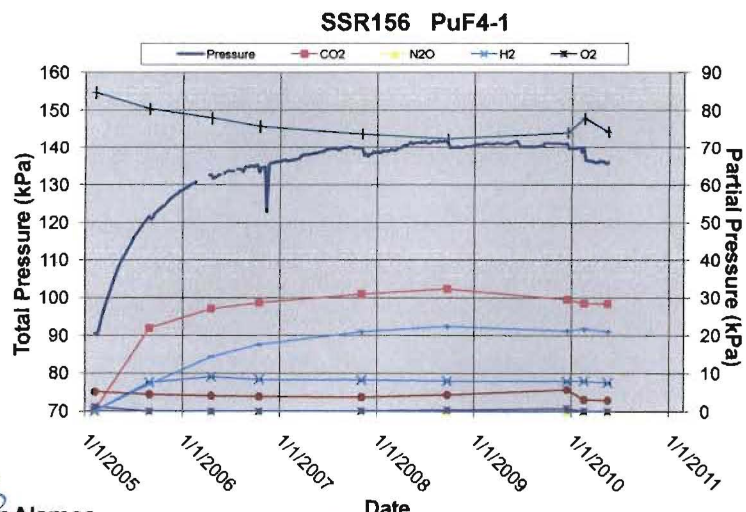
LANL 72% Pu



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LANL material loaded

Material	SSR	Pu (%)	Cl (%)	Pyc. Den. (g/cm³)	Bulk (g/cm³)	SSA (m2/g)	Moisture Added (%)
CXLPROD091901	203	87.6	0.03	11.2	2.2	7.9	0.4
CXLPROD021202C	204	87.9	0.02	11.5	2.6	4.4	0.48
CXLPROD091802A	205	77.2	2.2		1.6		0.49
04272-CC-220-AS	207	(Th)					0.02/15%
04272-CC-220-AS	208	(Th)					0.06/50%

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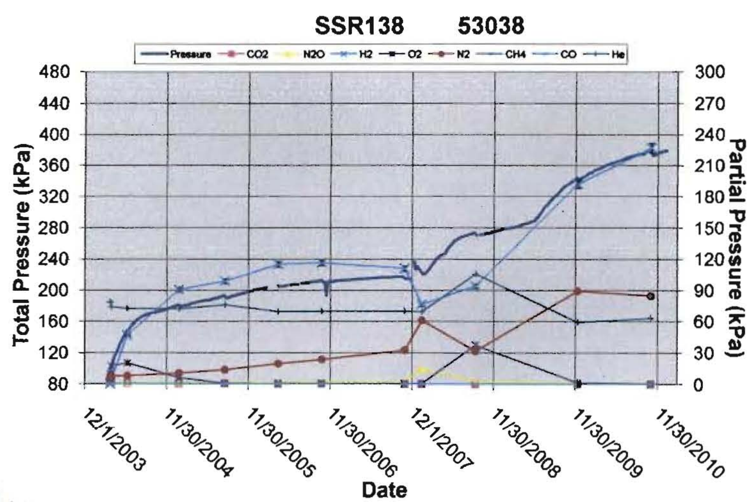
Temperature excursion changed behavior



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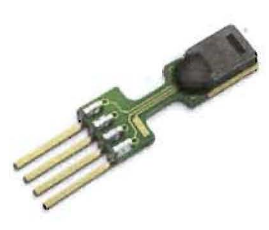
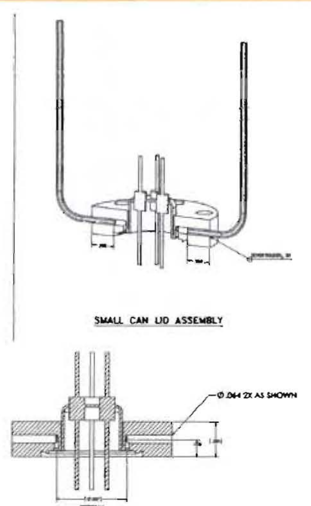
Materials to be reviewed for removal

- SSR 125 MT-1490 RFETS 86% Pu
- SSR128 7242201 RFETS 63.5% Pu
- SSR132A BLO-39-11-14-004 Hanford 87.5% Pu
- SSR139 520610020 RFETS 33.7% Pu
- SSR150 TS707013 RFETS 69.7% Pu
- SSR151A 7032282 RFETS69.4% Pu
- SSR153D 63-88-06-121 Hanford 35% Pu
- SSR155HT ARF-102-85-295 Hanford 39.7% Pu (leaked)

Indicated Pu content but represented class is more relevant

Humidity sensor for small scale lid





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Work to do

- Reports on each material (or should it be a composite report? Or a composite summary report with all details in individual reports)
- Use empty slots to repeat materials with corrosion potential with RH measurements.

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SAVANNAH RIVER NATIONAL LABORATORY
We Put Science To Work

DE Analysis Reductions

G. F. Kessinger
Separations & Actinide Science Programs
SRNL
January 2011

3013 Surveillance and Monitoring Program Review

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Introduction

Continuous Improvement Process

- **"Traditional" suite of DE analyses**
  - Pycnometry
  - Bulk & Tapped Density
  - Surface Area Analysis
  - Carbon/Sulfur Analysis
  - Thermogravimetric Analysis-Mass Spectrometry
  - Acid Dissolution
  - Aqueous Leaching
- **Reviewed all aspects of DE analyses**
  - Results from FY07 – FY10

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3013 Surveillance and Monitoring Program Review 2

Introduction

Continuous Improvement Process

- **Determined that some analyses/results were:**
  - Redundant
  - Not necessary
- **Concluded that some analyses could be reduced or eliminated**
  - Blank Gas analysis – eliminated
  - Direct Inlet MS – eliminated
  - Bulk & Tapped Density – eliminated
  - Carbon/Sulfur Analysis – eliminated
  - Acid Dissolution – some aqueous solution analyses
    - ICP-MS – reduced
    - RadChem – eliminated
  - SEM/EDX - reduced

Continuous Improvement Process

Gas Analyses

- **Blank Gas analysis – eliminated (data not needed)**
  - The blank gave a measure of the effectiveness of the last flush of the CPD with N_2 (not the actual background present just prior to puncturing).
  - Four years of results indicated that the flushing procedure was adequate
- **Direct Inlet MS – eliminated (redundant)**
  - The species of interest detected via DIMS can also be determined via FTIR and μGC
  - The instrument is still present and available for data collection when additional data are required.

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Continuous Improvement Process

Solids Analyses

- **Bulk & Tapped Density – eliminated (redundant)**
  - Redundant information - pycnometry is used for GEST calculations.
- **Carbon/Sulfur Analysis – eliminated (data not needed, redundant)**
  - It does not appear that the carbon and sulfur content are related to package performance.
  - H_2O – soluble sulfate is detectable by IC
  - Crystalline carbon phases are detectable by XRD
  - The instrument is present and available for data collection.
- **SEM/EDX – reduced (data not needed)**
  - When no corrosion or anomalous conditions exist, these results are not needed.
  - The instrument is available for data collection when additional data are required.

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Continuous Improvement Process

Solids Analyses

- **SEM/EDX – reduced (data not needed)**
  - Data collected on five cans (of seven) this year:
    - S002129 and S001105 – engineering judgment items
    - H003337 - high Cl^-, small amount of coating on headspace of convenience can (no can analysis)
    - H003343 – high moisture, small amount of coating on headspace of convenience can (no can analysis)
    - H003371 – corrosion-looking product on convenience can (extra analyses of can will be done)
  - Expect more SEMs early in FY (engineering judgment cans)

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Continuous Improvement Process

Aqueous Solution Analyses

- **Analysis of Acid Dissolution Product**
  - ICP-MS – reduced
    - The primary reason for collecting these data was mass balance (for actinide content).
    - Pu & Am content determined by a superior method (Cal-Gamma) prior to packaging.
    - The instrument is available for data collection when additional data are required (when U is present).
    - ICP-MS data have been requested for three cans
      - *H002592 – UO_3 and $NaUO_3(OH){\cdot}H_2O$ in XRD*
      - *S001105 – engineering judgment*
      - *H003371 – corrosion-looking product on convenience can*

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Continuous Improvement Process

Aqueous Solution Analyses

- **Analysis of Acid Dissolution Product**
  - RadChem – eliminated
    - The primary reason for collecting these data was mass balance (for Pu & Am content).
    - Pu & Am content determined by a superior method (Cal-Gamma) prior to packaging.
    - This technique is available for data collection when additional data are required.

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Conclusions

- Reviewed all aspects of DE analyses, including four years of experimental results
- Concluded that some analyses could be reduced and/or eliminated
- Instrumentation is available to perform these analyses (as needed).
- Cost savings = $500K

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Collaborators

Kerry Dunn

Chip McClard

Dave Missimer

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FY10 Prompt Gamma Update

Joshua Narlesky

January 26, 2010

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FY10 Activities

- Routine Analysis
  - LLNL
  - LANL
- Surveillance Data Review
- Hanford File ID Matching
- Analysis of New Hanford Data
- PG Software Updates

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Prompt Gamma Analysis (α-Particle Induced)

Capability

- **NDA method to detect low-Z elements (Z < 20) present in Pu bearing materials.**
  - Uses self-interrogation: gamma rays produced in (α,nγ), (α,pγ), and (α,α'γ) reactions
  - Requires 5+ MeV α-particles from Pu & Am
  - Cannot detect Ca
- **Uses**
  - Semiquantitive analysis for some elements
  - Screening tool
  - Representation
  - Binning of 3013 containers

60-Minute Detection Limits*

Element	Isotope Detected	Isotopic Abundance (%)	Element $LLD_{60\,min}$ (%)	Semi-Quantitative Analysis
Li	^{7}Li	92.5%	0.026%	No
Be	^{9}Be	100.0%	0.008%	Yes
B	^{10}B	19.9%	0.046%	No
N	^{14}N	99.6%	No data	No
O	^{18}O	0.2%	13.0%	No
F	^{19}F	100.0%	0.200%	Yes
Na	^{23}Na	100.0%	0.014%	Yes
Mg	^{25}Mg	10.0%	0.056%	Yes
Al	^{27}Al	100.0%	0.130%	Yes
Si	^{28}Si	92.2%	No data	No
P	^{31}P	100.0%	0.820%	Yes
Cl	^{35}Cl	75.8%	0.640%	Yes
K	^{39}K	93.3%	2.0%	Yes

*Can determine as a function of count time

Routine Data Analysis

- **LLNL—completed 40**
  - Results:
    - 7 Chlorides: 0.5 to 2.5 wt% Cl
    - 7 Fluorides: 0.01 to 0.3 wt% F
    - 13 Other: Be, Na, Mg
    - 13 No impurities detected
  - Notable results: 2 cans with high Al—11 wt% and 15 wt%
- **LANL—completed 27**
  - Results
    - 3 Chlorides: 2.5 to 5.5 wt% Cl
    - 3 Fluorides: 0.03 to 0.2 wt% F
    - 10 Other: Be, Na, Mg
    - 12 No impurities detected
  - Notable results: None

Review of Surveillance PG (FY10)

- **Following review, surveillance results match baseline for all DE items**

ID	3013 ID	Cl% AC	Be wt%		Cl wt%		F wt%		Mg wt%		Na wt%		K wt%	
			BL	FS	BL	FS	BL	FS	BL	FS	BL	FS	BL	FS
10DE01	H004251	14.7-15			11.3	10.0			2.2	1.6	3.9	3.4	4.0	2.9
10DE02	H002496	0.27-0.42			0.9		3.7	3.2	1.4	0.6	0.1	0.1		
10DE03	H003710	6.3-6.4	0.02		8.5	6.6	0.1	0.1	1.5	0.8	2.6	2.2	3.3	3.1
10DE04	H003655	6.3-7.1			8.2	6.6			1.4	0.7	2.7	2.1	3.3	3.2
10DE05	H002447	10.7-11.2	0.04	0.02	1.5	1.3			1.3	0.8	0.5	0.4		
10DE06	R610627	16.7-18.5	0.05	0.03	10.2	8.8		0.1	2.1	1.0	2.8	2.7	5.4	1.9
10DE07	H003900	12.3-12.5			13.5	8.6	0.2	0.2	2.2	1.1	4.7	3.2	5.6	3.9
10DE08	H003650	3.7-3.8			4.4	3.7			0.7	0.4	1.3	1.2	2.0	2.1
10DE09	H002567	<0.03	0.16	0.07					1.1	0.2	1.7	1.4		
10DE10	H002728	6.5-7.3			7.8	6.2			1.6	0.6	2.3	1.8	2.7	4.1
10DE11	H002786	7.3-7.4			9.4	7.8			1.5	0.8	3.0	2.4	3.6	2.5
10DE11	H002786	7.3-7.4			7.3	7.8			1.0	0.8	2.5	2.4	3.5	2.5
10DE12	H003077	0.46-0.48			0.6	0.8			1.0	0.6	0.3	0.3		
10DE13	H003367	0.82-0.86			0.5	1.4	2.1	2.9	0.8	1.3	0.1	0.2		
10DE14	H003704	8.6-8.8			9.3	7.3			1.3	0.6	2.8	2.4	3.8	3.6
10DE15	R610785	9.6-10.0	0.05	0.03	7.6	7.8			1.4	0.8	3.1	3.1	2.9	3.5
10DE16	R610826	14.3-15	0.05	0.04	9.9	8.8	0.3	0.2	1.7	0.9	3.0	3.0	4.2	3.2
10DE17	R610853	5.2-5.7			7.0	6.2			1.5	0.7	1.9	2.0		1.6
10DE18	S001721	0.61-0.62			2.3	1.9	0.2	0.1		0.2	0.0	0.0		

Review of Surveillance PG (FY11)

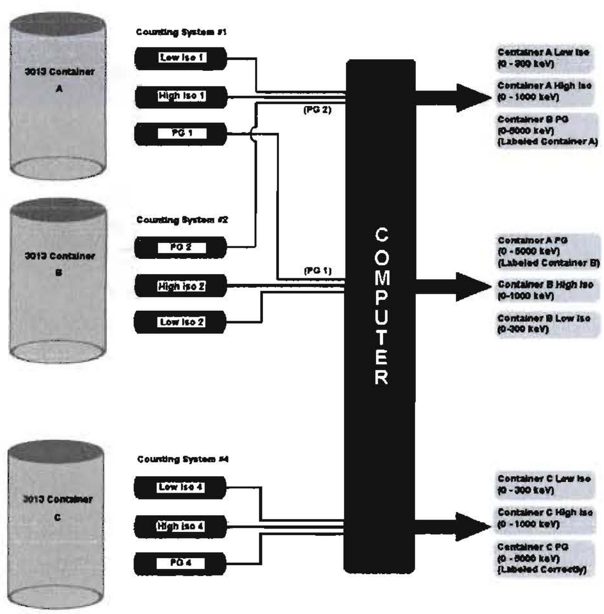
ID	3013 ID	Al wt%		Be wt%		Cl wt%		F wt%		Mg wt%		Na wt%		K wt%	
		BL	FS	BL	FS	BL	FS	BL	FS	BL	FS	BL	FS	BL	FS
11DE01	H003443														
11DE02	S002129			0.10	0.06			0.4	0.3	0.5	0.4	0.05	0.03		
11DE02	S002129			0.10	0.06			0.4	0.3	0.5	0.3	0.05	0.05		
11DE02	S002129			0.10	0.04			0.4	0.3	0.5	0.4	0.05	0.04		
11DE02	S002129			0.10	0.06			0.4	0.2	0.5	0.4	0.05	0.04		
11DE03	H002592														
11DE04	H003337					14.8	9.7			2.6	1.2	4.8	3.0	4.7	5.1
11DE04	H003337					14.8	9.6			2.6	1.0	4.8	3.2	4.7	2.3
11DE05	S001105	0.20				0.4		0.3	0.2	0.3	0.3	0.03	0.03		
11DE06	H003343														

Hanford Spectrum ID Corrections

- **A counting system issue resulted a set of Hanford PG spectra being labeled with incorrect spectrum IDs**
  - Affected measurements on counting systems #1 and #2 from 11/20/2003 to 3/4/2004
  - Result: IDs for the items systems #1 & #2 were swapped
- **<u>258</u> Items affected (250 oxide & 8 metal)**
- **Matching corrected for 230 spectra (A→B & B→A)**
- **Containers without PG analysis: 34**
  - A→NDA STD & NDA STD→
  - A →Bkg & Bkg →
- **Example**

3013 ID	Type	Measurement Type	Date	Al%	Be%	Cl%	F%	Mg%	Na%	K%
H003928	ARF	Original	09-Dec-03	0.16			0.31	0.11	0.03	
H003928	ARF	Input Item Screening	19-Nov-03	0.12		3.76		1.38	0.44	
H003928	ARF	Input Item Screening	18-Nov-03			8.92		0.89	2.62	3.55
H004099	PFP Scrap	Original	09-Dec-03			6.52		1.36	1.72	3.30
H004099	PFP Scrap	Surveillance	10-Sep-08	0.24			0.31	0.05	0.03	

Schematic



Impact

- **Surveillance Binning (70 affected)**
  - Innocuous → Engineering Review (no PG result): 15
  - Innocuous → Pressure and Corrosion 1
  - Pressure → Engineering Review (no PG result): 1
  - Pressure → Pressure and Corrosion 13
  - Pressure and Corrosion → Engineering Review 22
  - Pressure and Corrosion → Innocuous 3
  - Pressure and Corrosion → Pressure 15
- **Items represented by 011589A (Mismatching: 4, PG updates: 12)**
  - Not Similar → Most Similar: 3
  - Not Similar → Potentially Similar: 5
  - Most Similar → Not Similar: 2
  - Potentially Similar → Most Similar 3
  - Potentially Similar → Not Similar: 3
- **Actions**
  - Update surveillance binning
  - 8 new items represented by 011589A, but none are expected to generate flammable gases (less than 0.3 wt% moisture)
  - Obtain PG meas. for 4 remaining "outliers" and 9 ARF/HNF scrap items without PG

New Hanford PG

3013 ID	ID	Type	Reason	PredCl%	PredF%	PredMg%	PredNa%
H002673	PG-13	HNF Scrap >80%	Outlier-Cl	0.9		0.2	0.4
H004009	PG-6	Oxalate Prod	Outlier-F		1.3	0.2	
H001863	PG-4	Mixed Ox	Outlier-Cl				0.02
H002543	PG-5	Oxalate Prod	Outlier-Cl				0.02
H002842	PG-2	ARF	No PG	5.4	0.7	0.7	2.4
H003284	PG-12	ARF	No PG		0.2	0.2	0.1
H004024	PG-10	ARF	No PG	9.5		0.9	2.6
H004096	PG-1	ARF	No PG	10.0		1.0	3.5
H004185	PG-11	ARF	No PG	8.7		0.9	2.3
H004220	PG-9	ARF	No PG		1.1	0.5	0.8
H004237	PG-3	ARF	No PG	3.9		0.5	1.3
H004392	PG-7	HNF Scrap <80%	No PG		1.6	1.2	5.0
H004415	PG-8	HNF Scrap <80%	No PG		0.4	1.9	5.0

PGA Software and Database Updates

- **Released PGA v 4.7 a,b,c (minor updates to v 4.7)**
  - Fixed issue with startup for some OSs (a)
  - Added automatic baseline correction for Be peaks (b)
  - Added redraw button for main plot window
  - Added "Save PGR" button and fixed issue with unreadable PGR files (c)
  - Added rename button (allow user to change spectrum file name) (c)
  - Revised code for calculating concentration (allow greater user control) (c)
- **Impact to user: more flexible & more robust**
  - Program is more robust for different OSs
  - More flexibility in selecting the element to display, the calibration parameters, and type of data (eg. detection limit only or concentration)
  - Allows user to calculate concentration from a peak other than primary
- **Impact to database: None,** but it is important that configuration file is set properly to feed correct data fields into database.

FY11 activities

- **Routine analyses—LLNL & LANL**
- **Issue final reports**
- **Support surveillance activities**
  - Review surveillance data
  - Software maintenance as necessary

Engineering Judgment Selection Process for FY11 DE Surveillance

Summary for MIS Annual Program Review,

Savannah River Site, Jan. 25-26, 2011

Presented by John Berg, LANL

NNSA

July 2010 discussions in Baltimore at INMM

- Participants
  - Chip McClard, L. Worl, K. Veirs, J. Duffey, K. Dunn, E. Kelly, J. Narlesky, T. Venetz (in spirit)
  - Three full afternoons of discussions in Baltimore
  - Input from database queries by Gary Friday
- Pick containers in storage that are most likely to show some corrosion using packaging, shelf-life and DE data.
- Items packaged at Savannah River Site were included for the first time.

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Selection criteria have evolved each year

- Initial focus on pressurization risk from high moisture shifted to a focus on corrosion risk in recent years.
- Early engineering judgment samples included containers produced at Rocky Flats that showed acid gases during the TGA moisture measurement.
- FY10 focused on packaging moisture content in conjunction with data on exposure to humid atmosphere between stabilization and packaging.
- For FY11 included the refinement that if moisture is present, liquid phase formation and hence corrosion would be more likely if the salt content is relatively low.

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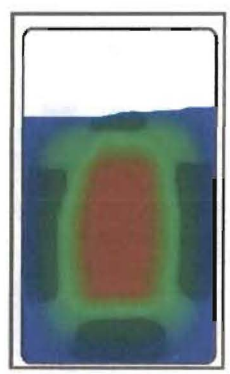
Factors leading to liquid phase in contact with container walls in sealed package.

- Hydrate formation during packaging.
- Temperature gradient may cause H_2O migration to walls.
- Total H_2O may exceed hydrate formation capacity of $MgCl_2$ and $CaCl_2$ and related salts.



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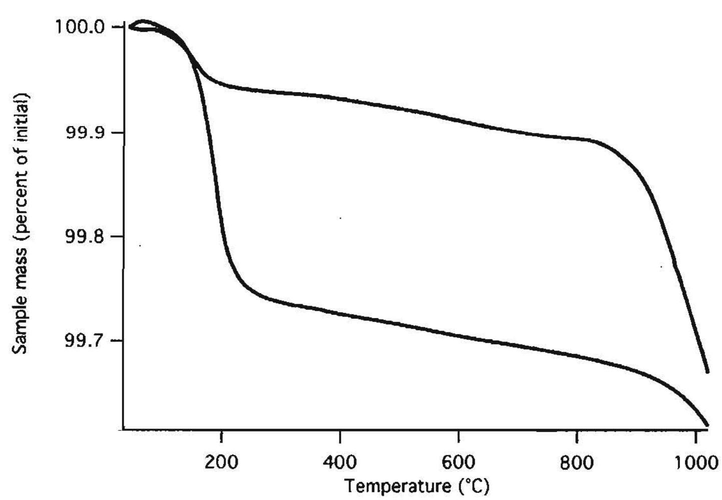
FY11 selection process

Calculate H_2O / chloride (PG) ratio

Pick the containers with highest ratio from those packaged at Hanford and SRS.

Pick highest-moisture containers from those with chloride below detection threshold – these probably have the highest actual ratio.

Moisture estimated by mass loss in TGA below temperature where salt evaporation dominates.



Necessary simplifications

- Mg and Ca chloride concentrations assumed proportional to total Cl.
  - Clearly not true – there is much variation.
- Prompt gamma can measure chloride low chloride accurately.
  - Hedge bets by including containers with non-detectable chloride.
- Despite shortcomings, we believe this selection method is better than moisture content alone.

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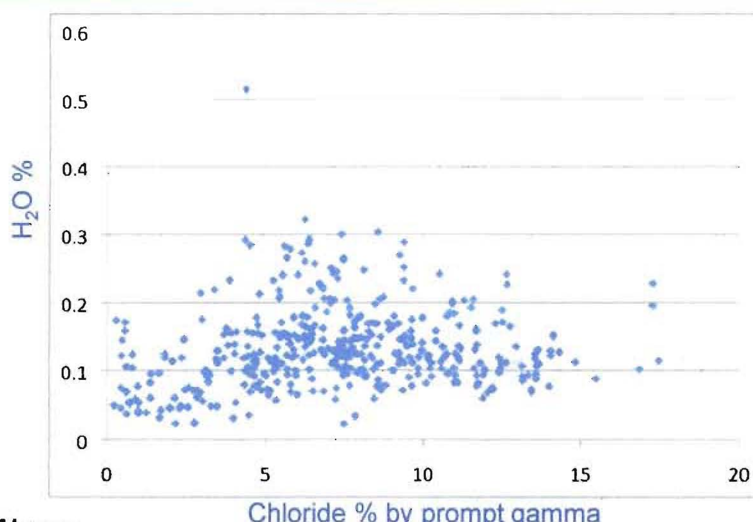
Hanford RMC moisture (tga to 650 °C) vs. chloride (PG)



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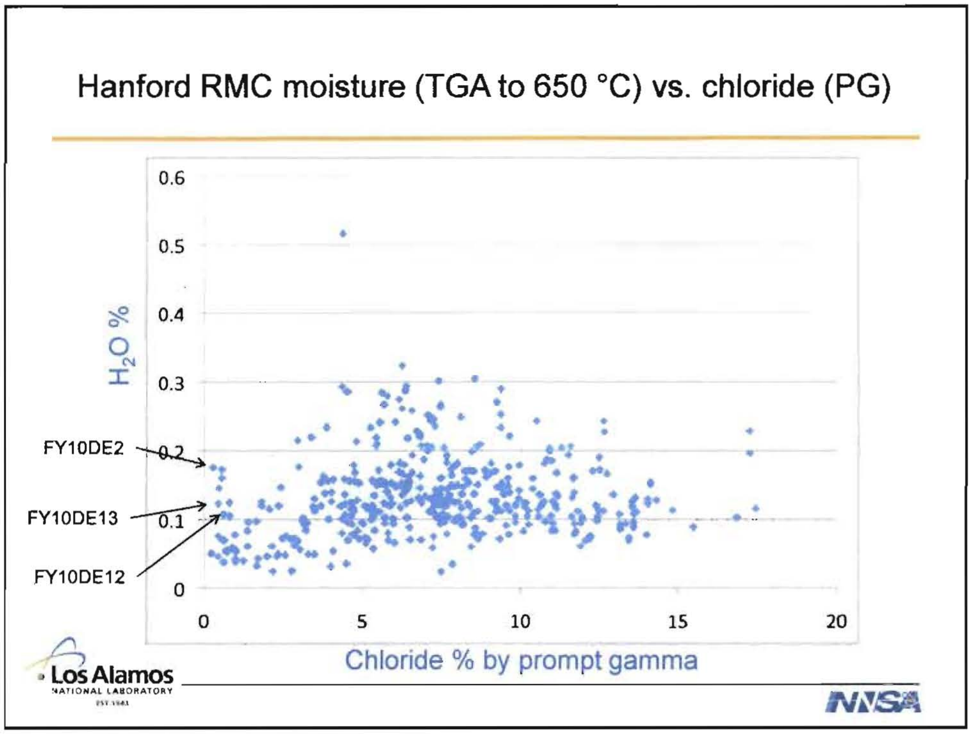
Hanford RMC moisture (TGA to 650 °C) vs. chloride (PG)
0.6
0.5
0.4
0.3
0.2
0.1
0
H_2O %
FY10DE2
FY10DE13
FY10DE12
0
5
10
15
20
Chloride % by prompt gamma
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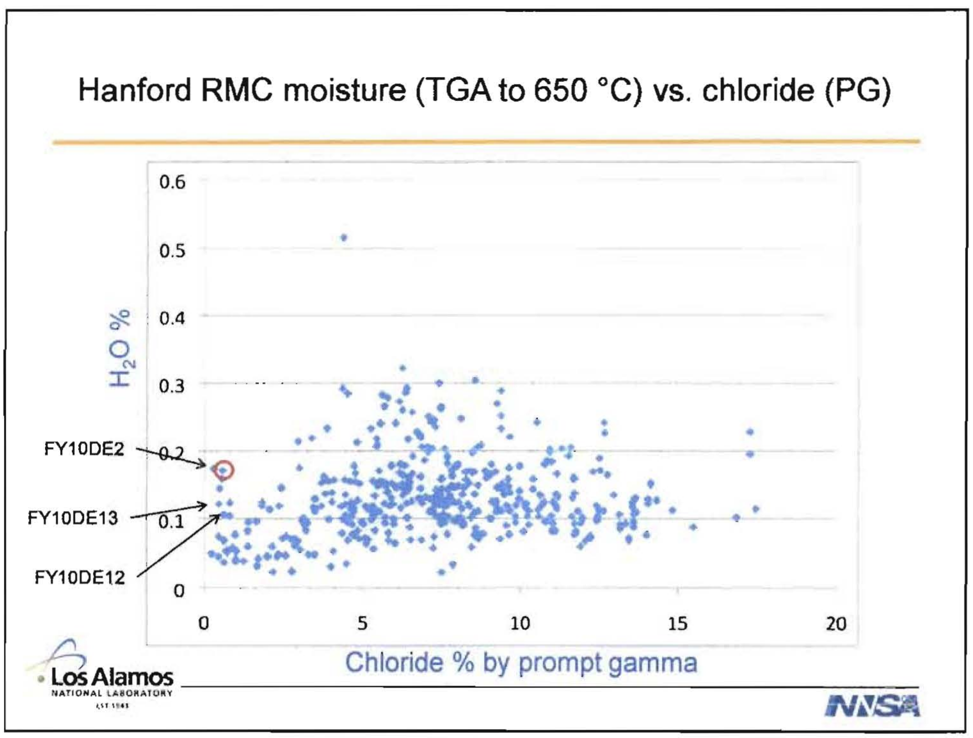
Hanford RMC moisture (TGA to 650 °C) vs. chloride (PG)
0.6
0.5
0.4
0.3
0.2
0.1
0
H_2O %
FY10DE2
FY10DE13
FY10DE12
0
5
10
15
20
Chloride % by prompt gamma
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3013 Container ID	Surveillance type	Glove Box Relative Humidity (%)	Duration_A (hrs) Stab End to First wt	TGA start to 650	Moisture (%) ; PCD value	Cl%	F%	Mg%	K%	Na%	ratio of moisture (TGA to 650) to Cl
Hanford candidates with non-detect Cl (PG) ranked by moisture (TGA to 650 or TGA-MS)											
H003371		30	109	0.18	0.27		1.180	1.587			#DIV/0!
H002574		27	18	0.14	0.24		4.385	1.385		0.110	#DIV/0!
H002103		25		0.13	0.22		0.166	1.038		3.053	#DIV/0!
H002766		25	20	0.13	0.17		3.319	1.104		0.098	#DIV/0!
H002631		20	22	0.12	0.26			1.096		0.094	#DIV/0!
H003870		21		0.12	0.22		0.153	0.403		0.335	#DIV/0!
H002103		25		0.11	0.22		0.166	1.038		3.053	#DIV/0!
Hanford candidates ranked by ratio of moisture (TGA to 650 or TGA-MS) to Cl (PG) – red indicates FY10 DE											
H002496	10DE2	41	29	0.17	0.25	0.300	3.694	1.409		0.094	0.581
H003343	NDE 2006	34	19	0.17	0.39	0.579	0.894	0.306		0.180	0.296
H003940	NDE 2006	30	17	0.14	0.33	0.490	0.385	0.650		0.110	0.295
H002543		40		0.16	0.19	0.574		0.139		0.270	0.277
H003367	10DE13	28	14	0.12	0.26	0.465	2.103	0.831		0.118	0.262
H003128		22	26	0.05	0.05	0.235		0.529		0.116	0.209
H003077	10DE12	21	241	0.11	0.13	0.617		1.012		0.295	0.172
H002286		26	108	0.07	0.27	0.453		0.210	0.697	0.223	0.164
H003390		30	145	0.12	0.18	0.811	0.599	2.158		0.206	0.152
H003328	LANL to DE	33	64	0.52	0.23	4.389	0.694	0.545		0.881	0.117
H002286		26	108	0.04	0.27	0.453		0.210	0.697	0.223	0.099
Hanford candidates remaining from FY10 list ranked by moisture (TGA to 650 or TGA-MS)											
H003443		35	28	0.29	0.37	6.400		1.213	3.782	1.866	0.046
H002575		36	26	0.28	0.36	5.621		1.444	3.480	1.680	0.050
H003368		32	99	0.28	0.36	5.798		1.347	3.091	1.751	0.048
H003737	NDE 2005	49	20	0.26		9.116		1.520	3.671	2.970	0.029
H002560		24	155	0.26	0.33	7.494		1.303	2.970	2.343	0.035
H003695	NDE 2006	38	27	0.25	0.35	7.275		1.076	2.827	2.196	0.034
H003896	NDE 2005	22	47	0.24	0.35	10.529		2.079	4.033	3.293	0.023
H002557	NDE 2005	24	70	0.24	0.33	5.563	0.206	0.824	2.715	1.460	0.043
H003670		38	23	0.23	0.27	3.879	0.134	0.619		0.835	0.060
H002468	NDE 2006	43	24	0.23	0.29	6.723		1.174	3.317	2.069	0.034

3013 Container ID	Surveillance type	Glove Box Relative Humidity (%)	Duration_A (hrs) Stab End to First wt	TGA start to 650	Moisture (%) ; PCD value	Cl%	F%	Mg%	K%	Na%	ratio of moisture (TGA to 650) to Cl
Hanford candidates with non-detect Cl (PG) ranked by moisture (TGA to 650 or TGA-MS)											
H003371		30	109	0.18	0.27		1.180	1.587			#DIV/0!
H002574		27	18	0.14	0.24		4.385	1.385		0.110	#DIV/0!
H002103		25		0.13	0.22		0.166	1.038		3.053	#DIV/0!
Hanford candidates ranked by ratio of moisture (TGA to 650 or TGA-MS) to Cl (PG) – red indicates FY10 DE											
H002496	10DE2	41	29	0.17	0.25	0.300	3.694	1.409		0.094	0.581
H003343	NDE 2006	34	19	0.17	0.39	0.579	0.894	0.306		0.180	0.296
H003940	NDE 2006	30	17	0.14	0.33	0.490	0.385	0.650		0.110	0.295
H002543		40		0.16	0.19	0.574		0.139		0.270	0.277
H003367	10DE13	28	14	0.12	0.26	0.465	2.103	0.831		0.118	0.262
Hanford candidates remaining from FY10 list ranked by moisture (TGA to 650 or TGA-MS)											
H003443		35	28	0.29	0.37	6.400		1.213	3.782	1.866	0.046
H002575		36	26	0.28	0.36	5.621		1.444	3.480	1.680	0.050
H003368		32	99	0.28	0.36	5.798		1.347	3.091	1.751	0.048
H003737	NDE 2005	49	20	0.26		9.116		1.520	3.671	2.970	0.029
Hanford Candidates on FY10 list for other reasons											
H003352	NDE 2006	34	71	0.27	0.38	6.169	0.336	0.962	2.532	1.825	0.044
H004228		20	112	0.12	0.20	10.690		2.248	3.937	3.151	0.011
H004194		28	20	0.13	0.24	11.199	0.081	2.034	4.370	3.601	0.012
SRS candidates with non-detect Cl (PG) ranked by moisture (TGA to 650)											
S002129				0.24	0.29		0.406	0.505		0.059	#DIV/0!
S002148				0.21	0.24			0.168			#DIV/0!
SRS candidates ranked by ratio of moisture (TGA to 650) to Cl (PG)											
S001105				0.20	0.23	0.413	0.306	0.279		0.029	0.476
S002277				0.22	0.29	0.506	0.327	0.187		0.056	0.441
S002187				0.21	0.23	0.625	0.657	0.599		0.058	0.341

Summary of selections for FY11

Engineering judgment selection of containers for DE in FY2011 sought to identify containers likely to be at the greatest risk for internal corrosion based on packaging conditions and material composition that could have led to formation of liquid water films or droplets within the container. The relevant packaging data available for this selection process are the total moisture and total chloride content. A high ratio of moisture to chloride was deemed to be the highest risk based on shelf-life studies. Two containers were selected based on having the highest such ratios from the Hanford and SRS packaging campaigns (H003343 and S001105). Two additional containers were selected based on high moisture but undetected chloride under the assumption that chloride is probably present but below the detection threshold of prompt gamma (H003371 and S002129). A fifth container was selected based solely on having the highest total moisture at the time of packaging (H003443) of the containers remaining in the surveillance program.

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Selections transmitted via letter 8/10/2010.

TO: Allen Gunter, Chairman of ISP Steering Committee August 10, 2010

FM: G.D. Roberson, Program Manager, MIS Working Group

RE: **FY11 Surveillance Recommended Destructive Examination Items.**

This letter is being sent on behalf of the Materials Identification and Surveillance Working Group (MIS WG). The MIS WG recommends the following 3013 containers as the minimum Destructive Examinations (DE) for FY11. The MIS WG does not request any Non Destructive Examinations (NDE) of 3013 containers for FY11.

Eighteen total DEs are specified in FY11 where five are selected for Engineering Judgment and thirteen are selected as part of the Random Sample for the Integrated Surveillance Program. The attached table lists the specific containers that have been selected by the MIS WG for surveillance.

Should you have any questions, please contact me at (202) 586-9681

G.D. Roberson

Nuclear Material Integration, PMP

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Selections transmitted via letter 8/10/2010.

FY11 Destructive Evaluation Surveillance Samples

Surv Year	Surv Type	ISP Bin	Surv Selection	Site (Packaged)	Surveillance Comment	3013 Container ID
2011	DE	Pressure and Corrosion	Judgmental	Hanford	Non-detect Cl with high moisture	H003371
					High ratio of water to Cl	H003343
					highest remaining TGA to 650 deg	H003443
				SRS	Non-detect Cl with high moisture	S002129
					High ratio of water to Cl	S001105
			Random	Hanford		H002592
						H003337
						H003526
						H003565
						H003625
						H003711
				LLNL		L000075
						L000178
				RFETS		R610960
						R610974
						R610989
						R611338
						R611131
	DE Total					18
2011 Total						18

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We Put Science To Work

Update on ISP Database Queries/FY2011 Binning

Gary Friday
26 January 2011

3013 Surveillance and Monitoring Program Review

Savannah River Site, Aiken, South Carolina

ISP Database

- Query Update
- FSM Data Dictionary
- FY2011 Binning Protocol

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ISP Database Query Protocol

Case Number

Date Received

Customer

Statement of the Problem

Resolution

Status

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ISP Database - Query Update

Completed Queries

2006 – 8

2007 – 22

2008 – 21

2009 – 22

2010 – 27

Total – 100

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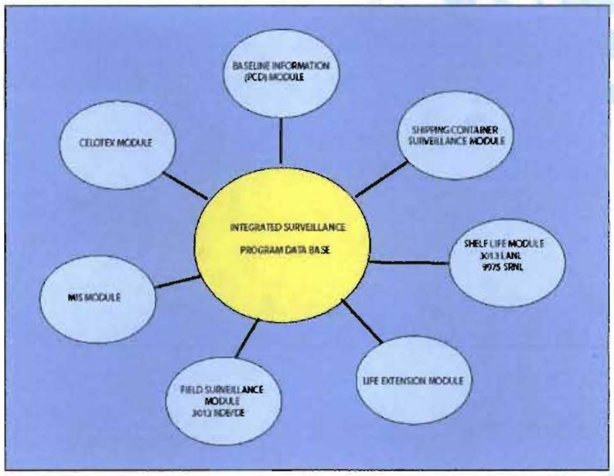
ISP Database Conceptual Model



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5

SRNL-STI-2010-00538

Data Dictionary for the Integrated Surveillance Program (ISP) Field Surveillance Module (FSM)

G.P. Friday

T.J. Paul

SRNL

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Field Surveillance Module (FSM)

- SRNL Elemental Isotopic Analysis
- SRNL Solid Oxide Analysis
- SRNL TGA Analysis
- SRNL Gas Analysis
- 3013 Contents Radiography
- 3013 Lid Deflection
- DE 3013 Photos
- DE 3013 Surveillance
- Survey Photos 3013
- DE Misc Documents
- DE Cutting
- DE Gas Sample
- DE Sample Vial
- NDE Surveillance 3013
- SRNL Microhardness
- SRNL Attachments
- SRNL Photos
- Survey Document Number
- FTIR Other Gases
- Pressure Surveillance

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Table 21. FSM Predicted Gas Values

Field Name	Data Type	Size	Description	n	Non-Zero	Zero's	Null
3013 ID	Number	10	Identification number on the 3013 container	43	43	None	0
GasN2	Number	50	Calculated percentage of nitrogen in the inner 3013 prior to puncturing as determined by GEST	43	43	None	0
GasN2EOR	Text	50	Explanation of result for nitrogen; < symbol signifies that the result was "less than the limit of quantification"; trace – visually a peak was greater than three times the background noise and integrated to 0.01 vol% or less	43	0	None	43
GasO2	Number	50	Calculated percentage of oxygen in the inner 3013 prior to puncturing as determined by GEST	43	4	None	39
GasO2EOR	Text	50	Explanation of result for oxygen; < symbol signifies that the result was "less than the limit of quantification"; trace – visually a peak was greater than three times the background noise and integrated to 0.01 vol% or less	43	8	None	35
GasH2	Number	50	Calculated percentage of hydrogen in the inner 3013 prior to puncturing as determined by GEST	43	10	None	33

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8

Binning

Why is binning performed?

- **Statistical Selection of 3013's for DE and NDE**
- **New Data Becomes Available**
- **Existing Data is Revised**
- **New Containers are Produced**

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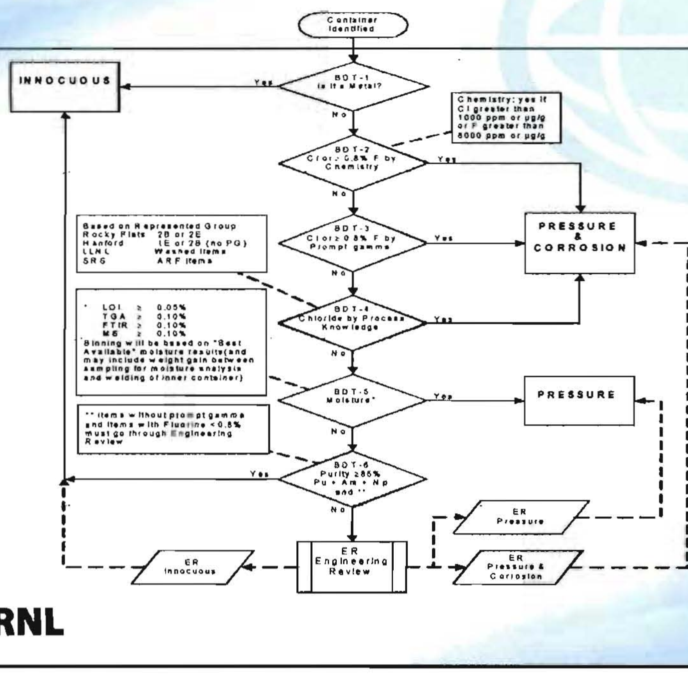

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Binning Protocol

Initial Binning Phase

- Physical Form
- Chemistry
- Prompt Gamma
- Process Knowledge
- Moisture
- Purity (Am + Np + Pu)

Final Binning Phase

- Engineering Review

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11

Bin and SubBin Hierarchy

Bins

- Innocuous
- Pressure
- Pressure and Corrosion

SubBins

- BDT-2-CI
- ER-C1-P (No PG)
- ER-C2-E-P

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Binning Macro

qry-MT_Binning_Data
qry-BDT-1
qry-BDT-2-CI
qry-BDT-3-F
qry-BDT-4-RF-2B
qry-BDT-4-SR-ARF
qry-BDT-5-P
qry-BDT-6-I
qry-BDT-6-ER

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Advantages of the Macro

- Faster
- Reduces Potential for Error
- Can Be Used for Future Rebinning Exercises

SRNL 14

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SRNS-STI-2011-00000

MIS DATABASE UPDATE

Jesse "Buzzy" Cheadle
Technical Advisor
January 26, 2011

Annual MIS Meeting

SRS, 766-H

Site Status

- **Rocky Flats**
  - 1888 of 1895 less 7 sent to Los Alamos
  - PCD Records for all 1895
  - 7 sent to Los Alamos have been marked as destroyed
  - 27 DEs and marked as destroyed
  - 1861 Active records

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Site Status Cont.

- **SRS**
  - 918 less 16 unpackaged and marked as destroyed
  - 16 were not supposed to be packaged
  - PCD Records for all 918
  - 2 DEs and one marked as destroyed
  - 44 3013s have been sent to H-Area for processing and have been marked as destroyed
  - 857 Active records

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Site Status Cont.

- **Hanford**
  - Received 2257 of 2257
  - PCD records for all 2257
  - 33 DEs and marked as destroyed
  - 2224 Active records

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Site Status Cont.

- **Livermore**
  - Received 164 of possible 285
  - Complete PCD records for all 164
  - 164 Active records

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Site Status Cont.

- **Los Alamos**
  - Received 12 of possible 268
  - PCD records for all 12
  - 12 Active records

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Surveillance Update

- **Non-Destructive**
  - Through FY10 222 NDEs, 9 done twice.
  - Data still to be added
- **Destructive**
  - Through FY10 62 DEs, 20 had previous NDE
  - Data still to be added

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Prompt Gamma and Moisture Data

- **Prompt Gamma data in the ISP is data provided by Josh Narlesky. Josh identifies the best PG record**
- **Moisture data comes from Los Alamos where the data is analyzed to provide the best and certified moisture values.**

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That's All Folks

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9

Selection of 3013 Containers for Field Surveillance – 2011 Update

Elizabeth Kelly, John Berg and Larry Peppers, LANL, Gary Friday and Chip McClard, SRS; David Riley, LLNL; Ted Venetz, Hanford

(LA-UR 11-00421)

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Surveillance Sampling Approach

- Combines random and judgmental sampling
  - Random selection based on bins (groups) defined by potential degradation mechanisms (or lack thereof) – Pressure Only, Pressure and Corrosion (P&C) and Innocuous
    - Pressure and P&C sampling criterion – 99.9%/5%
    - Innocuous – check assumption of no pressurization and minimal variability in measurements
    - Judgmental: MIS working group and other experts select containers deemed to have the greatest potential for degradation
    - Random sampling better at finding surprises, judgmental sampling better at finding "worst case"
- Key component of random sampling is binning process
  - Cl and F (chemistry, prompt gamma, process knowledge), moisture content, purity, engineering review)

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Background (Checkered Past)

- 2005
  - Three reports documenting (1) binning approach, (2) sampling approach and (3) items in statistical and judgmental samples
- 2007
  - Three 2005 reports combined into one document (LA-14310) and binning and sampling information updated
- 2009
  - Revision 1 of LA-14310 (LA-14395). This report contains all of the 14310 report plus new binning and sampling information
- 2011
  - LA-14310/14395 Update. This report will contain new binning and sampling (both statistical and judgmental) information only

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What's Changed

- Focus is now on P&C bin sampling, since the Pressure and Innocuous bin sampling was completed in 2009
  - Over 320 containers have had NDE pressure measurements (132 randomly sampled from Pressure bin and 10 from Innocuous bin)
  - Approximately 70 have had DE pressure measurements
  - No significant pressurization in any container
  - Shelf-life studies will guide future sampling
- Changes affecting binning
  - Hanford mismatch (250 containers with incorrect prompt gamma information)
  - Prompt gamma calibration curves changed
  - New items from LANL and LLNL
  - Other new information (e.g., washed / not washed info from LLNL, ARF assignments)
- New judgmental sampling criteria

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How Changes Affect Binning

	Hanford		LANL		LLNL		RFETS		SRS	
	2008	2011	2008	2011	2008	2011	2008	2011	2008	2011
Innocuous	928	939	25	525*	117	84	808	809	744	724
Pressure	778	769	83	83	9	9	718	721	103	95
P&C	551	549	160	160	159	108	362	358	71	83
Total	**2257**	**2257**	**268**	**768**	**285**	**201**	**1888**	**1888**	**918**	**902**

*500 ARIES

	2008	2011
Grand Total	**5616**	**6016**

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Details for 2011 Binning

Site	Innocuous	Pressure	Pressure and Corrosion	Total
RFETS	809	721	358	1,888
Hanford	938	770	549	2,257
LLNL Shipped as of Dec, 2010	57	9	101	
Future	27	0	7	
Total planned	84	9	108	201
SRS	724	95	83	902
LANL Shipped as of Dec, 2010	8	3	1	
Future	517	80	159	
Total Planned	525	83	160	768
Containers packaged as of December, 2010	2,537	1,597	1,092	5,226
TOTAL PLANNED	3,081	1,677	1,258	6,016
3 LLNL Innocuous were shipped to LANL to be archived Note that 2 items in the bin are pending a final ER decision	LANL Innocuous includes 500 ARIES containers			

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What is the Impact On the Statistical Sample Allocation Between Sites?

Site	Pressure and Corrosion Sample Size		Difference*
	2008	2011	
RFETS	35	36	1
Hanford	54	56	2
LLNL	16	11	-5
SRS	7	9	2
LANL	16	16	0

*Select 5 LLNL randomly and replace.

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Other Impacts on Samples

3013Container	FY11Bin	FY08ISPBin	Comment	FY11SubBin	FY08ISPSubBi	Destroyed	SiteID	SurveyFY	SurveyType	SurveillanceR
[illegible]	Pressure and Corrosion	Pressure	New Data	BDT-4-LLNL-WASHED	ER-C3	N	3	2005	N	Random
H003094	Pressure and Corrosion	Pressure	Mismatch	BDT-3-F	ER-C3	N	1	2006	N	Random
S001682	Pressure and Corrosion	Pressure	New Data	BDT-4-SR-ARF	BDT-5	N	5	2008	N	Random
H003119	Pressure and Corrosion	Pressure	PG Update	BDT-3-Cl	BDT-5	Y	1	2009	D	Random
S001756	Pressure and Corrosion	Innocuous	New Data	BDT-4-SR-ARF	BDT-6	N	5	2009	N	Random
R610548	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-F-HCl	N	4	2005	N	Eng Judgement
R611398	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl-HCl	Y	4	2005	N	Eng Judgement
R611398	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl-HCl	Y	4	2008	N	Eng Judgement
R611398	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl-HCl	Y	4	2009	D	Eng Judgement
H004309	Pressure	Pressure and Corrosion	Mismatch	BDT-5-P	BDT-3-Cl	N	1	2010	N	Eng Judgement
H004099	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl	Y	1	2006	N	Highest wt gain
H004099	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl	Y	1	2009	D	Judgemental
R601285	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl	Y	4	2007	D	Random
H003157	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-F	Y	1	2008	D	Random
H002195	Pressure	Pressure and Corrosion	PG Update	BDT-5-P	BDT-3-Cl	Y	1	2009	D	Random
R601957	Innocuous	Pressure and Corrosion	PG Update	BDT-6-I	BDT-3-Cl	Y	4	2007	D	Random

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Items Needing Replacement in P&C Statistical Sample

- 4 DE sample items need to be replaced (added on in 2017?)

Container ID	2011 Bin	2008 Bin	DE Year	Reason for Change
R601957	Innocuous	Pressure and Corrosion	2007	PG Update
H002195	Pressure	Pressure and Corrosion	2009	PG Update
H003157	Pressure	Pressure and Corrosion	2008	PG Update
R601285	Pressure	Pressure and Corrosion	2007	PG Update

- One future (2015) DE sample item needs to be replaced - H002862 (now in Pressure Bin)

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Issues for Discussion

- May need to adjust LANL sample items
  - Sampling plan calls for 2 LANLP&C items in 2014 – 5th and 10th (do these exist? / packaged in '09?)
  - LANL sample items in 2016 and 2017 (packed by 2011 and 2012)
    - 2016 calls for 18th, 27th, 34th, 35th, 41st, and 44th
    - 2017 calls for 54th, 67th, 71st, 74th, 78th 84th, 90th 148th
- Need to determine bins for H001863 and H002543 (Josh's PG outliers/wrong spectrum)

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Additional Info for "Update"

- *S001721 (scheduled for DE in 2011) was switched for R611131 in 2010)*
- Change binning diagram for LANL / Oxalate Precipitation - Aqueous Chloride, Dissolution Residuals - Chloride heel, and any Pyrochemical process group material are suspected to contain chlorides from process knowledge and should be assigned BDT-4 even if PG does not show chloride.
- In 2010 there were also 16 foreign material inspection containers (all with NDE and some with DE and NDE
- **Please provide suggestions for additional content for the "update."**

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Understanding Interactions Between Stainless Steel and Plutonium Metal

Savannah River Site
January 2011

Plutonium metal – steel interactions

Safety issue addressed:

- Plutonium metal is stored across the DOE complex in stainless steel containers. Temperatures could exceed the Pu-Fe eutectic temperature of 410°C yet remain below the melting point of plutonium metal at 640°C during a fire.
- A DOE review of 2005 and 2006 ORPS reports concluded "While concerns about the potential Pu-Fe eutectic failure mode have been around for years, there appears to be no DOE consensus on what conditions (e.g., temperature, duration, and oxidation) Pu-Fe eutectics will realistically form and cause failure."

Contributors

- Pu metal – Kane Fisher
- Test design and test conduct – John Dunwoody
- Metallography – Fred Hampel
- Microprobe – Angelique Neuman
- Analysis - John, Angelique, Kirk, Laura, and Ric

Presentation Outline

- Test Description
- Phase Diagrams
- Post Test Results & Analysis
  - Component Condition
  - 304L/Pu interactions
  - 316L/Pu Interactions
  - Plutonium Condition
- Scoping Test Results Summary
- Proposed Future Work

Sponsorship

- Testing by SRS
- Examination of post test material by NNSA
- Analysis and reporting SRS & NNSA

Test Conditions

- Test components
- Scoping Test Configuration
- Test Profile

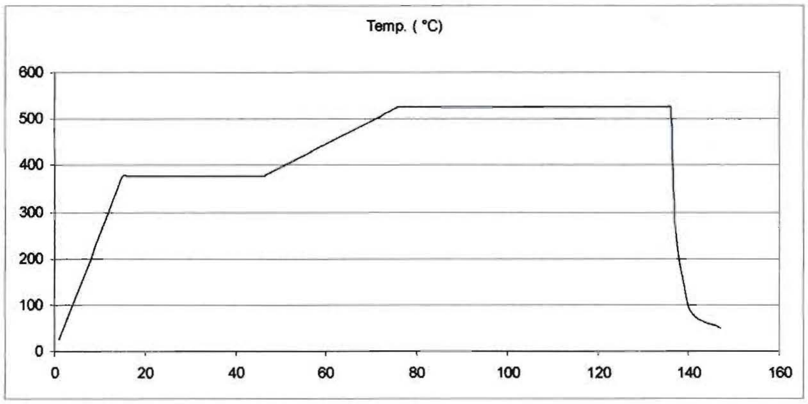
Physical Configuration Of Stainless Steel Pieces Pre-test Dimensions

	316 SS bar	Plutonium	304 SS bar
length - mm	26.92	4.95	25.65
Diameter - mm	6.36	5.073	6.36
Mass - g	6.76	1.96	6.39
SS length lost if all of the Pu is converted to Pu_6Fe (mm)		0.30	
SS length lost if all of the Pu is converted to $PuFe_2$ (mm)		3.61	

Steel – Plutonium Diffusion Couple

- Left side: 316L ss annealed cold drawn
- Center: machined α-Pu metal
- Right side: 304L ss annealed cold drawn
- Furnace ramp: 25°C/min in purified Ar atmosphere
- Furnace holds: 380°C ½ hr; 525°C 1 hr

Scoping Test Furnace Profile



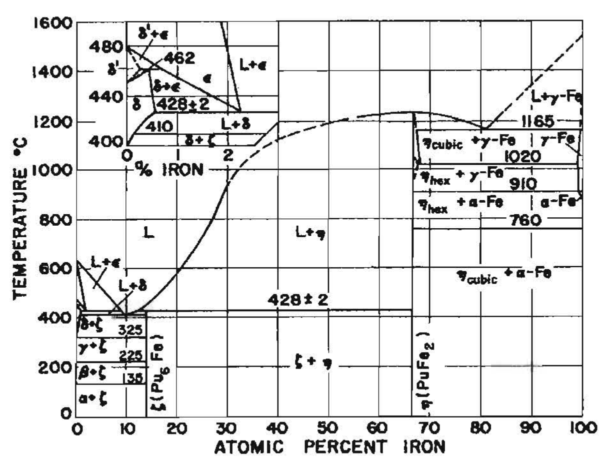
Composition of Stainless Steel

	304L(%)	316L (%)
C	0.03	0.03
Mn	2	2
Si	0.75	0.75
P	0.05	0.05
Si	0.03	0.75
Cr	20	18
Mo		3
Ni	12	14
N	0.1	0.1
Fe	65.0	61.33

Equilibrium Phase Diagrams

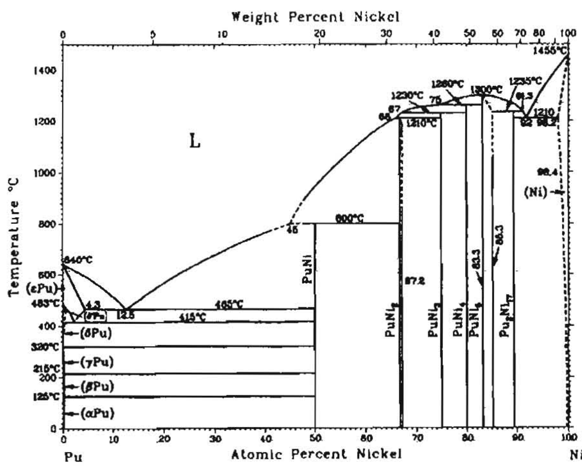
- Iron – Plutonium
- Nickel – Plutonium
- Chromium – Plutonium
- Molybdenum - Plutonium

Plutonium-Iron Phase Diagram



- LA-3870 & LA-4638

Ni-Pu Phase Diagram



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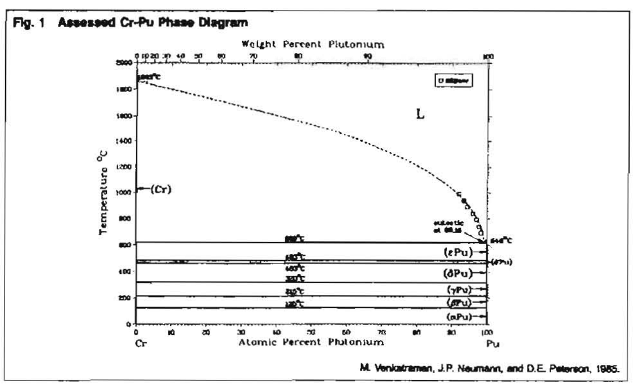
Cr-Pu Phase Diagram

Cr metal is a Face-centered-cubic crystal



420 Bulletin of Alloy Phase Diagrams Vol. 6 No. 5 1985

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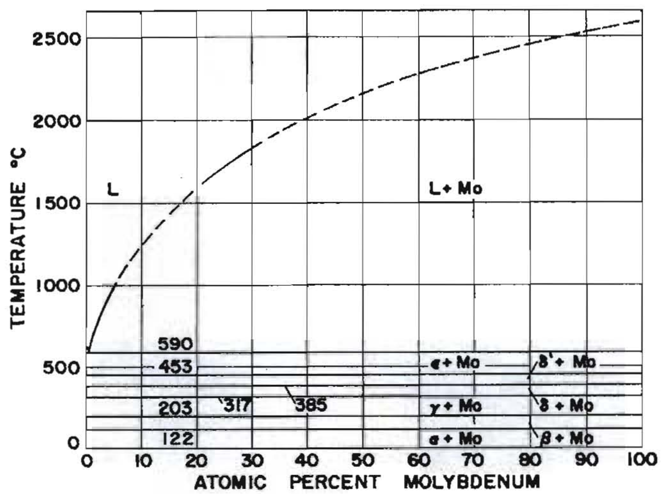
Molybdenum-Iron Phase Diagram



LA-3870

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Post Test Results & Analysis

- Component Condition
- 304L/Pu interactions
- 316L/Pu Interactions
- Plutonium Condition

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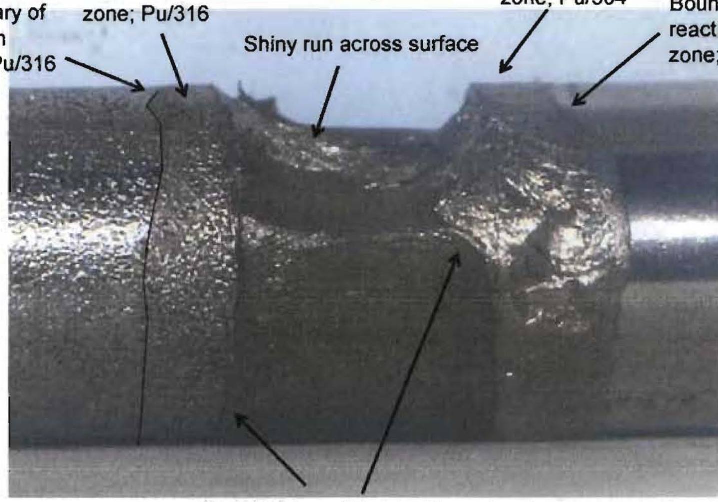
Preliminary Results; Steel – Plutonium Diffusion Couple



John Dunwoody, Steve Willson, Ric Mason

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Preliminary Results: 304L/Pu Interface

Pu

304L

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Slide 18

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Preliminary Results: 316L/Pu Interface

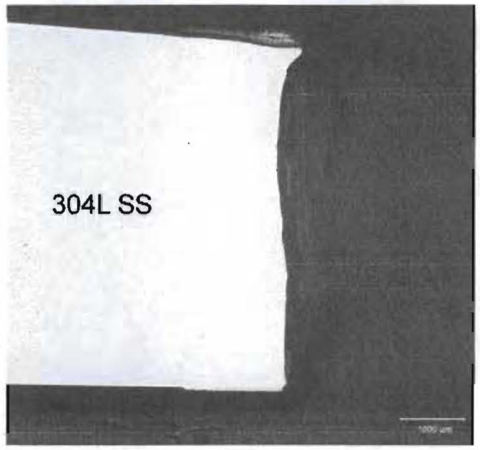
316L

Pu

304L/Pu Interactions

- Significant corrosion of the steel face
- Wetted surface
- Iron movement into the plutonium
- Iron/Plutonium/Chromium dense layer
- Chromium metal found in reaction layer
- $PuFe_2$
- Pu_6Fe

304L Face



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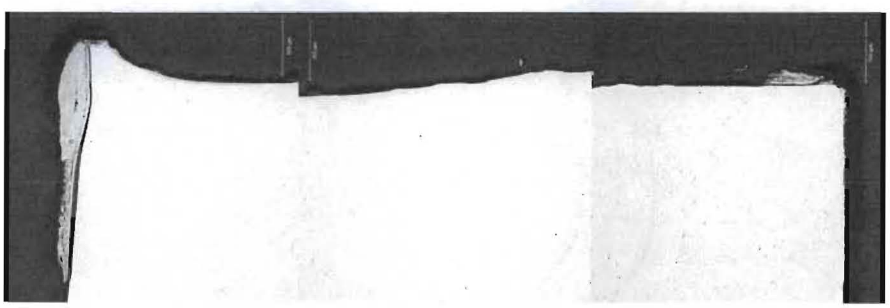
Three Sections of the 304L Face



About 330-µm (0.3mm) of SS dissolved

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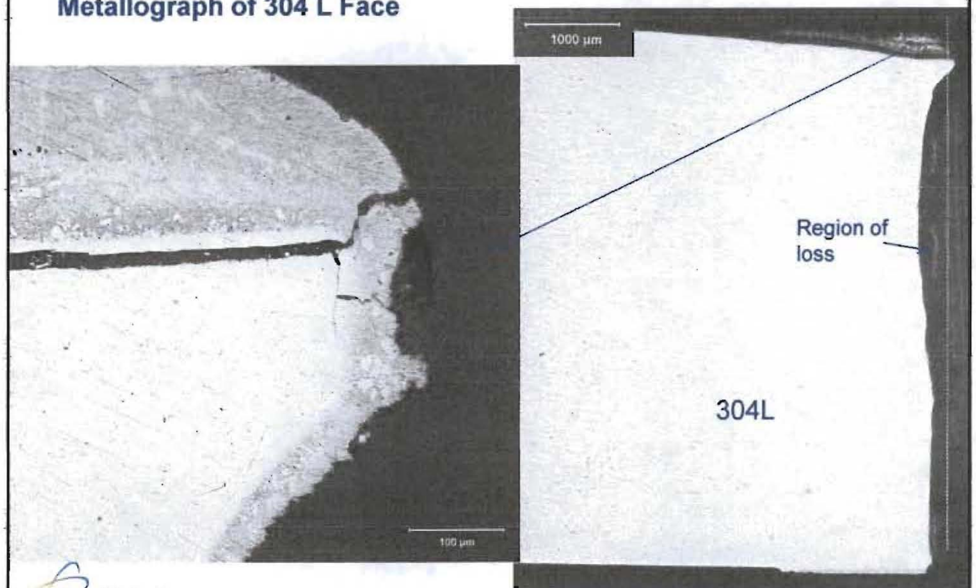
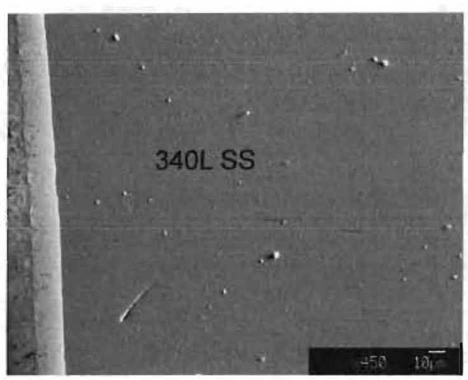
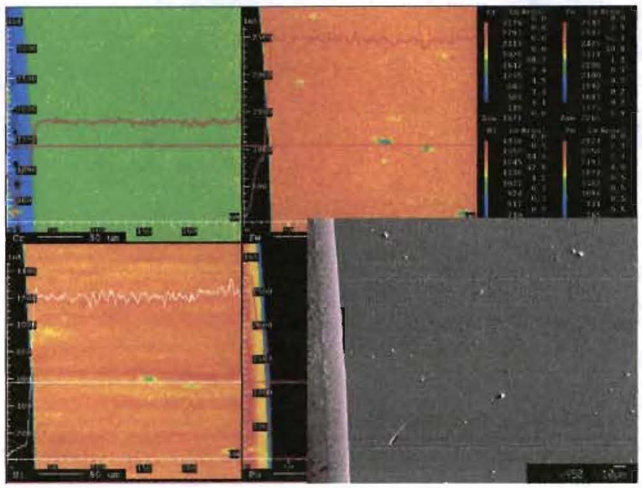
Metallograph of 304 L Face



340L Corrosion Interface



Reaction Layer Composition



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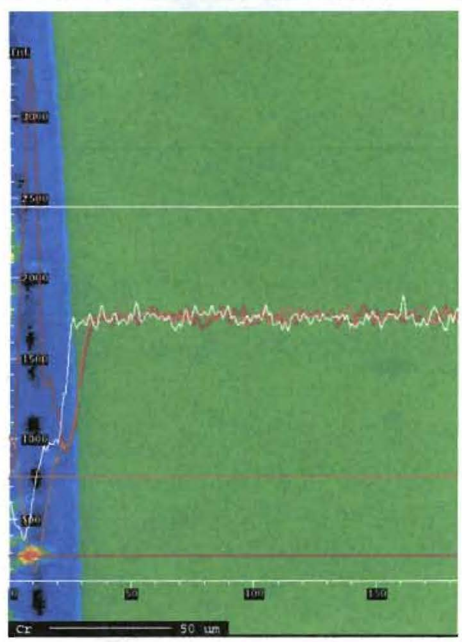
3 Chrome Scans



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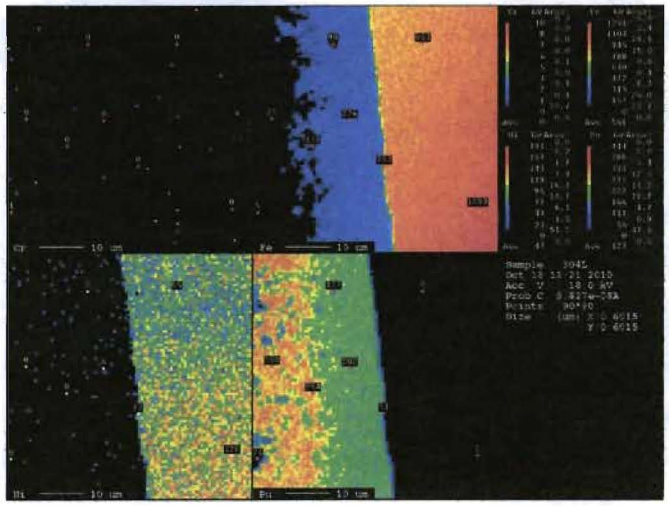
Reaction Layer on 304L Stainless Steel



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Reaction Layer

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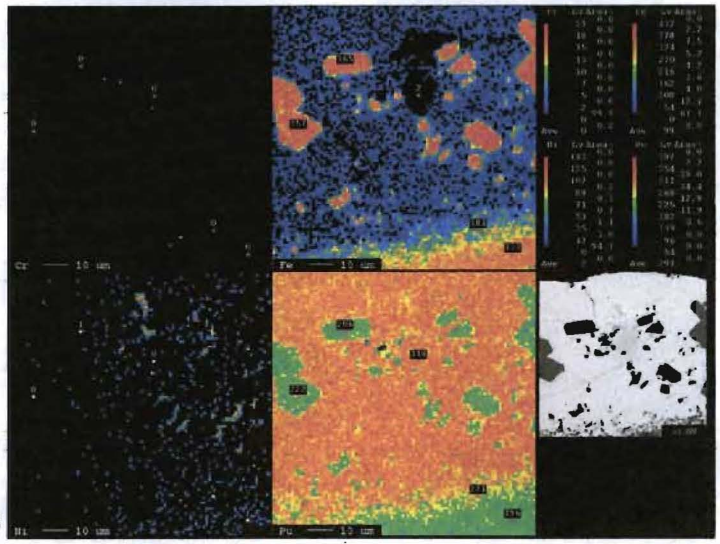
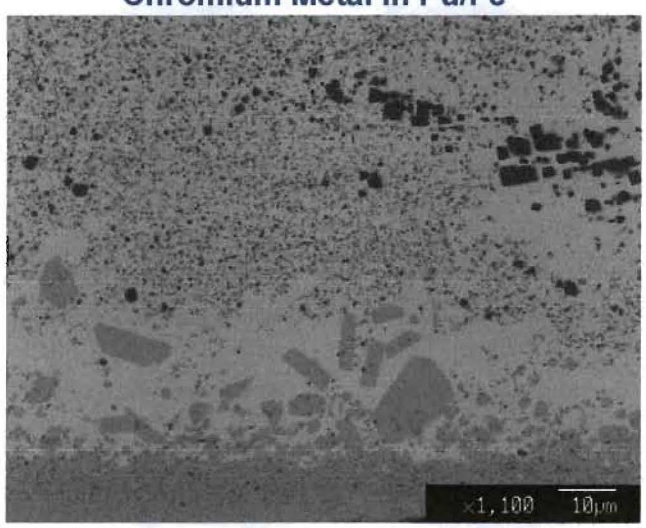
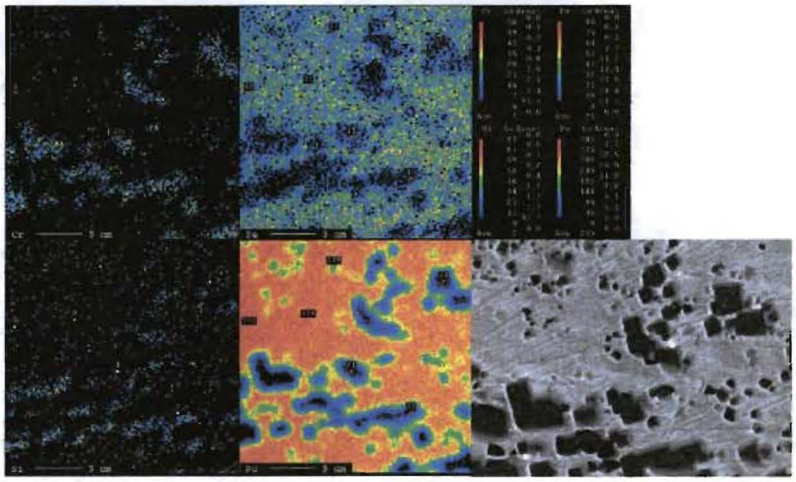
Wetted Surface Interaction Layers on 304L



Chromium Metal in Pu/Fe



Chromium Metal in Solidified Liquid Matrix



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316 Interactions

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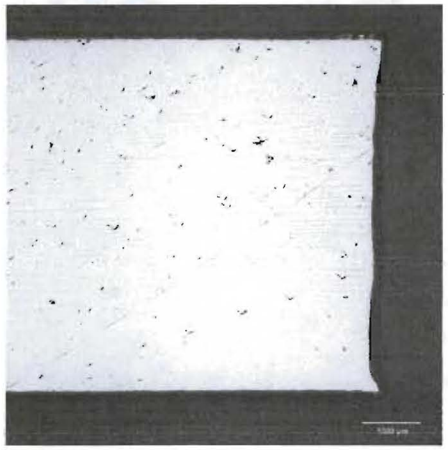
316L Face



316L Reaction Layers

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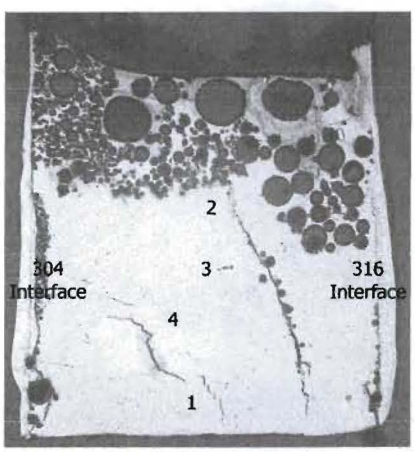
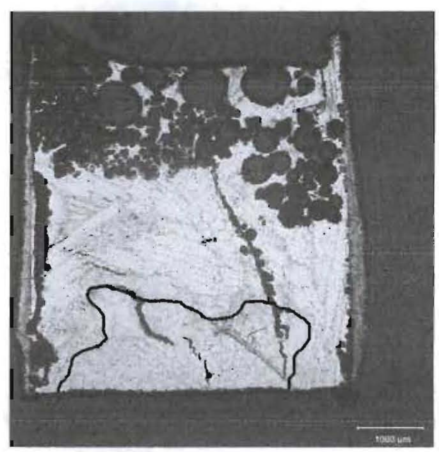
Plutonium Condition

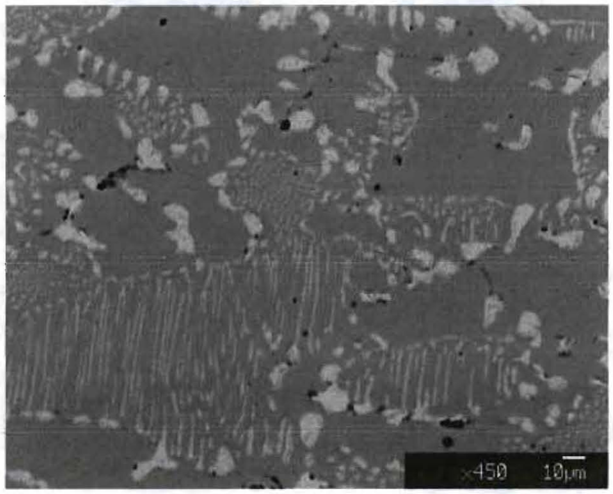
- 304L/Pu reaction layer
- 316L/Pu reaction layer
- Iron/Nickel/Chromium throughout the matrix of the plutonium piece
- The entire plutonium piece was probably liquid
- Gases in the plutonium formed bubbles and the bubbles floated to the top of the plutonium liquid

Melted Plutonium

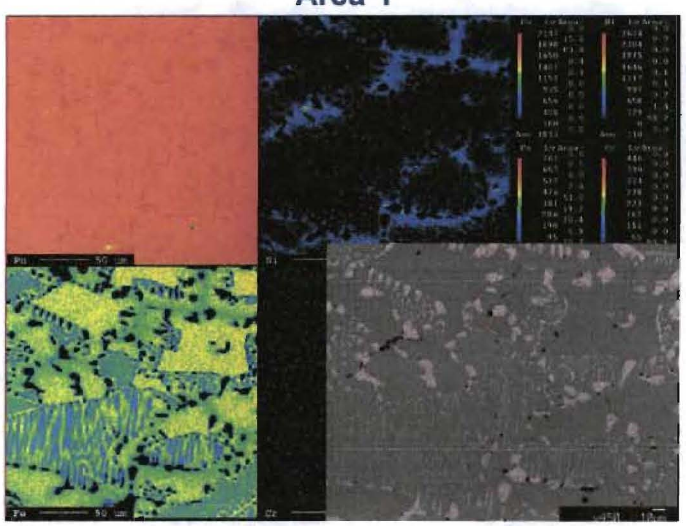




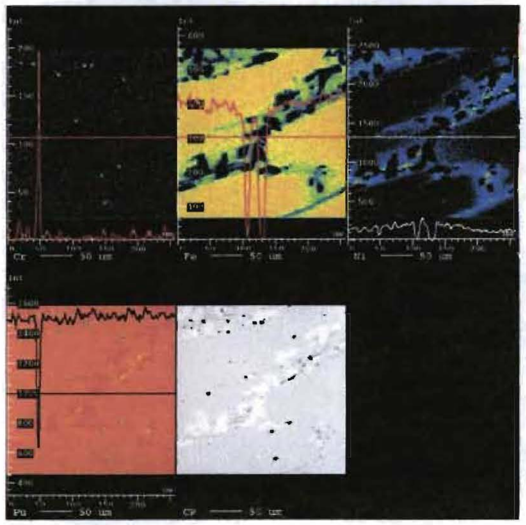
Plutonium Near the Bottom of Plutonium Piece Area 1 (back scatter image)



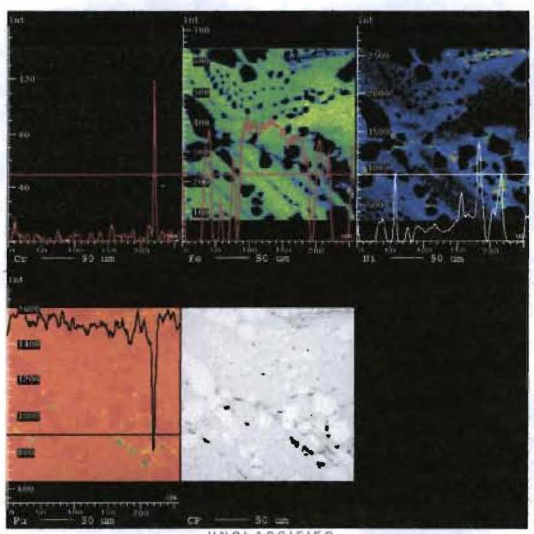
Plutonium Near the Bottom of Plutonium Piece Area 1



Plutonium Near the Bubbles in the Plutonium Piece
Area 2



Matrix Near the Middle of the Plutonium Piece
Area 3



Scoping Test Results Summary

- 1 hour at 525C is sufficient to convert most of a ~2-g cylinder of Pu into a liquid
- The 304L was more wetted with the liquid than the 316L
- A boundary layer of Cr/Fe/Pu forms but it does not stop iron diffusion into the Pu/Liquid
- The eutectic liquid is iron rich because the iron diffuses more rapidly into the plutonium than the plutonium into the iron.
- Next to the steel, the liquid freezes forming $PuFe_2$ precipitates and then Pu_6Fe precipitates as the entire matrix freezes when temperatures drop below the eutectic temperature.
- Chromium was found in the interaction zone and the chromium forms crystals in the eutectic liquid
- In the plutonium, plutonium dendrites freeze in the liquid until the matrix temperature drops below the eutectic temperature and then the Pu_6Fe liquid freezes.
- In the plutonium, some chromium and nickel agglomerations are apparent.

Questions to be Answered

- Did the reaction go to completion?
- Was the diffusion of the Fe or Pu beginning to slow the reaction?
- Would the liquid continue to dissolve the iron until all of the Plutonium had reacted to $PuFe_2$?

Future Tests

- **Future Tests**
  - Only use 304L SS
    - Iron diffusion is so rapid that contribution from both steels make the results less certain.
  - Scoping test profile with 1 hour hold temperature at 420°C
    - Eliminates melting of the $PuFe_2$
  - Scoping test profile with 1 hour hold temperature at 450°C
    - Evaluates the reaction above 428°C but significantly below the 525°C scoping test temperature.
  - Long test to determine how far the dissolution will go
    - Time & Temperature will be determined based on the tests above
- **Future analysis**
  - Complete both tests and then evaluate how much analysis is required on each piece.
- **Report findings in a Journal**

LANL 3013 Packaging for 00-1 Materials & AFS Demo Project

MIS Working Group
SRL, Savannah River, SC
January 25-26, 2011

Jim Rubin
Technical Project Manager

Actinide Process Chemistry Support Group (MET-1)
Manufacturing Engineering & Technology Division
Los Alamos National Laboratory
Mail Stop E511, Los Alamos, NM 87545

LANL 3013 Packaging – Current Status

- In FY10 seventeen 3013 containers were fabricated
- In FY11 we intend to ship ten of these containers
- Data packages are currently under Project-level QA evaluation, to include
  - Traveler completion and consistency against requirements
  - PCD checklists for completion and accuracy
  - Path forward for any identified discrepancies, for example
    - LOI used for items < 80% total Pu
    - Training records
    - Negative Pu value from a neutron multiplicity measurement !

AFS Demo Project

- In most cases, material destined for 3013 containers & long-term storage requires aqueous processing to establish a process history.
- The majority of the excess material to be processed (>90%) is chloride-based salts and residues.
- The storage site (SRS) is requesting that future material sent by LANL be of MOX-able grade, meeting the Alternate Feedstock (AFS) specification.
- AFS specification requires ≥80% Pu assay for optimal loading of 3013 containers. (Note : ≥72% Pu assay is permitted, but with reduced 3013 loading.)

Possible oxide products for LANL 3013 packaging

	Total Impurities (Max impurity basis)	Cl^- (max, ppm)
1) Polished MOX[1]	0.35%	220
2) ARIES/PCDF[2]	1.6%	220
3) DOR	≤ 1% (desired)	100 (nominal)
4) AFS[3]	≤ 28%	176,211 (as Cl^-)
5) 3013 (minimum)[4]	≤ 70%	400,000 (as NaCl)

1. *Characteristics of the Plutonium Dioxide Powder*, DCS02 FQJ PU SPE W 00001 A, U.S. Department of Energy, Chicago Operations Office
2. *Plutonium Dioxide Powder Interface Control Document*, National Nuclear Security Administration, ICD-02-001-01, (March, 2008)
3. *Interface Control Document: Alternate Feedstock (AFS) Plutonium Oxide Transfers From The K-Area Complex (KAC) to MFFF*, National Nuclear Security Administration, G-ESR-K-00011 ICD-07-025-01, (March 2008)
4. *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials*, DOE-STD-3013-2004, U.S. Department of Energy, Washington, DC (2004)

The AFS Spec

AFS Specification[1]

$^{238}Pu \leq 0.05$ wt.%

$90\% \leq {}^{239}Pu \leq 95$ wt.%

$5\% \leq {}^{240}Pu \leq 9$ wt.% [2]

$^{241}Pu \leq 1$ wt.%

$^{242}Pu \leq 0.1$ wt.%

$^{(241)}Am \leq 6{,}167$ µg/g PuO_2

DU,NU $\leq 440{,}528$ µg/g PuO_2

Packaging must meet DOE-STD-3013

1. The total impurities are calculated by subtracting actinides (Pu, U, Np, Am) as oxides from the net weight and counting all unexplained mass as impurity.
2. Note that ^{240}Pu limit does not allow for fuels grade material

Can we make AFS grade from residues ?

- The ***traditional*** aqueous chloride flowsheet, which includes solvent extraction and calcination to 850°C, easily satisfies the AFS spec :

3013 outer can #		MASS % SNM/NET	Fe	U	Am	Np	C	F	Cl
			conc. (ppm)						
A000699	RBXSFY05-1	87.57	218	113				100	40
A000684	RBXSFY05-6	87.02	278	115				120	250
A000839	04272-CC-075	86.87	111	105				50	30
A000695	RBXSFY05-3	87.05	215	102				40	70
A000793	RBXSFY06-1	86.57						<90	<90
A000690	RBXSFY06-2	87.66						<90	140
A000758	RBXSFY06-4	87.13						160	170
A000634	RBXSFY06-5	87.64						60	150
A000731	RBXSFY06-6	86.50						60	90
A000833	RBXSFY05-8	84.75	99	112				50	30
A000755	RBXSFY05-15	87.18	66					120	60

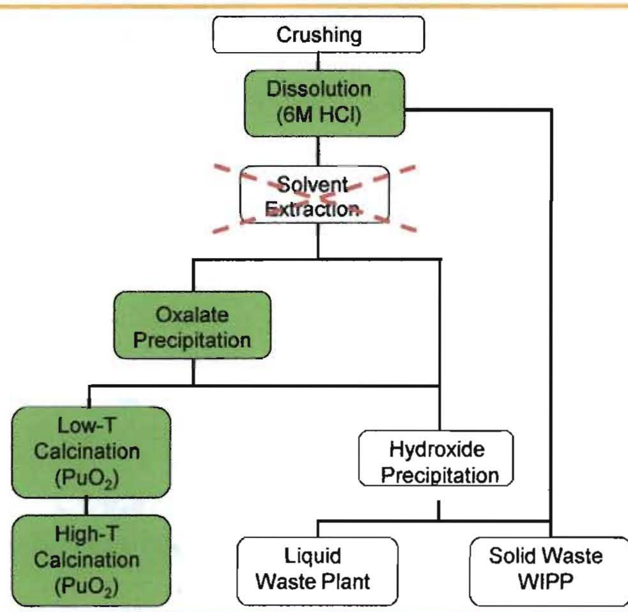
- At present, however, aqueous chloride processing is being conducted without the solvent extraction step, due to failure of the (18 year old) centrifugal contactors. Critical replacement parts are no longer available from the manufacturer.
- ***Question : Can we meet the AFS specification without solvent extraction ?***

Can we make AFS grade from residues (cont) ?

- New centrifugal contactors have been fabricated and are currently undergoing cold testing.
- These new contactors are expected to be introduced in-line in FY11.

- However, the absence of solvent extraction capability has given us the opportunity to examine and optimize the dissolution and oxalate precipitation processes.

Standard Aqueous HCl Flowsheet



Can we make AFS grade from residues (cont) ?

- At the 3013 Surveillance and Monitoring Program Review (February, 2010), the analytical chemistry results for an MIS item was presented, which was assumed to represent the processes and output product we are evaluating :

CXLOX091802A
(Item created 10/02)

Analyte	Conc.
F	15,000 µg/g
Cl	22,000 µg/g
Al	698 µg/g
Be	1 µg/g
Ca	29,000 µg/g
Fe	3,430 µg/g
K	24,000 µg/g
Y	3,430 µg/g

Typical Chloride Feed Items


ER salt


ER Crucible


Anode heel


MSE metal and salt

Dissolution– Refining the Technique

- Traditionally, dissolution has used 6M HCl

- As ER salts are highly-concentrated, equimolar NaCl/KCl, we have looked at increasing the HCl molarity (decreasing the water content), taking advantage of the common-ion effect :

Concentrations are in g/100 g

R.W. Potter 11 and M.A. Clynne. "Solubility of NaCl and KCl in Aqueous HCl from 20 to 85°C", J. Chem. Eng. Data (1980) pp. 50-51.

T, °C	[HCl]	[NaCl]	T, °C	[HCl]	[KCl]
34.70	3.97	20.56	24.86	4.02	19.61
35.29	8.61	13.94	23.89	8.70	12.97
32.90	13.79	8.08	24.88	13.88	7.49
36.26	19.26	3.68	25.93	19.21	3.93

- This has shown positive results in the dissolution of some ER crucible feeds

Dissolution– Refining the Technique (cont.)

- In FY11, we are pursuing the installation of PTFE dissolution pots, to assist in the dissolution of the more intractable residues, i.e.
  - Previously leached resides
  - Partially-oxidized ER salts
  - Low-assay, calcined oxides

- Will allow for heated dissolution and the addition of ~ 0.1M HF additions

- PTFE dissolution pots are operating within the Aqueous Nitrate flow sheet, and this can be used as a basis, but must be made robust for the more corrosive HCl environment.

Oxalate Precipitation – Refining the Technique

- In the past, the product was washed with 60 g of oxalic in 2 L of water after precipitation.
- Currently, we are washing with 150 g of oxalic acid in 3 L of water.
- So far, with good operator technique and our new method of washing, we have been able to achieve > 80% Pu assay, ***relatively independent of incoming feed assay***.
- *Can we further increase our Pu assay by further optimization of the oxalate washing recipe ?*

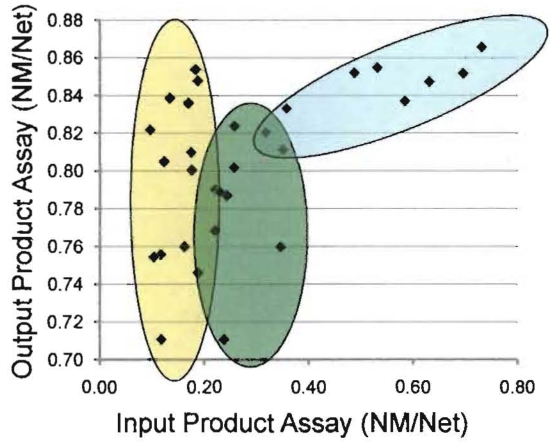
Low-T Calcination – Refining the Technique

- Criticality safety and MC&A requires a post-precipitation calcination.
- This post-precipitation calcination utilizes the following recipe

Step #1: 2 hour ramp time to 200°C
Step #2: 3 hour soak time at 200°C
Step #3: 2 hour ramp time to 400°C
Step #4: 3 hour soak time at 400°C
Step #5: 2 hour ramp time to 650°C
Step #6: 4 hour soak time at 650°C
Step #7: All Off

- Is there an opportunity here ?

Aq. Cl⁻ Ops - Input vs Output Pu Assay



Data spans 2/10 to 9/10

Input items come from

1) ER salts (NaCl/KCl)
2) ER crucibles (NaCl/KCl)
3) MSE salts ($PuCl_3$/^{241}Am)
4) Coalescence crucible

Output product is calcined only to 650°C for approximately 4 hrs. Subsequent 3013-type calcination (≥ 950°C for ≥ 2 hrs) should further increase output product assay.

Next, High-T Calcination as Purification

- Oxide produced from the traditional aqueous chloride flow sheet has been calcined at 850°C for 12 hrs (for DOR use).

- Recent DOR calcination experience with CXLOX has produced significant weight loss.

- Subsequent 3013 calcination (> 950°C) of the same items resulted in "bricking".

- This suggests that opportunities exist for assay enhancement through a controlled pre-treatment.

Next, High-T Calcination as Purification (cont.)

•Therefore, we will look at a set of T-t calcination parameter combinations to determine an optimal pre-treatment profile.

(i.e., PuSPS Feed Oxide Pretreatment Activities, PRO-1605-PuSPS Pretreat-371)

– Which temperature removes the most chloride, and does it change for each input feed type, and how long does it take ?

– This should be guided by a knowledge of what is being removed during calcination and approximately by how much, i.e.

→ Development of an at-line, semi-quantitative analysis technique

– Finally, how do chloride-based oxide produced with and without solvent extraction and nitrate-based oxide products compare ? (We do have nitrate-compatible residues, albeit to a far lesser extent)

We plan to look at combinations of 750°C < T < 950°C
8 < t < 16 hrs

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Analytical Scheduled for FY11...

- During FY11, analytical samples will be taken of the oxalate product and will be analyzed for the following:
  - Metals: ***Fe***, ***Ga***, ***Al***, ***B***, ***Cr***, ***Zn***, ***Ni***, ***Ca***, ***Mg***, ***K***, ***Na***, ***Nb***, Be, Cd, Cu, Si, Li, Mo, Pb, ***Ru***, Sn, Ta, Ti, W, ***Zr***
  - Non-metals: C, F, Cl
  - Actinides: (Pu by assay), ***Am***, ***Np***, ***Th***, U

Comments ?

i. Be, Cd, Cu, Si, Li, Mo, Pb, Sn, Ta, Ti, W, U are expected to be relatively efficiently removed by a $Pu_2(C_2O_4)_3$ precipitation only (without SX)

ii. Fe, Ga, Al, B, Cr, Zn, Ni, Ca, Mg, K, Na are known to be less well removed by $Pu_2(C_2O_4)_3$ precipitation only

iii. Am, Th, Np, Zr, Nb, Ru and the lanthanides are not efficiently removed by $Pu_2(C_2O_4)_3$ precipitation only

iv. C pass through will depend on form (organic/inorganic)

v. Cl is expected to act as a "bystander" ion in $Pu_2(C_2O_4)_3$ precipitation

vi. F, even if added as dissolution aid, is not expected to produce mixed metal fluoride/oxalate species during $Pu_2(C_2O_4)_3$ precipitation, at the low levels that would be used.

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Los Alamos Oxide Production Campaign

Steven McKee
Technical Project Manager

MET-1, Manufacturing Engineering and Technology Division

3013 Surveillance and Monitoring Program Review
January 26, 2011

Plutonium Science and Manufacturing
Los Alamos National Laboratory

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Oxide Production

Los Alamos will produce 2 MT of unpolished plutonium as plutonium oxide to support MFFF start up.

- Joule Metrics – cumulative annual amounts in kgs Pu converted to certified oxide.
- FY2010, Los Alamos converted 52 kgs Pu into PuO_2.
- In FY2011, Los Alamos has converted 61 kgs Pu into PuO_2 (30% of our target of 200 kgs).
- Working to certify 37.6 kgs of FY2010 material with MOX services and awaiting analytical chemistry on 43.2 kgs of FY2011 material.

2011	225
2012	375
2013	675
2014	975
2015	1275
2016	1575
2017	1875
2018	2000

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Oxide Production

- Schedule Requirements – Production Targets defined in the ICD

Milestone	ICD Date	Schedule Date	Note
500 kg Pu Production Target	6/30/2015	4/22/2013	ICD defined milestone
1500 kg Pu Production Target	12/31/2017	7/11/2016	ICD defined milestone
2000 kg Pu Production Target	12/31/2018	7/2/2018	ICD defined milestone

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Product Oxide

- unmilled DMO product
  - 80% greater than 200 μm

- milled and blended DMO product
  - 100.0 % less than 200 μm
  - surface area = 0.28 m^2/g
  - tap density = 6.4 g/cm^3
  - moisture = 0.007 wt% (by TGA)

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Blend Lots #1 - #8

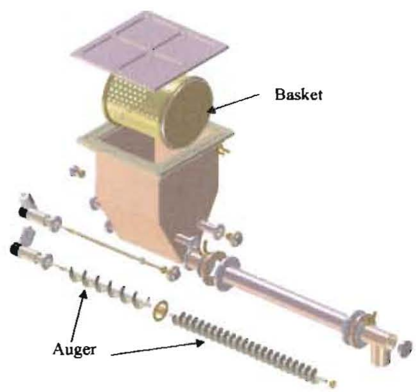
- Blend Lots #1 - #7 consists of 20 3013 containers, with each can holding less than 4800 g PuO_2.
    - Blend Lot #8 will be packaged this week.
- Completion of FY2011 production campaign will yield an additional 36 containers by early August.
- Expectation is to have the material in 56 containers certified and accepted by MOX services by September 30, 2011.
    - Blend Lot #3…?
- Draft shipper-receiver agreement in review and comment period.
- No plans to ship material in FY2011.

DMO Furnace Auger

- DMO-2 furnace currently installed in PF-4.
- Current equipment uses an alonized Inconel 600 auger for the calcination furnace for the processing of Blend Lots #1 - #7.

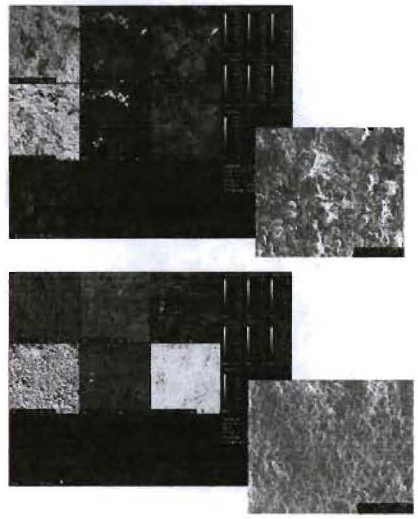
September 2010

- Auger replaced with Inconel 600 in December 2010 for processing of Blend Lot #8.



DMO Furnace Auger

- Flakes appear to be oxidized, alonized material.
  - Flakes are easily broken up.
  - Microprobe shows that one face of the flake is primarily aluminum and oxygen and that the other side is primarily chromium, oxygen, iron and nickel.
  - Flakes are about the thickness of alonized layer (~ 0.010").



Plutonium Oxide Product

	Measured Product (μg/g Pu)				ICD	
	Blend Lot #1	Blend Lot #2	Blend Lot #3	Blend Lot #4	Maximum	Maximum exceptional
Cr	268	223	471	237	100	500
Fe	1047	957	1508	660	500	2500
Ni	1081	746	5916	873	200	2500
Al (AES)	60	57	71	55	150	10000
Al (MS)	61	60	53	49	150	10000
Be (AES)	<0.6	<0.6	< 0.6	6.1	100	2000
Be (MS)	<2.3	<2.3	< 2.3	7.7	100	2000
Total impurities	9405	7087.5	16147	9838	18600	n/a

- Product meets all other specifications identified in the ICD.

Dissolution

- Some small amount of material remained undissolved for Blend Lots #1 - #3; Blend Lot #4 dissolved completely.
    - Lot 1: 0.4 mg of 250 mg = 0.16%.
    - EDS indicated that the material was analogous to dissolved material (Pu plus Fe, Cr , Ni).
    - SEM data points to undissolved material as oxide and not metal.
    - Chemical analysis indicates that sample has same composition as dissolved sample.

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Final Thoughts

- Oxide production underway at Los Alamos.
    - Working issues as we transition from an R&D mentality to a production mentality.
    - On target to deliver oxide product per our committed schedule.
    - Looking forward to ship certified product from Los Alamos to K Area in FY2012.
    - Executing most of the processes for pit disassembly and conversion.

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Low-temperature Stabilization Alternative for Oxide Produced by Metal Oxidation

John Berg, LANL

MIS Program Annual Meeting

SRS, Jan. 27-28, 2011

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Background

- Oxide for storage is currently stabilized to 950 C.
- Lower temperatures may achieve the same technical goals.
- Potential time and cost savings in stabilization and future processing after storage.
- LANL was requested to develop a test plan and to conduct tests pending plan approval.
- Scope of tests is to determine whether 3013 stabilization criteria are met at lower temperatures, and what temperatures and stabilization times are sufficient.

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3013 Stabilization Objectives for Oxides

- DOE-STD-3013-2004, Section A.6.1.2.1:
  1. eliminate reactive materials such as finely divided metal or sub-stoichiometric plutonium oxides;
  2. eliminate organic materials;
  3. reduce water content to less than 0.5 wt.% and similarly reduce equivalent quantities of species such as hydrants and hydroxides that might produce water;
  4. minimize potential for water re-adsorption above 0.5 wt.% threshold; and
  5. stabilize any other potential gas-producing constituents.

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3013 Stabilization Objectives for Oxides

1. eliminate reactive materials such as finely divided metal or sub-stoichiometric plutonium oxides;
2. eliminate organic materials;
3. reduce water content to less than 0.5 wt.% and similarly reduce equivalent quantities of species such as hydrates and hydroxides that might produce water;
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Performance criteria for eliminating reactive materials?

- 3013 Standard requires measurement of moisture.
- Qualitative criterion to stabilize to "avoid energetic events ... when storage containers are opened".
  - Complete oxidation of metal is presumed assured by
    - 950 °C stabilization temperature for at least 2 hours
    - Requirement for an "oxidizing atmosphere"
- Could a lower temperature stabilization be as effective in fully oxidizing metal?
- Would the product oxide behave the same in subsequent processing (dissolution)?

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What are "reactive materials" in the context of oxide from metal oxidation?

- Un-oxidized metal
  - Thermodynamically capable of reacting with air to release heat.
- Finely divided
  - Kinetically capable of reacting fast enough to release heat at a rate that might be of concern.
- Sub-stoichiometric oxide – PuO_{2-x}
  - How large could average *x* be in DMO product?
    - Thermodynamic and kinetic factors.
    - Importance of stabilization temperature and stabilization time.
  - How much of a deviation from average of PuO_2 is of concern?
    - Could it react rapidly upon exposure to air?
    - Would it generate significant H_2 upon dissolution?

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What makes a good stabilization process?

- Stabilization conditions thermodynamically favor oxide.
- Stabilization time is sufficient for complete reaction.
- Sufficient delivery of oxidizer so as not to limit reaction.
- Minimal effect of process upsets – a robust process.
- Product testing and performance criteria?
  - 3013 Standard only requires measurement of moisture
  - Complete oxidation of metal is presumed, and the control is the 950 °C stabilization temperature and the specification of an "oxidizing atmosphere".

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Proposed test plan

- Sample ARIES DMO product oxide.
- Measure the product oxide average stoichiometry to establish bound for trace unreacted metal.
- Measure specific surface area to assess the capacity of the product oxide to adsorb moisture from credible atmospheric exposures.
- Sample intermediate product after oxidizer stage.
- Repeat measurements to determine effect of calcination.
- Batch calcine at other temperatures and repeat measurements.

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Outline of approach

- Define tests to verify adequate stabilization.
- Benchmark tests on available pure oxide samples
  - Material stabilized to 950 °C.
  - Material only fired to lower temperatures.
- Obtain ARIES metal oxidation product prior to calcination.
  - Split and batch calcine portions at intermediate temperatures.
    - 600 °C, 675 °C and 750 °C
  - Size reduce as necessary.
  - Run samples through the same tests for completeness of oxidation and moisture uptake behavior.

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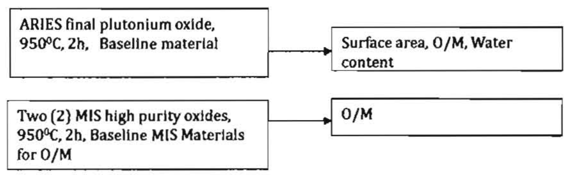
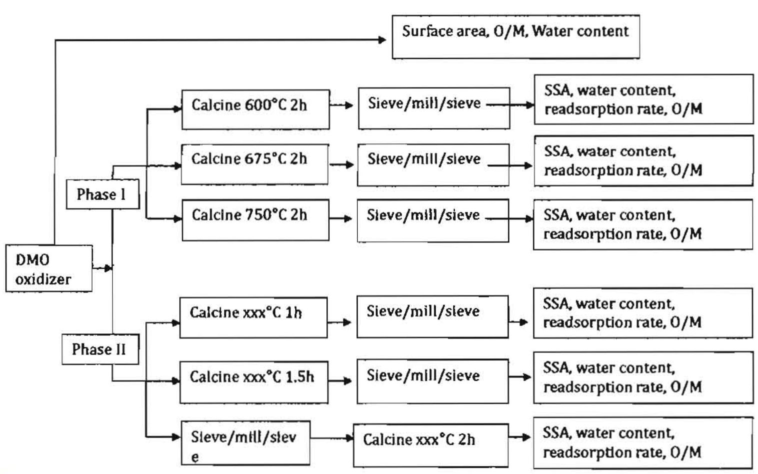
Baseline tests (Task 1)

- Conduct proposed measurements on recent ARIES product and on well-characterized oxide in MIS program.



Batch calcine DMO oxidizer intermediate product at different temperatures and measure.



Oxygen-to-metal ratio (O/M) measurement

- Propose to use ASTM Standard Test Method C697-10
  - Designed to measure adherence of powders and pellets to nuclear fuel specifications.
  - Section 106 is gravimetric method for O/M.
  - Expose oxide to flowing Ar + H_2O + H_2 at 800 °C.
  - Mass change indicates deviation of the O/M ratio from 2.000.
- Details
  - Powder samples are dried before initial and final weights to exclude adsorbed moisture from the measurements.
  - Hold time at 800 °C is 6 hours.
  - Thermodynamically, conditions are less oxidizing than air.

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Oxygen-to-metal ratio (O/M) measurement

ASTM Standard Test Method C697-10

Initial mass
- 1.5 – 2 gm sample
- Dry at 150 °C
- Cool and weigh

Oxidize any residual to PuO2
- Heat to 800 °C
- Flow Ar/H2/H2O 6 hrs
- Cool and re-dry at 150 °C

Final mass
- Cool and hold at 150 °C under flowing Ar to re-dry
- Cool to RT in dry atmosphere
- Re-weigh

Solve for x in PuO_{2-x}, $x = (1 – m_{initial}/m_{final}) \times (239+32)/16$

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Oxygen-to-metal ratio (O/M) measurement

ASTM Standard Test Method C697-10

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Final mass
- Cool and hold at 150 °C under flowing Ar to re-dry
- Cool to RT in dry atmosphere
- Re-weigh

Solve for *x* in PuO_{2-x}, $x = (1 - m_{initial}/m_{final}) \times (239+32)/16$

To determine x to 0.01, need < 1 ppt uncertainty in mass ratio.

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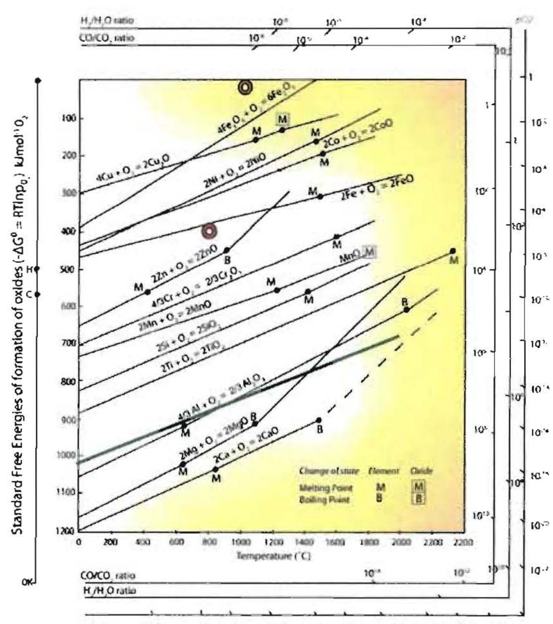
Ellingham diagram provides a useful summary of oxidation thermodynamics

$n M + O_2 \rightarrow M_nO_2$

$Pu + O_2 \rightarrow MO_2$

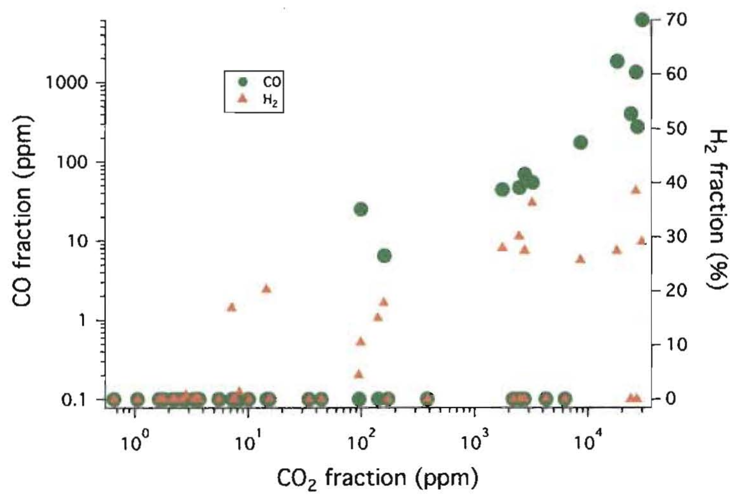
ASTM method uses $H_2O + H_2$ to oxidize
Diagram allows us to compare with O_2

$2 H_2 + O_2 \rightarrow H_2O$



Trace CO and CO_2 measured in DE gas analysis may indicate redox potential

$Pu + O_2 \rightarrow MO_2$ $2 H_2 + O_2 \rightarrow H_2O$ $2 CO + O_2 \rightarrow 2 CO_2$



$Pu + O_2 \rightarrow MO_2$

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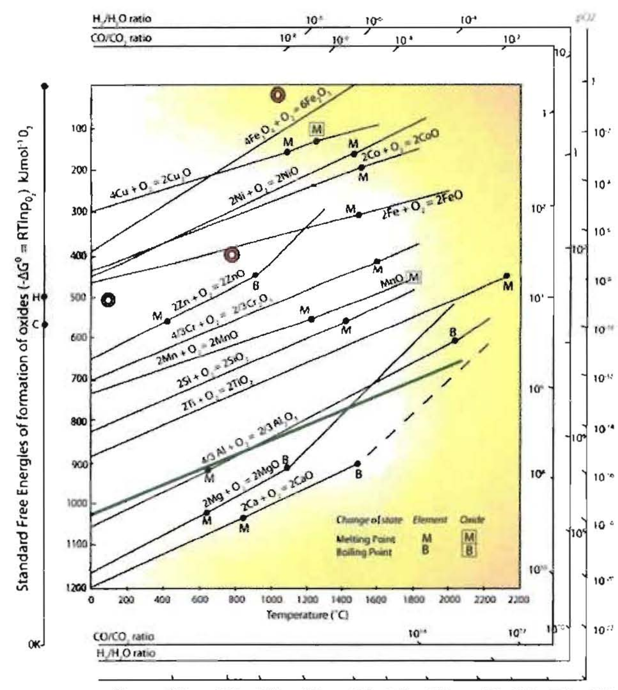

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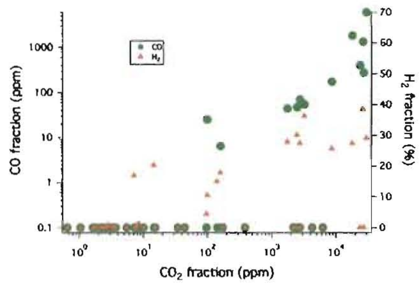

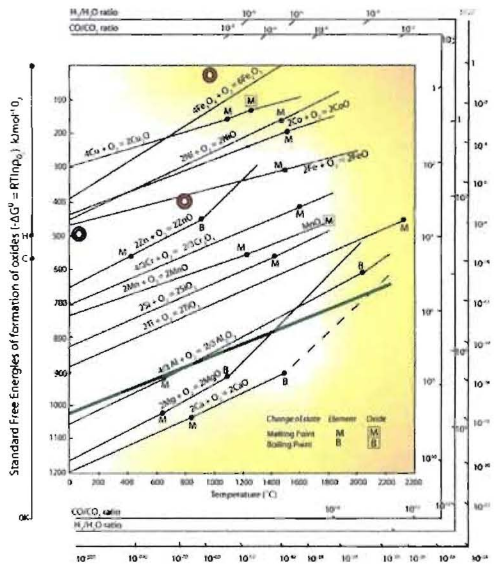

O/M measurement status

- Equipment in place at LANL and approved for use by Fuel Fabrication Team.
- Expect baseline results this month on DMO product.
  - Short delay to replace tube furnace heating element
- Initial results will provide benchmark for results from later tests on lower stabilization temperatures.
- Discussion of acceptable result for storage is needed.
  - Acceptable range of deviation of measured value from O/M = 2
  - Acceptable uncertainty

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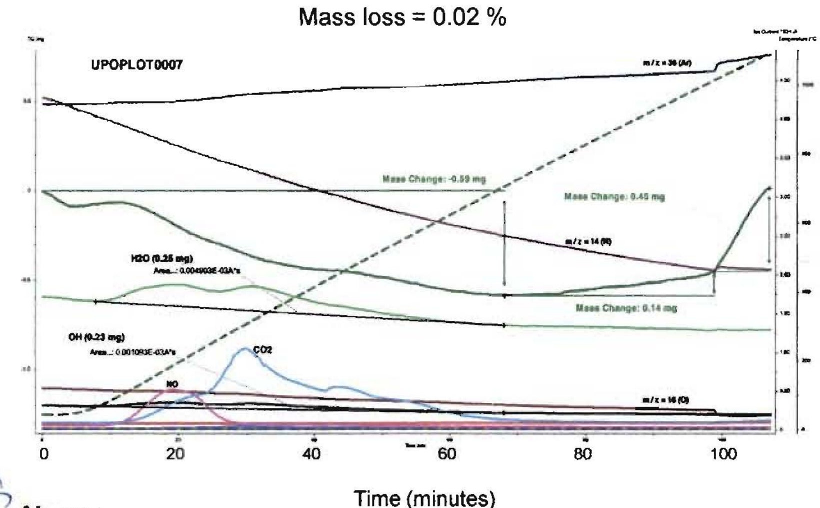
Pre-packaging TGA of ARIES blend batch



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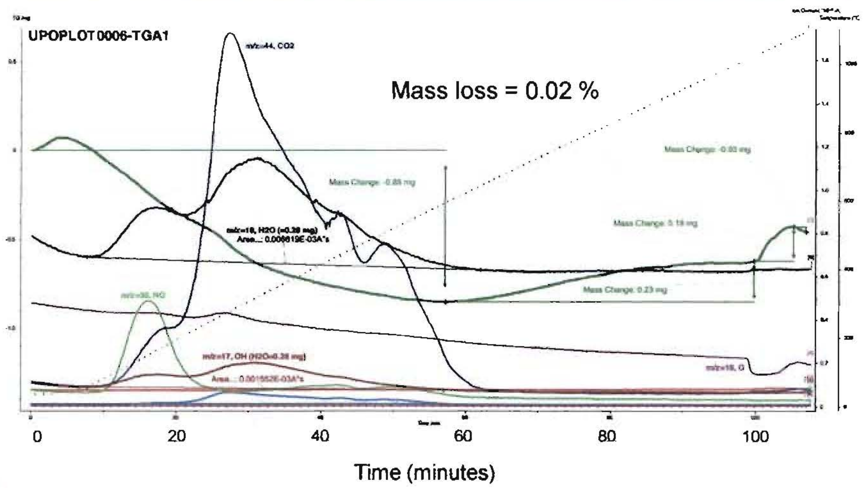
Pre-packaging TGA of ARIES blend batch



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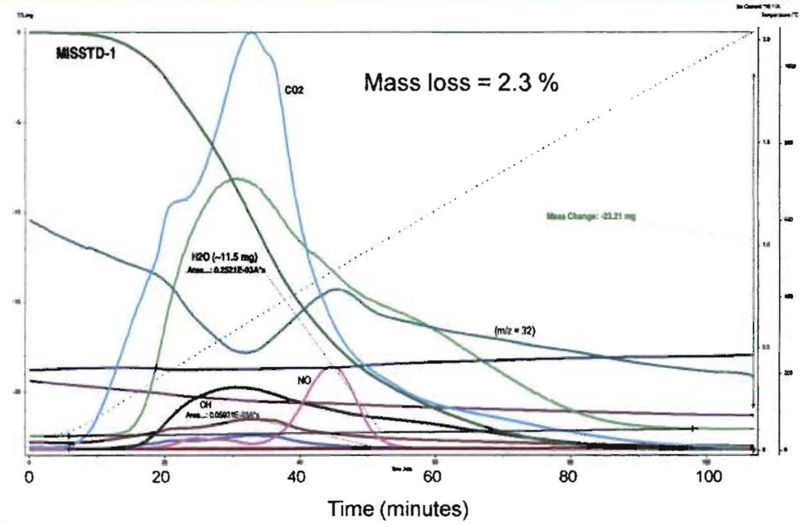
TGA of MISSTD-1 sample after opening



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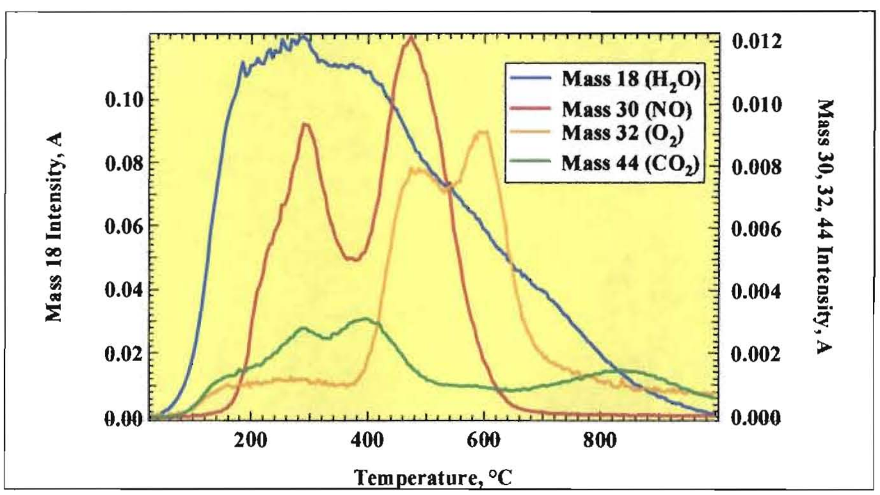
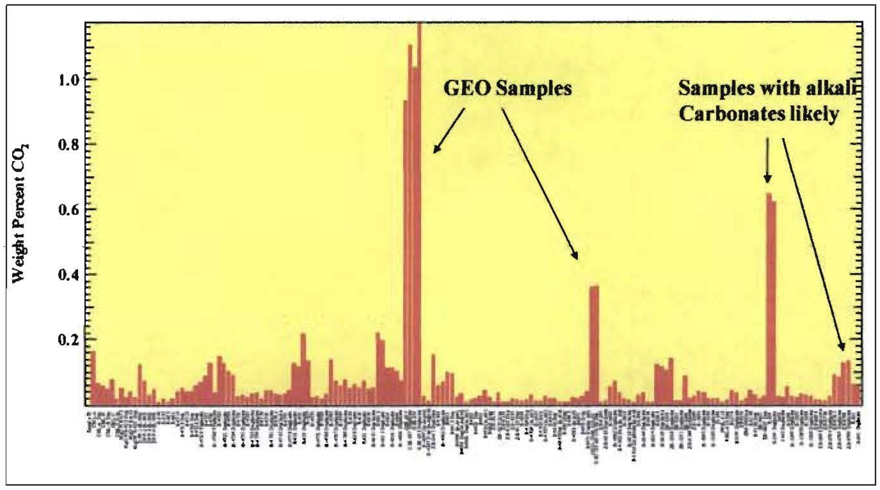
Mass Intensities for a Pure PuO_2 Sample (GEO-110-2) Stored 20+ Years



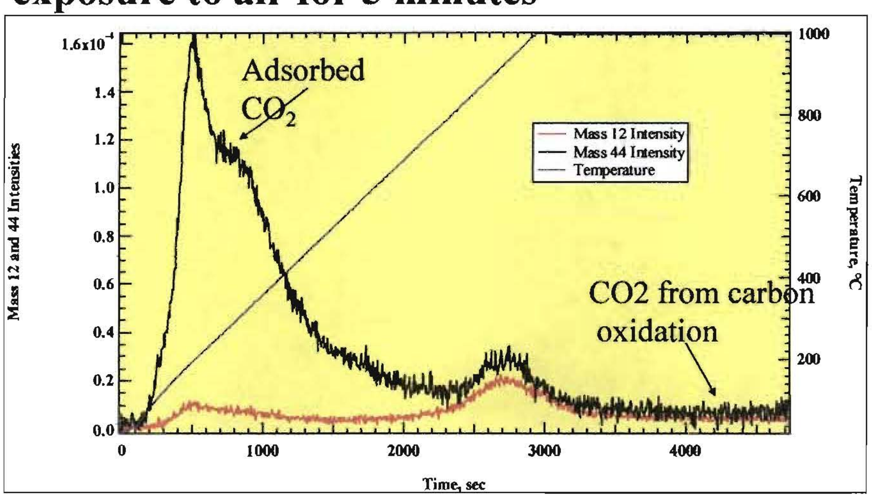
G. Scott Barney, Hanford, 2003

Weight Percent CO_2 in Stabilized Hanford Oxides (Analyzed by TGA-MS)



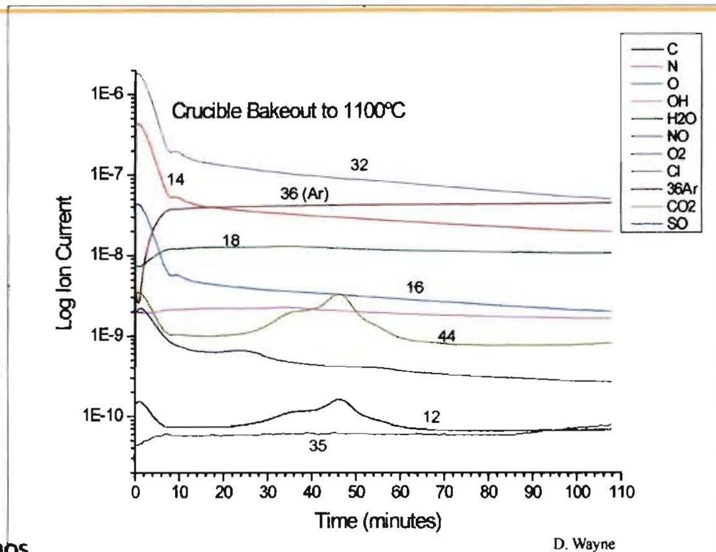
G. Scott Barney, Hanford, 2003

Mass intensities for C^+ and CO_2^+ during heating of activated carbon in argon after exposure to air for 5 minutes



G. Scott Barney, Hanford, 2003

TGA of empty crucible



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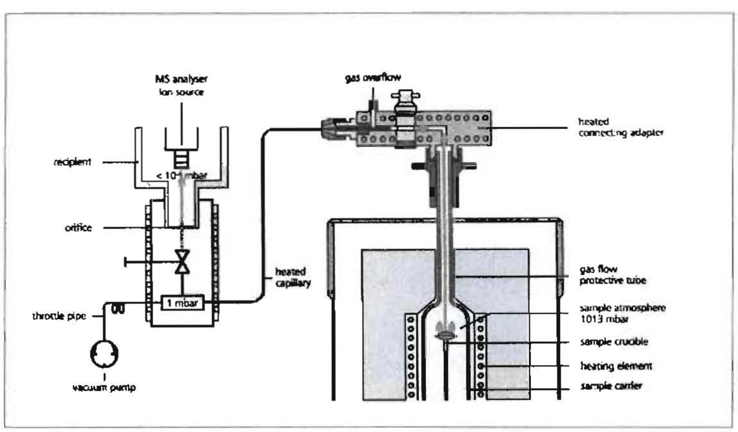
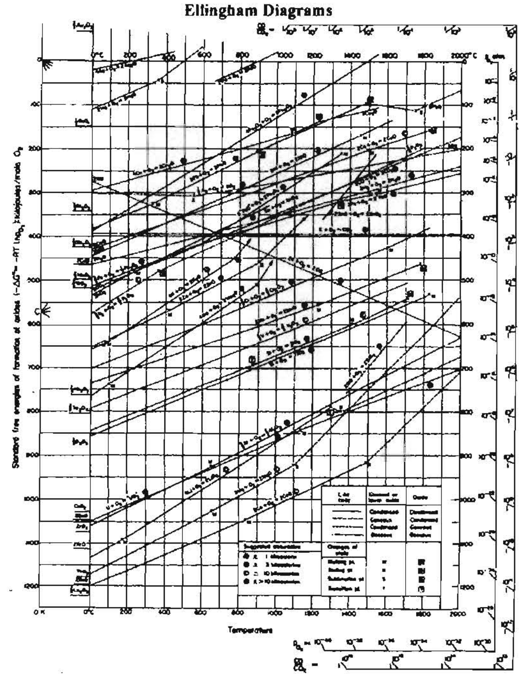
Schematic of the Netzsch TA-409 TA-MS Interface



Ellingham Diagrams



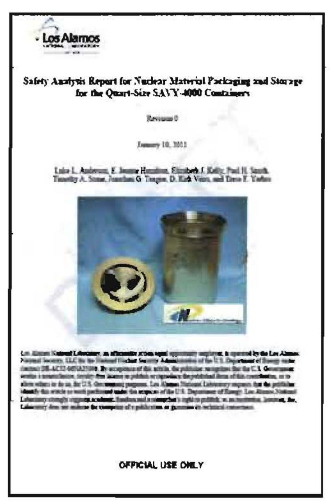
Status of LANL's M441.1-1 container

D.K. Veirs

3013 Surveillance and Monitoring Program Review
Jan. 25-27, 2011
Savannah River Site

SAR Submitted to LASO

- 1392 pages!!! (main report 78 pages with over 1300 pages of Appendices)
- LASO determined they did not have expertise to evaluate container design, requested help from Packaging Certification Division (PCD), PCD provided guidance document QA-10-105-ABL (Feb. 2010) Nuclear Material Packaging and Storage Review Plan.
- Review Plan requires 10 Chapters including Design Criteria, Structural Analysis, Thermal Analysis, Containment Analysis, Operating Procedures, Maintenance Program, Surveillance Program, and QA.


Safety Analysis Report for Nuclear Material Packaging and Storage for the Quart-Size SAVY-4000 Containers

Revision 0

January 10, 2011

OFFICIAL USE ONLY

Table 1-2. Summary Table of Allowable Material Contents

Non-actinide material identification

- Specification of the non-actinide materials is difficult because there are so many of them.
- Identified material not allowed using the LANMAS Item Description (IDES) codes.

Content	Bounding Case
Identification and maximum quantity of radioactive material	Heat source plutonium oxide Any actinide material with A_2 quantity in grams greater than heat source plutonium oxide is allowed up to 25 watts or by other existing limits (container weight, criticality, external dose limit)
Maximum heat load	25 watts
Chemical form	Allowed: All materials unless specifically not allowed Allowed with restrictions: metals that can undergo oxidative expansion are required to be in hermetically sealed inner containers Not Allowed: Materials with IDES codes C02, C19, C39, C40, C61, GXX, KXX, LXX, N69, R12, and R59 (X is generic for any number or letter, see Appendix B).
Physical form	Allowed: Solids; Prohibited: liquids and gases
Maximum Normal Operating Pressure	Differential pressure across container boundary of 1 kPa for quart-size containers
Maximum payload weight	See Table 1-1

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New Container Qualification, Production and Deployment

- Qualification
  - Submit quart-size Safety Analysis Report to DOE (Jan, 2011)
  - Submit gallon-size Safety Analysis Report addendum (May, 2011)
  - DOE-LASO approval of quart-size container Safety Analysis Report (July, 2011)
  - DOE-LASO approval of gallon-size Safety Analysis Report addendum (Aug, 2011)

- Deployment
  - EstablishTA-55 handling procedures for initial production lot (February, 2011)
  - Receive 5-QT production at risk (Mar 2011)
  - Manufacture first production lot - low rate initial production (May, 2011)
  - Establish surveillance testing and maintenance procedures (June, 2011)
  - Procure/install surveillance testing equipment (August, 2011)
  - Deploy database tracking system for containers (September, 2011)
  - Manufacture second production lot - full rate initial production (September, 2011)

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Weld issues

- Evaluation by Edison Welding Institute found the laser welder to be inadequate for reliable production operation – laser beam intensity too low.
- Drop tests described in SAR done with this laser welder. Production will be using a new, more powerful laser welder with slightly modified weld.
- Drop tests on product from new laser welder anticipated along with a SAR addendum.
- Gallon size containers failed drop test and were redesigned. New test units will use the new laser welder.
- New laser welder has been received at NucFil and is being setup by manufacturer.

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New Laser Welder at NucFil

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Lifetime issues

- Design life in SAR specified as five years; desired lifetime of forty years.
- Two design elements are of concern: polymers and the filter.
- LANL has added a polymer SME (Mike Blair) and a filter SME (Murray Moore) to the team to assist in design and execution of Surveillance Program with the goal of extending the lifetime.

Polymer (o-ring) status

- Procurement
  - High-temperature accelerated aging testing completed on special Viton formulation.
  - World-wide Viton shortage resulted in inability to procure o-rings in a timely fashion.
  - Considering commercial grade Viton as well as other materials such as ethylene propylene (EP) in addition to special formulation Viton.
  - Commercial grade o-rings would require additional high-temperature accelerated aging testing.
- Lifetime extension – Laboratory studies
  - Need tests that can be conducted at in-service temperatures to validate the high-temperature tests. Considering room temperature oxygen consumption tests.
  - Need to consider radiation and the synergy between radiation and room temperature aging mechanisms.
  - Currently o-ring replaced each time container is opened. Develop approach to justify multiple opening and closings.

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Survellance Program

- Completed to date
  - Statistical sampling plan for 3 different container populations
  - Procured mostly automated leak test system and procedures
  - Identified key components and tests required to extend service life
    - Filter in PF-4: flow and efficiency
    - O-ring in PF-4: Visual inspection, Shore M hardness, and compression set
    - O-ring special tests: FTIR and tensile properties
- Near Term Plans (FY11)
  - Establish Surveillance and Maintenance to include:
    - Visual inspection, helium leak testing and key component tests
    - Database tracking of containers (history, content, usage statistics, etc.)
  - Procure additional testing equipment and establish surveillance testing capability
- Long Term Plans (FY12-16)
  - Gather and analyze surveillance data
  - Adjust surveillance testing as appropriate
  - Establish justification for long term service life

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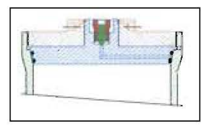
SAVANNAH RIVER NATIONAL LABORATORY
Operated by Savannah River Nuclear Solutions, LLC
We Put Science To Work

O-Ring Surveillance and Life Prediction

T.E. Skidmore, E.N. Hoffman, W.L. Daugherty, K.A. Dunn
Materials Science & Technology
January 26, 2011



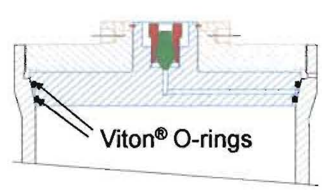



3013 Surveillance & Monitoring Program Review

Plutonium Storage at SRS

- DOE-STD-3013, shipped in Model 9975 shipping packages (Type B)
- 9975 packages stored in KAMS
- Nested stainless steel containment vessels (PCV, SCV) sealed with dual O-rings
- Outer O-rings credited as leak tight per ANSI N14.5 ($\leq$ 1E-07 ref cc/s)
- Initially approved for 10 yrs, recently extended to 15 yrs

PCV = primary containment vessel
SCV = secondary containment vessel

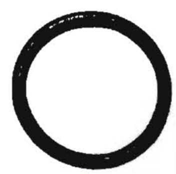



SRNL 2

O-Ring Compound

- Parker Seals V0835-75, based on Viton® GLT, introduced ~1976
- GLT = peroxide-cured, low temperature fluoroelastomer (FKM)
- Service temperature: - 40 to +204 °C
- Hardness: 75+/-5A
- Size AS568 2-244 (PCV), 2-252 (SCV)
- Meets AMS-R-83485
- 2006: GLT replaced by GLT-S, new Parker compound (VM835-75)
- 2008: SRNL approved GLT-S O-rings for transportation and storage

9975 primary containment lid



SRNL

3

STORAGE CONDITIONS

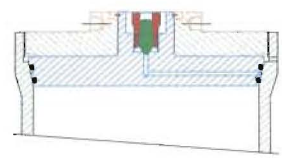
• Normal ambient:	13 - 29 °C (55 - 85 °F)
• Normal O-ring temp (19W):	52 - 68 °C (124 - 155 °F)
• Peak recorded ambient:	41 °C (106 °F)
• Peak O-ring temp:	80 °C (176 °F)
• At 106 °F ambient, 19W	
• Peak O-ring temp:	93 °C (200 °F)
• At 130 °F ambient, 19W	
• Loss of ventilation:	116 °C (240 °F)
• Fire condition bounded by storage	
• Dose Rate (gamma):	20 mGy/hr (2 rad/hr)

SRNL

4

GENERAL APPROACH

- Field Surveillance
  - Examination of actual O-rings
- Simulated laboratory tests
  - Sealed mock-9975 vessels aged at bounding temperatures
  - Purpose: to bound storage and loss of ventilation scenarios, advanced notice to facility
  - Periodic He leak tests to verify performance
- Accelerated-aging methodology
  - Compression stress relaxation
  - Time-temperature superposition



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5

Field Surveillance Results

- ~ 780 O-rings examined (195 packages, 4 O-rings per package)
- O-ring profile (installed) and thickness measured in field after removal (within 30 minutes). Thickness also measured in SRNL.
- Average compression set ~ 23%, based on nominal initial dimensions
- Thickness slightly reduced due to ID stretch (18-20% vs. 3-5% manufacturer)
- O-rings exhibit no degradation

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6

Laboratory Leak Tests

- 62 fixtures assembled with GLT O-rings, aged at 93 °C or 149 °C. Additional fixtures at 177, 204, 232 °C.
- Modified to allow testing of either upper or lower O-rings.
- Stainless steel tubing attached to leak test port via welded high pressure fitting. Threaded hole machined in the bottom of the fixture.
- Wire heaters around the fixture, insulated with fiber batting.
- LabView™ software monitoring with feedback from a type-K thermocouple attached to the PCV body.

Sealed Mock-PCV in aging storage rack

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7

Leak Test Approach

- He leak tests every ~3 to 6 months, 93 °C and 149 °C
- Leak tests on fixtures > 177 °C every ~ 3 weeks
- Leak rate recorded at 3 min (same as for shipping)
- All fixtures tested once to show permeation (proves He flow)
  - one fixture not showing permeation after ~ 1 hour
- Fixture variables:
  - Temperature — 93, 149, 177, 204, 232 °C
  - Radiation Dose — 2 kGy ~ 12 yr dose (0.2 Mrad)
  - Lubricant — silicone, none, Krytox® 240AC
  - Backfill — none, >75% CO_2

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8

Leak Test Results

- No failures at 93 °C after ~4.5 years
- 8 O-rings in 6 GLT fixtures aged at 149 °C have failed within 3 – 4 yrs. Other O-rings remain leaktight after up to 4.5 yrs.
- Both GLT and GLT-S failures after aging at 177, 204, and 232 °C (several days to <1 year)
- At higher temps, O-rings adhere to metal surfaces, leaving residue and oxidized grease. Significant compression set observed.

Flat O-ring profile, 45 days at 204 °C (oxidized Viton®/silicone grease residue)

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9

Compression Stress Relaxation (CSR)

- Industry standard for elastomeric seals (ASTM D6147, ISO 3384)
- Seal is compressed to fixed strain (25% per standard or as-installed)
- Measures force to deflect the seal 0.001”-0.002” at constant compressive strain
- Tests at isothermal conditions
- Inserts designed to mimic 9975 design (ID stretch, squeeze)

Shawbury-Wallace jig

Mark IV Relaxometer

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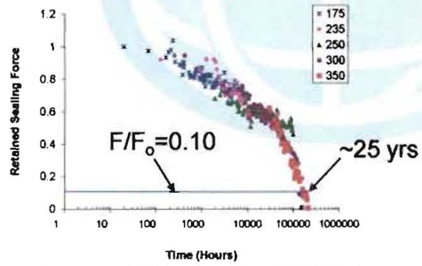
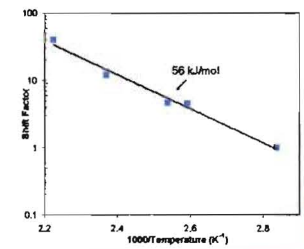
10

Preliminary CSR Aging Model

- Assume failure criterion (90% loss)
- Determine time to failure at multiple temperatures
- Use time-temperature superposition based on WLF principles to develop "master curve".
- Uses all experimental data, allows translation to any temperature desired using shift factors
- Activation energy is less than typical for oxidation processes (80-120 kJ/mol). Indicates physical relaxation is dominant.
- Non-Arrhenius aging behavior possible due to:
  - Diffusion-limited oxidation
  - Antioxidant depletion
  - Change in degradation mechanism



Superposed CSR data at T_{ref}= 175 °F (80 °C)



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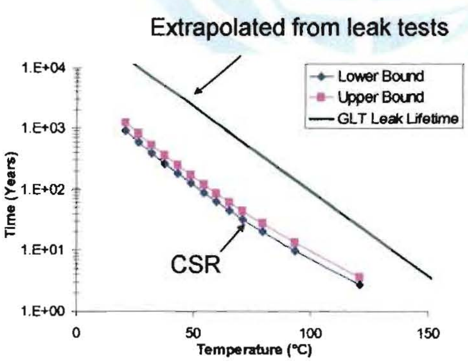
11

SEAL LIFE PREDICTION

- CSR model predicts shorter seal life than leak test data (no failures yet below 149 °C)
- At 93 °C, CSR seal life is ~12 years. Leak test data suggests ~150 years.
- At 80 °C, CSR life is ~ 25 years. Leak test data suggests ~ 300 years.
- Average storage temperatures and reduced payloads further increase seal life.
- Assumptions:
  - seal temp is continuous
  - single degradation mechanism



Estimated Seal Lifetime

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12

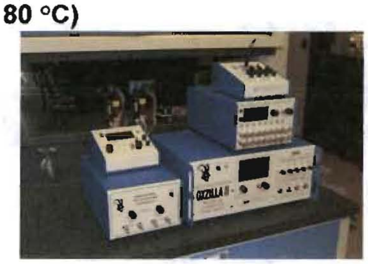
CONCLUSIONS

- 9975 O-rings are not challenged in storage. No degradation has been observed in field-aged O-rings.
- Storage temperatures are well bounded by aging temperatures. Peak temperatures are transient.
- Viton® GLT and GLT-S O-rings are expected to show similar aging behavior.
- No leak failures in ~4.5 years at 93 °C. Recent failures at 149 °C after ~3-4 years. Failures within days to 1 year at 177-232 °C, some at or below vendor "continuous" limit (204 °C).
- Relationship between CSR and leak rate is unknown. Leak rate depends on many factors. CSR aging model is believed to be conservative.

SRNL 13

PATH FORWARD

- Additional leak tests at higher aging temperatures
- Validation of mock-PCV leak tests with full-size PCV tests
- Continue CSR tests – failure criterion not reached at lower temperatures (only ~20% loss at 80 °C)
- Is there a "cliff"?
  - Evaluate non-Arrhenius behavior via oxygen consumption analysis (baseline data in progress)
  - Possible change in the degradation mechanism?
  - Long-term effect of ID stretch?



Ultrasensitive oxygen analyzer (Oxzilla II respirometer, Sable Systems)

SRNL 14

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We Put Science To Work

9975 Surveillance Program - Fiberboard

W. L. Daugherty
Materials Science & Technology
January 26, 2011



3010 Surveillance & Monitoring Program Review

9975 Surveillance (Specific to SRS)

The 9975 shipping package is part of the approved storage configuration at SRS

KAMS credits the 9975 package to perform several safety functions and provide

Fiberboard
- Criticality control → Weight, Density
- Impact resistance → Energy absorption (compression), Fiberboard layer buckling strength
- Fire resistance → Thermal conductivity, Specific heat capacity

O-rings
- Containment

SRNL 2

Scope

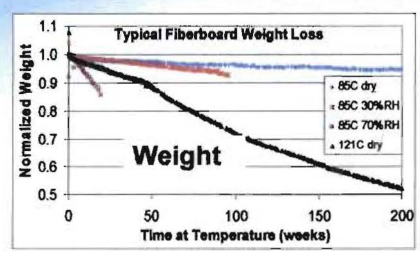
- Laboratory testing of fiberboard samples (SRNL)
- Field surveillance of 9975 packages (KAMS)
- Destructive examination of 9975 packages (SRNL)
- Integrated testing of instrumented packages (SRNL)

- Goal – service life prediction for long-term storage of 9975 packages in KAMS, with intention to extend approved storage life from 10 years to 15 years or beyond

SRNL

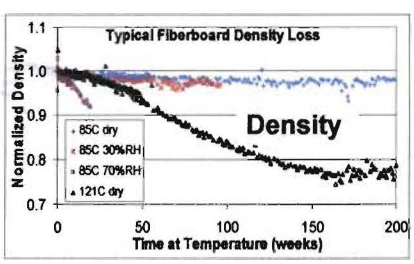
3

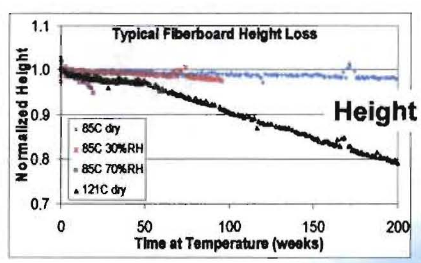
Small-Scale Laboratory Testing



Degradation rate increases with increased temperature, increased humidity

Absolute values vary with package, but rates of degradation more consistent





SRNL

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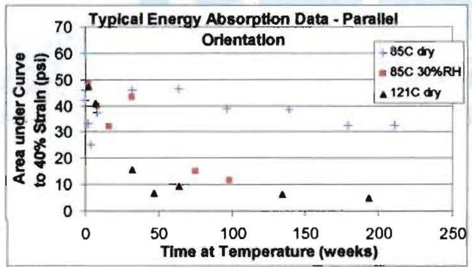
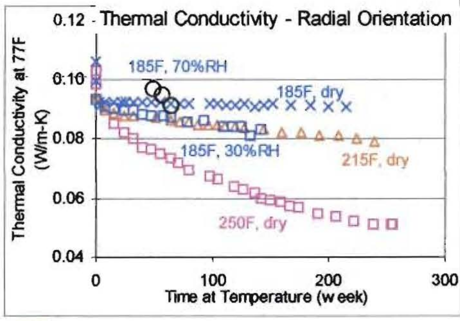
Small-Scale Laboratory Testing

Degradation rate increases with increased temp., increased humidity





Statistical modeling in progress to develop models for predicting service life under storage conditions

SRNL

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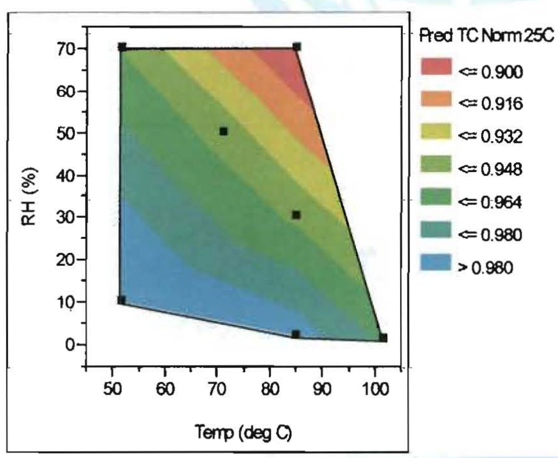
Thermal Conductivity Model

Radial orientation

25 C

Normalized change over 100 weeks



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Laboratory Testing – Trends to Date

- **Up to >4 years conditioning in several environments**
- **Significant change in mechanical and thermal properties only in environments bounding to KAMS**
- **Modest change in properties in environments closer to actual KAMS conditions, not yet a threat to functional requirements**

SRNL 7

Field Surveillance

-Package data following storage at actual storage conditions

-Verify key parameters and develop trends

Dimensional measurements of fiberboard and shield
Fiberboard moisture content
Visual examination of components
Component temperatures
Post-load leak test of containment vessels
Dimensional measurements of O-rings
O-rings sent to SRNL for further examination and measurement

SRNL 8

Field Surveillance

- **195 packages over the last 6 years**

FY05 – 27 pkgs *FY08 – 44 pkgs*
FY06 – 24 pkgs *FY09 – 45 pkgs*
FY07 – 21 pkgs *FY10 – 34 pkgs*

- **Only 1 finding with potential to impact fiberboard integrity:**
  - Mold - upper and lower assemblies
  - Higher local moisture levels
  - Fiberboard intact, ~4.5 yrs service

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Destructive Examination

- **6 packages (1 per year) following up to 7 years storage**
- **Provides a sanity check by comparing laboratory test results to full package data**
- **Destructive examination of fiberboard:**
  - Visual, weight and dimensions
  - Thermal properties
  - Compression test

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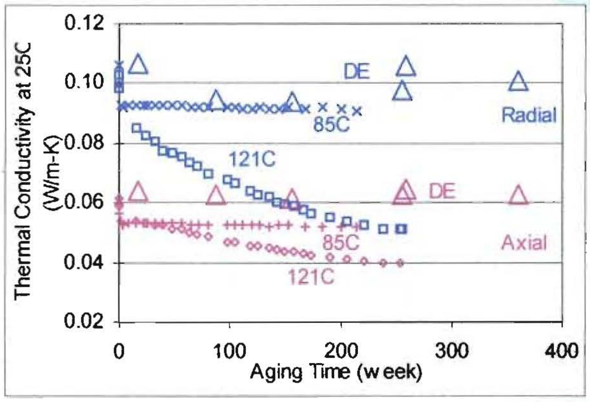
Destructive Examination - Thermal Conductivity

Fiberboard thermal conductivity measured during DE and after laboratory aging



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Destructive Examination Conclusion

- **Results comparable to lab samples with minimal environmental aging**

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Full-Scale Integrated Tests - Instrumented Packages

Modify and instrument 9975 packages for real time measurements

- Bounding conditions
- Monitor material changes and validate against models developed from small scale accelerated aging tests
- Continuous monitoring – temperatures, moisture accumulation
- Periodic monitoring –fiberboard dimensions, humidity, weight and moisture, lead shielding, other components

LE3 at 15 weeks

LE1 – 12 watt internal, 142F 80%RH external

LE2 – 19 watt internal, ~250F max fiberboard temperature

LE3 – 19 watt internal, ~160F max fiberboard temperature

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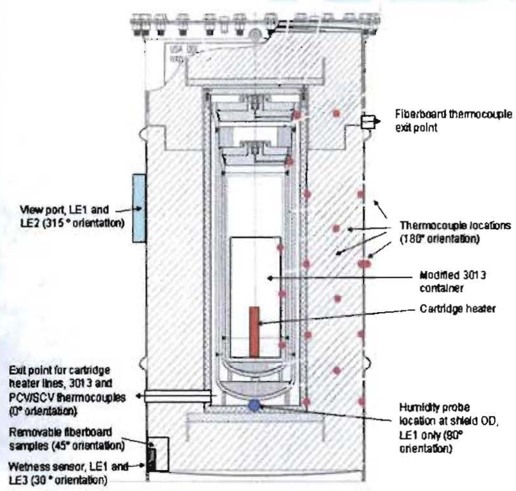
Full-Scale Integrated Tests



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Full-Scale Integrated Tests

Moisture segregation due to temperature gradient

Axial shrinkage / settling of fiberboard – axial gap at top of package

Mold growth in high moisture, moderate temperature regions

Consistent with field experience

Leaching of minerals, etc from fiberboard

LE2

~250F max. fiberboard temp.

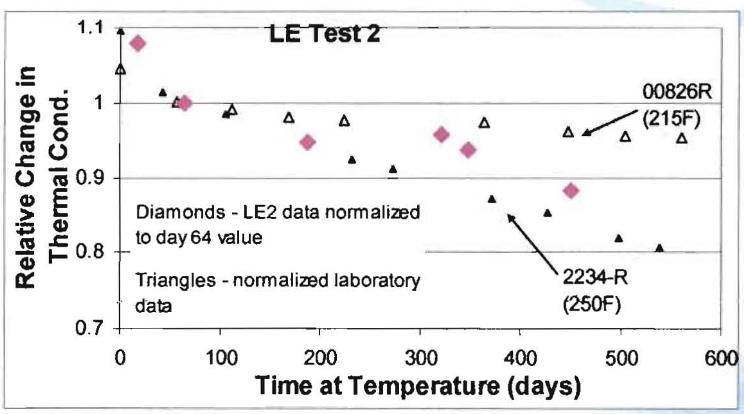
LE3

~160F max. fiberboard temp.

Full-Scale Integrated Tests – Validation of Lab Data

Fiberboard weight loss comparable to lab samples

Thermal conductivity change comparable to lab samples



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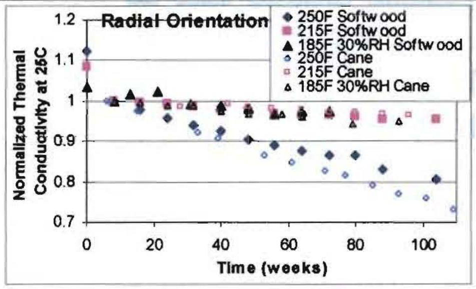
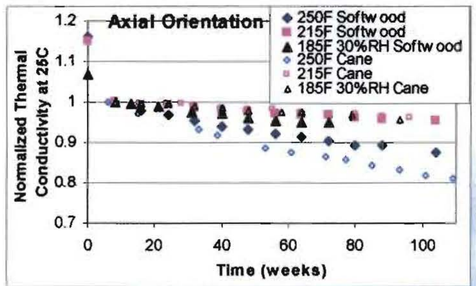
Cane Fiberboard vs Softwood Fiberboard

Comparable behavior with some minor differences

- 250F, less decrease in thermal conductivity with softwood
- 185F, 30%RH, greater decrease in ax. thermal conductivity, compression strength, weight, height with softwood

Thermal conductivity





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Summary

Lab-scale tests – basis for aging models and service life predictions

Field surveillance – no significant degradation to date for nominal storage conditions (caveat for elevated moisture levels)

Destructive examination – fiberboard properties consistent with non-degraded material

Full scale integrated tests – correlates with lab-scale data and field experience, confirms potential for several degradation scenarios

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Summary

The 9975 package is robust

Continuing goals include

- models for service life prediction
- continue aging tests to validate models and conclusions
- extension of approved storage period beyond 10 years

SRNL 19

Questions?

SRNL 20