LA-UR-13-23179

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Title:	FY12 Surveillance and Monitoring Program Review
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FY12 Surveillance and Monitoring Program Review

Laura A. Worl

3013 Surveillance and Monitoring Annual Program Review*
Savannah River Site, Building 766-H, Room 2138
February 27 - 28, 2013
Preceded by Corrosion Working Group Meeting on February 26

Tuesday Feb 26	Duration		
Corrosion Working Group			
8:30 AM	8:00	**Corrosion Working Group Meeting**	Corrosion Working Group
Wednesday Feb 27			
8:00 AM	0:15	Welcome/ Introductions	C. McClard
3013 Field Surveillance Update			
8:15 AM	0:30	K Area FY12 status and FY13 plans	C. McClard, Hackney
8:45 AM	0:20	Sample Selection of 3013 Containers from K-Area	C. McClard/ E. Kelly
9:05 AM	0:45	Oxide Analysis in DE	D. Missimer / J, Duffey
9:50 AM	0:20	DE Gas Analysis and Pressures in 3013 containers	B. Nguyen / Crapse
10:10 AM	0:15	**Break**	
10:25 AM	0:20	Gradients of Thermal conductivity, Relative Humidity and Moisture in 3013 Containers	B. Nguyen
10:45 AM	0:45	3013 Can analysis from DE	J. Mickalonis, K. Dunn
11:30 AM	0:30	Update to prompt gamma calibrations	J. Narlesky
12:00 PM	**1:00**	**Lunch**	
Corrosion Work			
1:00 PM	0:30	Review of Corrosion Conditions, Pitting, SCC and Ties to 3013 Inventory	K. Veirs
1:30 PM	0:30	Overview SRNL Corrosion Shelf Life Studies	J. Mickalonis, J. Duffey
2:00 PM	0:20	Overview and Status of Large Scale Corrosion Containers	J. Narlesky
2:20 PM	0:20	Summary Corrosion Pit Depth Statistical analysis	E. Kelly
3013 Equivalencies	0:15	**Break**	
2:55 PM	0:20	3013 Equivalency / Low Temp Stabilization for Oxalate precipitation Material	J. Duffey
3:15 PM	0:15	Review Team Comments	T. Venetz
3:30 PM	0:30	Experimental results to date - effect of RH and O2 generation	K. Veirs
4:00 PM	0:30	Oxide Studies - Test Plan	J. Berg, Veirs et al.
4:30 PM	0:30	3013 Equivalency /Low Temp Stabilization for Metal Oxidation Material	J.Berg / R. Livingston
5:00 PM	0:30	Low Temperature Material Analysis	J. Berg
Thursday Feb 28			
MIS - WG			
8:00 AM	2:00	**MIS-Working Group Meeting (Meeting Action Items, SRNL and LANL AOPs)**	MIS WG
Corrosion Working Group			
10:00 AM	6:00	**Continued from 2/26. Corrosion Working Group - SCC Plan Status**	Corrosion Working Group

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K-Area FY12 Status

J. W. McClard, E.R. Hackney

Savannah River Nuclear Solutions, LLC

February 27, 2013

MIS Program Review

FY12 DE Status

- MIS Requested 12 DEs
  - 9 total DEs Completed
  - 1 DE originally scheduled for FY14
    - Swapped to collect samples for Vacuum Salt Distillation Testing
  - SRNL Analyses recently completed for 9 DEs

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FY13 Plans

FY13 Plans

- MIS Requested 9 DEs
- Budget Issues Impacted Activities
- 1 Limited Scope DE Forecasted for April 2013
  - Standard DE for KAC (gas samples, oxide samples and can pieces generated)
  - SRNL will receive and store samples(visual observation of can pieces only)
    - Potential impacts of delaying SRNL analyses
      - Data obtained from TGA/MS of oxide sample will be suspect
      - Implementation of LEAN event program improvement: extending lifetime of gas cylinder prior to analysis

FY14 Plans

- Perform 9 DEs in KAC
- SRNL will perform 10 Analyses
  - 9 DEs from 2014
  - 1 DE from 2013

SELECTION OF 3013 CONTAINERS FOR FIELD SURVEILLANCE: 2013 UPDATE (LA-UR-13-21195)

Elizabeth Kelly, Los Alamos National Laboratory
John Berg, Los Alamos National Laboratory
Jesse Cheadle, Savannah River Nuclear Solutions
David Riley, Lawrence Livermore National Laboratory
Theodore Venetz, Washington River Protection Solutions
Laura Worl, Los Alamos National Laboratory
James McClard, Savannah River Nuclear Solutions

MIS Program Review
February 25-28, 2013
SRS

History

- **This update is the seventh in a series of reports that document the field surveillance program for 3013-type containers.**
  - **2005**. Three reports documenting the binning approach (Peppers, et al., 2005a) the sampling approach (Kelly, et al., 2005) and the items in the statistical (random) and judgmental samples were published (Peppers, et al., 2005b).
  - **2007**. These three reports were combined into one document (LA-14310) (Peppers, et al., 2007) and the binning and sampling information was updated.
  - **2009**. Revision 1 of LA-14310 (LA-14395) (Peppers, et al., 2009) was published.
    - Binning update and resulting changes to surveillance sample.
  - **2011**. LA-UR-11-04417 was published, providing an update of the information in LA-14395 (Kelly, et al., 2011).
    - Surveillance focused on P&C bin, binning update and resulting changes to surveillance sample.

What Are the Major Changes in 2013?

- **Updated numbers of containers from LANL and LLNL and SRS (AFS-2)**
  - Re-allocation of remaining random samples between sites
- **Changes in schedule due to budget restrictions**
  - Reduced DEs from 12 to 9 per year
  - Deferred FY13 DEs to FY14
  - Extended end date from FY22 to FY25
- **New prioritization for scheduling random items based on moisture measurements**

SRS Containers

- **SRS currently plans to generate approximately 1000 new 3013 containers.**
  - The material in these containers will be product oxide for shipment to the Mixed-Oxide Fuel Fabrication Facility (MFFF).
  - These containers will likely be binned into the Pressure bin.
  - The intent is to only store these containers for a short time prior to processing in MFFF.
    - If storage becomes extended (greater than the three year threshold for NDE), these containers should be evaluated to determine if surveillance of these containers is prudent.

New numbers for LLNL and LANL

Table 3. Summary of binning results for P&C Bin as of January 2013.

<table>
<tr><th>Site</th><th>Pressure and Corrosion</th><th>Total</th></tr>
<tr><td>RFETS</td><td>358</td><td>358</td></tr>
<tr><td>Hanford</td><td>546</td><td>546</td></tr>
<tr><td>LLNL</td><td>111</td><td>111 (108 previously)</td></tr>
<tr><td>SRS</td><td>83</td><td>83</td></tr>
<tr><td>LANL Shipped to SRS as of Jan, 2013</td><td>4</td><td rowspan="2">9 (160 previously</td></tr>
<tr><td>LANL 3013 Containers at LANL</td><td>5</td></tr>
<tr><td>TOTAL</td><td></td><td>1007</td></tr>
</table>

Changes to Site Sample Sizes Resulting from New Numbers from LANL and LLNL

Table 4. Distribution of sample sizes in the Pressure and Corrosion (P&C) bin across sites for the previous surveillance sampling and the current plan

Site	Previous P&C Sample Size (Kelly, et al., 2011)	Current P&C Sample Size	Difference
RFETS	37	41	4
Hanford	56	63	7
LLNL	11	13	2
SRS	8	10	2
LANL	16	1	-15
TOTAL	**128**	**128**	

Changes to DE Schedule

- **Budgetary Constraints**
  - **FY 2011**. DEs reduced from 18 to 12 per year.
  - **FY 2012.** DEs reduced from 12 to 9
  - **FY2013.** DEs delayed until FY2014
    - 7 random 2 EJ
- **Prioritization of P&C Bin Sample Based on Moisture Content**
  - There is a stronger correlation between corrosion and the material moisture content than with other parameters.
  - Therefore, DE's prioritized in order of decreasing moisture content, in order to maximize the rate of acquiring data that better define the bounds of the potential for corrosion in the overall population.

New Schedule – Table 7

- **Between FY07 and FY12 DE has been performed on 48 of 128 containers in P&C bin random sample**
- **80 DE containers in the random sample remain to be examined from 2014 to 2025**
  - Current plan is to perform 9 DE surveillances per year consisting of 7 random and two EJ items.
  - Table 7 prioritizes DE's according to known or estimated moisture content with the highest moisture items evaluated first.
  - If SRS finds that it needs to swap the specific random items in a given year, they will document the changes and the reason for the changes in a letter to MIS.

Table 7

3013ContainerID	Site	TGA650 or dbase Moisture	ISP Sub-bin	DE Year
H003064	Hanford	0.300	BDT-3-Cl	2014
S002116	SRS	0.180	BDT-3-Cl	2014
H003307	Hanford	0.165	BDT-3-Cl	2014
H003052	Hanford	0.162	BDT-4-H-1E	2014
H003898	Hanford	0.159	BDT-3-Cl	2014
H004219	Hanford	0.158	BDT-3-Cl	2014
H004024	Hanford	0.158	BDT-4-H-1E	2014
H003896	Hanford	0.393	BDT-3-Cl	2015
S002162	SRS	0.370	BDT-4-SR-ARF	2015
R610156	RFETS	0.320	BDT-3-Cl	2015
H004302	Hanford	0.301	BDT-2-Cl	2015
H001979	Hanford	0.295	BDT-3-Cl	2015
H003181	Hanford	0.285	BDT-4-H-1E	2015
H003258	Hanford	0.279	BDT-3-Cl	2015
H002556	Hanford	0.232	BDT-3-Cl	2016
R601875	RFETS	0.197	BDT-3-F	2016
H004173	Hanford	0.169	BDT-3-Cl	2016
H004247	Hanford	0.168	BDT-3-Cl	2016
H003775	Hanford	0.165	BDT-3-Cl	2016
H003652	Hanford	0.149	BDT-3-Cl	2016
H003711	Hanford	0.145	BDT-4 (LLNL Washed)	2016
H003970	Hanford	0.143	BDT-3-Cl	2017
S002121	SRS	0.130	BDT-3-Cl	2017
H004100	Hanford	0.130	BDT-3-Cl	2017
H004104	Hanford	0.123	BDT-3-Cl	2017
H003326	Hanford	0.118	BDT-3-Cl	2017
H003910	Hanford	0.118	BDT-3-Cl	2017
H003313	Hanford	0.117	BDT-3-Cl	2017
H004152	Hanford	0.103	BDT-3-Cl	2018
S002132	SRS	0.100	BDT-4-SR-ARF	2018
H004014	Hanford	0.100	BDT-4-H-1E	2018
R611307	RFETS	0.094	BDT-3-Cl	2018
H004248	Hanford	0.093	BDT-3-Cl	2018
H004164	Hanford	0.091	BDT-3-Cl	2018
S002288	SRS	0.090	BDT-3-Cl	2018
H003312	Hanford	0.080	BDT-4-H-1E	2019
R611068	RFETS	0.079	BDT-3-Cl-HCl	2019
H004213	Hanford	0.077	BDT-3-Cl	2019
R600600	RFETS	0.074	BDT-4-RF-2B	2019
R611207	RFETS	0.073	BDT-3-Cl	2019
S001150	SRS	0.070	BDT-4-SR-ARF	2019
H004162	Hanford	0.069	BDT-3-Cl	2019
H004010	Hanford	0.068	BDT-3-Cl	2020
H003276	Hanford	0.064	BDT-3-Cl	2020
L000282	LLNL	0.060	BDT-4 (LLNL Washed)	2020
R610989	RFETS	0.054	BDT-3-Cl	2020
S001766	SRS	0.050	BDT-4-SR-ARF	2020
S002160	SRS	0.050	BDT-4-SR-ARF	2020
R610396	RFETS	0.041	BDT-3-Cl	2020
R610913	RFETS	0.041	BDT-3-Cl	2021
R611225	RFETS	0.036	BDT-4-RF-2B	2021
R610667	RFETS	0.033	BDT-3-Cl	2021
R610974	RFETS	0.028	BDT-3-Cl	2021
R611417	RFETS	0.028	BDT-3-Cl	2021
R611402	RFETS	0.017	BDT-3-Cl	2021
H002792	Hanford	0.017	BDT-3-F	2021
L000196	LLNL	0.015	BDT-4 (LLNL Washed)	2022
H003280	Hanford	0.014	BDT-3-F	2022
H002862	Hanford	0.012	BDT-3-F	2022
R611306	RFETS	0.012	BDT-4-RF-2B	2022
R611019	RFETS	0.011	BDT-3-Cl-HCl	2022
H003439	Hanford	0.010	BDT-3-Cl	2022
A000551	LANL	0.010	BDT-3-Cl	2022
H004220	Hanford	0.008	BDT-4-H-1E	2023
H002706	Hanford	0.008	BDT-3-Cl	2023
L000223	LLNL	0.007	BDT-3-Cl	2023
H003106	Hanford	0.006	BDT-4-H-1E	2023
R611244	RFETS	0.004	BDT-4-RF-2B	2023
L000274	LLNL	0.004	BDT-4 (LLNL Washed)	2023
R610728	RFETS	0.003	BDT-4-RF-2B	2023
R610906	RFETS	0.003	BDT-3-Cl	2024
L000377	LLNL	0.003	BDT-3-Cl	2024
L000207	LLNL	0.002	BDT-4 (LLNL Washed)	2024
L000421	LLNL	0.001	BDT-3-Cl	2024
L000202	LLNL	0.001	BDT-4 (LLNL Washed)	2024
L000185	LLNL	0.001	BDT-4 (LLNL Washed)	2024
L000172	LLNL	0.001	BDT-4 (LLNL Washed)	2024
L000159	LLNL	0.001	BDT-4 (LLNL Washed)	2025
R611338	RFETS	-0.017	BDT-3-Cl	2025
R611101	RFETS	-0.042	BDT-3-Cl-HCl	2025

Where Are We?

- **48 random DEs completed**
- **Approximately a 90% probability of detecting a 5% problem**
- **Approximately a 99.9% probability of detecting a 15% problem**

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Oxide Analysis in DE

J. M. Duffey

Separations & Actinide Science Programs

February 27, 2013

3013 Surveillance & Monitoring Program Review

Annual Meeting

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

S&ASP FY12 DE Oxide Analyses

- **Received 9 DE oxide samples**
- **Analyses performed**
  - Pycnometry
  - BET surface area analysis
  - TGA-MS moisture analysis
  - Acid dissolution
  - Aqueous leaching

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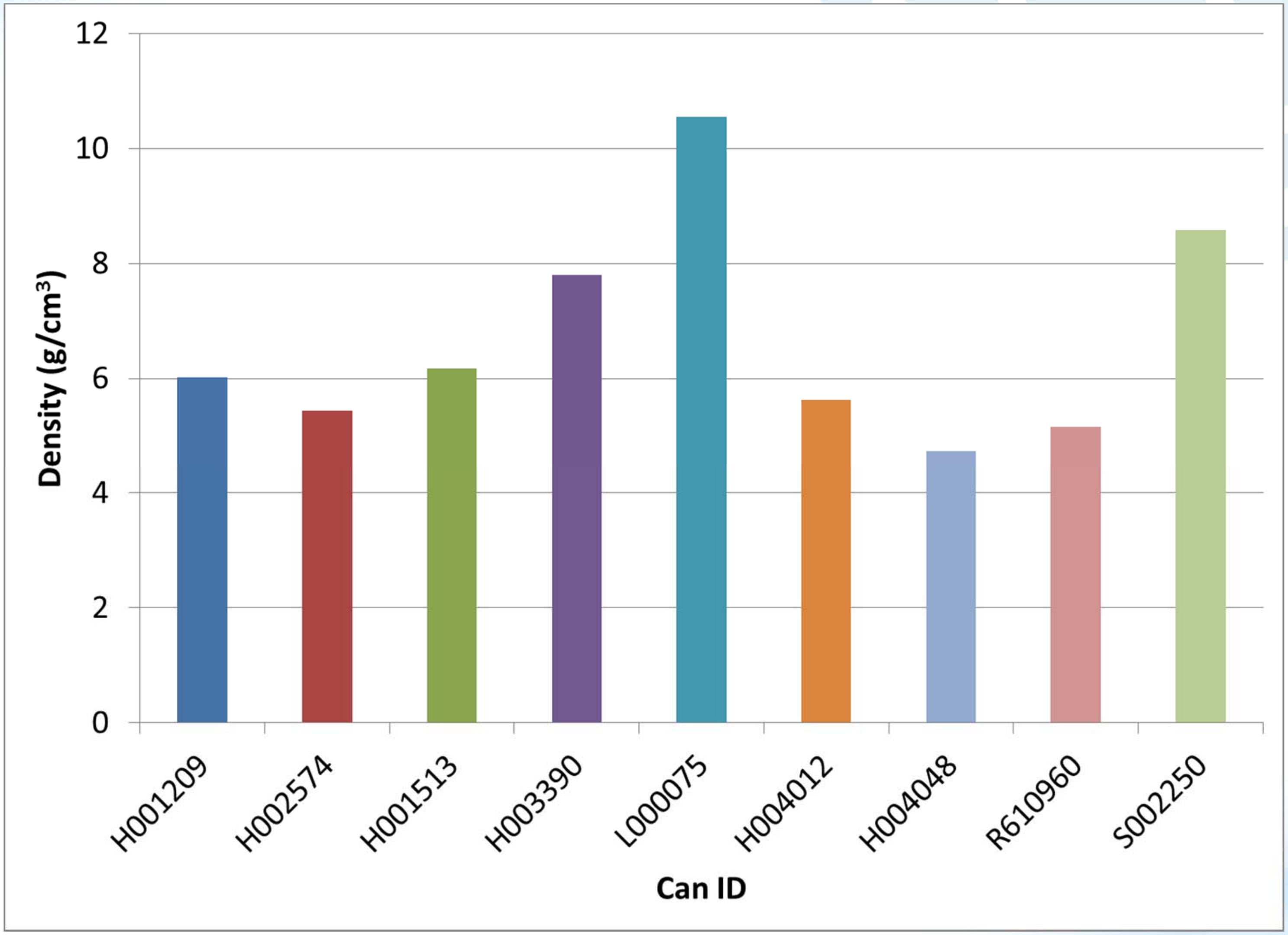
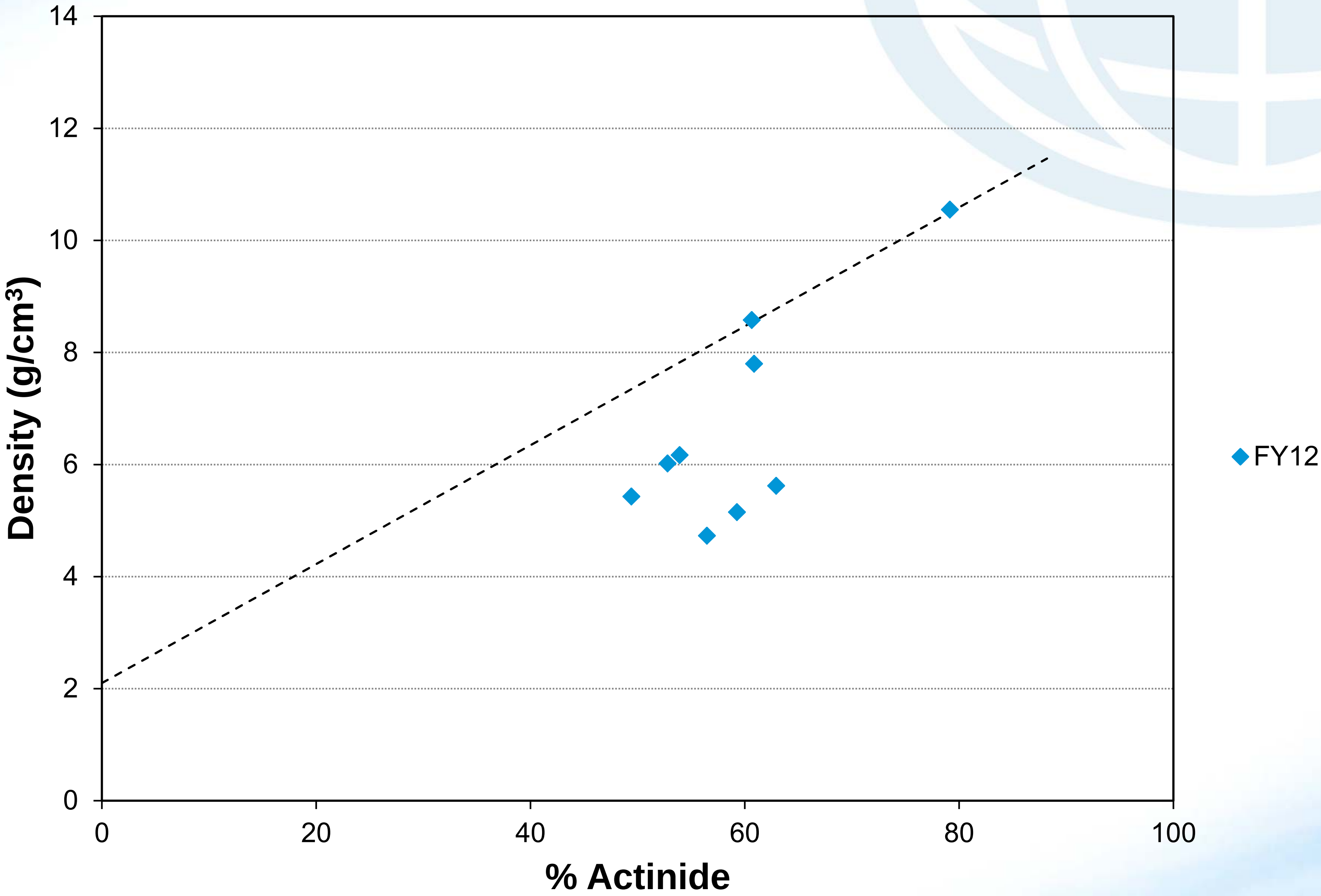
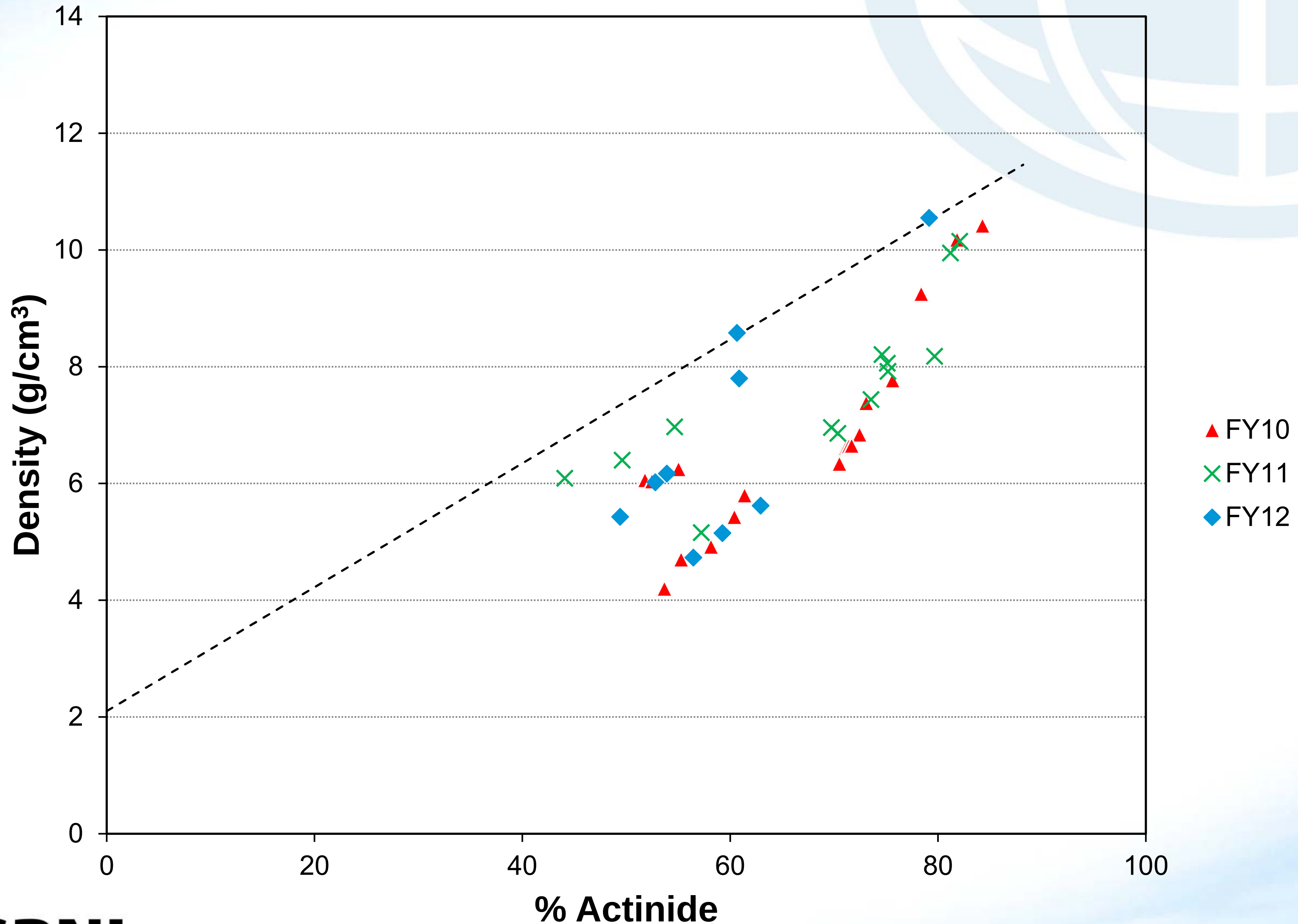
FY12 Pycnometry Results



FY12 Pycnometry Results



FY10, FY11, and FY12 Pycnometry Results



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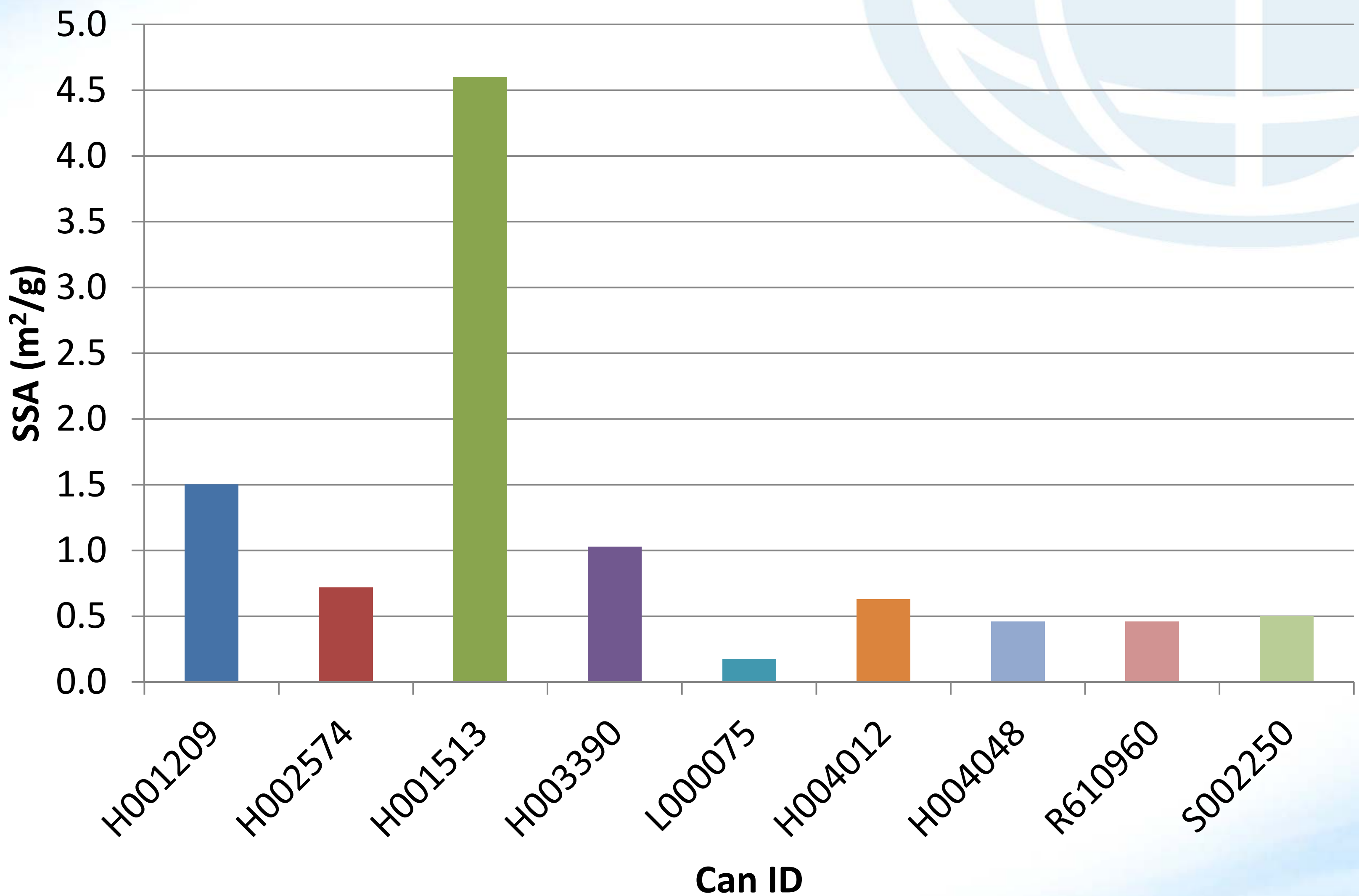
BET Surface Area Results



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12DE03 and 12DE04 Photos

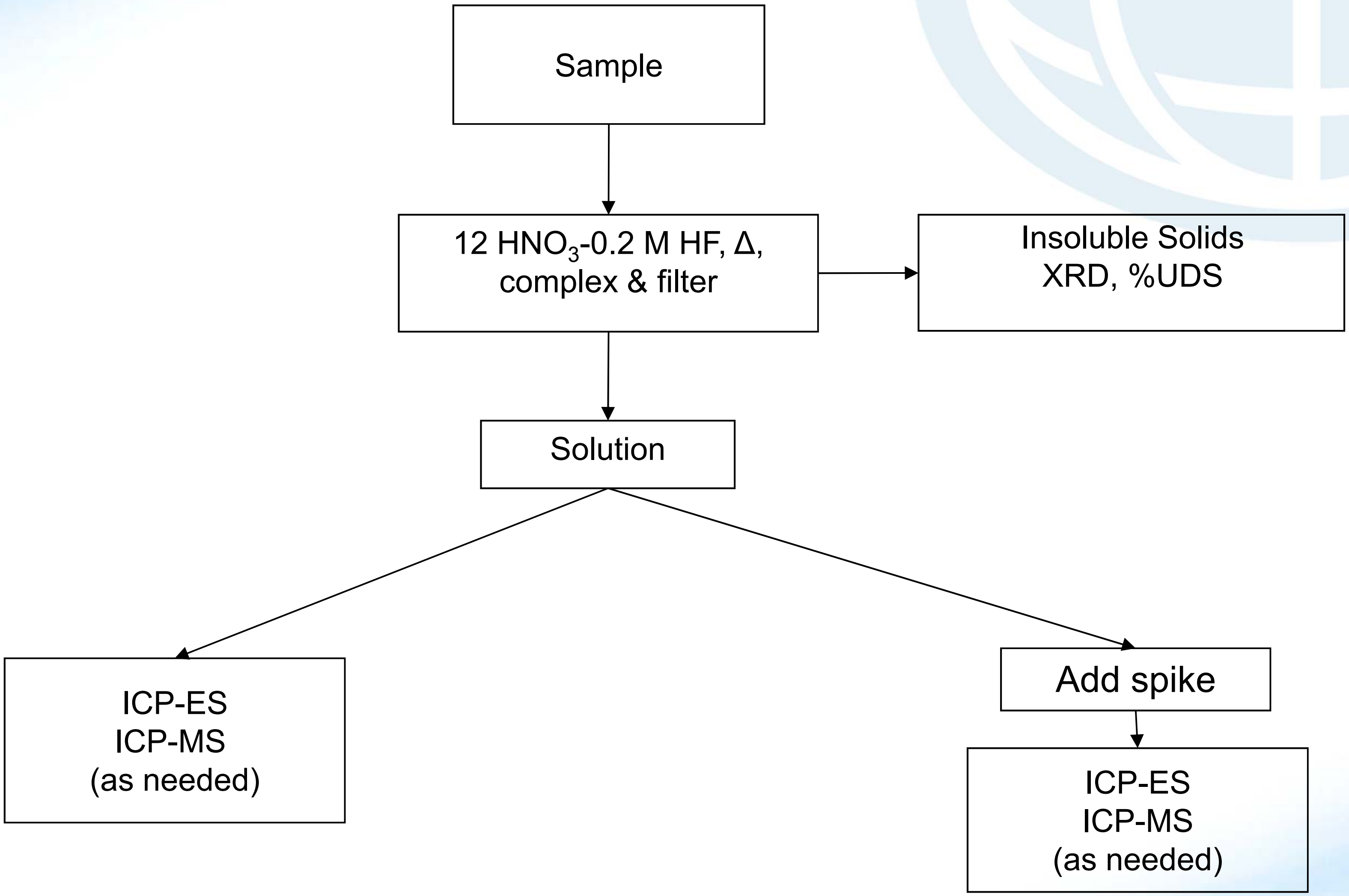
12DE03 – H001513

12DE04 – H003390

Dissolution Flowsheet

- **No changes to dissolution flowsheet in FY12**
  - 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 (sometimes)
  - Insoluble fraction: XRD, %UDS

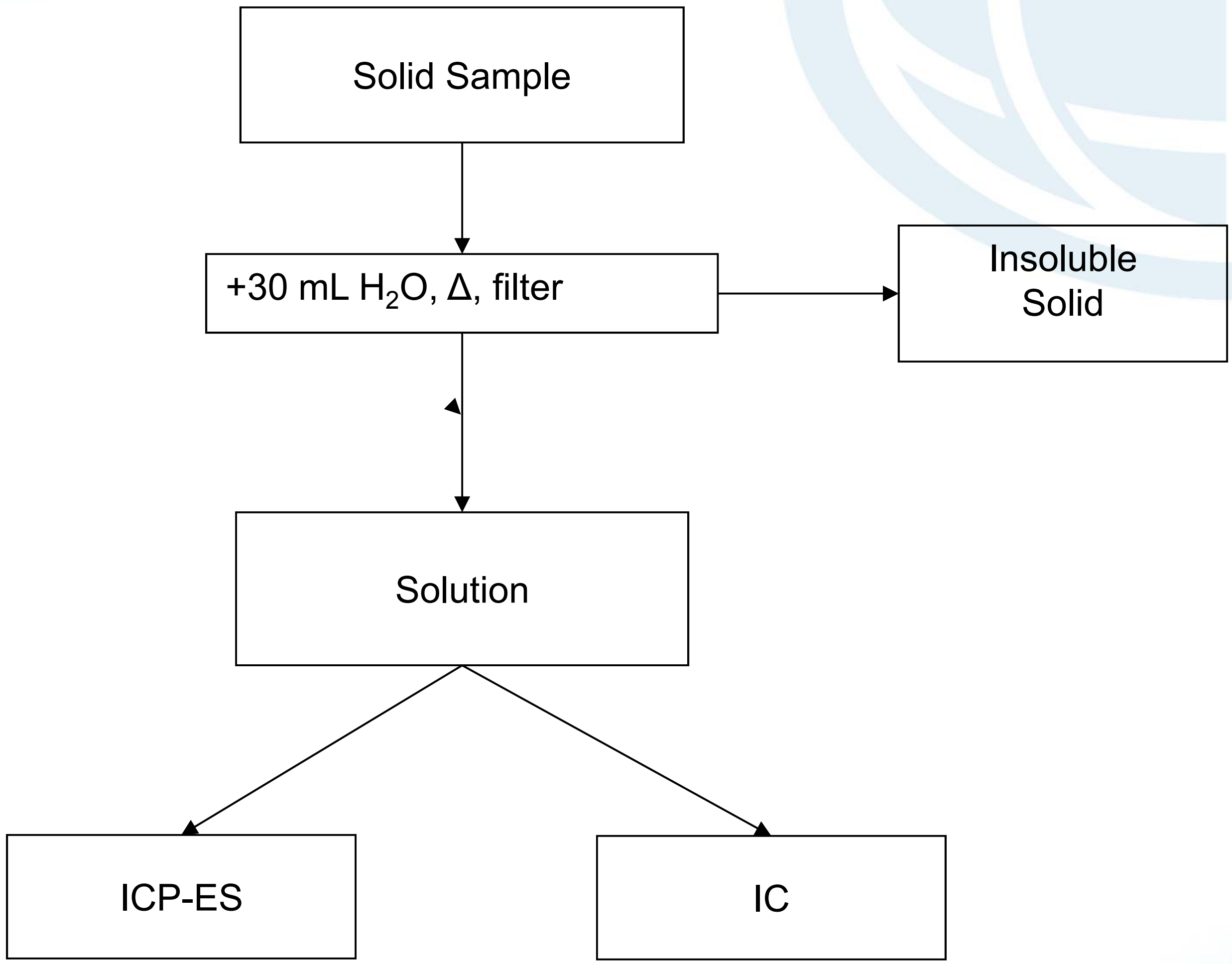
Dissolution Flowsheet



Aqueous Leach Flowsheet

- **No changes to leaching flowsheet in FY12**
  - 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: solids retained until aqueous results reviewed

Leaching Flowsheet



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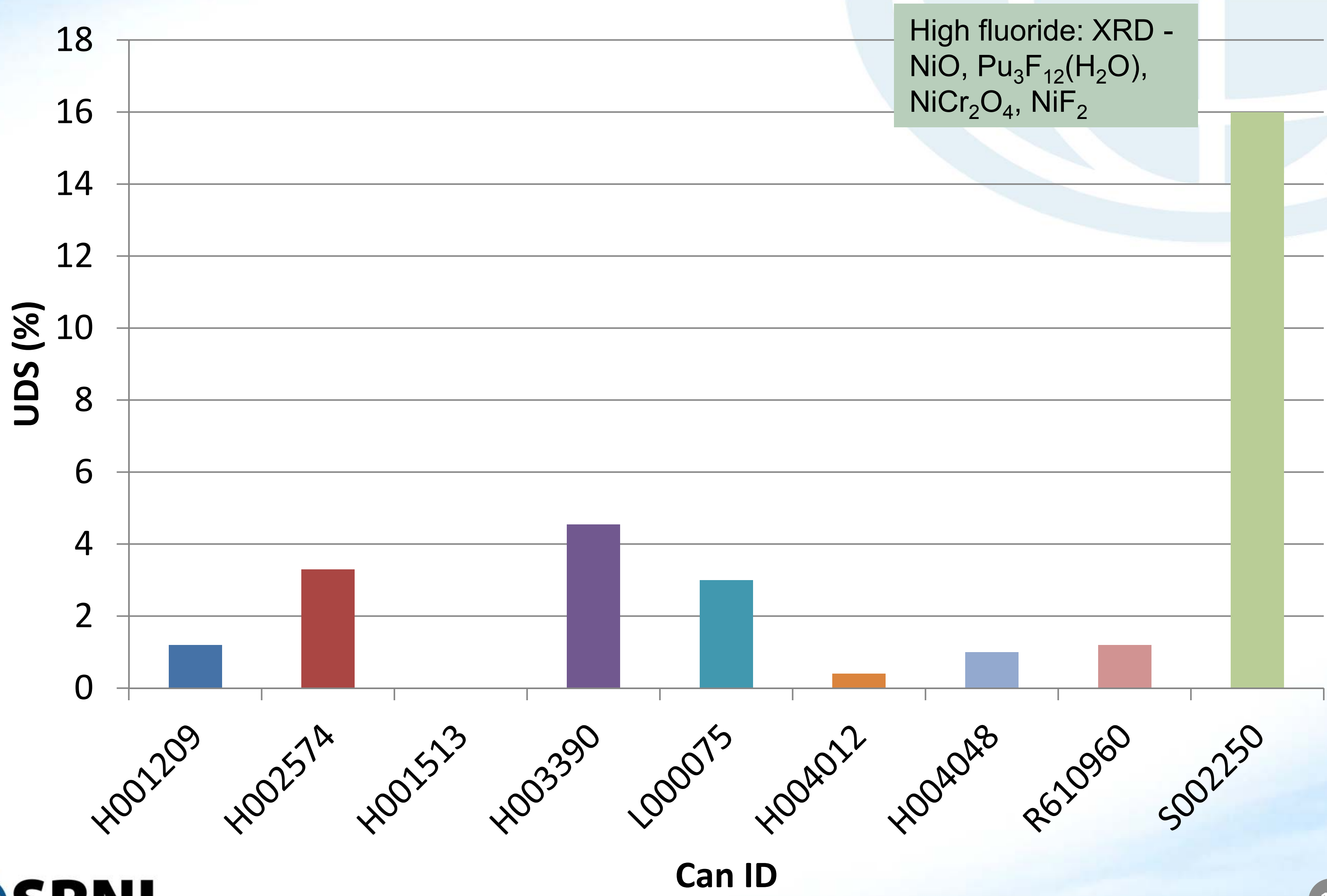
Undissolved Solids



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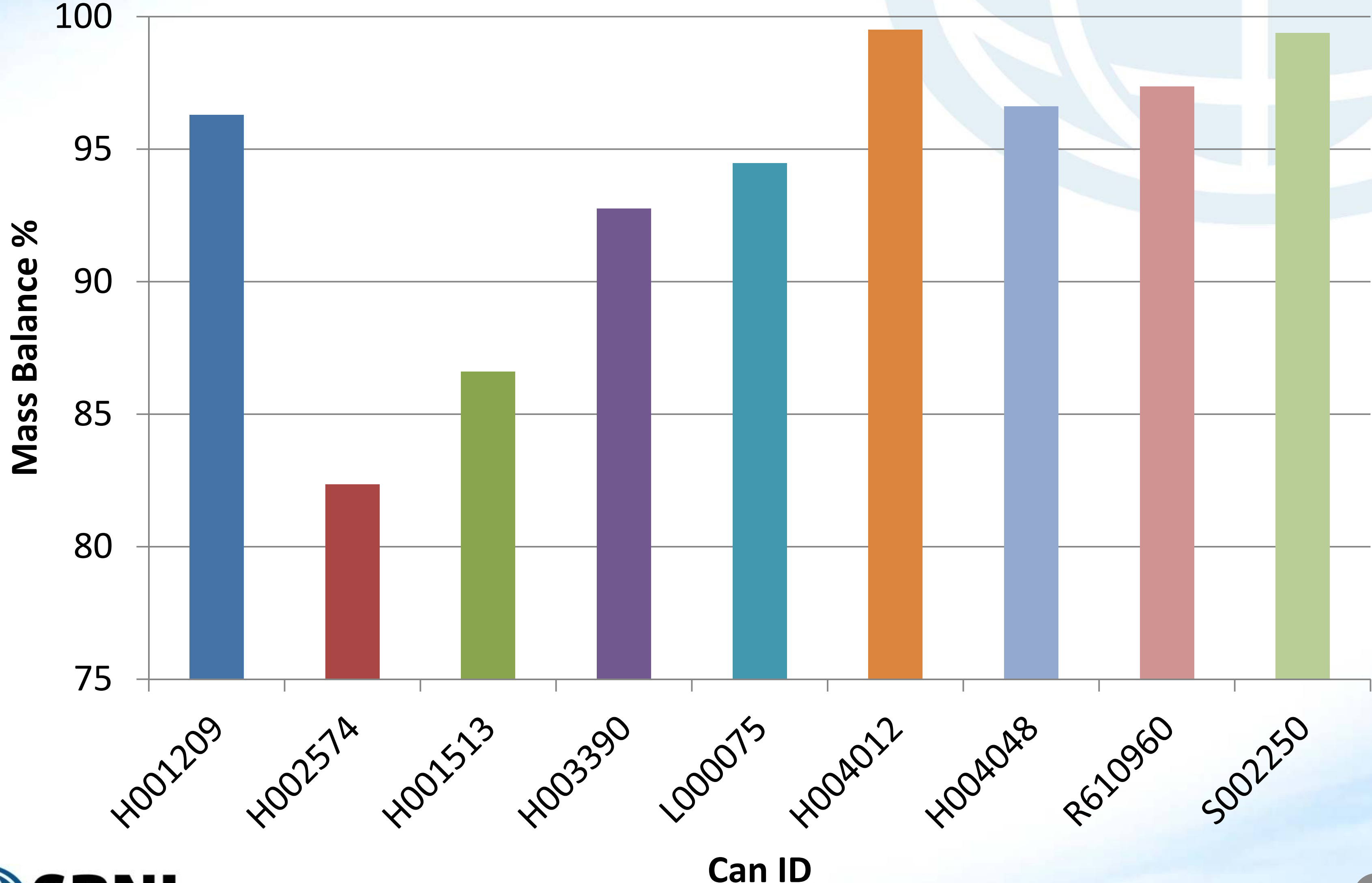
Mass Balance Calculations



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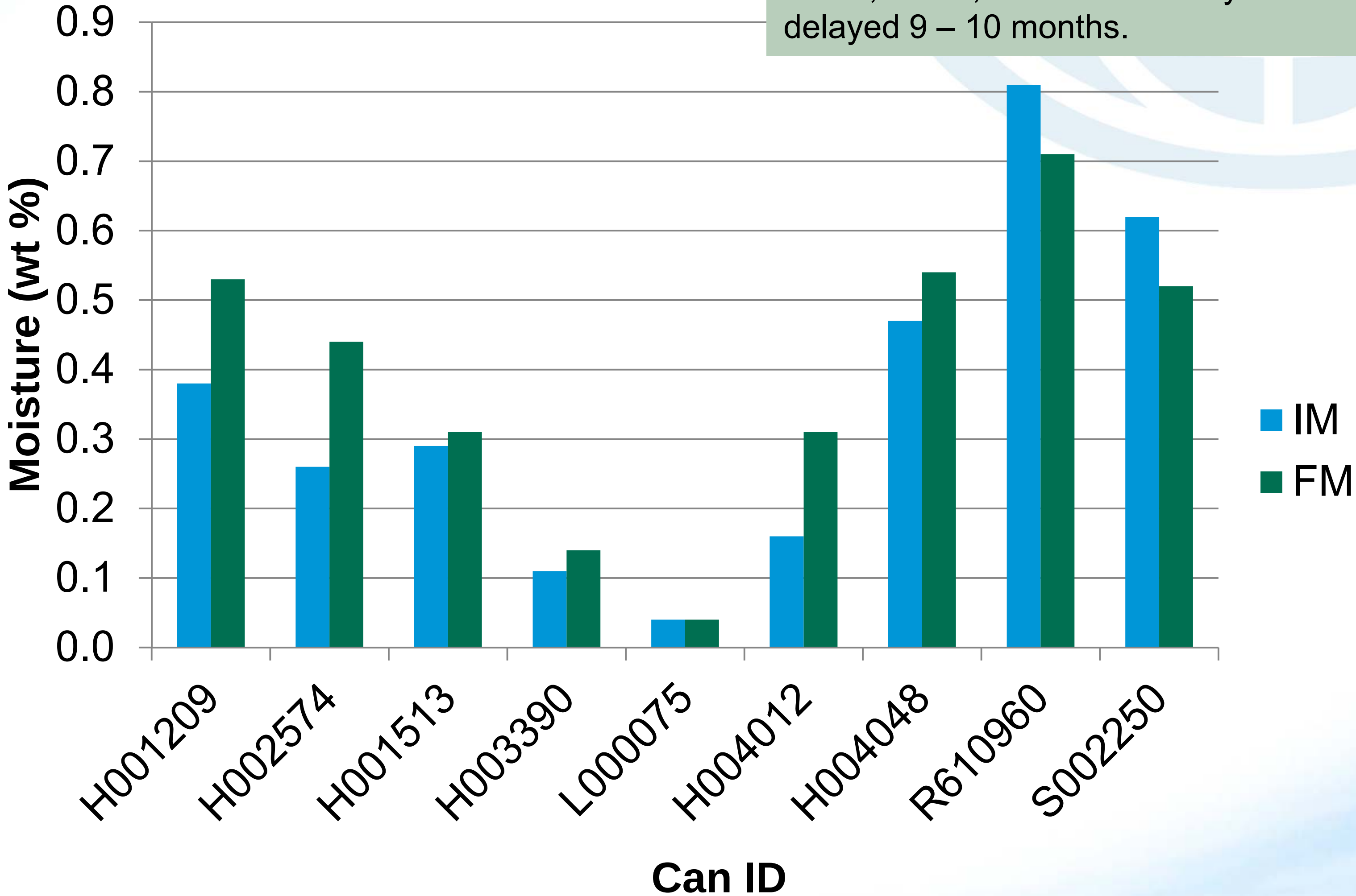
TGA-MS Moisture Measurements

Preliminary data – not yet reviewed for 12-07, 12-08, and 12-10. Analysis was delayed 9 – 10 months.



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Conclusions

- **Two IM samples, four FM samples >0.5 wt % H_2O**
  - Moisture analysis of last three DE samples delayed approximately 9-10 mos.
  - Comparison of packaging moisture values and H_2 generation results suggests some moisture uptake during sample storage likely
- **Densities range from 4.7 g/cm^3 to 10.6 g/cm^3 and generally increase with increasing actinide content**
- **SSAs range from 0.2 to 4.6 m^2/g (one >1.5 m^2/g – H001513)**
- **One sample (S002250 – high F content) had >5% UDS**
- **Mass balances generally good (five >95%; two <90%)**

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Acknowledgments

Technical Assistants:

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

Scientists/Engineers:

Mike Bronikowski, Mark Crowder, Fernando Fondeur, Kim Crapse, John Scogin, Tom Shehee

Specialists:

Angela Bowser, Patrick Westover, Shirley Brunson-Brown

Managers:

Sam Fink (S&ASP), Tim Brown (Acting), Dave Mitchell (FLS)

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FY2012
Gas Sample Results & Lean Initiatives

Binh Nguyen & Kim Crapse

KAC Process Engineer & SRNL Researcher

Savannah River Nuclear Solutions, LLC
Date: 2/27/2013

Can Puncture Device

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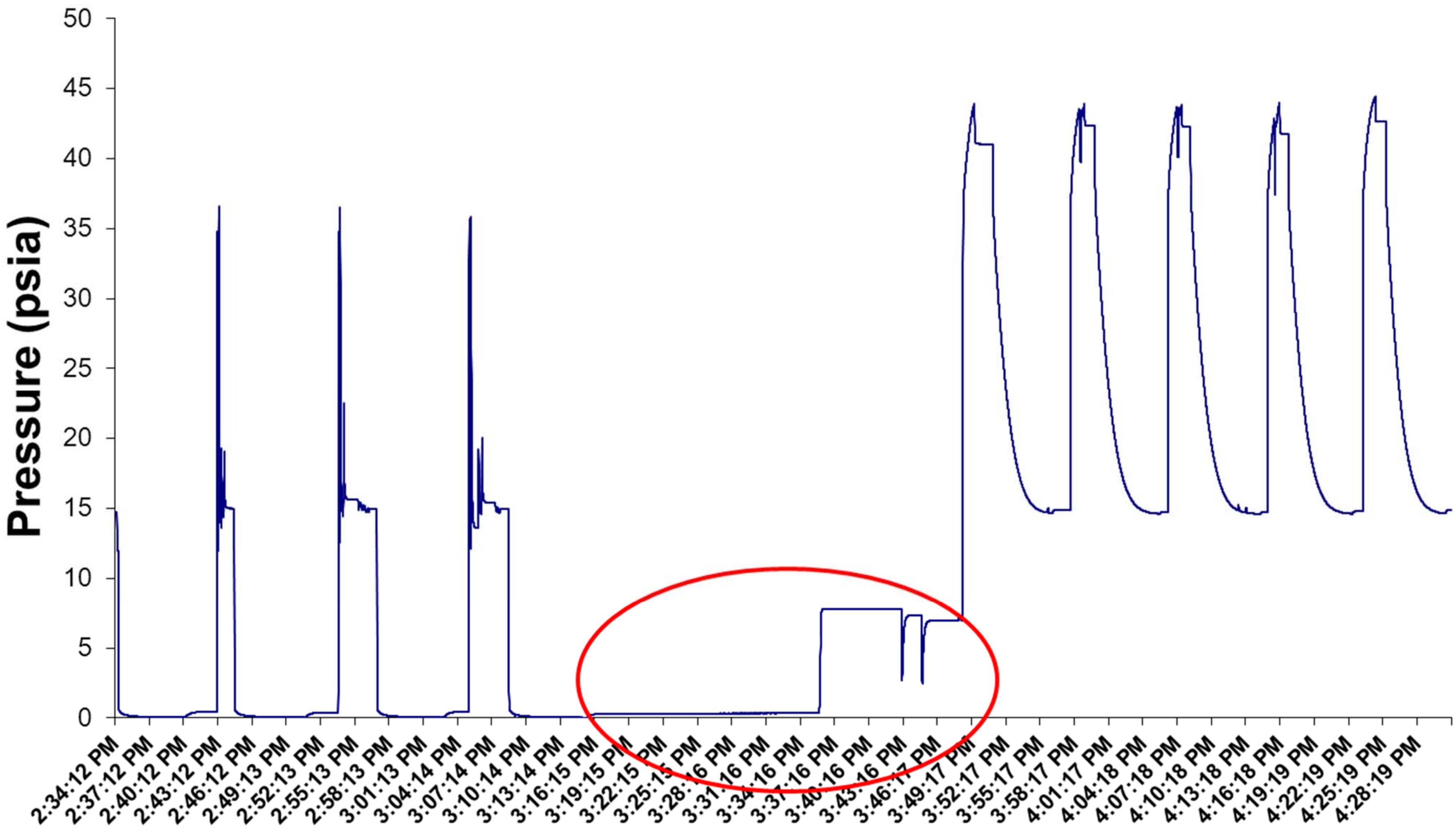
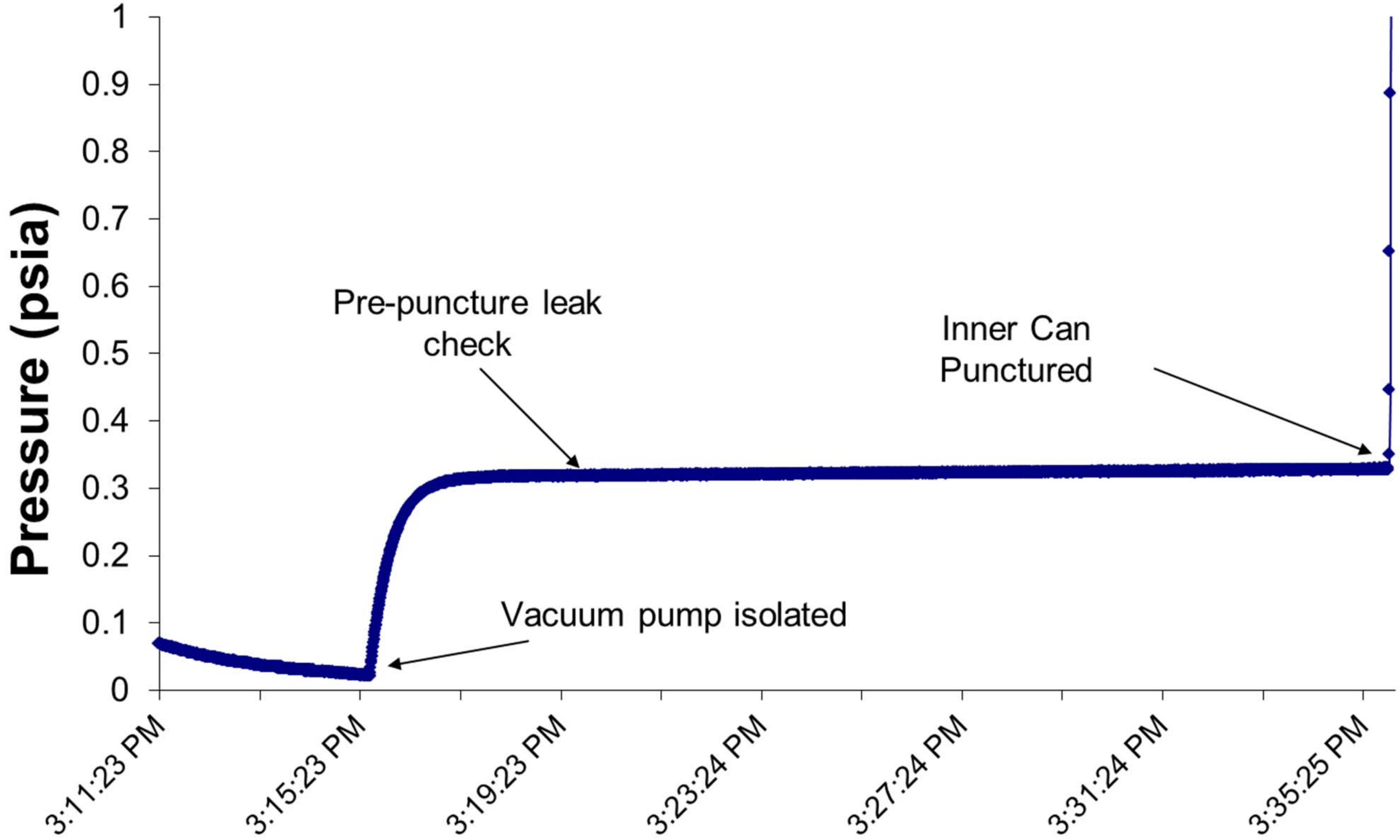
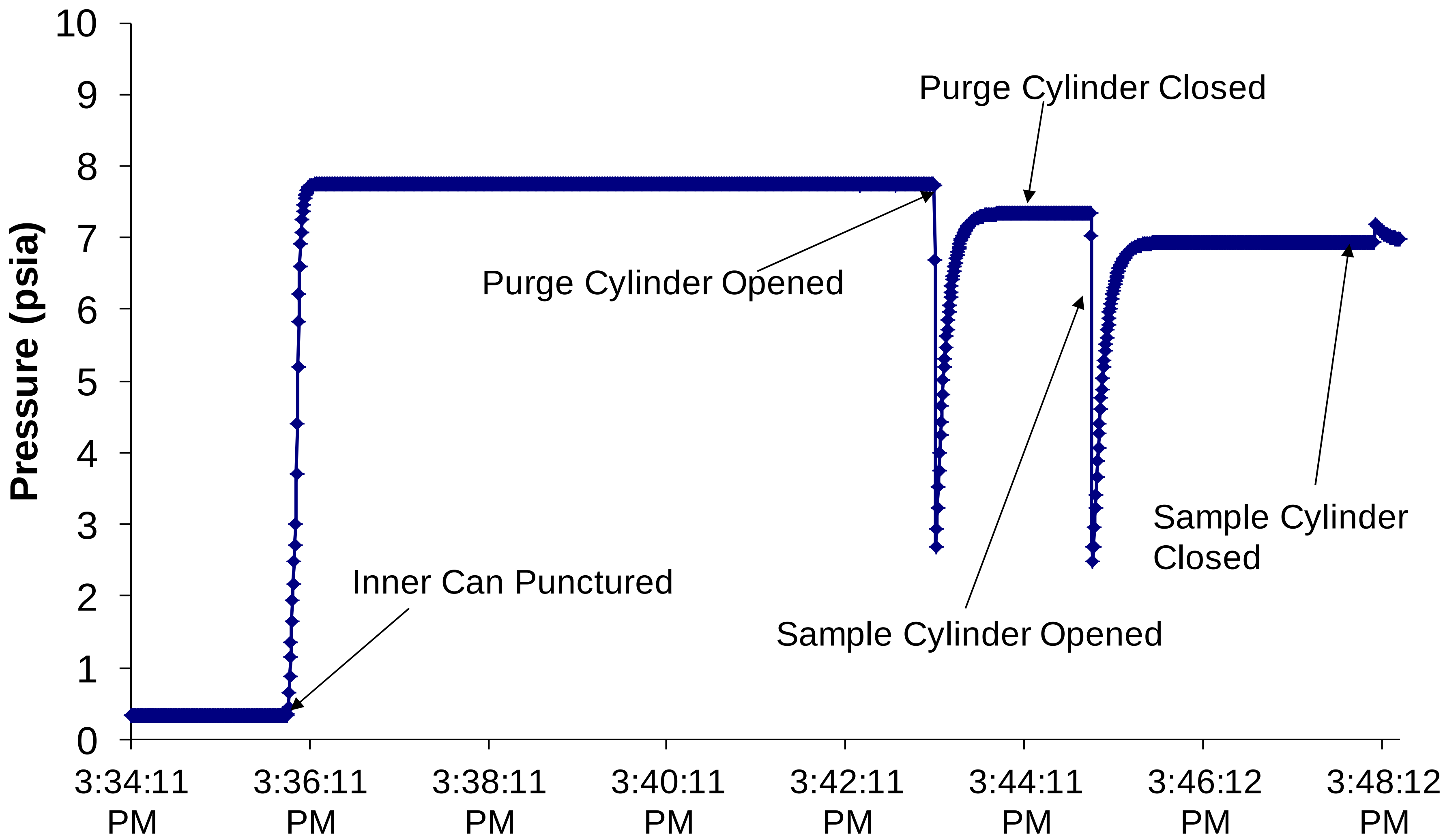
Typical Pressure Curve



Leak Check


Pressure (psia)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
3:11:23 PM
3:15:23 PM
3:19:23 PM
3:23:24 PM
3:27:24 PM
3:31:24 PM
3:35:25 PM
Pre-puncture leak check
Inner Can Punctured
Vacuum pump isolated

Gas Sampling



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Gas Processes and Results

- Captured gas from outer-inner (OI) and inner can (IC) sent to SRNL for analysis (150 mL sample cylinders)
  - Micro-Gas Chromatography
  - 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; ***typically*** sealed with moisture
- To date, no flammable mixture has been measured

Micro-Gas Chromatography CP-4900

- Typical pressures as received sample cylinders in FY11-12;
  - OI sample cylinders ~2-3 psia
  - IC sample cylinders ~5-7 psia
- Further expanded: at least 1 psia sample pressure in manifold
- Argon push gas: 18-22 psia
- Columns:
  - PoraPlot Q (10 m):
    - » Carrier gas: He
    - » CH_4, CO_2, N_2O
  - Molsieve 5 Å (20 m):
    - » Carrier gas: Ar
    - » He, H_2, O_2, N_2,(CH_4), CO

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GEST Overview

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

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FY12 Gas Composition Results

(Values in %vol)		CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO	Ar	Pressure (Psia)
DE#1	H001209	ND	ND	ND	55.02	0.42	Trace	44.55	ND	-	12.15
DE#2	H002574	ND	ND	< 0.1	91.83	ND	Trace	8.09	ND	-	12.82
DE#3	H001513	ND	ND	0.54	52.80	< 0.1	< 0.1	46.52	ND	-	11.31
DE#4	H003390	ND	ND	0.17	57.69	0.21	< 0.1	41.91	ND	-	11.43
DE#5	L000075	ND	3.54	0.89	2.90	Trace	< 0.1	77.15	< 0.1	15.48	14.20
DE#6	H004012	ND	< 0.1	Trace	48.42	< 0.1	< 0.1	51.52	ND	-	10.92
DE#7	H004048	< 0.1	0.40	Trace	51.92	4.09	< 0.1	43.50	< 0.1	-	9.82
DE#8	R610960	< 0.1	Trace	ND	87.42	11.74	Trace	0.81	ND	-	13.01
DE VSD	S002250	ND	3.58	0.39	73.24	Trace	0.98	21.50	0.31	-	13.65

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Rocky Flats Cans

FYDE	Container	He	N2	H2	Pressure (psia)	Packaging Moisture Method	Packaging Moisture Percent	Initial Moisture TGA/MS Percent
2007DE01	R600885	90.8	9.2	Trace	12.8	LOI	0.10	0.05
2007DE02	R601722	87.2	12.7	Trace	12.5	LOI	0.18	0.04
2007DE03	R601957	89.6	10.4	Trace	12.8	LOI	0.03	0.04
2007DE04	R600719	83.8	16.2	Trace	12.9	LOI	0.10	0.04
2007DE05	R610735	82.3	17.5	Trace	12.4	FTIR Recalc	0.36	0.19
2007DE06	R610697	82	18	Trace	12.5	FTIR Recalc	0.28	0.14
2007DE07	R601285	77.4	22.5	Trace	13.4	LOI	0.15	0.1
2008DE01	R602731	83.9	16.1	Trace	12.3	LOI	0.07	0.03
2008DE02	R601318	91.5	8.5	Trace	12.6	LOI	0.17	0.02
2008DE04	R610327	82.8	16.7	Trace	12.4	FTIR Recalc	0.00	0.04
2008DE05	R610298	84	16	Trace	13	FTIR Recalc	0.00	0.14
2008DE06	R610324	82.3	17.7	Trace	13.1	FTIR Recalc	0.01	0.1
2008DE09	R610584	84.6	14.8	Trace	13.7	FTIR	0.14	0.07
2008DE10	R610578	82.1	17.8	Trace	12.5	TGA	0.04	0.19
2008DE16	R610679	70.3	26.7	Trace	11.7	TGA	0.26	0.03
2009DE05	R602498	87.5	12.5	ND	12.3	LOI	0.26	0.13
2009DE09	R611398	80.6	18.9	<0.10	11.4	FTIR Recalc	0.29	0.02
2009DE13	R610700	82.9	14.2	<0.10	11.5	TGA	0.23	0.03
2009DE14	R610764	83.3	16.8	<0.10	12.2	TGA	0.06	0.05
2009DE15	R610573	85.5	14.2	Trace	13.7	TGA	0.25	0.22
2009DE16	R610558	81.8	17.2	Trace	12.3	TGA	0.04	0.01
2009DE17	R610806	84.3	15.1	<0.10	12.2	TGA	0.28	0.27
2010DE06	R610627	85.1	14.8	Trace	14.7	FTIR Recalc	0.02	0.09
2010DE15	R610785	84.8	14.5	0.7	13.9	FTIR Recalc	0.01	0.19
2010DE16	R610826	88.5	11.5	ND	12	FTIR Recalc	0.01	0.28
2010DE17	R610853	86.8	13.2	Trace	12.3	FTIR Recalc	0.03	0.12
2011DE10	R611131	86.1	13.9	ND	13.8	LOI	0.01	0.09
2012DE08	R610960	87.42	0.81	11.74	13.01	LOI	0.03	0.81

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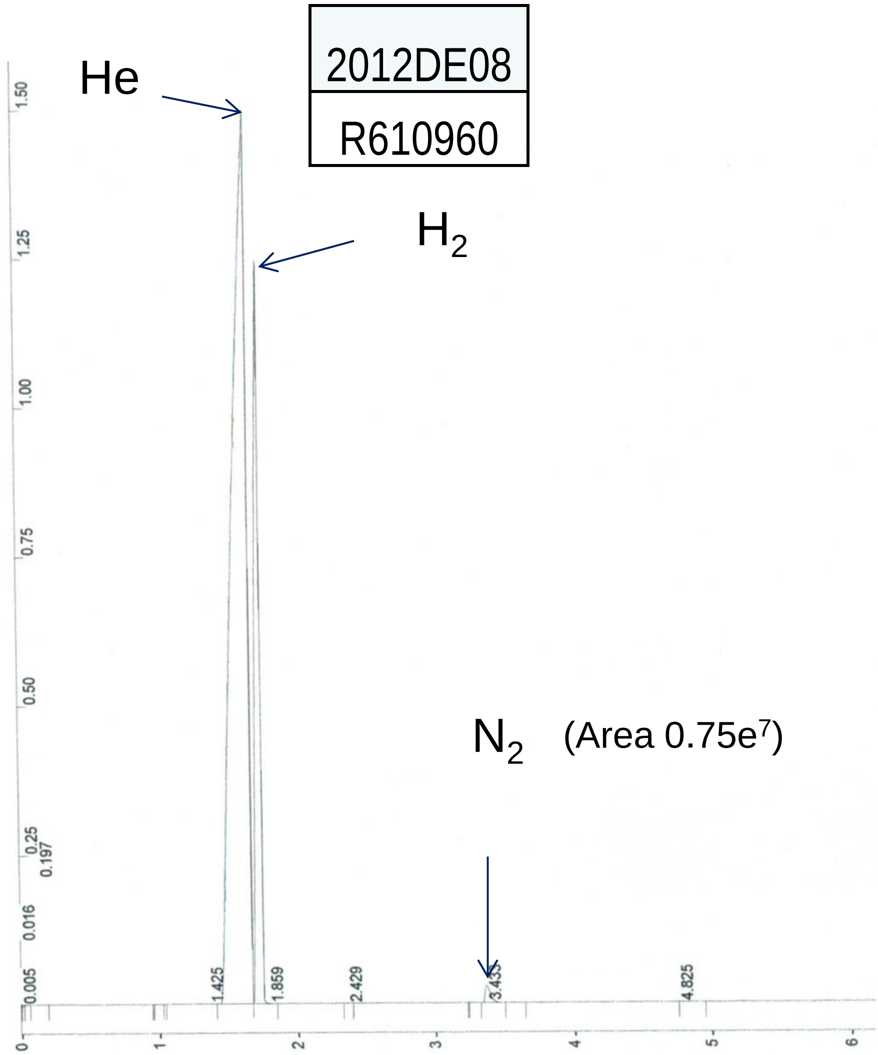
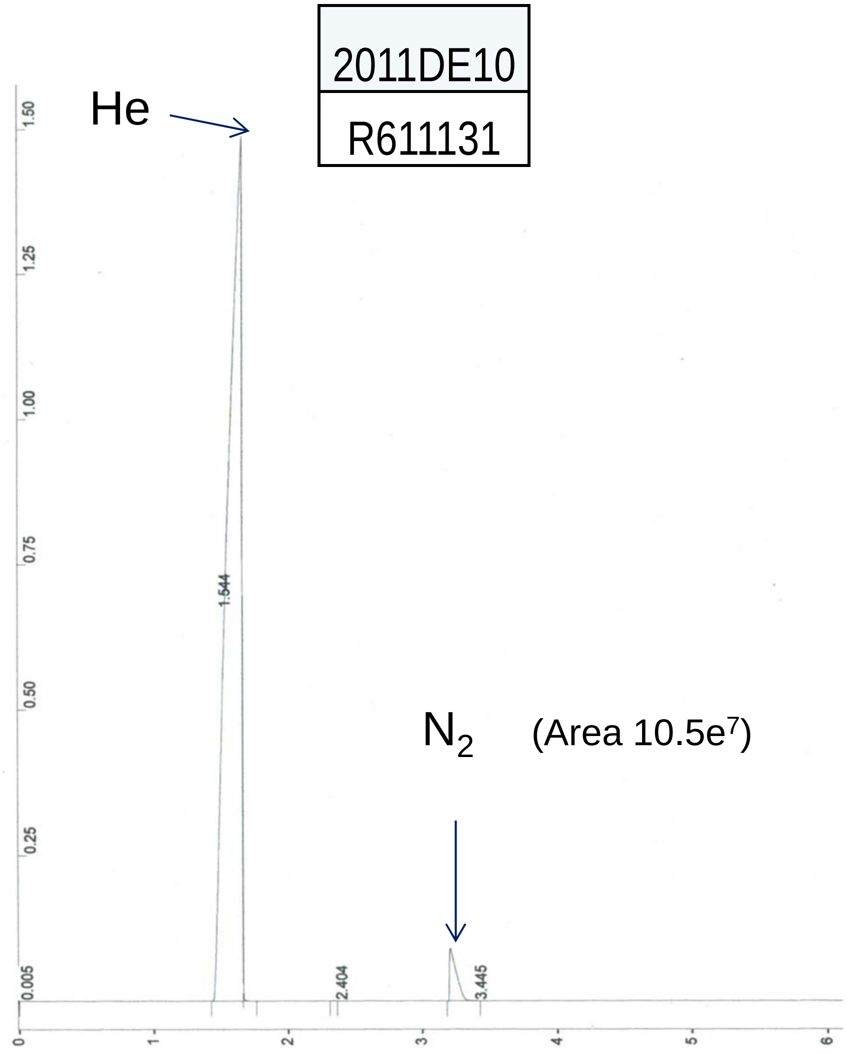
MicroGC Data Comparison





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Lean Initiative – Eliminate OI Analysis

Currently collecting and analyzing OI samples

Proposal: collecting OI sample but
DON'T analyze the sample unless..

1. OI puncture pressure abnormally high (inner can leak)
2. Corrosion seen on the outer can or outside of inner can

Benefit: cost saving on OI sample analysis

Lean Initiative – Extend Gas Sample Shelf Life

Current Shelf Life: 45 days all gas samples

New Shelf Life:

Refined calculation (X-CLC-A-00090) shows 100 days for OI sample and 300 days for IC to reach 0.1% O_2 criteria

- 60 days for OI sample
- 180 days for IC sample

Benefits:

- More operational flexibility
- Cost saving from running GC in batch

End of Presentation

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BACK-UP SLIDES

(slides from 2012 MIS meeting)

GEST Input/Output

Post-Puncture 3013 Gas Compositions (FY11 DE#9)

Gas	CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO
Composition (Volume %)	0.000	0.001	0.001	65.361	0.913	0.067	33.657	0.000

GEST Calculated Pre-Puncture 3013 Gas Compositions (FY11 DE#9)

Gas	CH_4	CO_2	N_2O	He	H_2	O_2	N_2	CO
Inner Can Composition (Volume %)	ND	Trace	Trace	67.9	0.9	< 0.1	31.1	ND
Uncertainty (±)	N/A	N/A	N/A	2.5	0.1	N/A	1.4	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%

3013 DE

7 in FY07
17 in FY08
19 in FY09
18 in FY10
12 in FY11
9 in FY12

48 Hanford
28 Rocky Flats
4 SRS
2 LLNL

CPD Pressures for Outer Can Puncture

Site	Range (psia)	Mean	Standard Deviation
RFETS	1.807 - 2.052	1.940	0.056
Hanford	2.259 - 2.561	2.429	0.068
SRS	2.430 - 2.495	2.471	0.036
LLNL	2.417 - 2.435	2.426	0.013

Note: For FY09 DE #3 (H002554) the inner can was unintentionally punctured with the outer can, resulting in a CPD pressure change of 8.832 psia.

RFETS		CPD Pressures (psia) for Outer Can Puncture		
DE #	Can#	Pre-Puncture	Post-Puncture	Post - Pre
FY07-01	R600885	0.462	2.269	1.807
FY07-03	R601957	0.172	2.063	1.891
FY07-04	R600719	0.186	2.167	1.981
FY07-05	R610735	0.287	2.281	1.994
FY07-06	R610697	0.297	2.269	1.972
FY07-07	R601285	0.243	2.112	1.869
FY08-01	R602731	0.531	2.435	1.904
FY08-02	R601318	0.34	2.273	1.933
FY08-03	H000898	0.616	2.522	1.906
FY08-04	R610327	0.366	2.385	2.019
FY08-05	R610298	0.4	2.353	1.953
FY08-06	R610324	0.502	2.37	1.868
FY08-09	R610584	0.467	2.389	1.922
FY08-10	R610578	0.425	2.477	2.052
FY08-16	R610679	-0.001	1.941	1.942
FY09-05	R602498	0.094	2.063	1.969
FY09-09	R611398	0.408	2.427	2.019
FY09-13	R610700	0.378	2.293	1.915
FY09-14	R610764	0.348	2.3	1.952
FY09-15	R610573	0.242	2.134	1.892
FY09-16	R610558	0.252	2.27	2.018
FY09-17	R610806	0.359	2.286	1.927
FY10-06	R610627	0.434	2.411	1.977
FY10-15	R610785	0.431	2.324	1.893
FY10-16	R610826	0.324	2.24	1.916
FY10-17	R610853	0.536	2.518	1.982
FY11-10	R611131	0.362	2.273	1.911

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Hanford		CPD Pressures (psia) for Outer Can Puncture		
DE #	**Can#**	**Pre-Puncture**	**Post-Puncture**	**Post - Pre**
FY08-07	H001992	0.592	3.045	2.453
FY08-08	H003157	0.479	2.982	2.503
FY08-11	H001916	0.649	3.079	2.43
FY08-12	H002088	0.577	3.045	2.468
FY08-13	H003409	0.597	2.955	2.358
FY08-14	H002573	0.629	2.972	2.343
FY08-15	H002534	0.673	3.02	2.347
FY08-17	H002750	0.674	3.024	2.35
FY09-01	H004099	0.689	3.015	2.326
FY09-02	H004111	0.9	3.159	2.259
FY09-04	H001941	0.119	2.68	2.561
FY09-06	H002509	0.081	2.607	2.526
FY09-07	H002565	0.084	2.594	2.51
FY09-08	H002657	0.36	2.731	2.371
FY09-10	H002200	0.446	2.822	2.376
FY09-11	H002667	0.475	2.81	2.335
FY09-12	H002715	0.396	2.803	2.407
FY09-18	H003119	0.354	2.842	2.488
FY09-19	H002195	0.342	2.856	2.514

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Hanford		CPD Pressures (psia) for Outer Can Puncture		
DE #	Can#	Pre-Puncture	Post-Puncture	Post - Pre
FY10-01	H004251	0.364	2.841	2.477
FY10-02	H002496	0.302	2.763	2.461
FY10-03	H003710	0.345	2.859	2.514
FY10-04	H003655	0.374	2.786	2.412
FY10-05	H002447	0.38	2.847	2.467
FY10-07	H003900	0.311	2.847	2.536
FY10-08	H003650	0.436	2.842	2.406
FY10-09	H002567	0.411	2.776	2.365
FY10-10	H002728	0.381	2.73	2.349
FY10-11	H002786	0.382	2.735	2.353
FY10-13	H003367	0.461	2.89	2.429
FY10-14	H003704	0.385	2.859	2.474
FY11-01	H003443	0.359	2.783	2.424
FY11-03	H002592	0.306	2.7374	2.4314
FY11-04	H003337	0.357	2.876	2.519
FY11-06	H003343	0.46	2.945	2.485
FY11-07	H003371	0.506	2.92	2.414
FY11-08	H003526	0.321	2.714	2.393
FY11-09	H003565	0.366	2.799	2.433
FY11-11	H003625	0.303	2.743	2.44
FY12-01	H001209	0.277	2.7	2.423
FY12-02	H002574	0.244	2.68	2.436
FY12-03	H001513	0.199	2.689	2.49
FY12-04	H003390	0.321	2.73	2.409

SRS		CPD Pressures (psia) for Outer Can Puncture		
DE #	Can#	Pre-Puncture	Post-Puncture	Post - Pre
FY10-18	S001721	0.365	2.854	2.489
FY11-02	S002129	0.306	2.736	2.43
FY11-05	S001105	0.469	2.964	2.495

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LLNL	CPD Pressures (psia) for Outer Can Puncture		
DE # Can#	**Pre-Puncture**	**Post-Puncture**	**Post - Pre**
FY11 #12 L000178	0.22	2.655	2.435
FY12 #5 L000075	0.305	2.722	2.417

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FY2012
Humidity Results & Lean Initiatives

Binh Nguyen

KAC Process Engineer

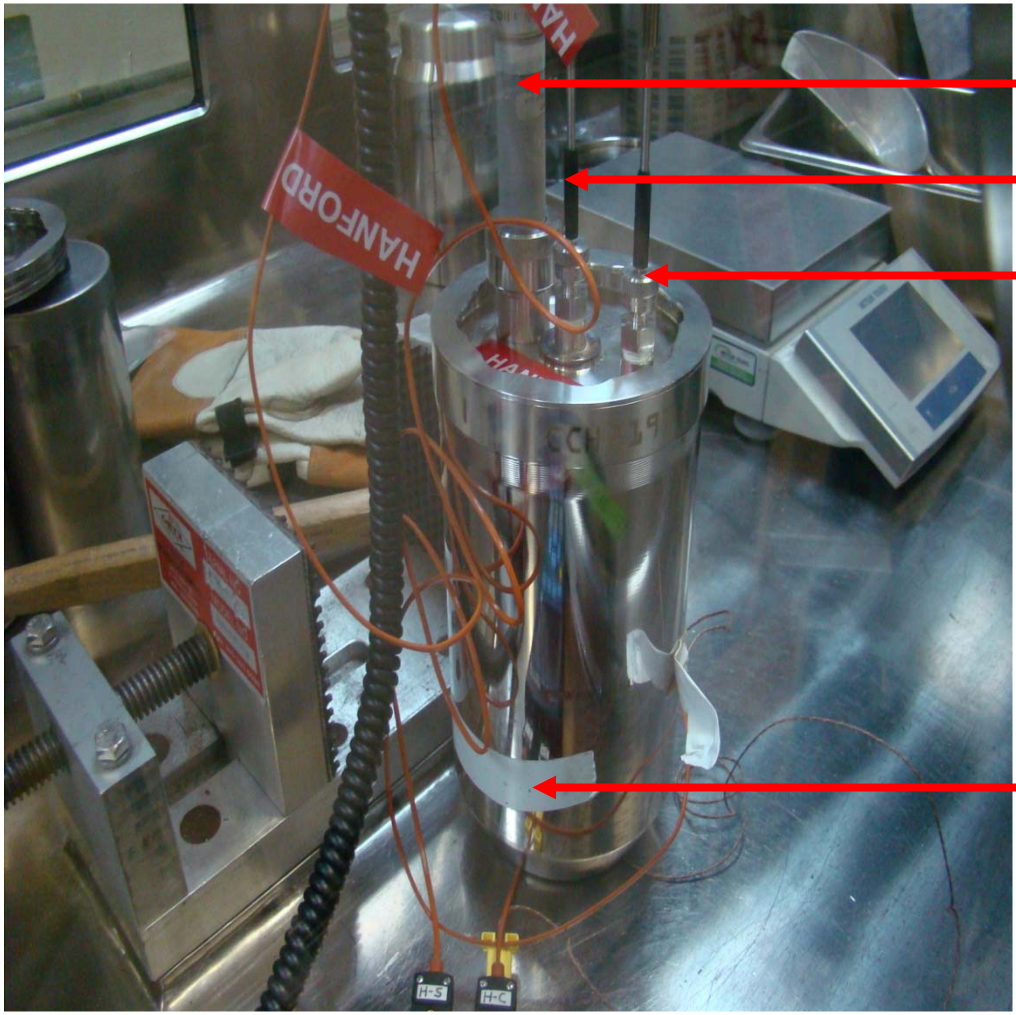
Savannah River Nuclear Solutions, LLC

Date: 2/27/2013

3013 Surveillance and Monitoring Program Review

766-H

Temperature & Relative Humidity



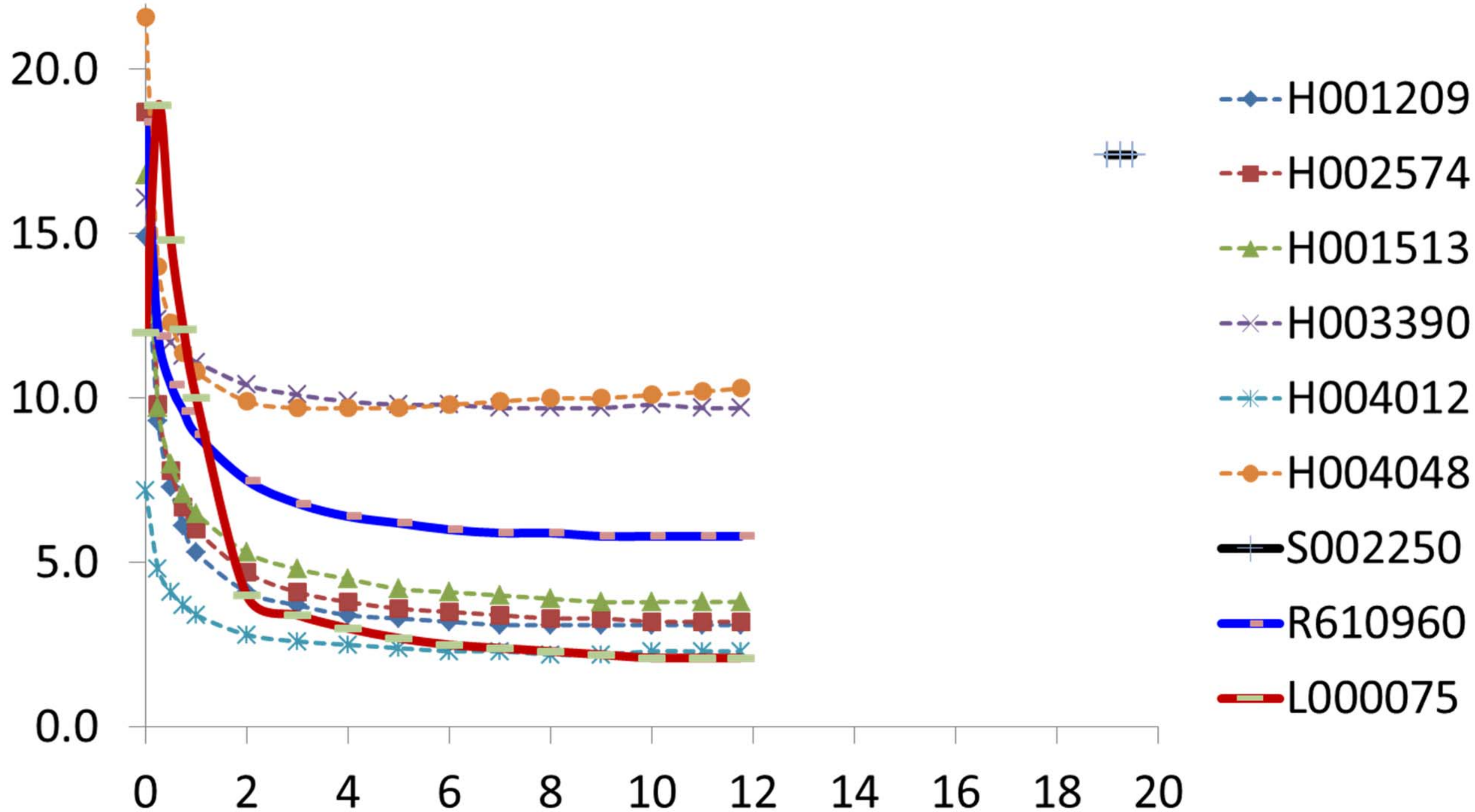
RH Probe

Center Temp Probe

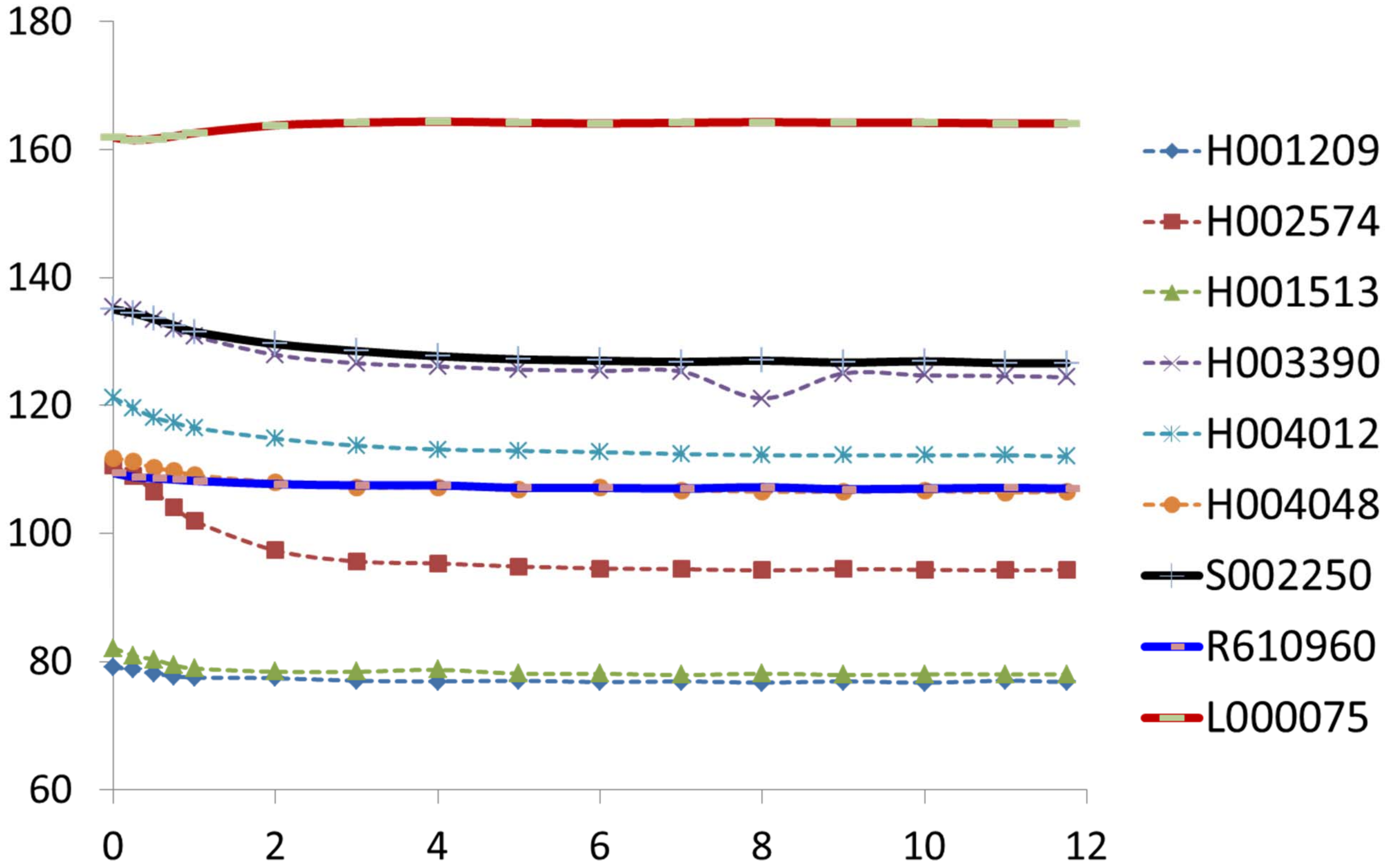
Side Temp Probe

Outer Wall Temp

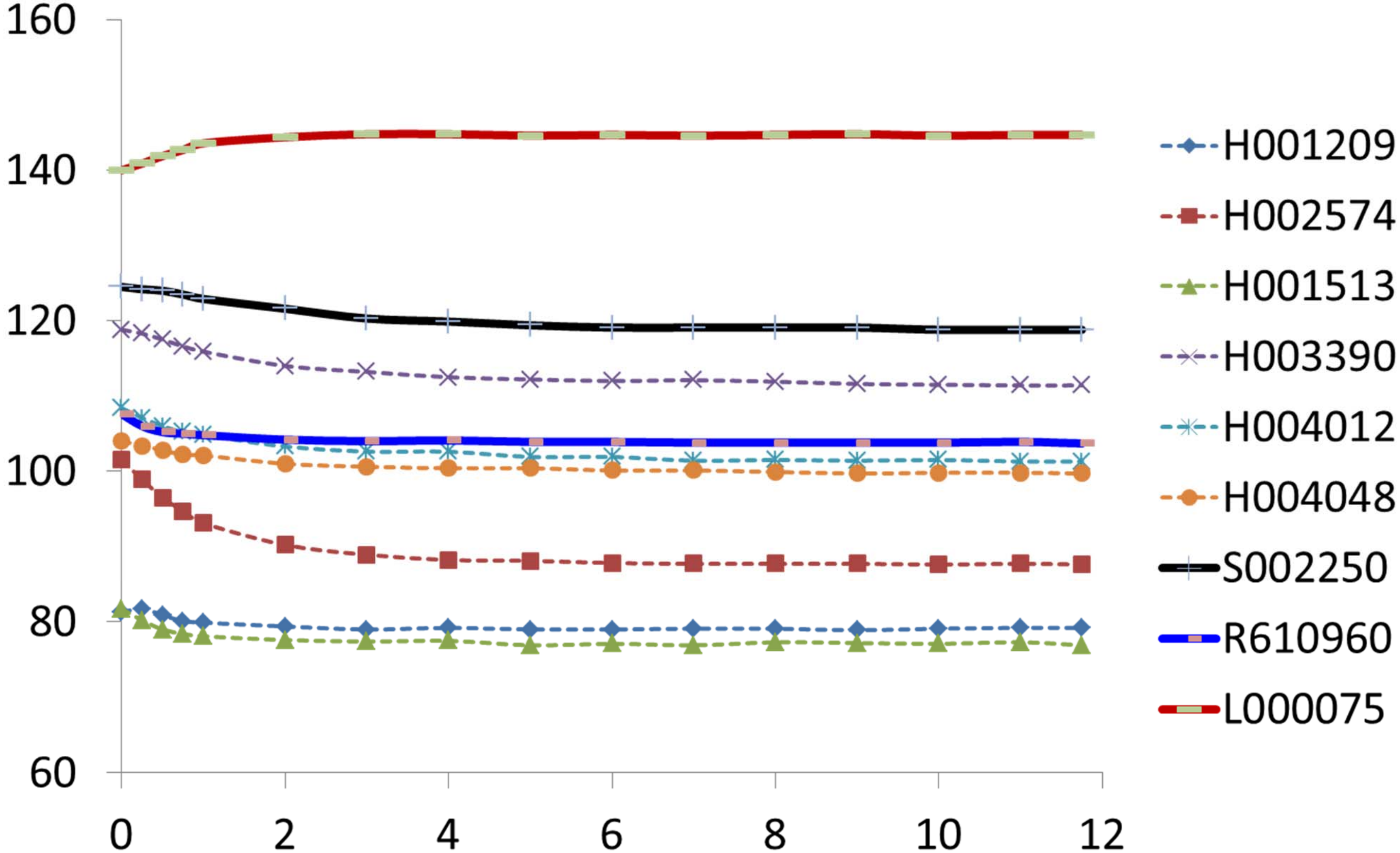
Relative Humidity (%) over Time (hr)



Center Temperature (°F) over Time (hr)



Side Temperature (°F) over Time (hr)



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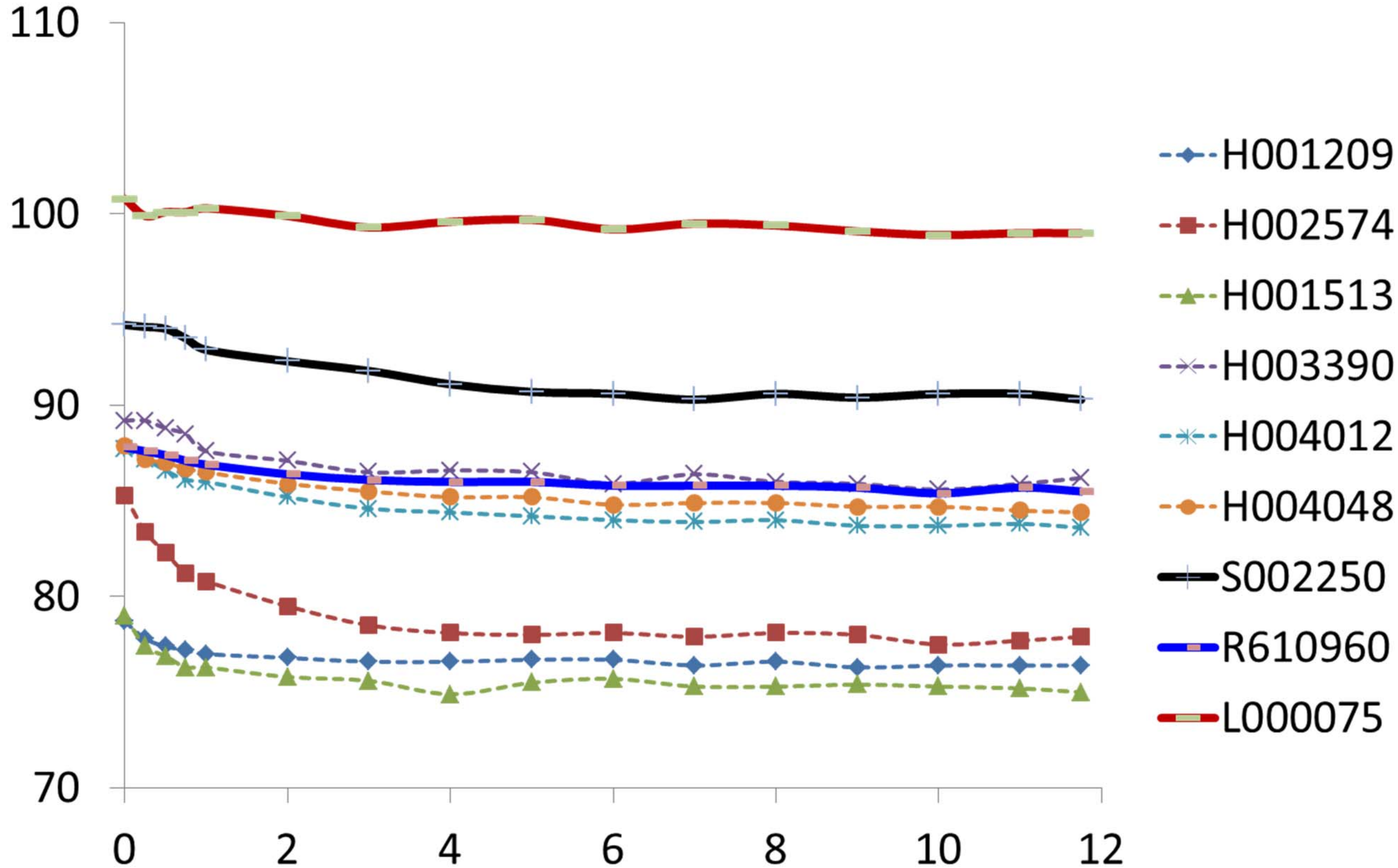
Wall Temperature (°F) over Time (hr)



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Lean Initiative – Eliminate Intermediate Readings

Currently:

- Collecting data every 15 minutes for at least 6 hours
- 20 minutes to program the instruments
- 40 minutes to retrieve and record the data

Proposal:

- Record the 1st and last data point (6th hr +)
- No program

Benefit: save approx. 1 hour

FY12 Humidity Results

		Heat Load (W)	Humidity (%RH)	Center (°F)	Side (°F)	Wall (°F)
DE#1	H001209	1.1	3.1	76.8	79.2	76.4
DE#2	H002574	2.4	3.2	94.3	87.6	77.9
DE#3	H001513	1.2	3.8	78.0	76.9	75.0
DE#4	H003390	4.7	9.7	124.4	111.4	86.2
DE#5	L000075	9.8	2.1	164.1	144.7	99.0
DE#6	H004012	3.8	2.3	112.0	101.3	83.6
DE#7	H004048	3.3	10.3	106.5	99.7	84.4
DE#8	R610960	4.6	5.8	107.0	103.7	85.5
DE VSD	S002250	6.7	17.4	126.6	118.8	90.3

All 39 DE's (1/5)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
S002250	6.7	17.4	126.6	118.8	90.3
S002129 (6)	9.6	1.0	154.3	136.2	98.1
S001721	8.3	0.7	164.2	n/a	106.1
S001105	9.7	0.8	169.9	147.7	99.1
R610960	4.6	5.8	107.0	103.7	85.5
R610806	8.2	0.3	138.6	123.4	93.6
R610573	4.5	0.6	n/a	n/a	n/a
L000178	3.0	1.3	103.3	98.3	77.5
L000075	9.8	2.1	164.1	144.7	99.0

All 39 DE's (2/5)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H004251	3.8	3.7	115.1	106.5	86.0
H004048	3.3	10.3	106.5	99.7	84.4
H004012	3.8	2.3	112.0	101.3	83.6
H003900	3.7	5.7	101.4	95.2	82.6
H003710	4.5	5.3	118.0	99.5	84.2
H003704	4.4	3.1	120.8	109.9	86.9
H003655	4.5	3.1	118.4	101.3	85.5
H003650	4.6	12.9	102.5	99.1	81.8
H003625	4.6	3.6	119.4	112.2	92.4

All 39 DE's (3/5)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H003565	4.6	1.4	123.7	110.1	87.3
H003526 (9)	4.3	4.2	112.6	103.1	84.2
H003443	4.2	8.0	108.8	100.1	84.9
H003390	4.7	9.7	124.4	111.4	86.2
H003371 (11)	3.0	11.8	107.5	96.2	77.3
H003367	2.7	14.4	99.5	93.6	78.8
H003343 (11)	3.7	1.2	112.6	86.8	78.9
H003337[9]	3.3	2.3	108.1	98.6	81.2

All 39 DE's (4/5)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H003119	5.5	2.8	129.8	119.1	93.6
H003077	6.9	4.1	146.4	121.7	82.4
H002786	4.3	3.2	115.7	97.4	80.9
H002728	4.4	4.2	123.8	102.0	84.1
H002592	1.8	11.6	93.1	87.0	79.0
H002574	2.4	3.2	94.3	87.6	77.9
H002567	1.2	11.8	79.2	78.8	77.5

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All 39 DE's (5/5)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H002496	2.5	12.1	95.2	85.1	77.4
H002447	4.8	5.3	n/a	n/a	n/a
H002195	8.2	n/a	131.8	97.8	87.2
H001523	1.2	3.8	78.0	76.9	75.0
H001513	1.2	3.8	78.0	76.9	75.0
H001209	1.1	3.1	76.8	79.2	76.4

End of Presentation

BACK-UP SLIDES

(slides from 2012 MIS meeting)

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

3013 Containers Collected To Date (FY09 to present)

- Two Rocky Cans (R610573*, R610806)
- Three SRS Cans (S001721, S002129, S001105)
- 27 Hanford Cans (H003119, H002195, H004251, H002496, H003710, H003655, H002447, H00390, H003650, H002567, H002728, H002786, H003077, H003367, H003704, H003443, H002592, H003337, H003343, H003371, H003526, H003565, H003625, H001209, H002574, H001523, H003390)
- One LLNL(L000178)
- Six more this year (1 LLNL, 2 Hanford, 2 Rocky, 1 SRS)

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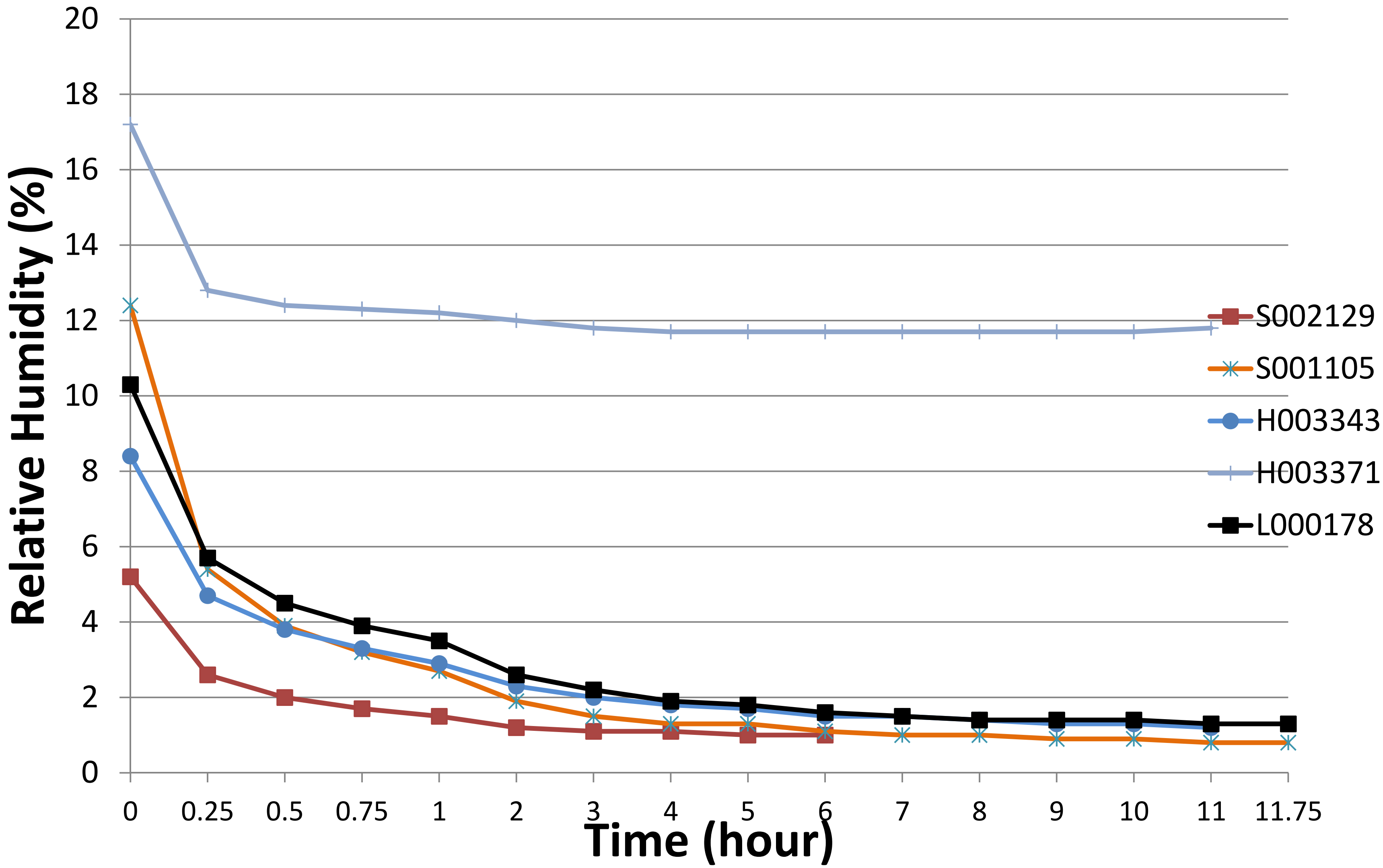
FY11 & FY12 Relative Humidity Over Time



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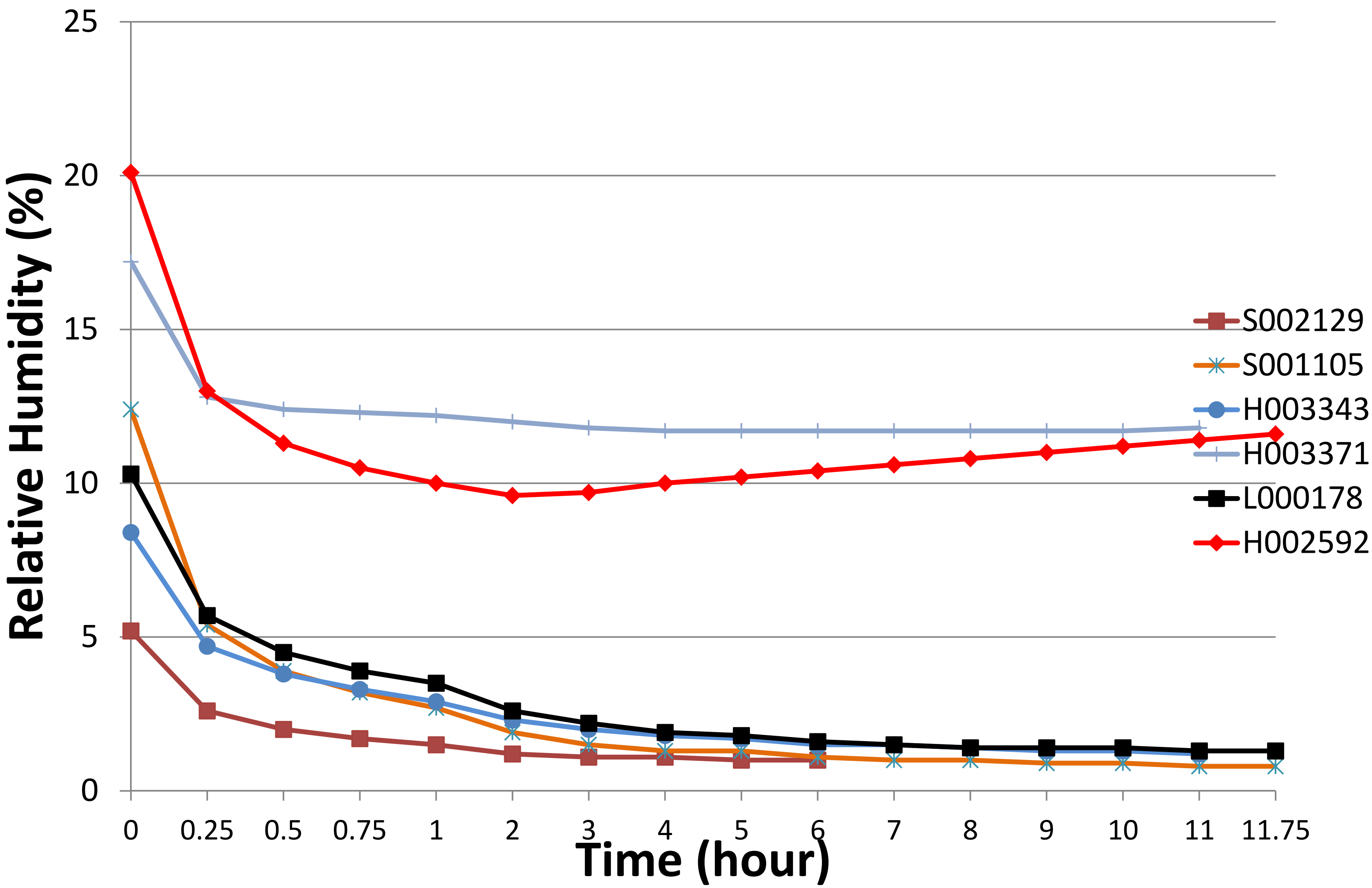
FY11 & FY12 Relative Humidity Over Time



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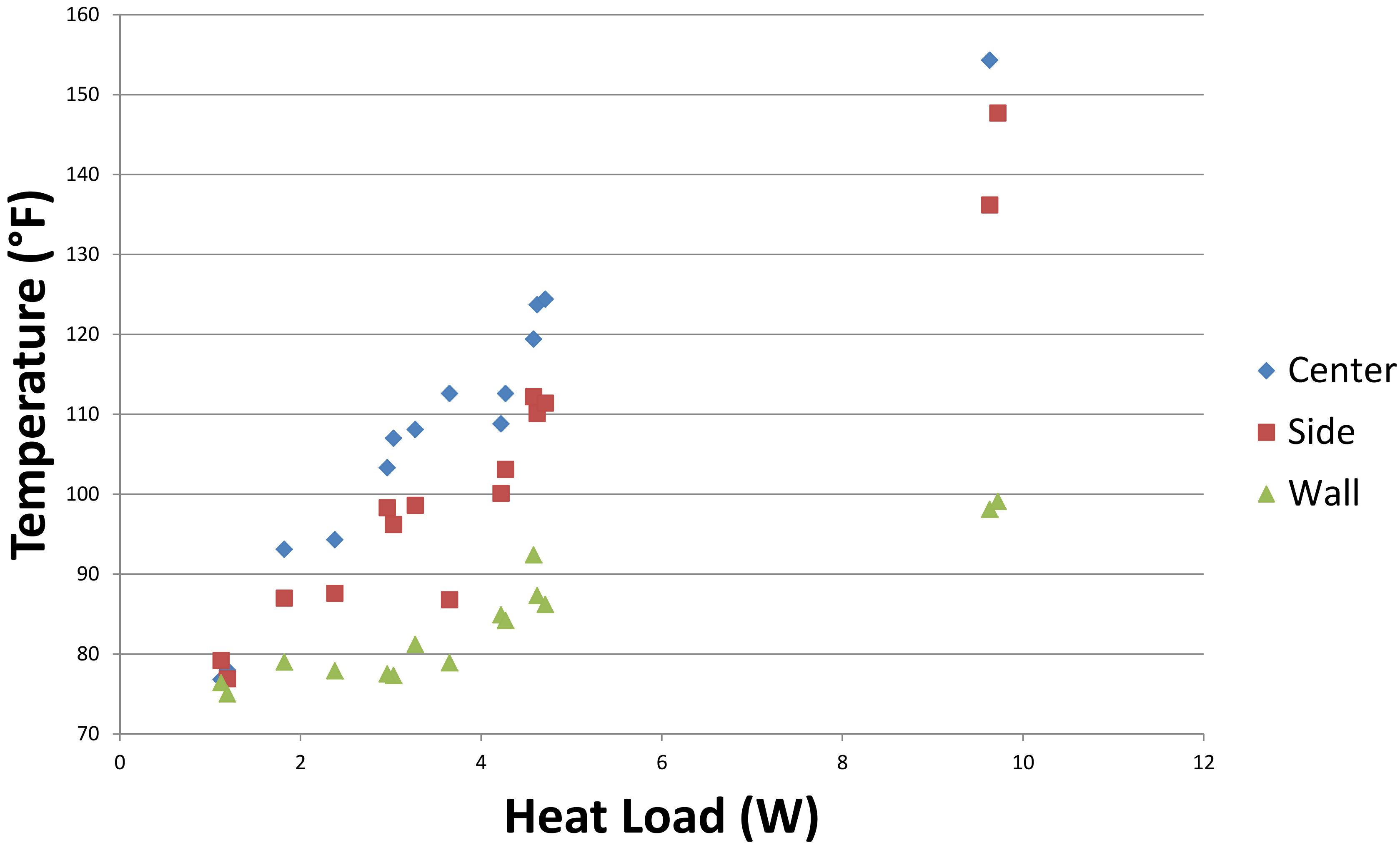
Temperatures vs. Heat Load



Data (1 of 3)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
L000178	3.0	1.3	103.3	98.3	77.5
R610573	4.5	0.6	n/a	n/a	n/a
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

Data (2 of 3)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H003650	4.6	12.9	102.5	99.1	81.8
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

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Data (3 of 3)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H003900	3.7	5.7	101.4	95.2	82.6
H003343 (1	3.7	1.2	112.6	86.8	78.9
H003371 (1	3.0	11.8	107.5	96.2	77.3
H003526 (9)	4.3	4.2	112.6	103.1	84.2
H003565	4.6	1.4	123.7	110.1	87.3
H003625	4.6	3.6	119.4	112.2	92.4
H001209	1.1	3.1	76.8	79.2	76.4
H002574	2.4	3.2	94.3	87.6	77.9
H001523	1.2	3.8	78.0	76.9	75.0
H003390	4.7	9.7	124.4	111.4	86.2

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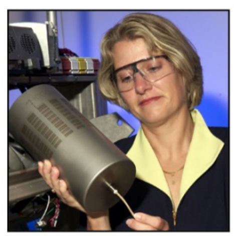
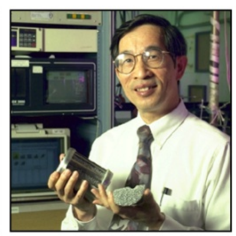
We Put Science To Work

3013 Can Analysis from DE

John Mickalonis and Kerry Dunn

February 26-27, 2013


3013 Surveillance & Monitoring Program Review

Annual Meeting

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Acknowledgements

DE Can Analysis

Thaddeus Reown, Vickie Timmerman, Josh Ziska, Robbie Garritano, Zane Nelson and Gregg Creech

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Mark Jackson

SRNL

Summary of FY12 DE Tasks

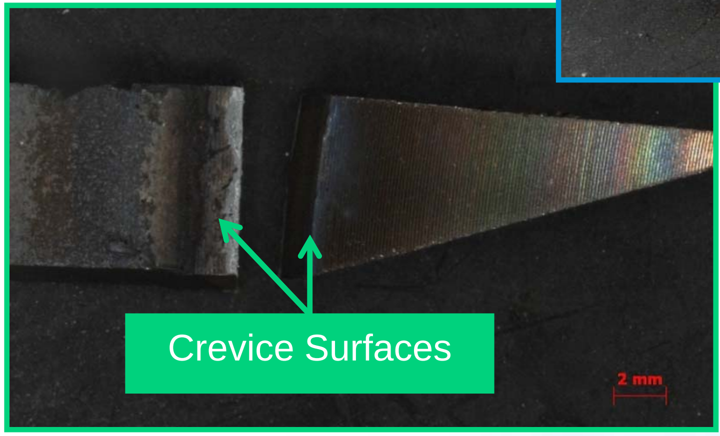
- **Nine 3013 containers destructively examined (DE) and analyzed in FY12**
- **Three cans (DE4, DE6 and DE7) received additional analysis with a focus on the inner can crevice region**
- **Additional analysis was continued for the Hanford High Moisture Can (HHMC) also in the inner can crevice region**

Sectioning Inner Can Lid

Pie-shaped sections from inner can are typically cut from 0, 90, 180 and 270° positions. The 0° position is the end point of the weld.

Closure weld removed along cut line close to lid external surface.

The weld is removed and the sample split into a side wall and lid section



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Summary of Can Visual Analysis FY12

DE #	3013 ID	Analyze	Categorization
FY12DE1	H001209	N	0
FY12DE2	H002574	N	0
FY12DE3	H001513	N	3A
FY12DE4	H003390	Y	IP (6)
FY12DE5	L000075	N	0
FY12DE6	H004012	Y	IP (6)
FY12DE7	H004048	Y	3A
FY12DE8	R610960	N	0*
FY12DE10 (VSD)	S002250	N	0

IP – Analysis in progress

Category	Description
0	Nothing or Wipeable coating
0*	Rocky Flat can if corrosion is observed
1	Adherent coating on convenience can
2	Pitting <50 µm on convenience can
3A	Suspected pitting >50 µm on convenience can – pit covered with corrosion product
3B	Confirmed pitting >50 µm on convenience can – generally confirmed with SEM
4	Adherent coating on inner can
5	Pitting <50 µm on inner can
6	Pitting >50 µm on inner can
7	SCC on inner can

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FY12DE4 H003390 Data

DE #	3013 ID	Analyze	Categorization
FY12DE4	H003390	Y	IP (6)

Package Information	
Bin	Pressure & Corrosion
Type	Engineering Judgment
TGA	0.183 wt %
Total Actinides	60.86%
Prompt Gamma (Cl)	<0.61 wt %

DE Data	
Gas Analysis (GEST) (Vol%)	He – 57.7 N_2 – 41.9 H_2 – 0.2
Gas Pressure (GEST) (psia)	11.4
TGA/MS (wt %)	Initial – 0.33 / 0.11 Final – 0.34 / 0.14
IC (µg/mL) (Leach)	F-179 Cl-2945
ICP/ES (µg/g) (Leach)	Ca – 526 K – 1535 Mg – 333 Na – 1565

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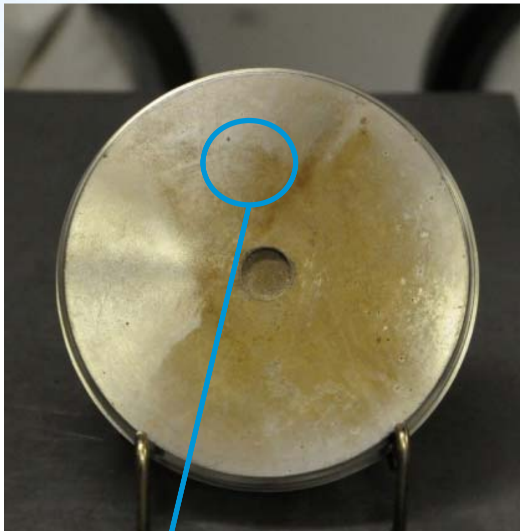
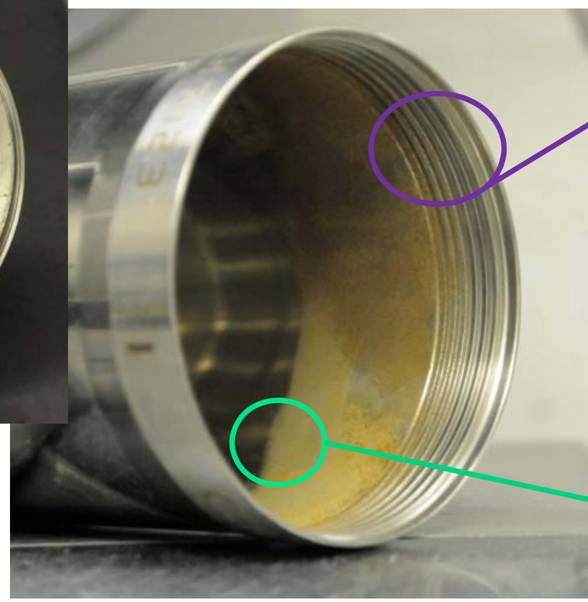
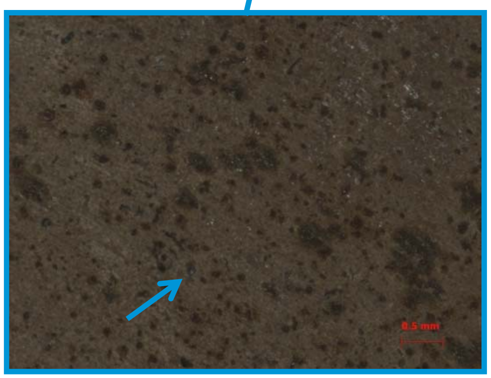
FY12DE4 H003390

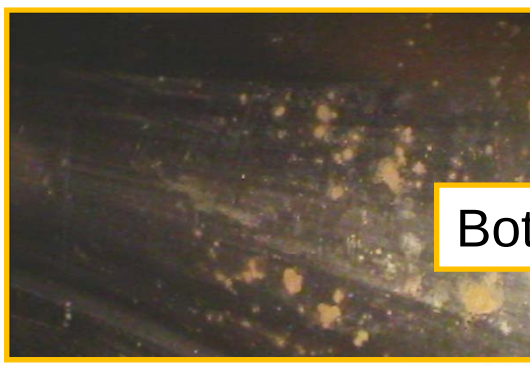
Convenience Can





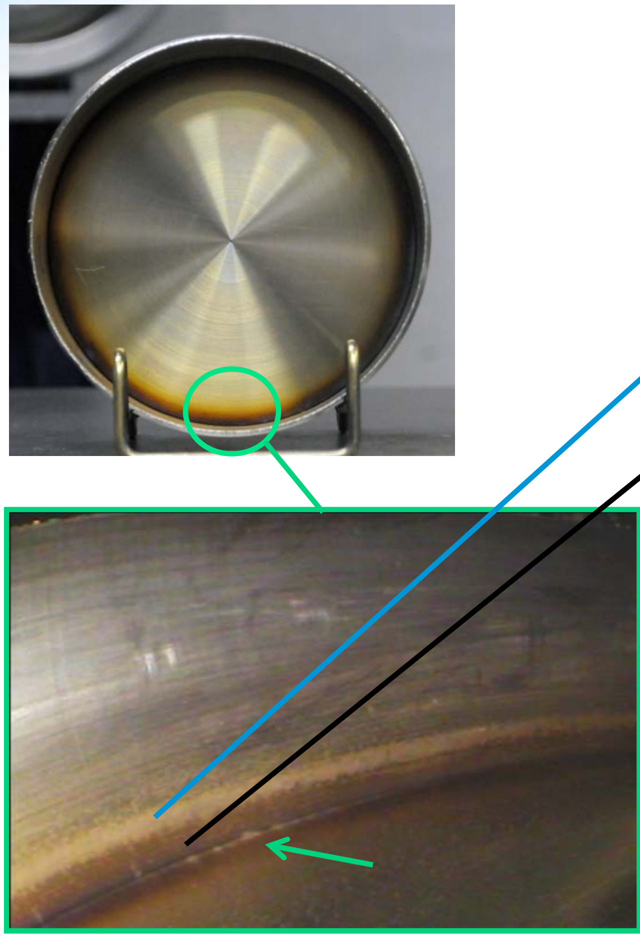


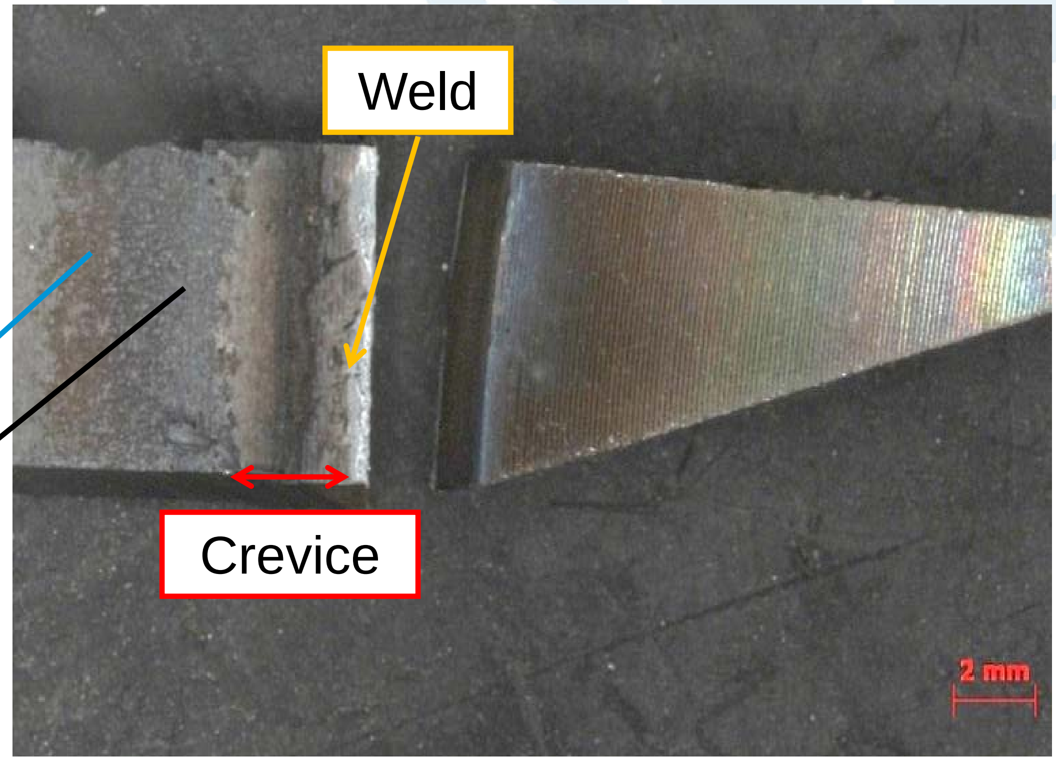
150 µm L, 83 µm W



Bottom of Convenience Can

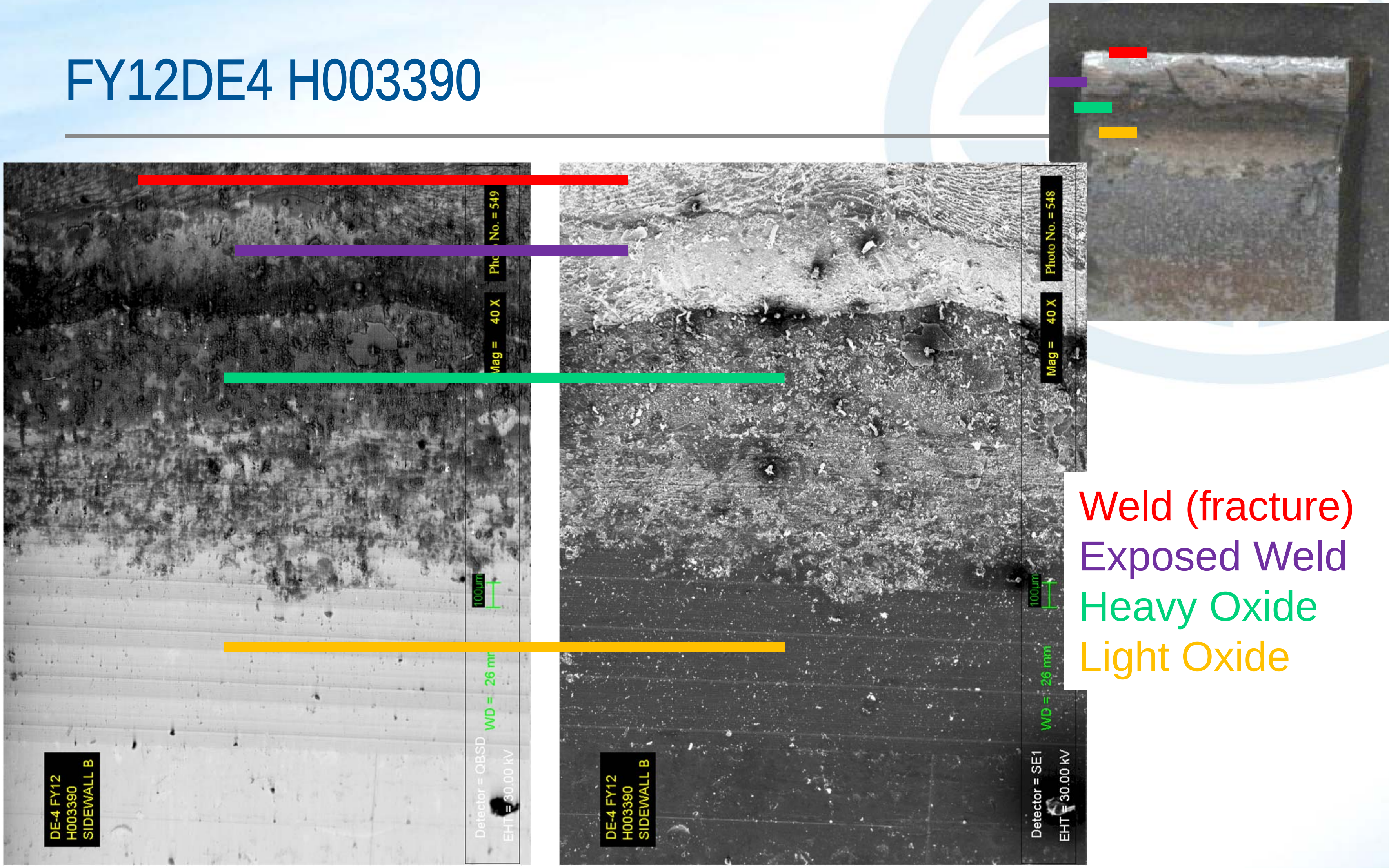
FY12DE4 H003390





Inner can was found to have a residue at mouth of crevice so can was sectioned for further analysis

FY12DE4 H003390



SEM micrographs of inner can sidewall within crevice

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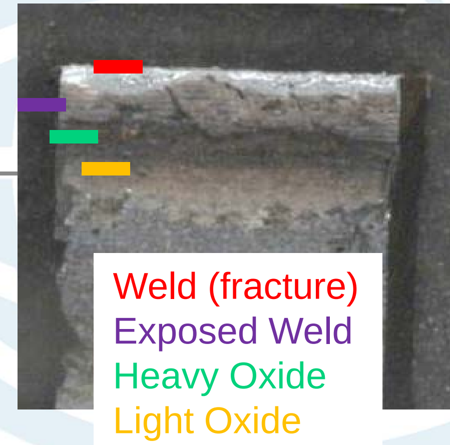
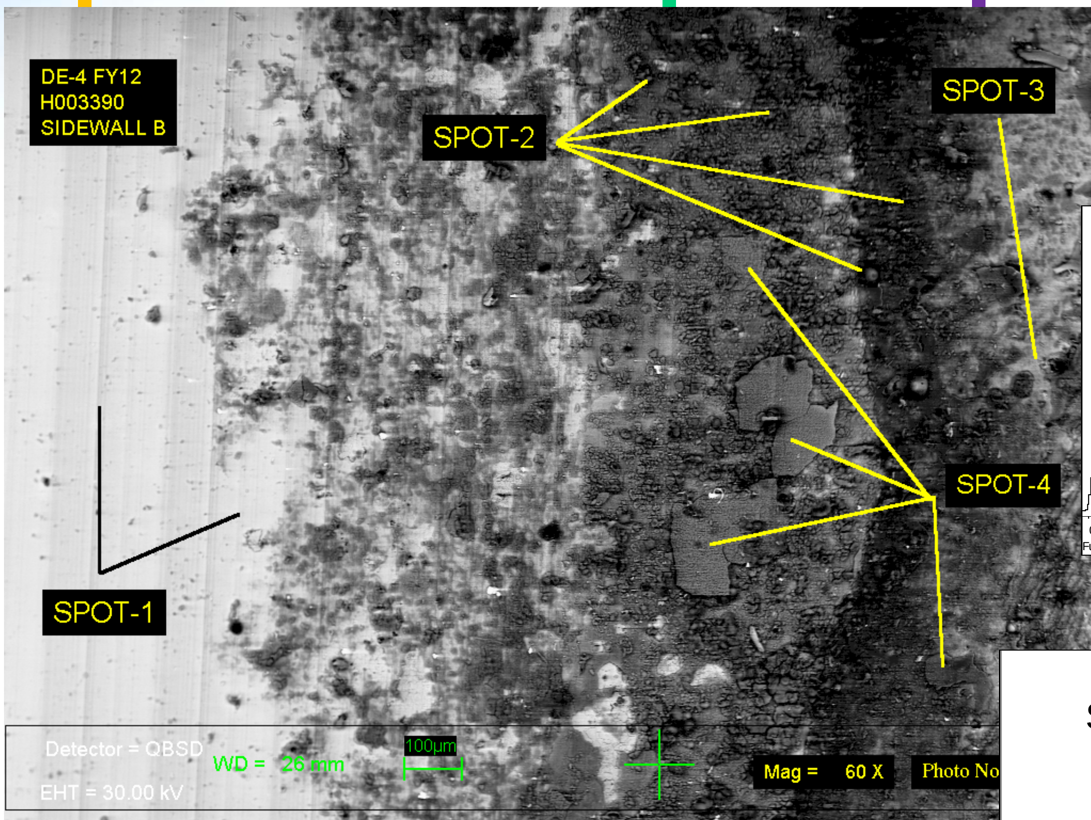
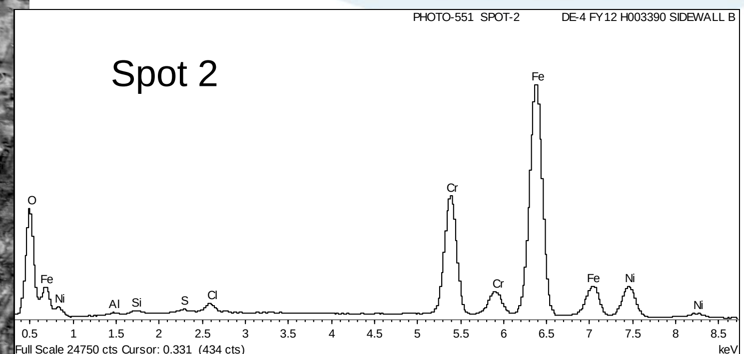
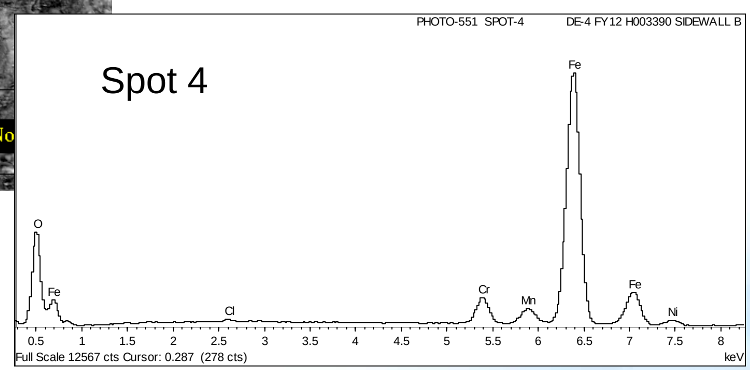
FY12DE4 H003390









SEM micrograph and EDS spectra of inner can sidewall within crevice

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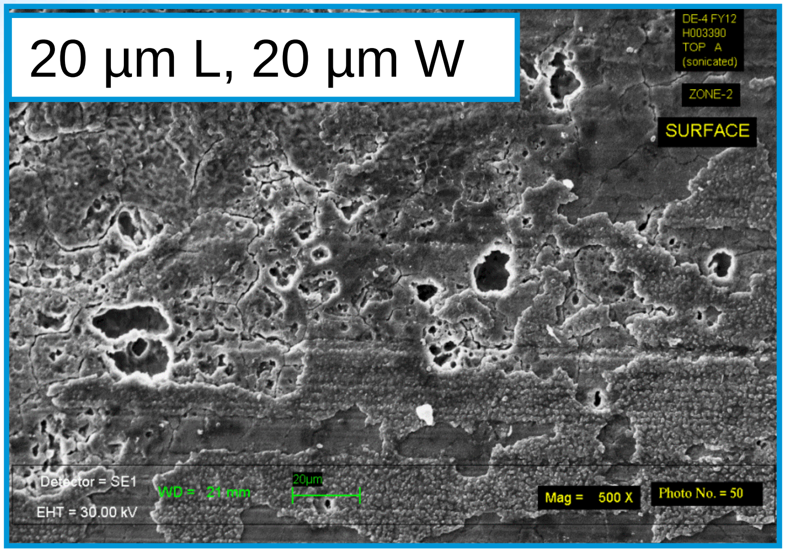
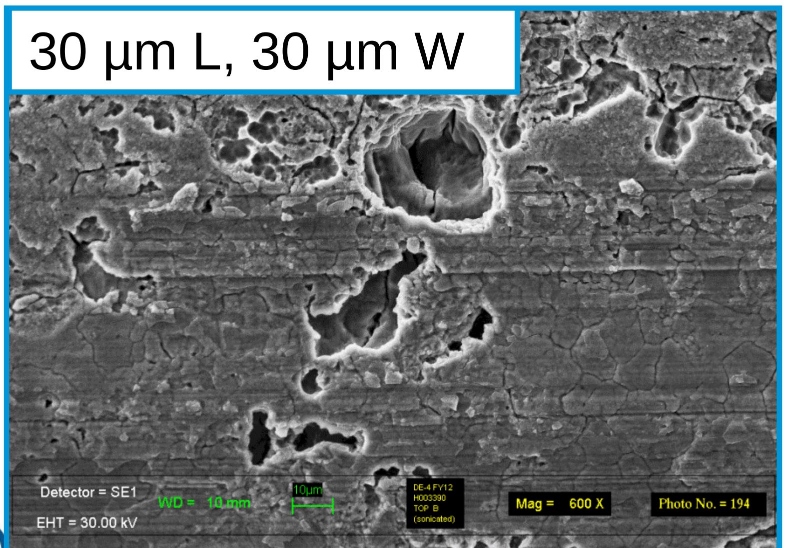
FY12DE4 H003390

Inner can lid

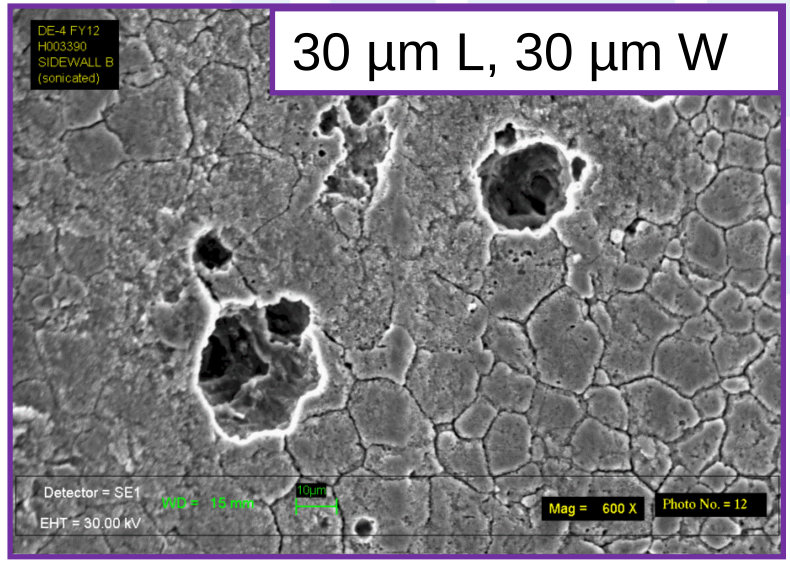


20 µm L, 20 µm W

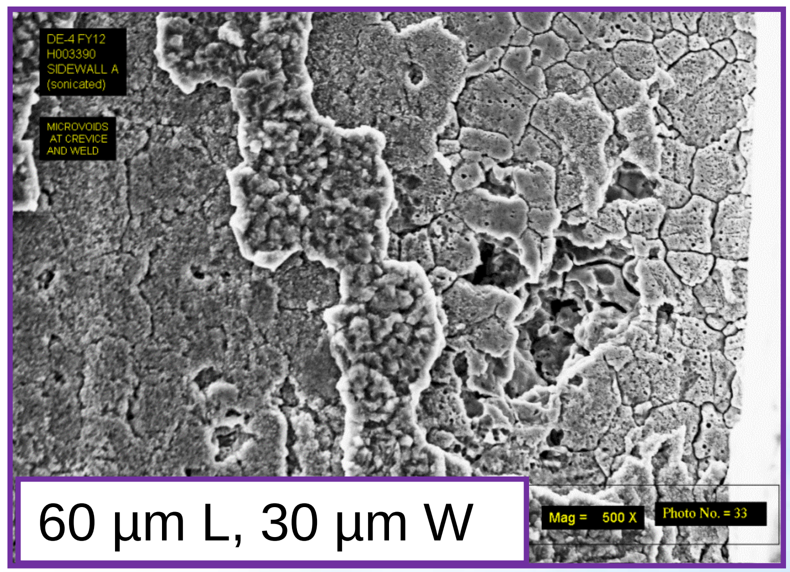


30 µm L, 30 µm W

Inner can sidewall



30 µm L, 30 µm W



60 µm L, 30 µm W

FY12DE6 H004012 Data

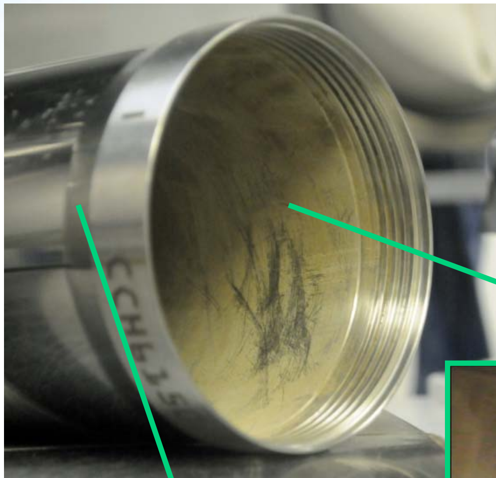
DE #	3013 ID	Analyze	Categorization
FY12DE6	H004012	Y	IP (6)

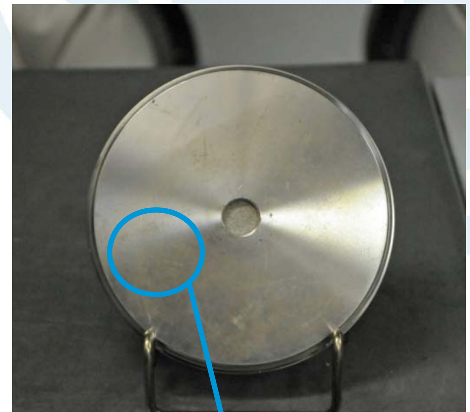
Package Information	
Bin	Pressure & Corrosion
Type	Random
TGA	0.238 wt %
Total Actinides	62.93%
Prompt Gamma (Cl)	12.8 wt %

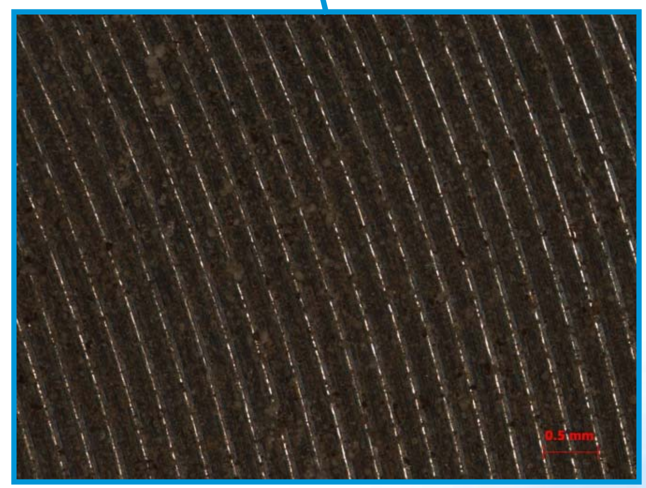
DE Data	
Gas Analysis (GEST) (Vol%)	He – 46.7 N_2 – 51.75 H_2 – <0.1
Gas Pressure (GEST) (psia)	10.9
TGA/MS (wt %)	Initial – 0.42 / 0.16 Final – 0.56 / 0.31
IC (µg/g) (Leach)	F – <150 Cl – 112500
ICP/ES (µg/mL) (Leach)	Ca – 5.55 K – 54850 Mg – 3520 Na – 32300

FY12DE6 H004012

Convenience Can





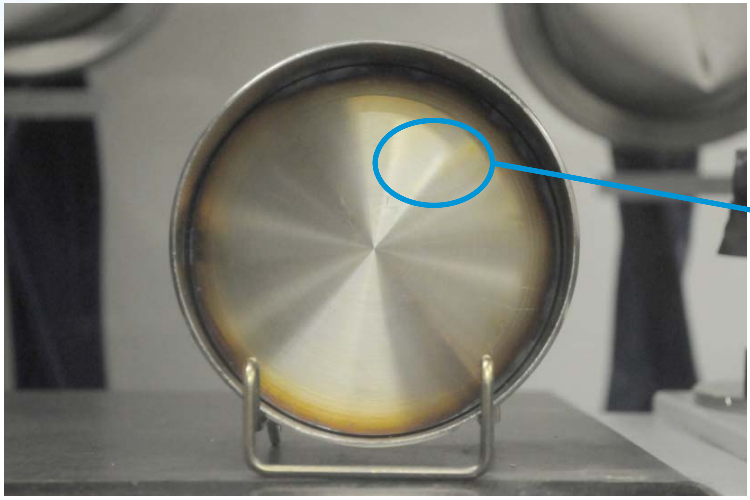


Borescope photographs

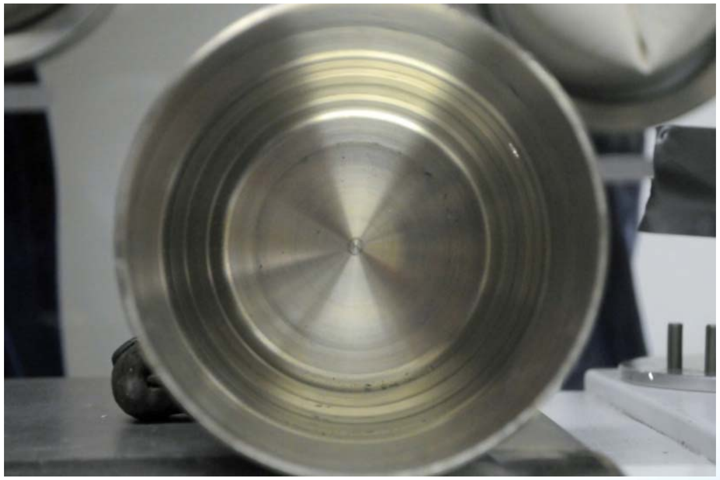
Stereomicrographs

FY12DE6 H004012

Inner Can

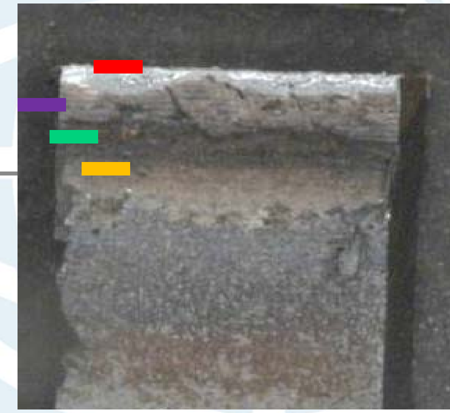


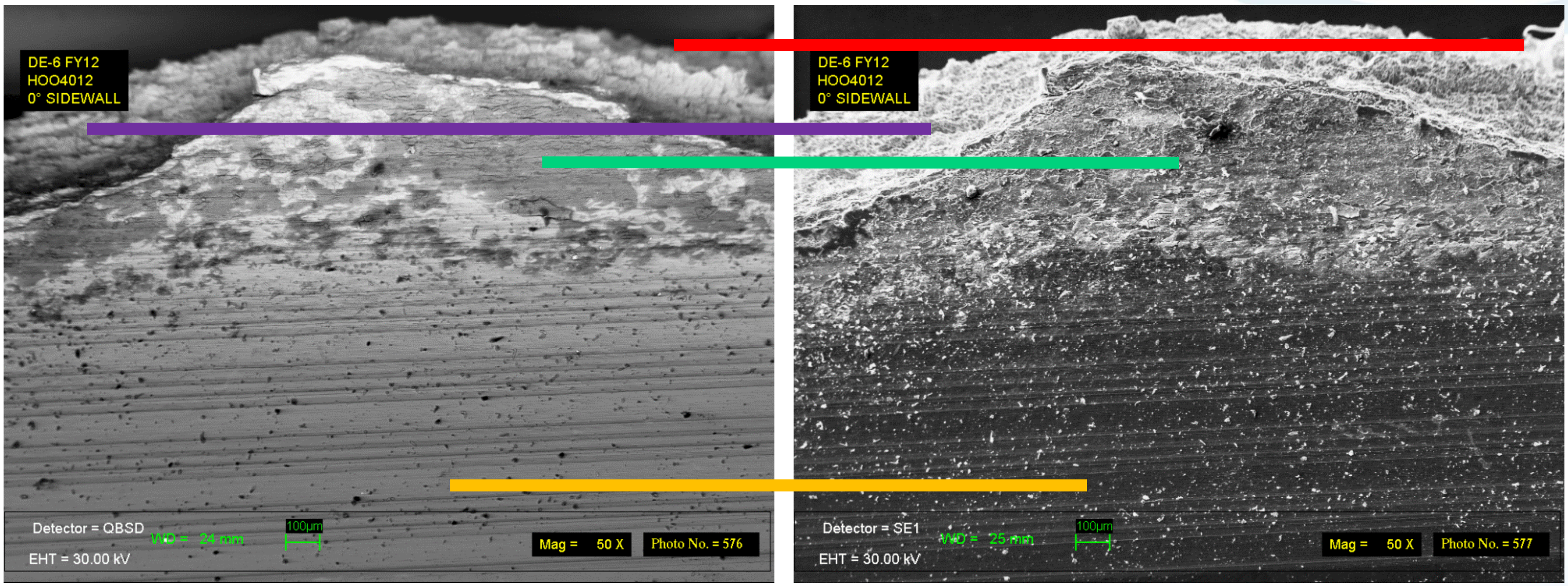
Stereomicrograph



FY12DE6 H004012

Weld (fracture)
Exposed Weld
Heavy Oxide
Light Oxide





SEM micrographs (50X) of inner can sidewall within crevice

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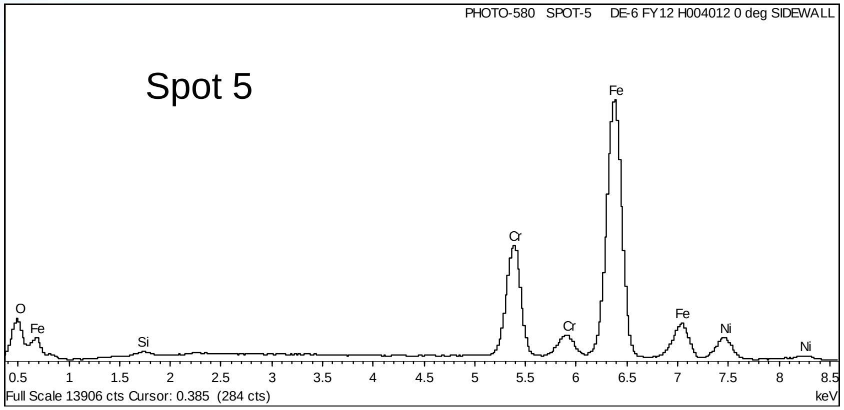
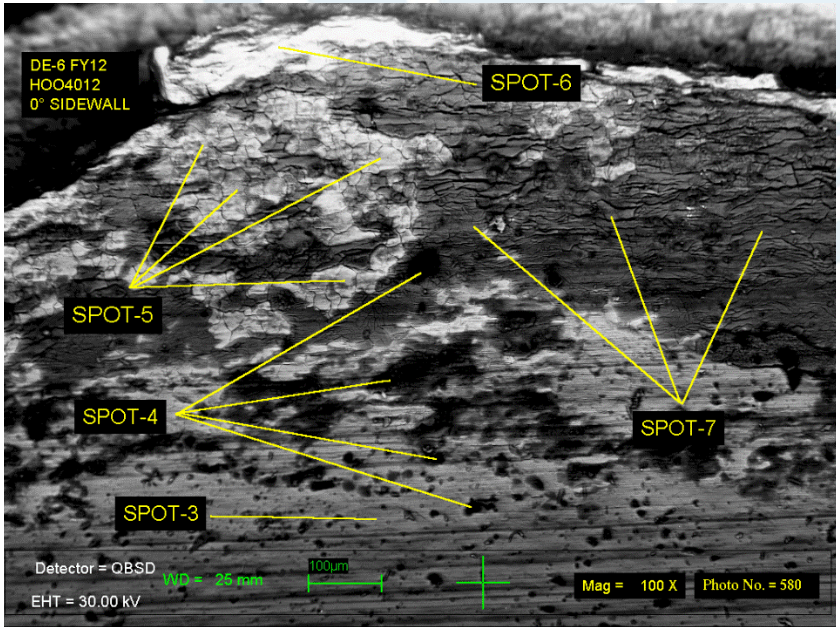
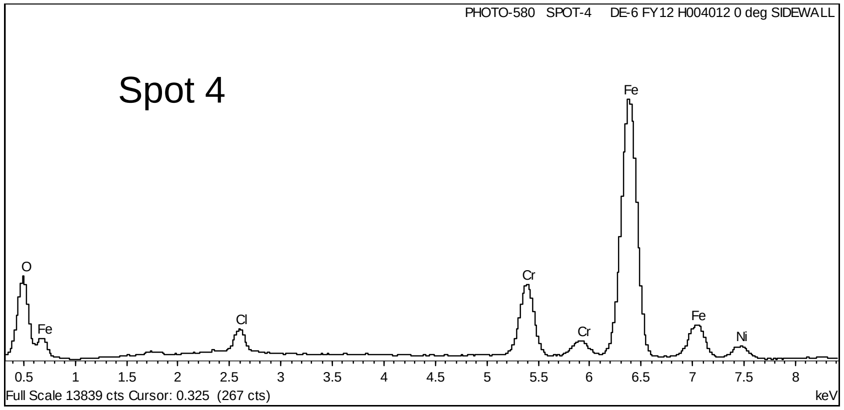
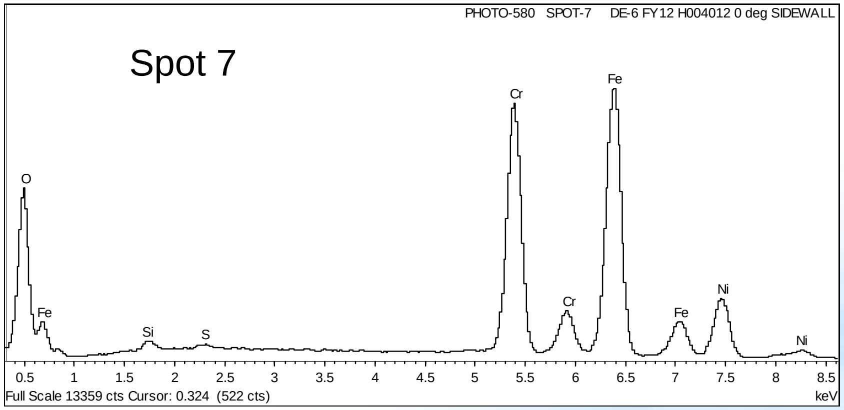
FY12DE6 H004012









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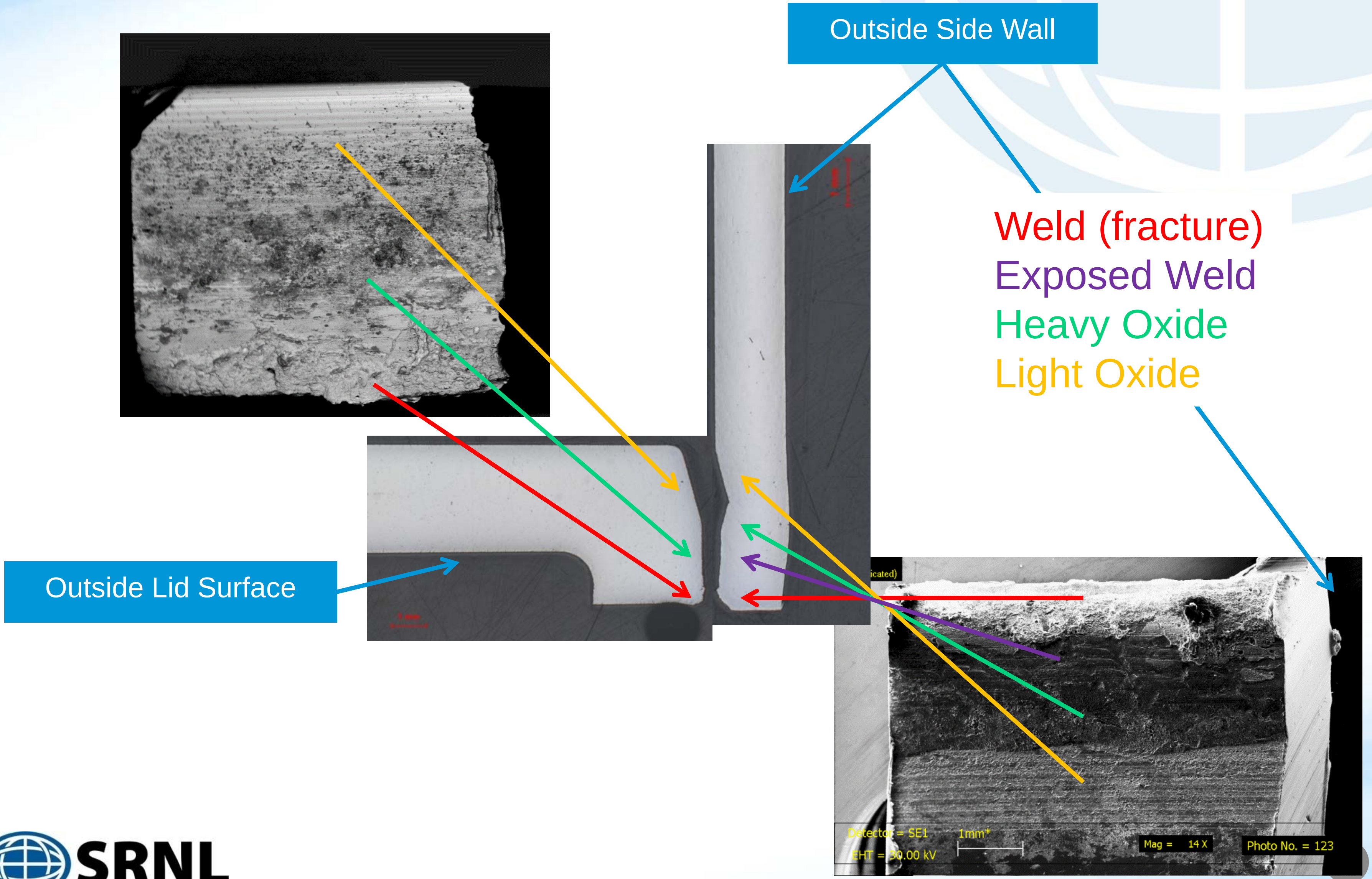
Cross Sectional Mounts



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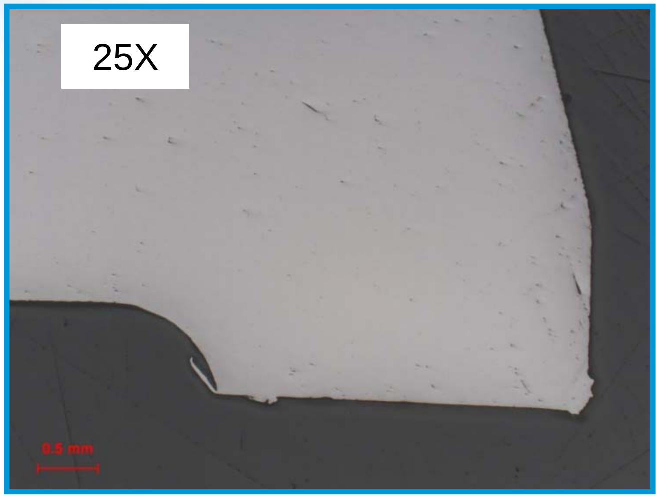
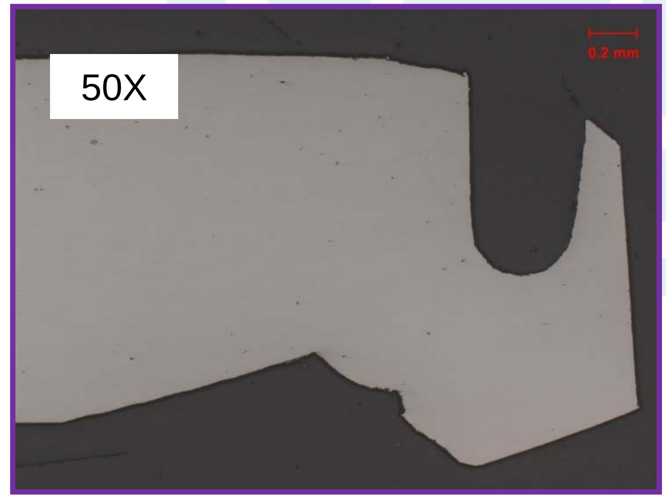
FY12 DE6 H004012

Inner can lid



Inner can sidewall



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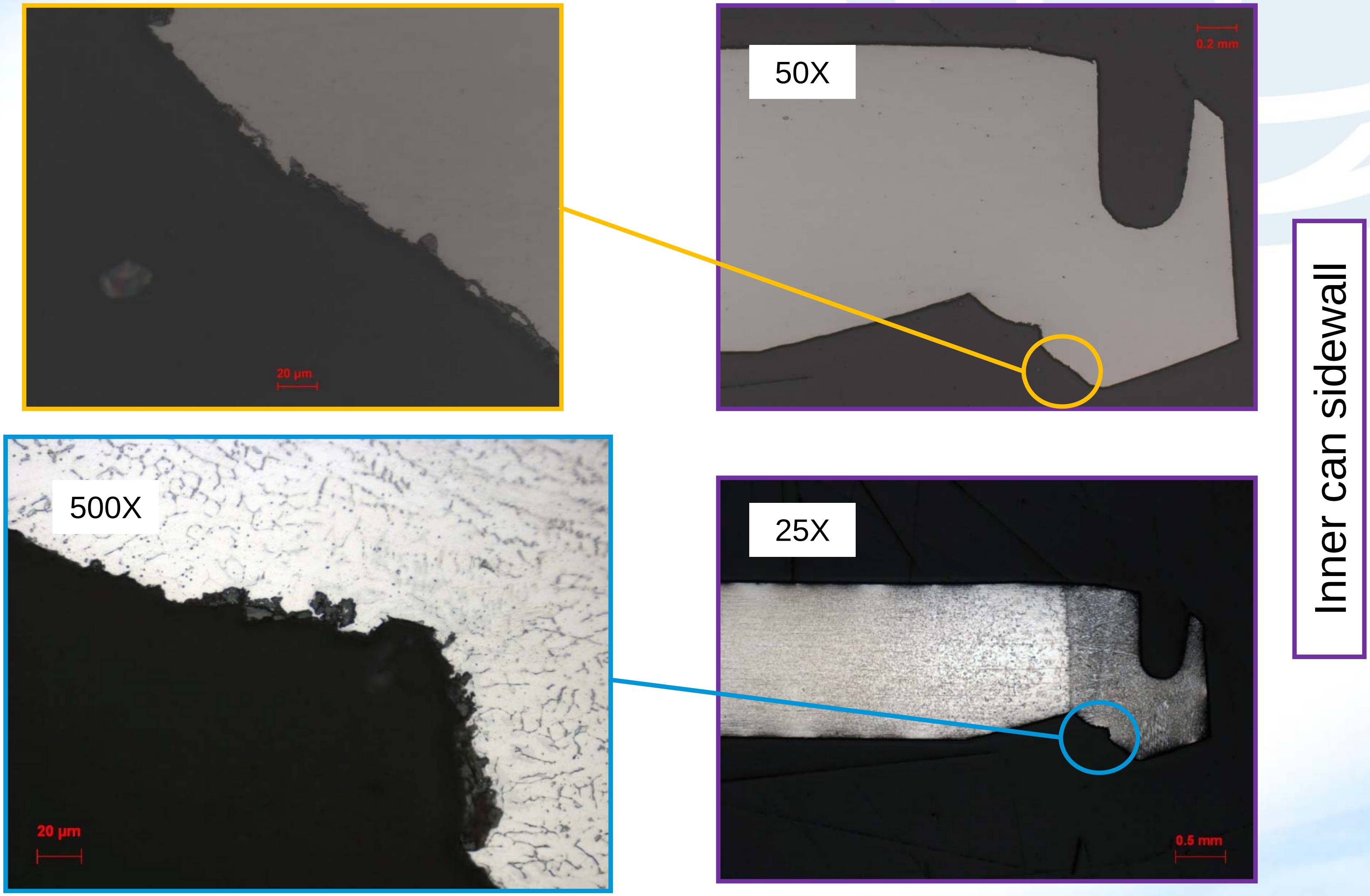
FY12 DE6 H004012



FY12DE7 H004048 Data

DE #	3013 ID	Analyze	Categorization
FY12DE7	H004048	Y	3A

Package Information	
Bin	Pressure & Corrosion
Type	Random
TGA	0.336 wt %
Total Actinides	56.46%
SRS Prompt Gamma (Cl)	16.17 wt %

DE Data	
Gas Analysis (GEST) (Vol%)	He – 50.5 N_2 – 43.75 H_2 – 4.1
Gas Pressure (GEST) (psia)	9.8
TGA/MS * (wt %)	Initial – 1.19 / 0.47 Final – 1.14 / 0.54
IC (µg/g) (Leach)	F – 90 Cl – 135500
ICP/ES (µg/g) (Leach)	Ca – 384 K – 71850 Mg – 3195 Na – 43600

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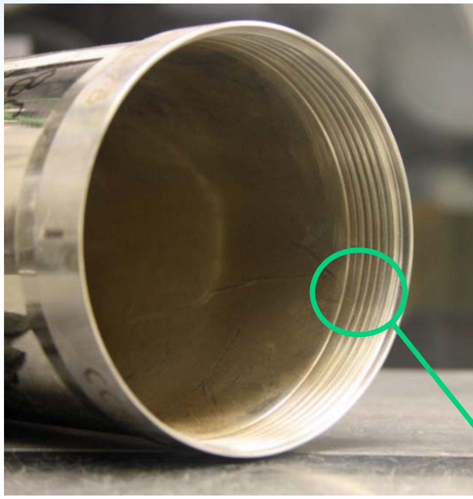
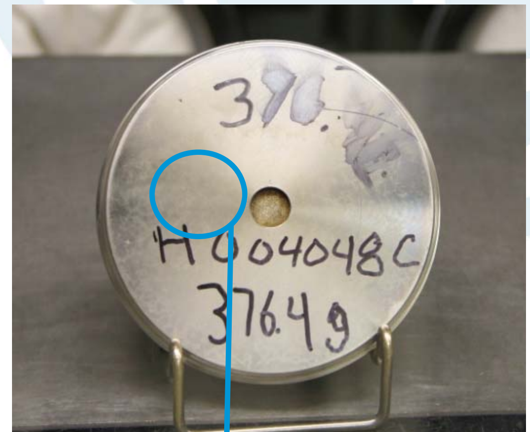
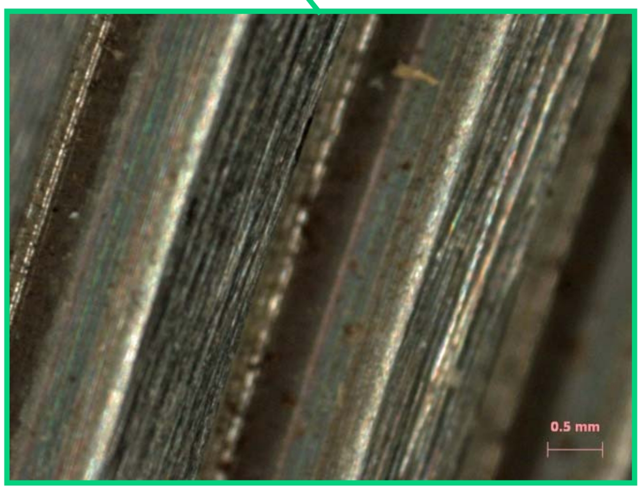
***Lab Work Complete – data not reviewed.**
Samples received 3/20/12 & analyzed 1/28/13

FY12DE7 H004048

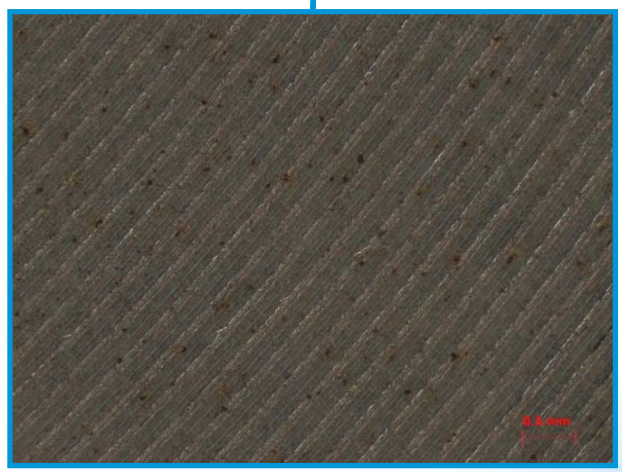
Convenience Can







Borescope photograph



Stereomicrograph

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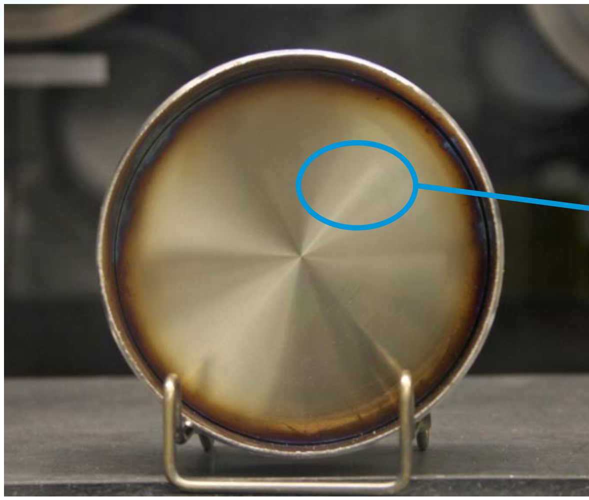
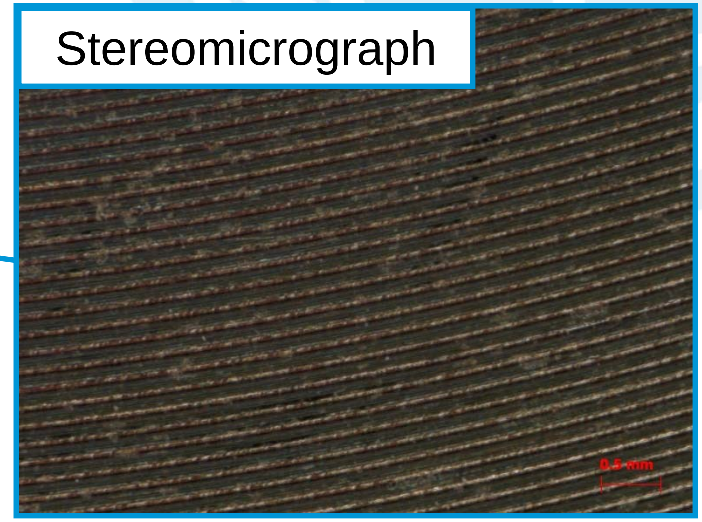
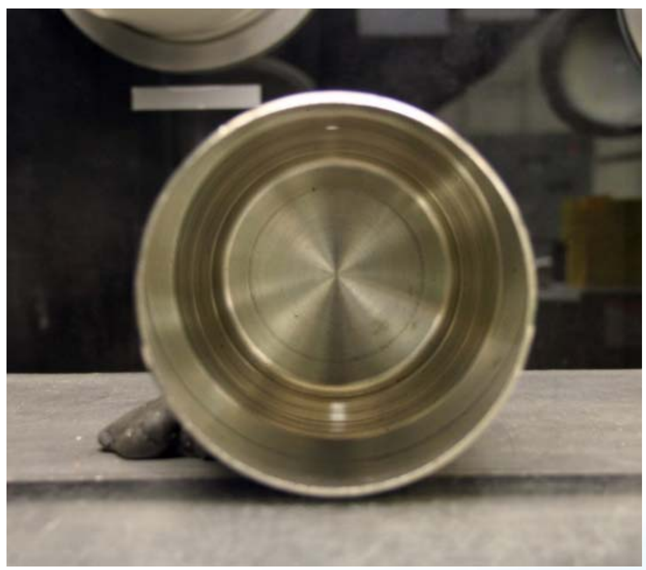
FY12DE7 H004048

Inner Can

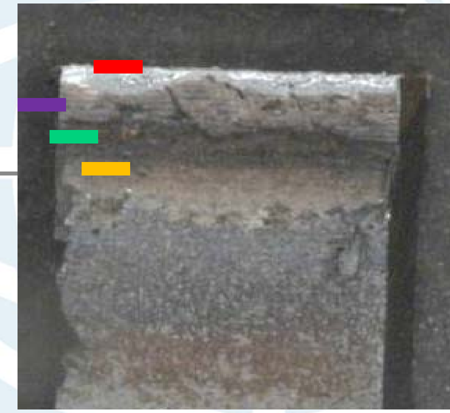


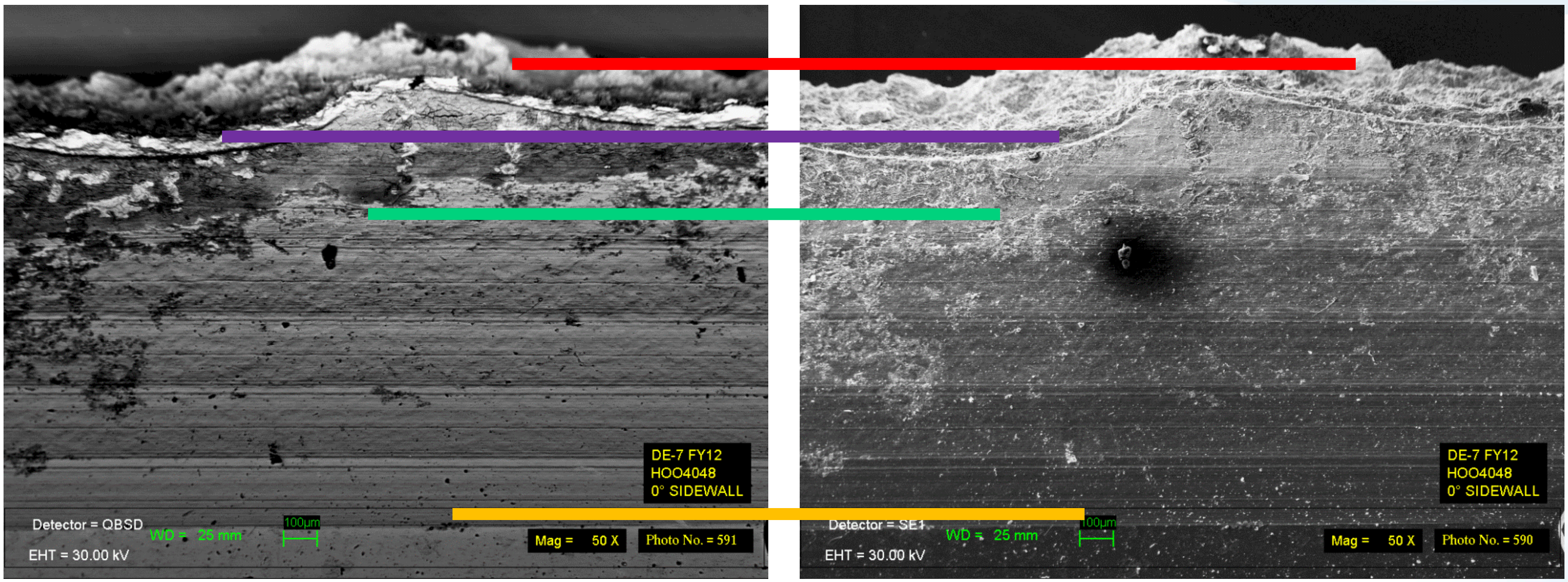




FY12DE7 H004048

Weld (fracture)
Exposed Weld
Heavy Oxide
Light Oxide





SEM micrographs (50x) of inner can sidewall within crevice

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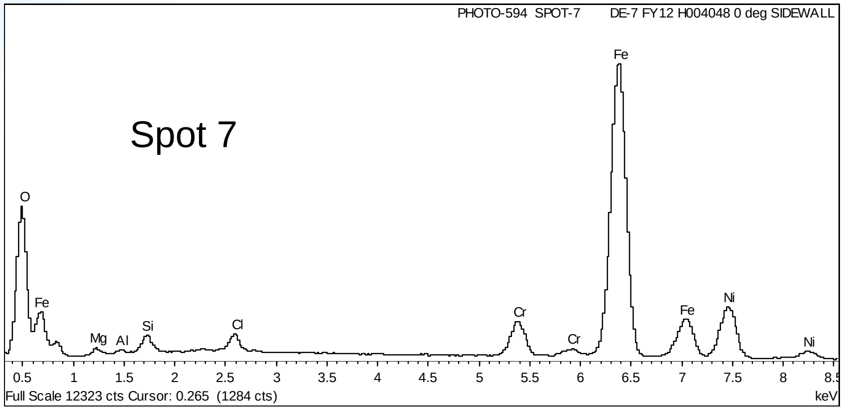
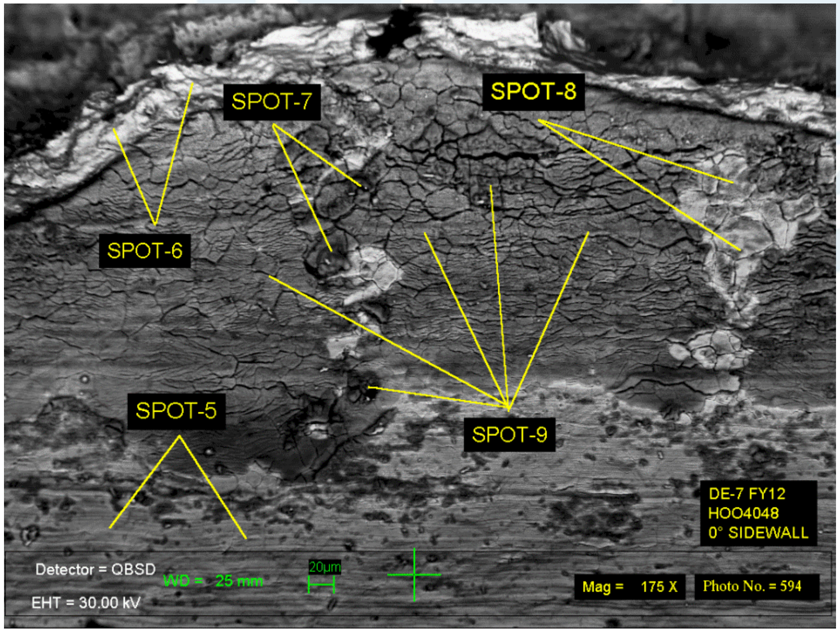
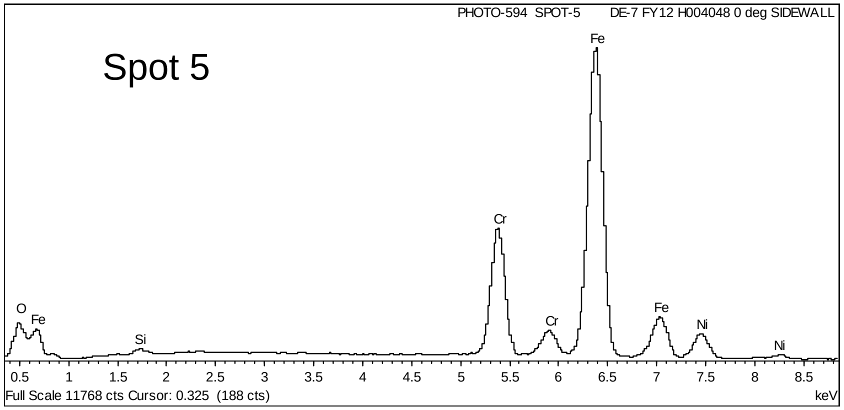
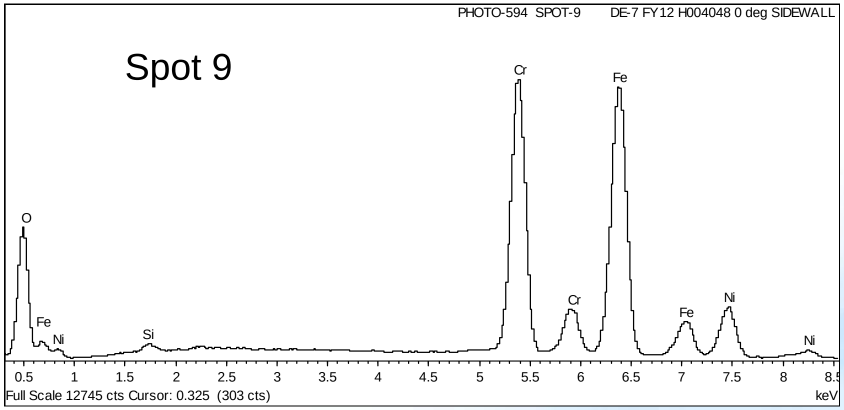
FY12DE7 H004048









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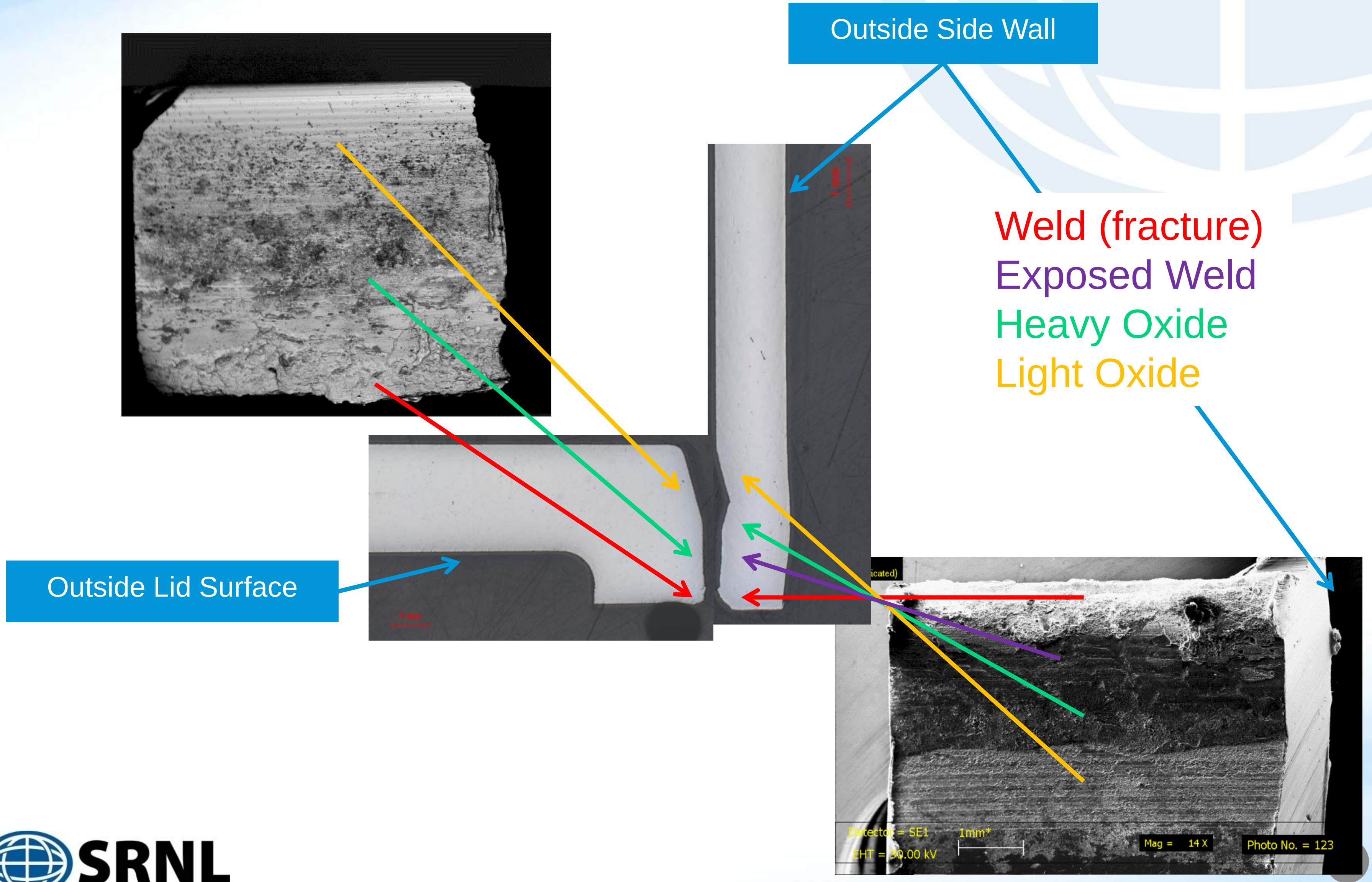
Cross Sectional Mounts



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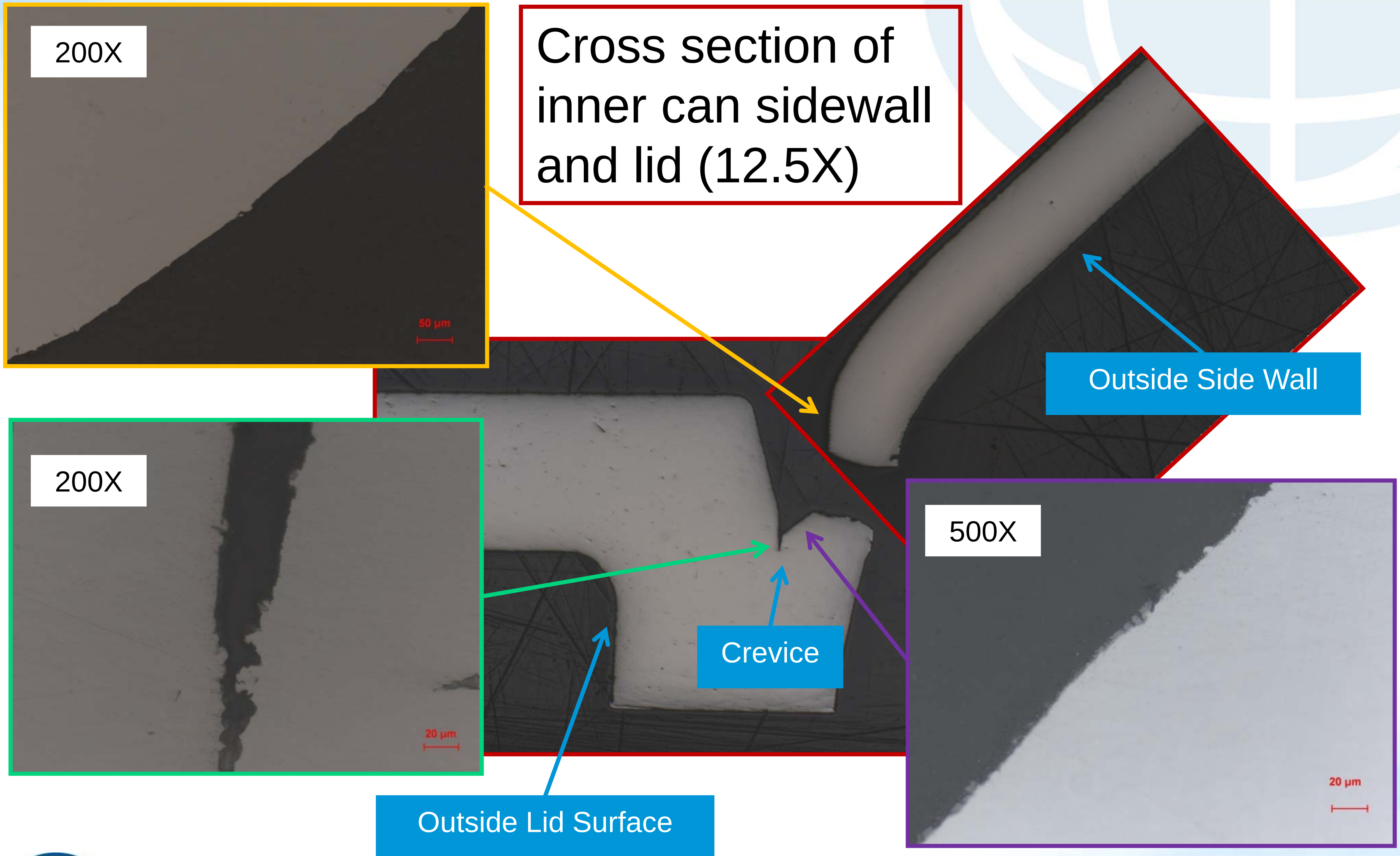
FY12 DE7 H004048



FY11 HHMC H003328 Data

DE #	3013 ID	Analyze	Inner	Convenience	Categorization
FY11 HHMC	H003328	Y	Lid	Lid, Body	IP (5)

Package Information	
Bin	Pressure & Corrosion
Type	ARF/High water
TGA	0.225 wt %
Total Actinides	75.11%
LANL Prompt Gamma (Cl)	3.69 wt %

DE Data	
Gas Analysis (GEST) (Vol%)	He – 14.2 N_2 – 11.34 H_2 – 74.38
Gas Pressure (LANL) (psia)	42
TGA/MS	TGA(0.9%) MS (0.24%)
IC (µg/g) (Leach)	F – 299 Cl – 32150
ICP/ES (µg/g) (Leach)	Ca – 3540 K – 13500 Mg – 310 Na – 7675

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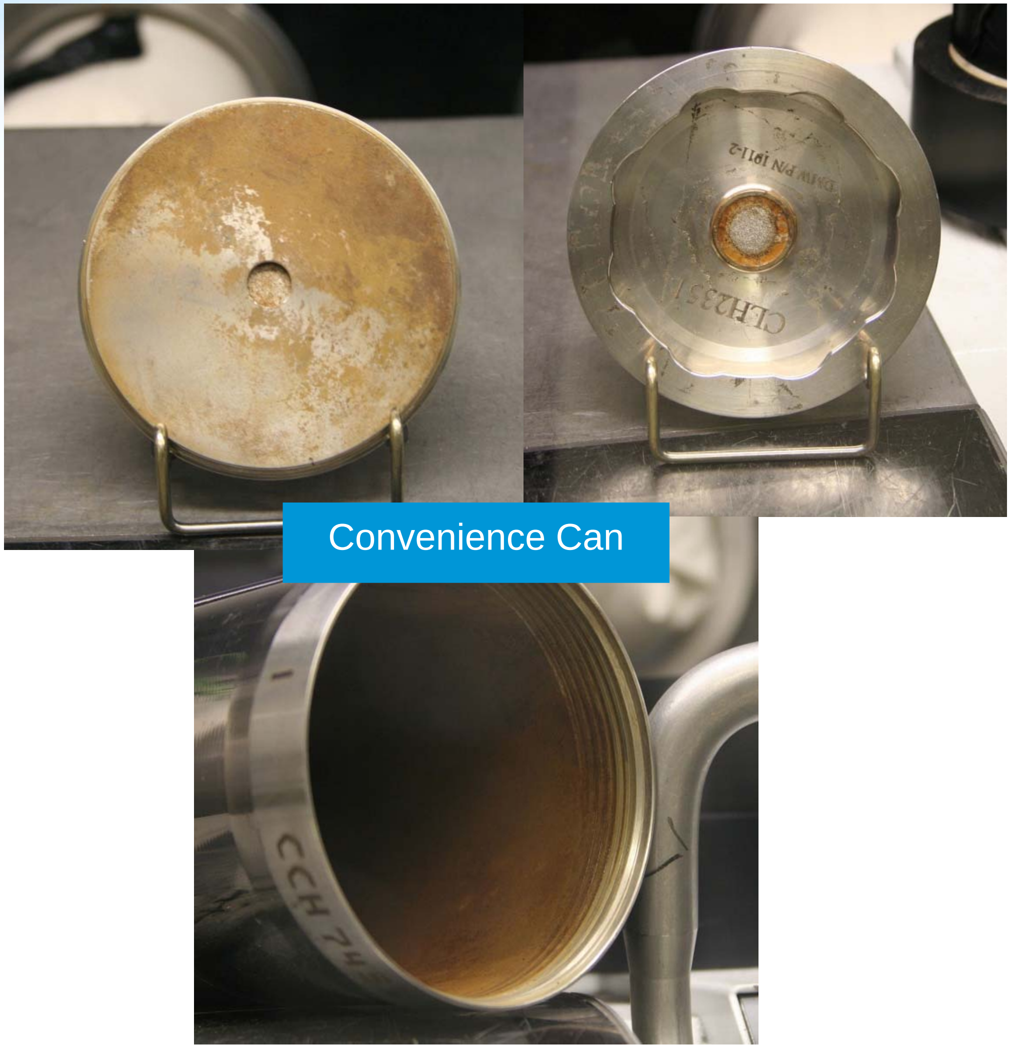
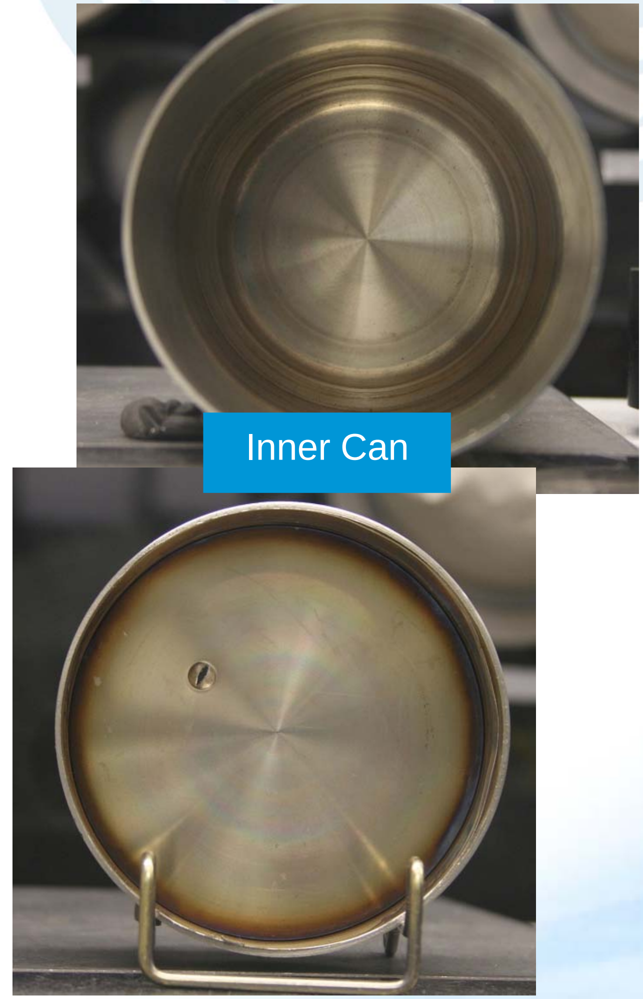
FY11 HHMC H003328 - As-Received Condition



Convenience Can



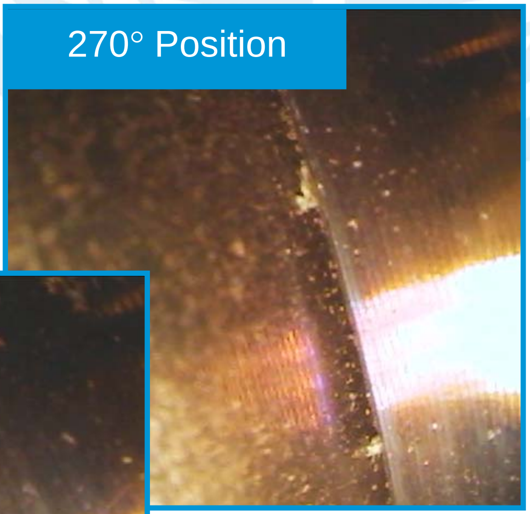
Inner Can

FY11 HHMC H003328 - Inner Can Lid – Interior Surface

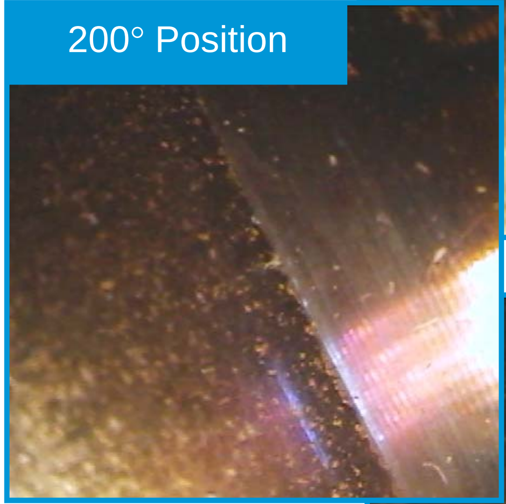
Stereomicroscope Image (25x)

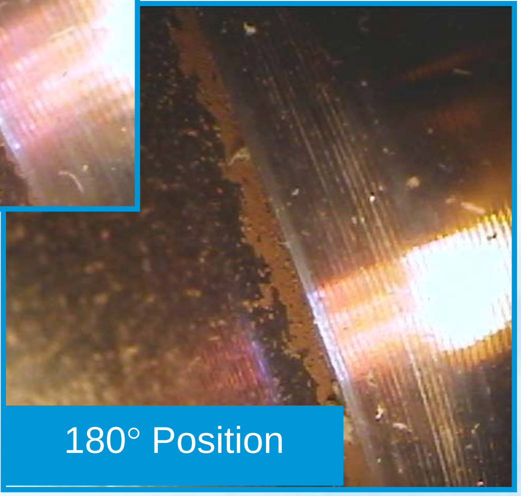
Borescope Images

270° Position



200° Position





180° Position

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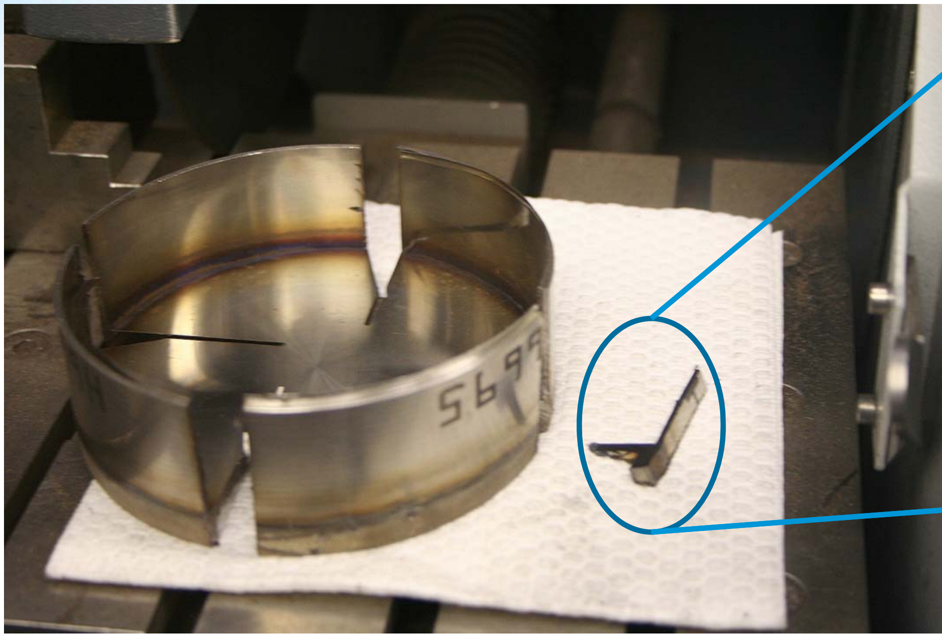
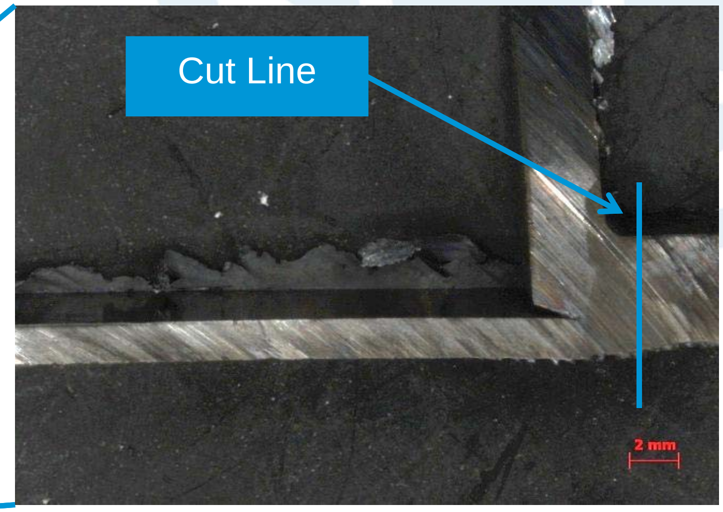
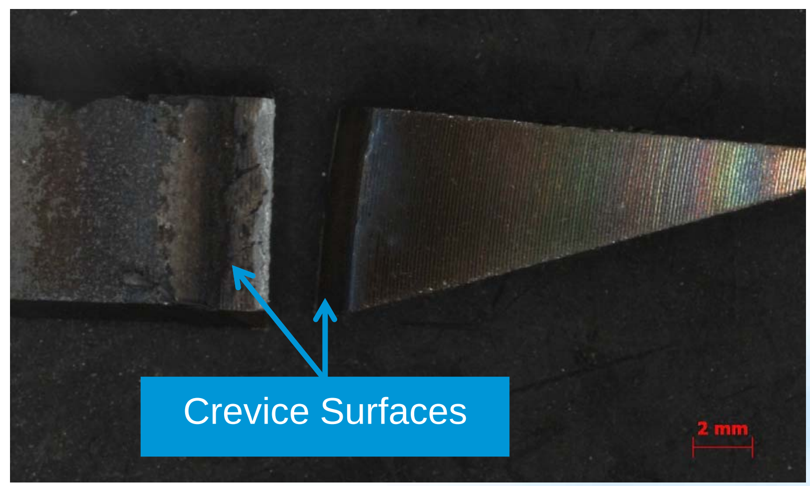
FY11 HHMC H003328 - Sectioning Inner Can Lid



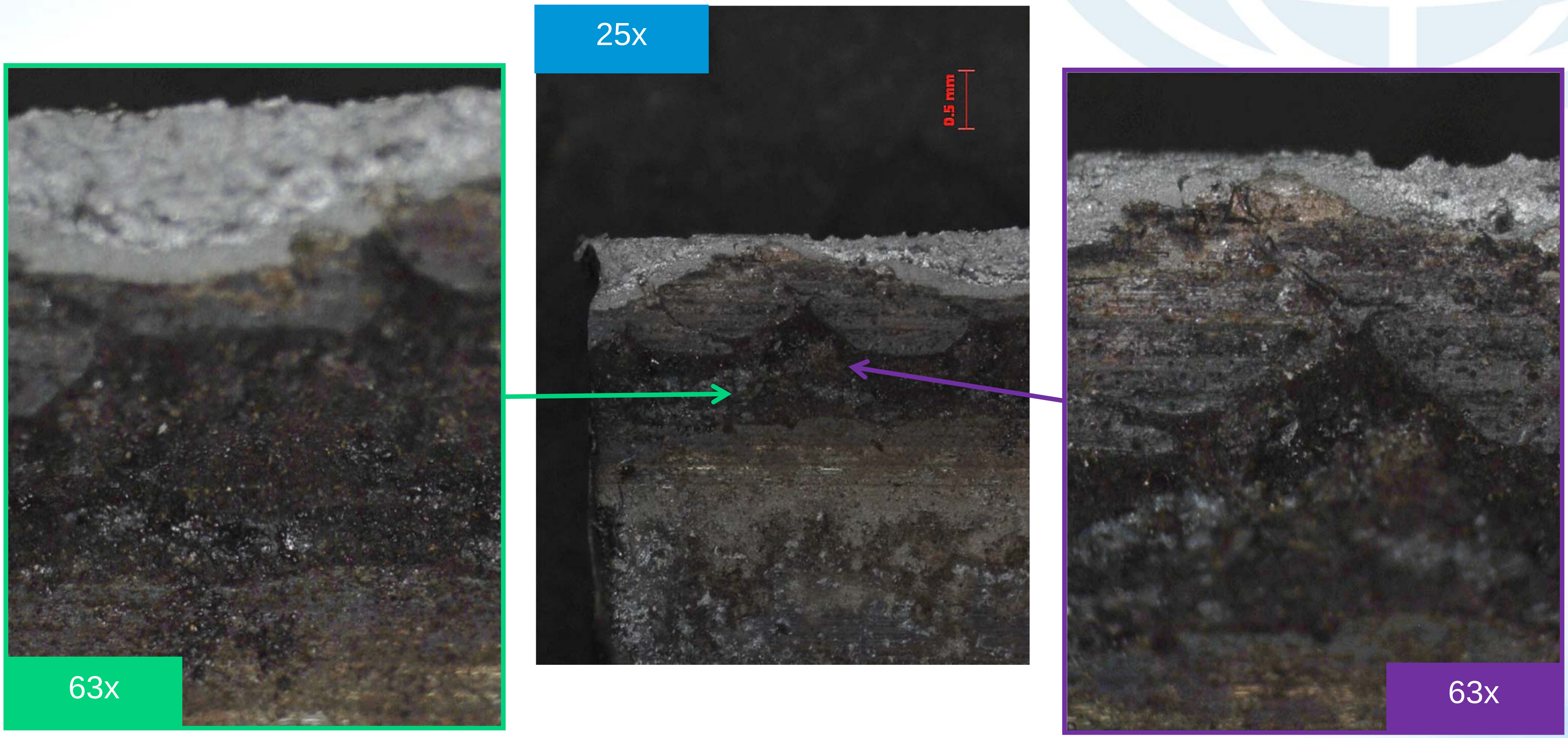




Inner can was sectioned to remove five pie sections: 0, 90, 120, 180 and 270° positions. The closure weld was removed along a cut line close to the external surface of the lid. This allowed the surfaces of the inner can crevice to be exposed.

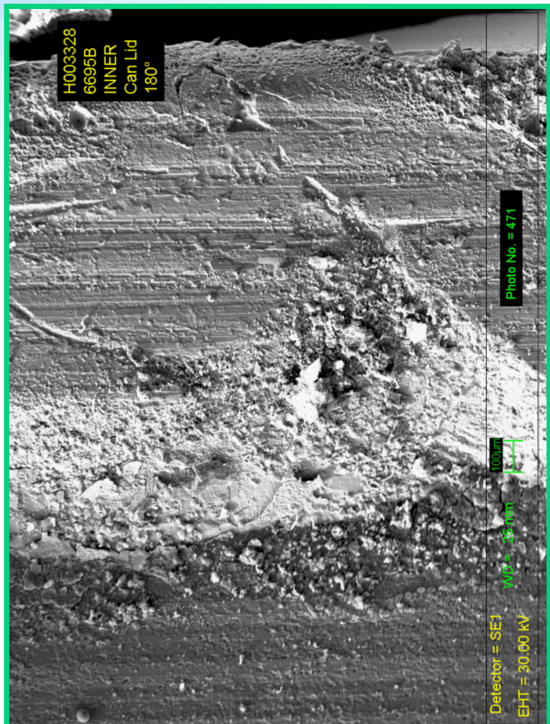
FY11 HHMC H003328 - Surface Morphology- 180° Position

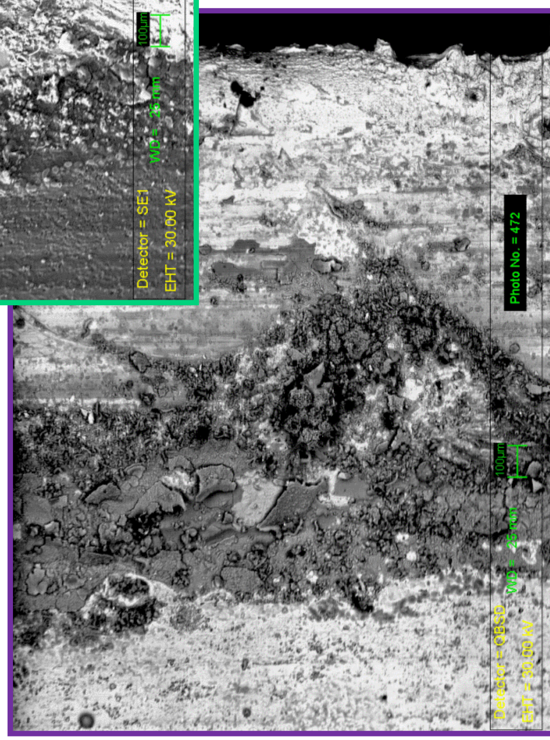
Inner Can Sidewall Stereomicroscope Image

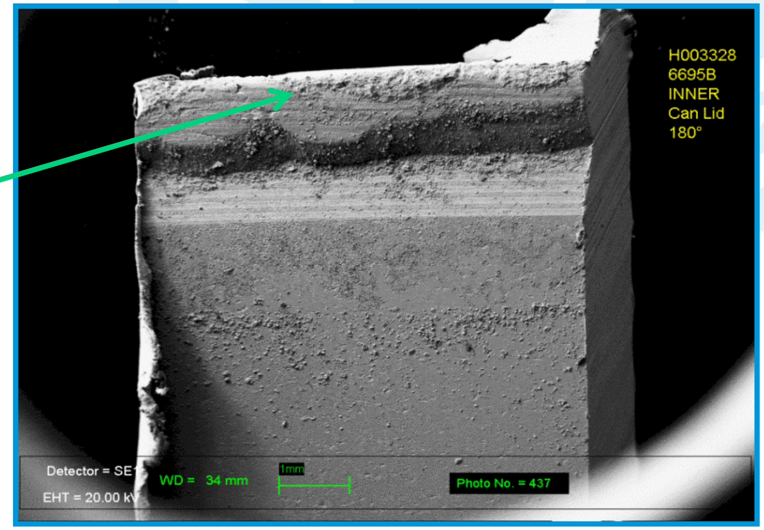


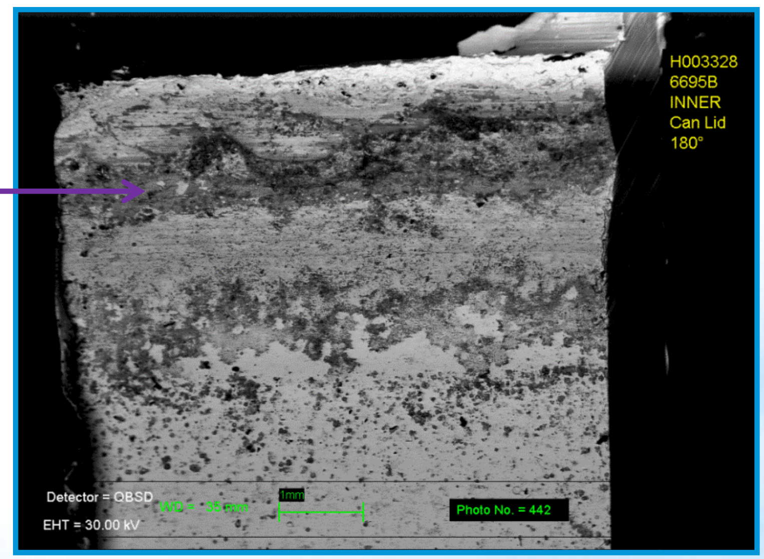
FY11 HHMC H003328 - Surface Morphology- 180° Position

Inner can sidewall SEM Micrographs

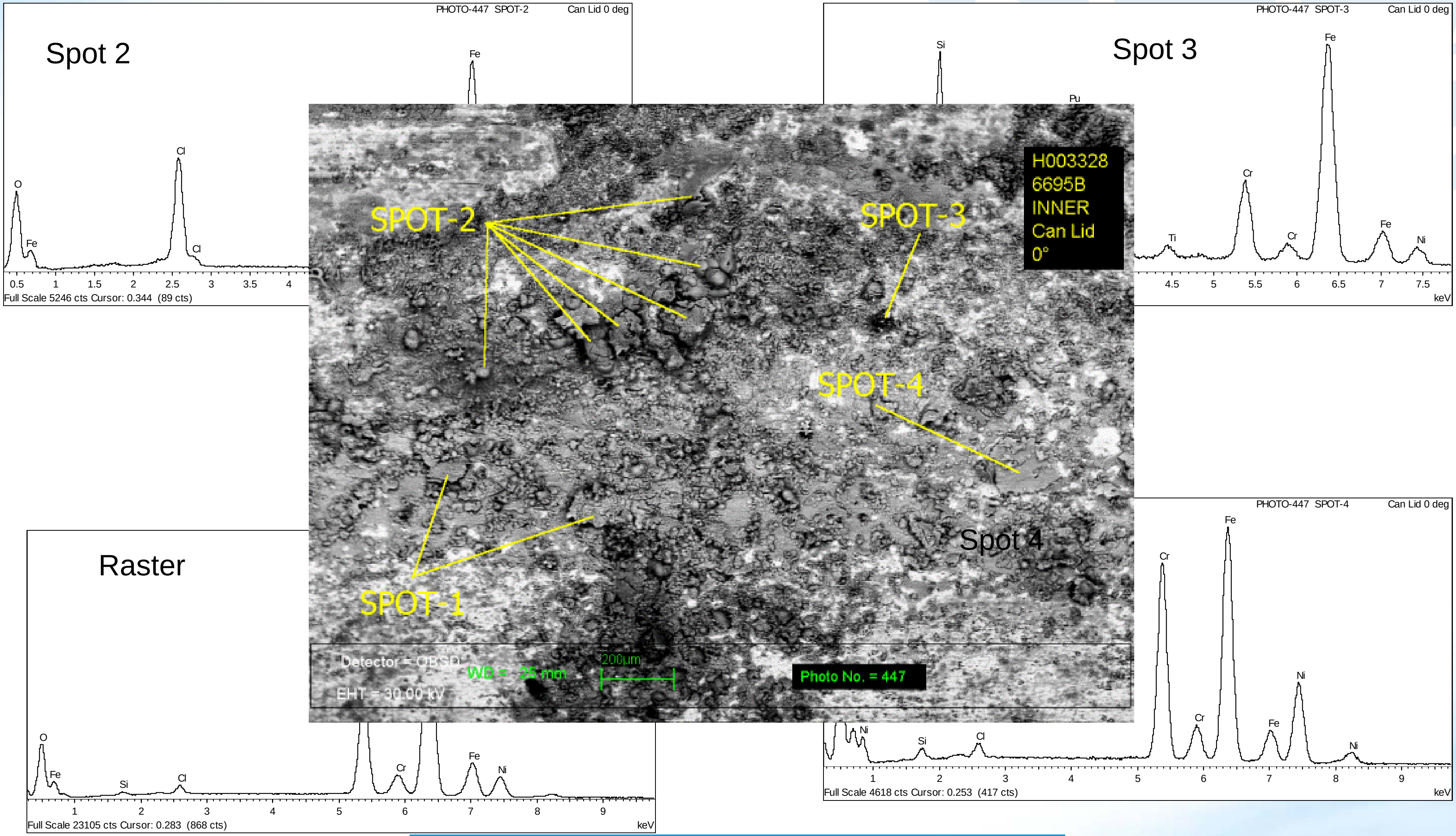








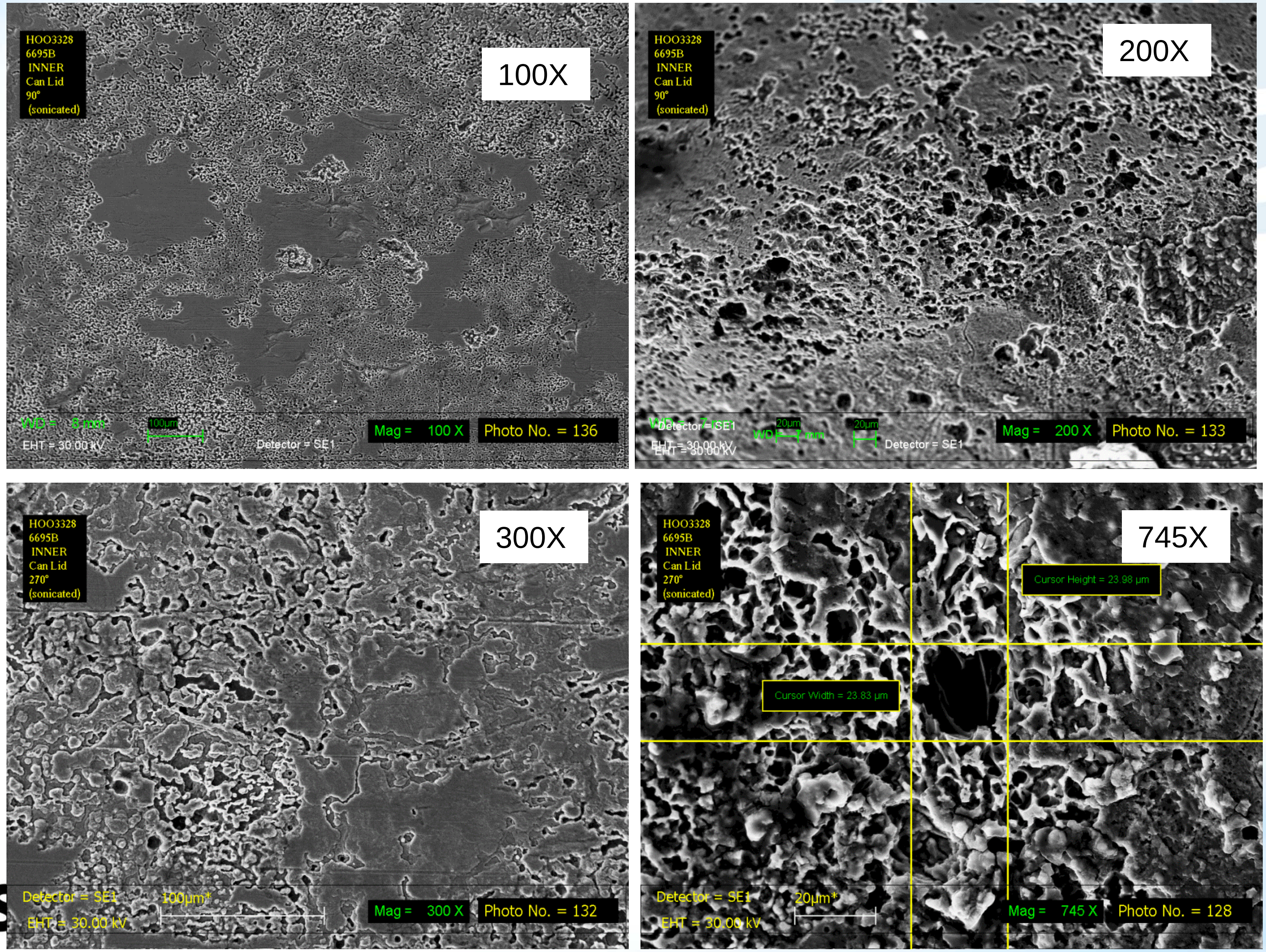
FY11 HHMC H003328 – Chemical Analysis



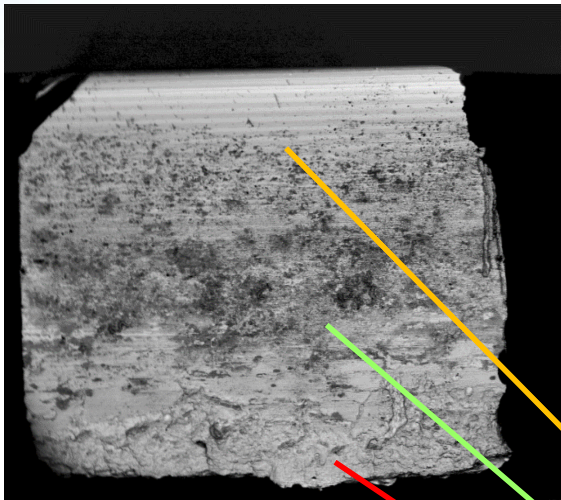
SRNL

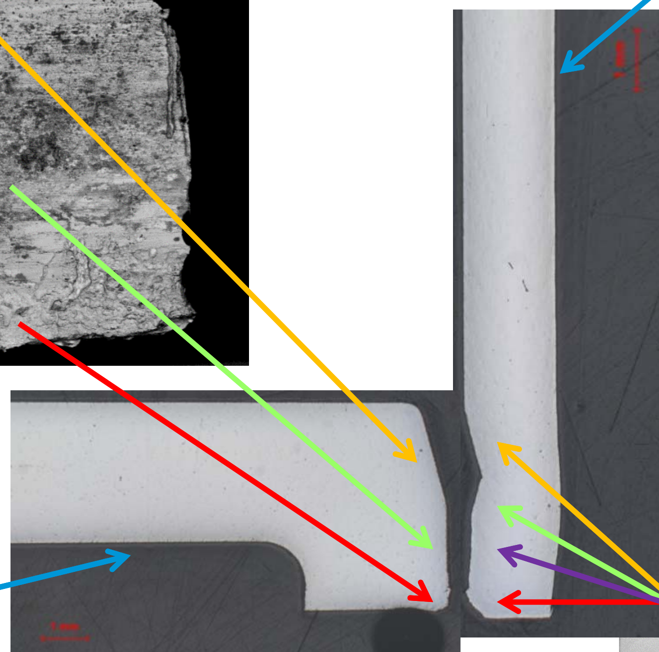
Inner can lid SEM Micrographs

FY11 HHMC H003328 - Corrosion Morphology

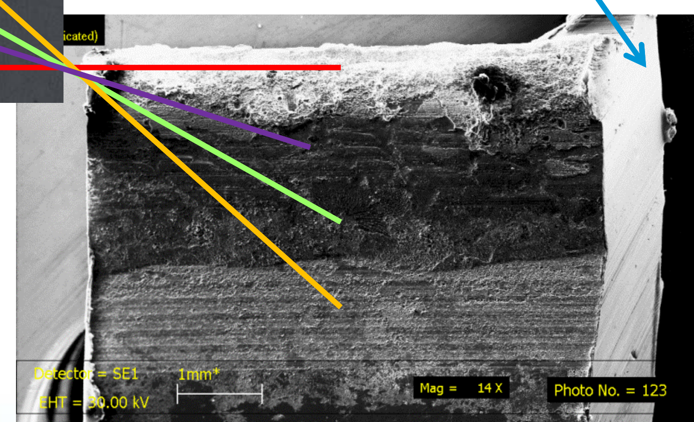


FY11 HHMC H003328 - Cross Sectional Mounts





Lid and Side wall sections from the 270° position showing correlation between surface locations and locations in cross sectional view.



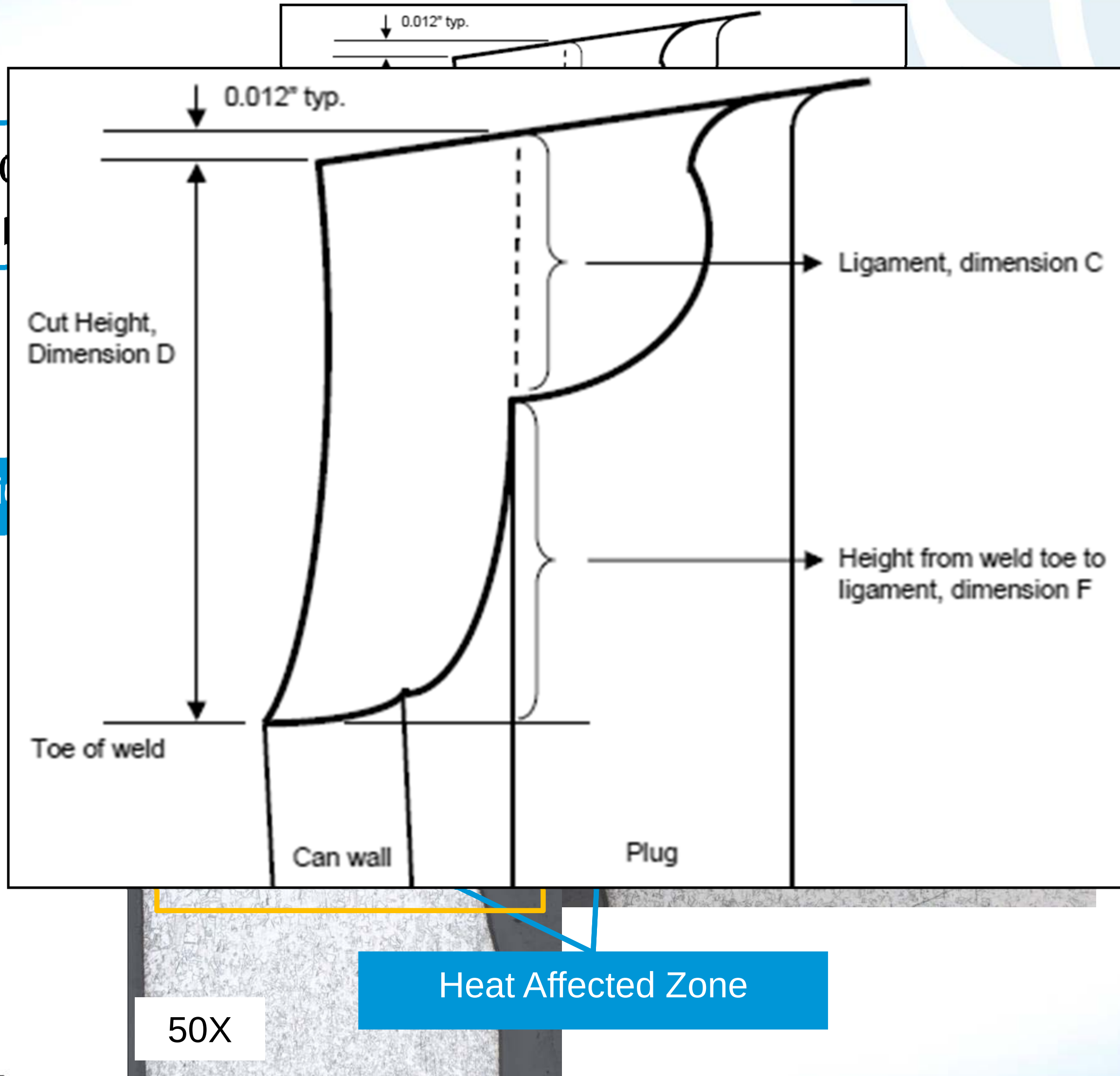
Lid and side wall sections from the 0, 90, 180 and 270° positions were mounted viewing in cross section.

SRNL

FY11 HHMC H003328 - Microstructure

Sections fr
90° Positio

Side Wall Secti

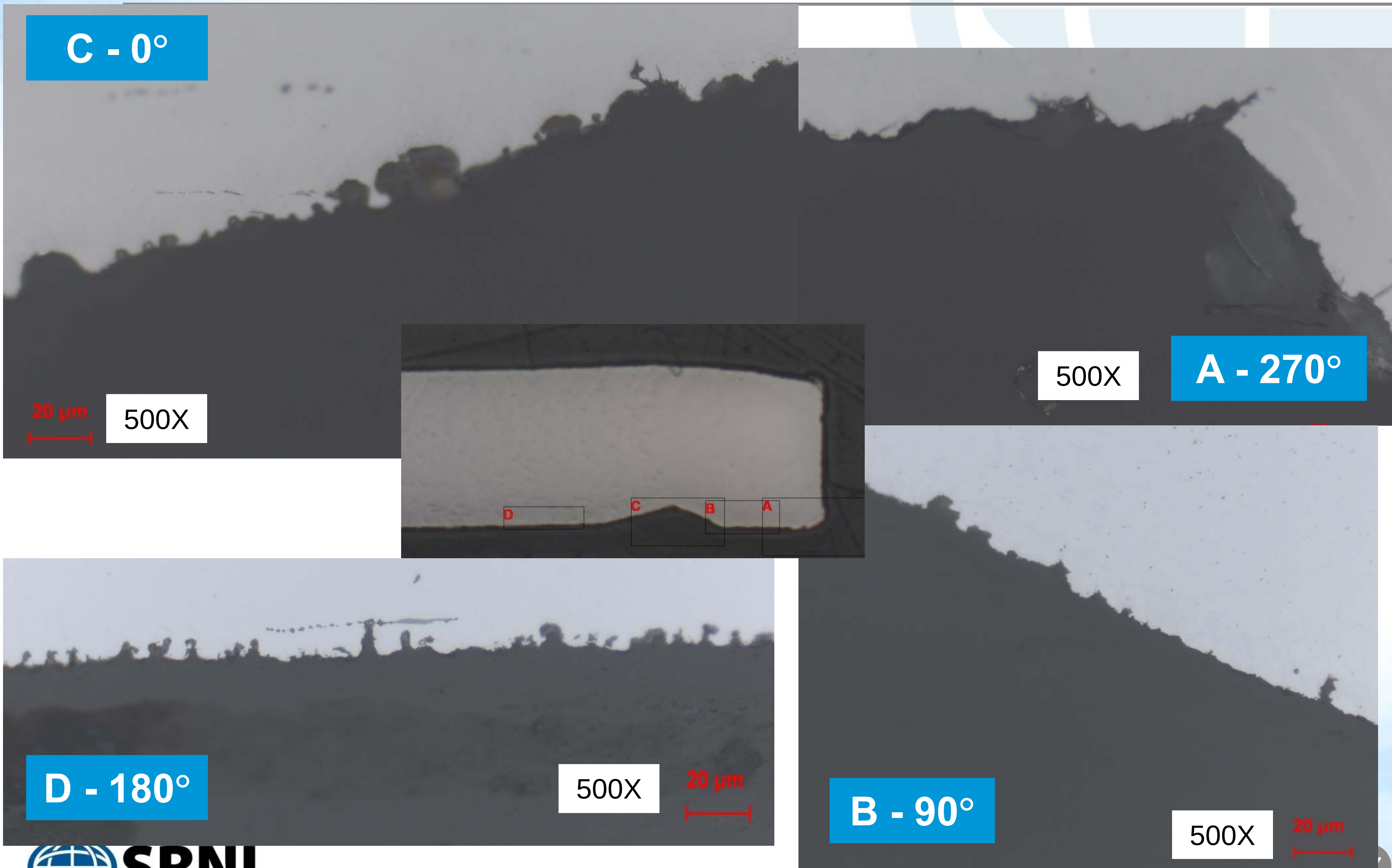


matic cross
on of inner
closure weld

Lid Section

SRNL

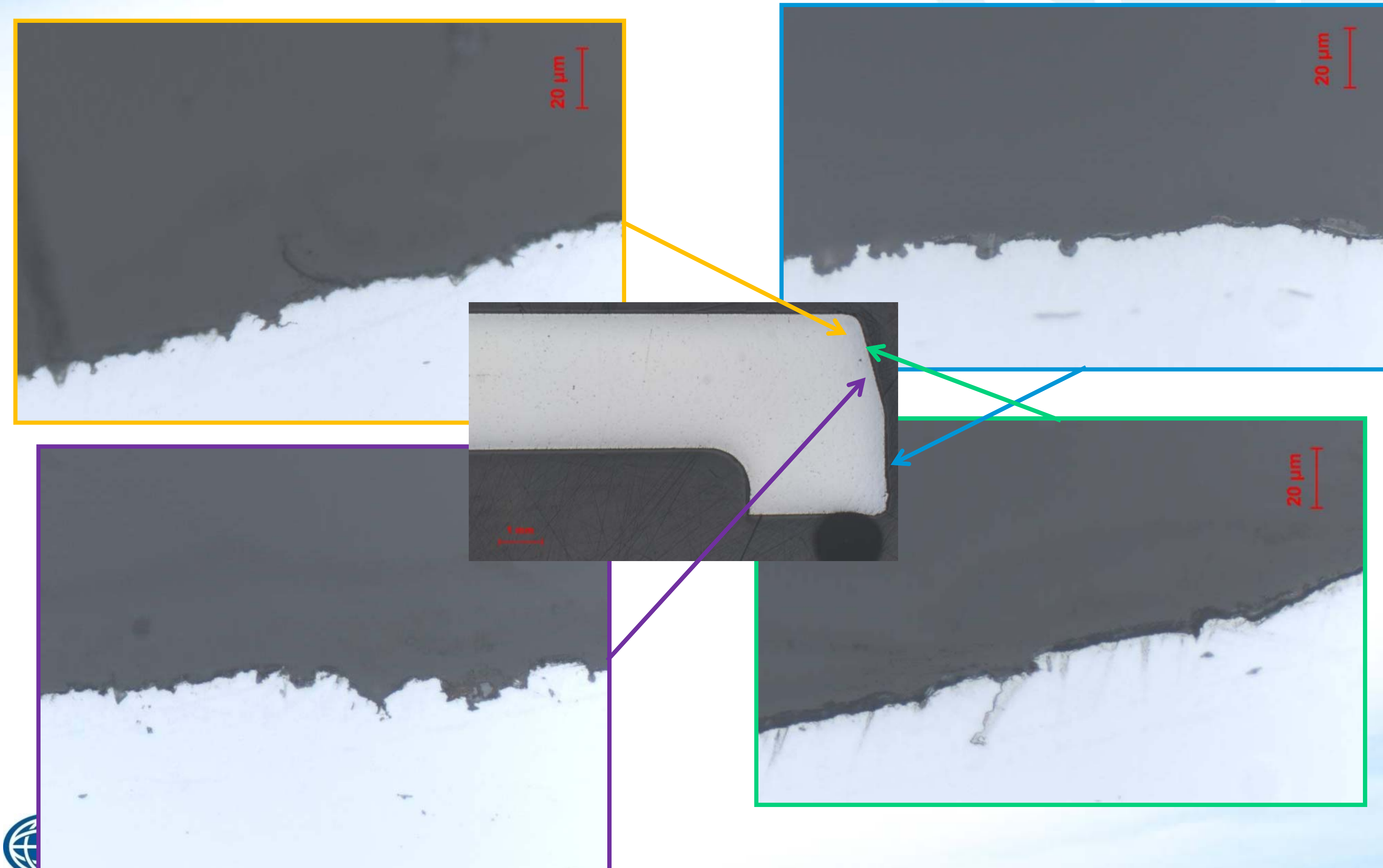
FY11 HHMC H003328 - Corrosion Morphology – Side Wall



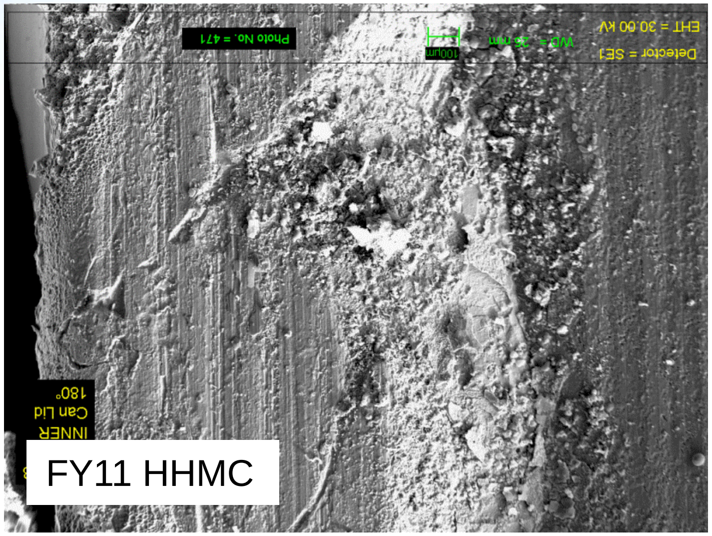
SRNL

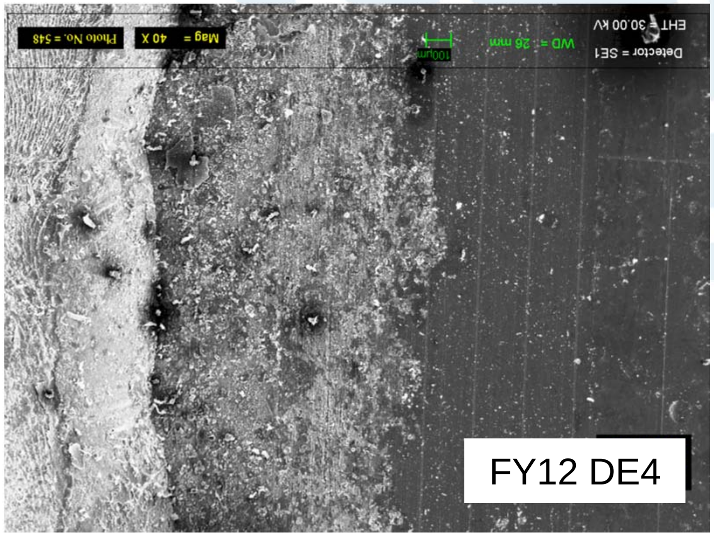
FY11 HHMC H003328 - Corrosion Morphology – Lid

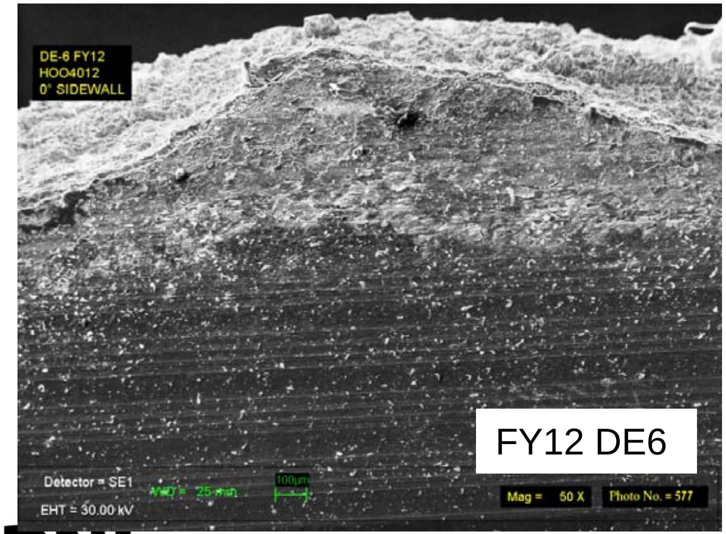
Sections from 90° Position

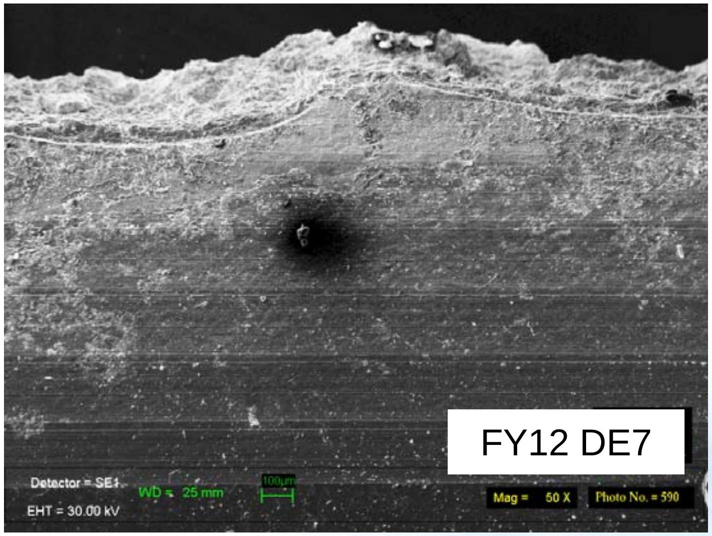


Comparison of Corrosion Morphology – Inner Can Side Wall









SRNL

Conclusion

Corrosion does not appear to occur in inner can crevice region when the convenience can has no degradation.

Corrosion does appear to occur in the inner crevice region when there is an interaction of the packaged material with the convenience can surface.

Qualitatively, the more degradation in the inner can crevice region the more chloride is found.

Prompt Gamma Analysis
Updates to Calibration

Joshua Narlesky and Elizabeth Kelly

February 27, 2013

Outline

- **Overview of Prompt Gamma Analysis**
- **Selection of Data**
- **Statistical Method**
- **Results:**
  - Chlorine
  - Magnesium
  - Fluorine
  - Others—let me know if you are interested
- **Discussion**

Overview

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
- 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 DL as a function of count time

Selection of Data
(Currently 166 Items with PG and Analytical Chemistry)

Data Source	Stabilization Temp	Analytical Method	Dissolution Method	Al	B	Be	Cl	F	Li	Mg	P	K	Na
Representative Items in MIS Program	As received by LANL	ICP-AES / ICP-MS	HNO_3/HF Dissolution	Y	Y	Y			Y	N	Y	N	N
		Ion Chromatography	Pyrohydrolysis				N	N					
	600ºC	ICP-AES / ICP-MS	HNO_3/HF Dissolution	Y	Y	Y			Y	N	Y	N	N
		Ion Chromatography	Pyrohydrolysis				N	N					
	800ºC	ICP-AES / ICP-MS	HNO_3/HF Dissolution	Y	Y	Y			Y	Y	Y	Y	Y
		Ion Chromatography	Pyrohydrolysis				Y	Y					
	950ºC	ICP-AES / ICP-MS	HNO_3/HF Dissolution	Y	Y	Y			Y	Y	Y	Y	Y
		Ion Chromatography	Pyrohydrolysis				Y	Y					
Hanford 3013 Container	750-950ºC	Ion Chromatography	Water Leach				N	N					
		Ion Selective Electrode	Na_2O_2-NaOH Fusion					N					
		ICP-AES / ICP-MS	Acid Leach	N	N	N			N	Y	N	Y	Y
		ICP-AES / ICP-MS	Na_2O_2-NaOH Fusion	Y	Y	Y			N	Y	Y	N	N
Hanford Input Item	Not Stabilized	Volhard Titration	Water Leach				Y						
	Not Stabilized	Ion Selective Electrode	Water Leach				Y						
	Not Stabilized	ICP-AES / ICP-MS	$NaHSO_3$ Fusion	Y	Y	Y			N	Y		Y	
Rocky Flats Input Item	450-850ºC	Ion Chromatography					Y						
	450-850ºC	ICP-AES										Y	Y
SRS 3013 Container	750-950ºC	ICP-AES / ICP-MS	HNO_3/HF Dissolution	Y	Y	Y			Y	Y	Y	Y	Y
		Ion Chromatography	Pyrohydrolysis				Y	Y					
3013 Container Destructive Analysis	750-950ºC	Ion Chromatography	Acid Leach				Y	N					
		ICP-AES	Acid Leach	N	N	N				N	N	Y	Y
		ICP-AES	HNO_3 Dissolution	Y	Y	Y				Y	Y	Y	Y
	750-950ºC	ICP-AES	HNO_3/HBO_3 Dissolution	Y	N	Y				Y	Y	Y	Y
	750-950ºC	ICP-AES	Na_2O_2-NaOH Fusion / H_2SO_4 Dissolution	Y		Y				Y			N
	750-950ºC	Ion Chromatography	Na_2O_2-NaOH Fusion / H_2SO_4 Dissolution				Y	Y					
				47	5	34	91	37	4	121	13	62	145

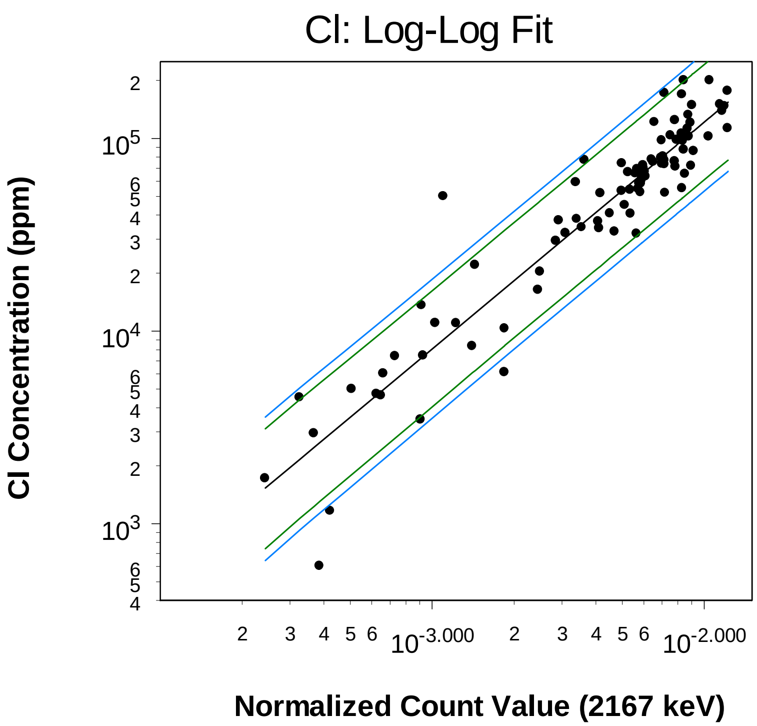
Statistical Method

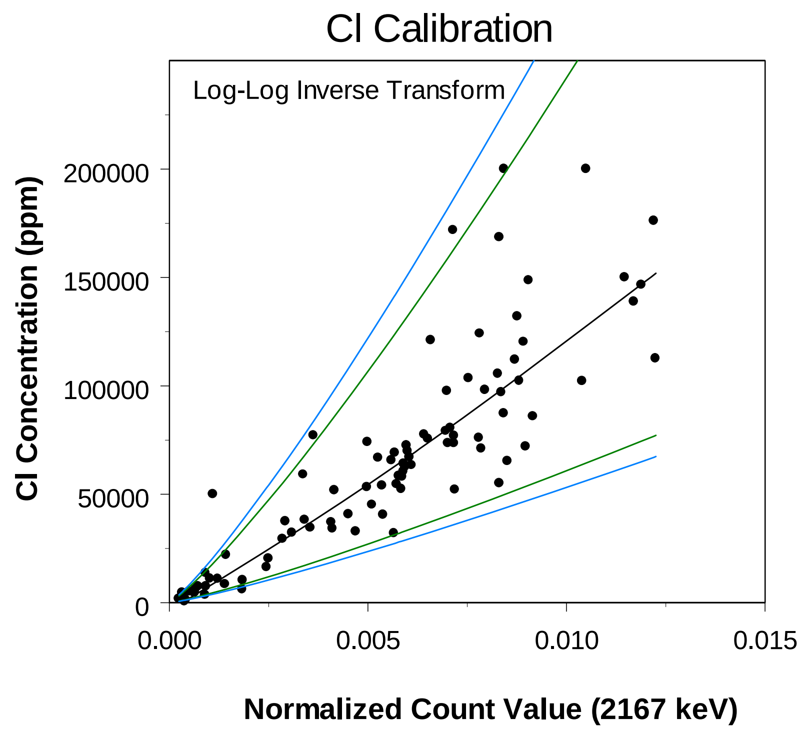
- **Method**
  1. Find PG as a linear function of impurity chemistry concentration (ICC)
  2. Use inverse regression to find ICC as a function of PG
  - Assume variability in ICC is small with respect to PG
- **Technique: weighted least squares (WLS)**
  - Why WLS?
    - In OLS, larger values of ICC have higher influence
    - Variability in our data increases with ICC
    - Bulk of data at low ICC
    - Give each data point proper influence—in our case 1/(ICC)
    - Defensible estimates of uncertainties
  - Earlier models
    - Applied log-log transform to data
    - Find log(PG) as a linear function of log(ICC)
    - Stabilized variance, but uncertainties unreasonable

Statistical Method

- **Sources of variability**
  - Primarily depends on degree of intimate contact between alpha-emitters and sensitive light elements.
    - Improve mixing by melting together (chlorides)
    - Better contact at higher Pu concentration
    - Chemical compounds affect detection ($MgCl_2$ better than MgO)
  - Element sensitivity: low sensitivity—weaker signal
- **Models using "better data"**
  - MOX model (>72% Pu <u>and</u> < 5% U): applied to Cl, Na, Mg
  - Low Mg concentration (<10% Mg): applied to Mg

Original Calibration (Chlorine)

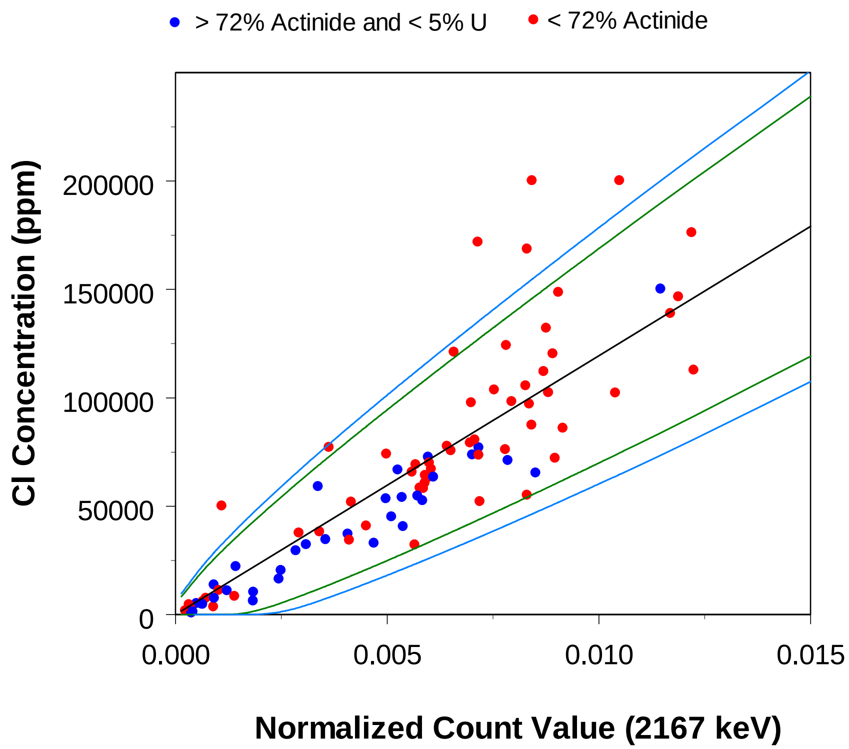




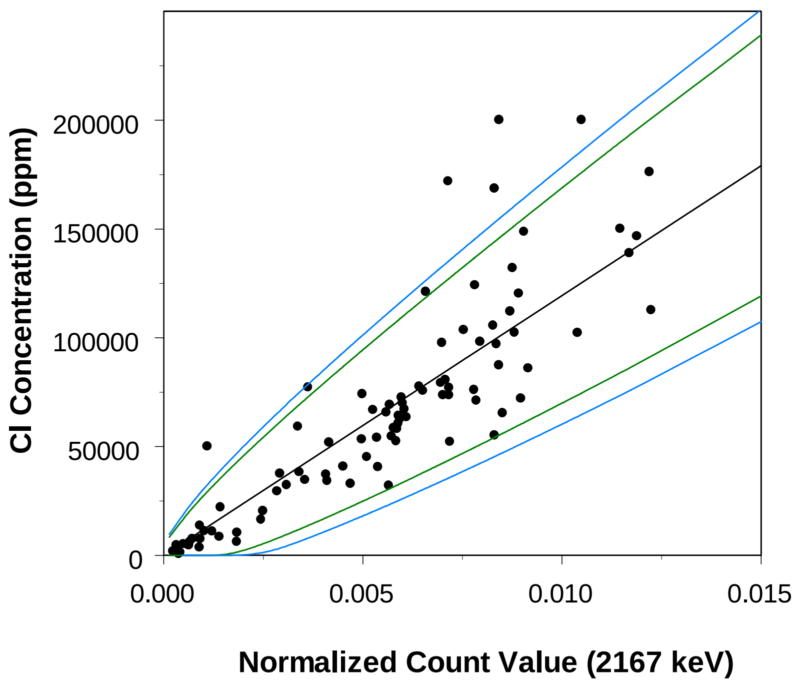
Linear fit to Log(data)

Inverse transform (power function)

Developing New Model

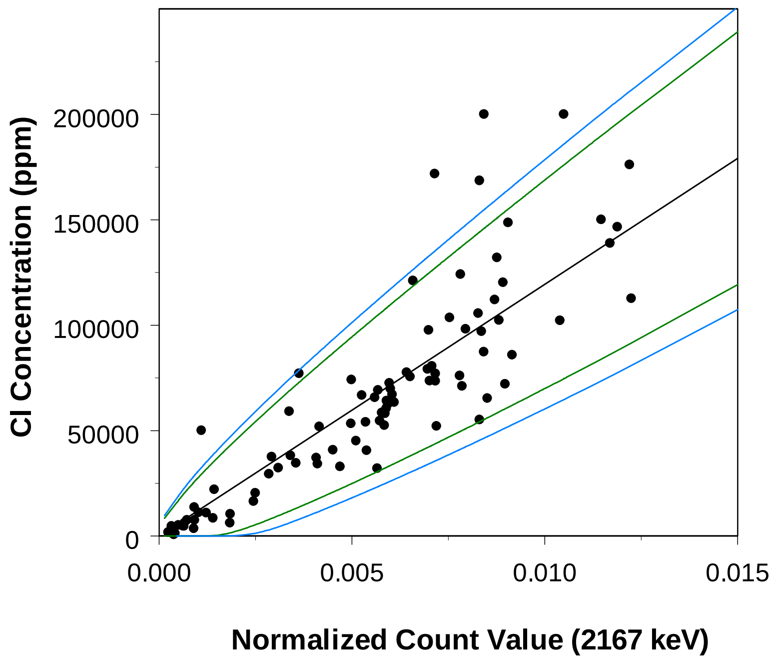


- New Model (WLS)

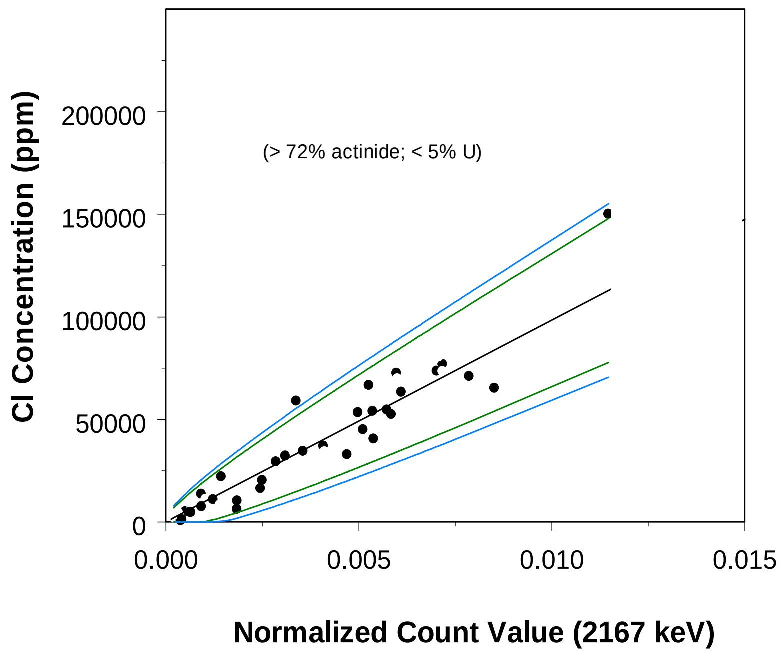


Chlorine

▪All Data

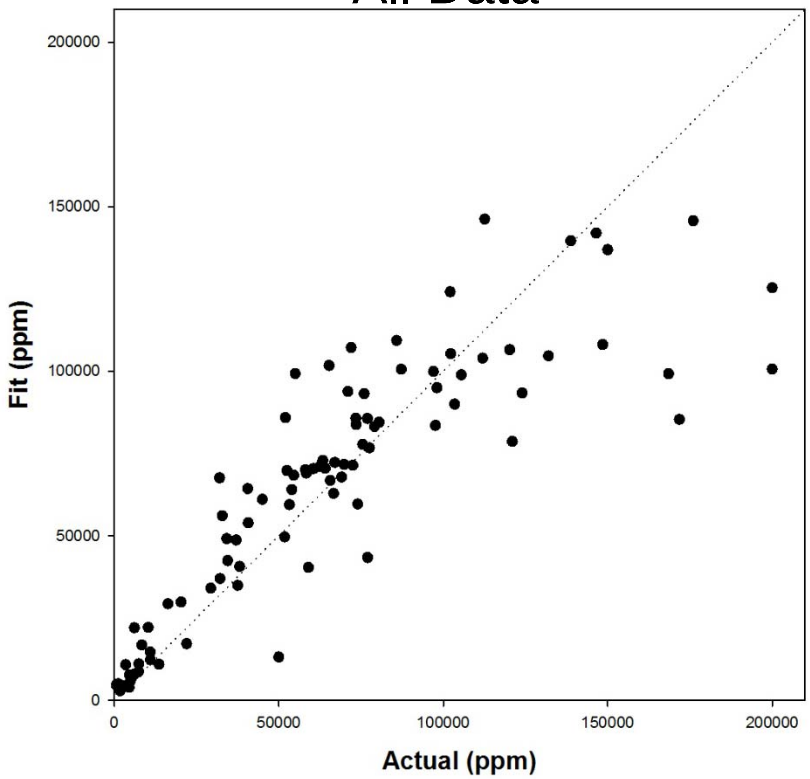


▪MOX Data

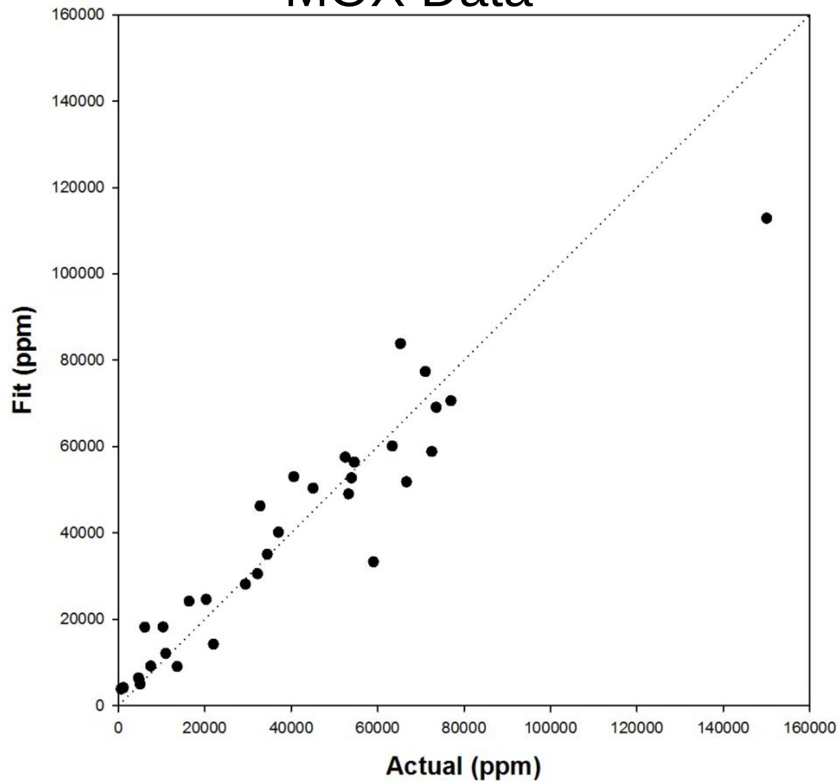


Diagnostic Plots

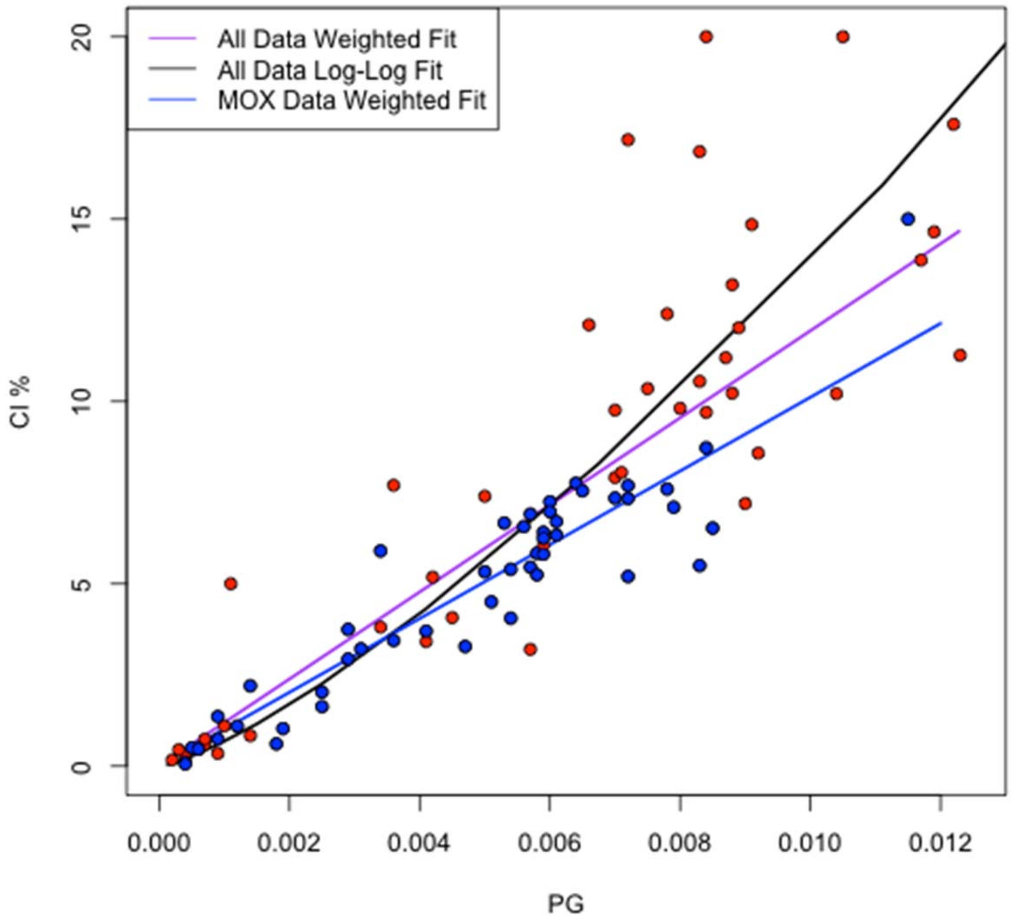
▪All Data



▪MOX Data



New Model vs. Original Model



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR Cl

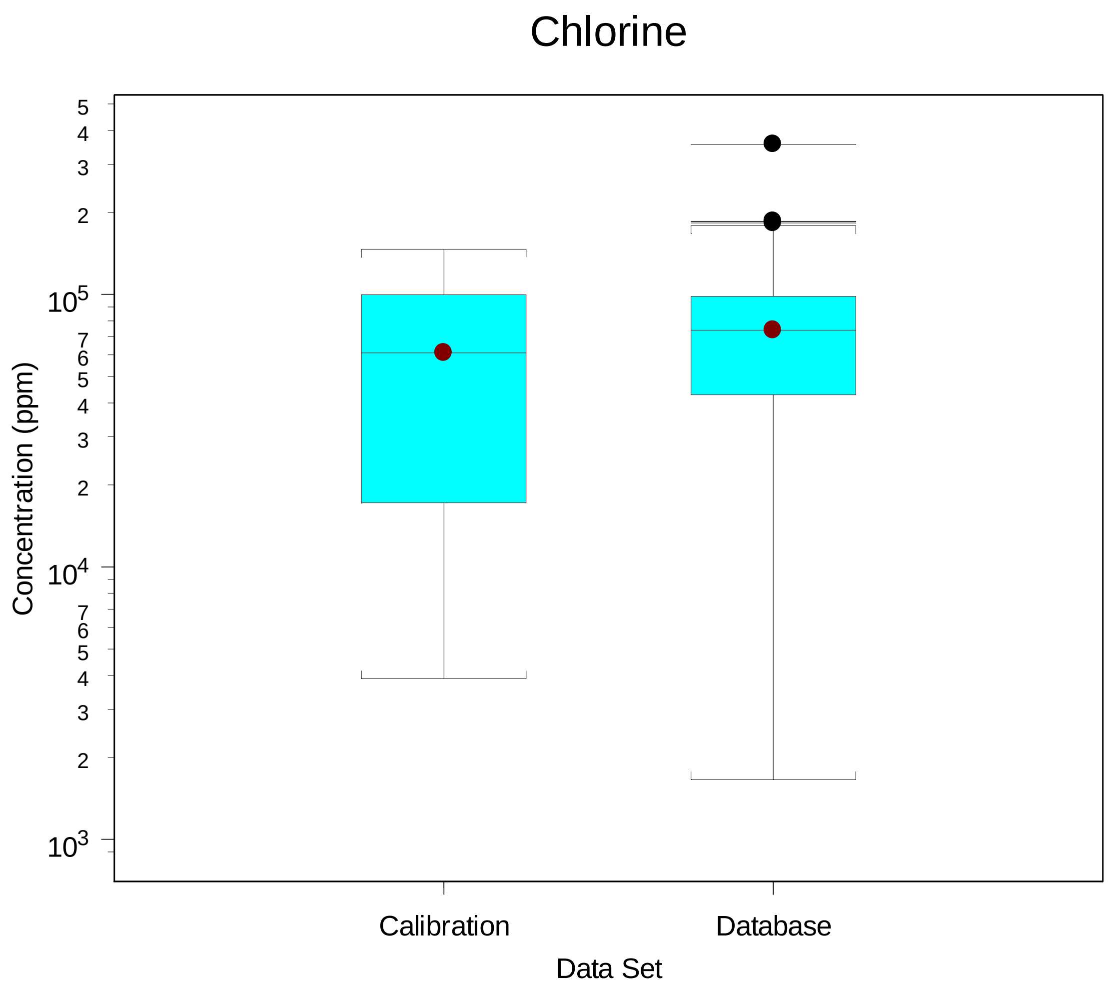
N	fit (WLS)	LCL95	UCL95	fit (WLS-MOX)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
7.50E-04	**8954**	0	25128	**7380**	0	17883	**5754**	2496	13254
1.00E-03	**11939**	0	30567	**9841**	0	21914	**8073**	3508	18565
2.50E-03	**29846**	489	59203	**24602**	5582	43621	**23731**	10365	54302
5.00E-03	**59693**	18117	101268	**49203**	22105	76301	**53650**	23523	122299
7.50E-03	**89539**	38489	140588	**73805**	40301	107309	**86456**	37992	196645
1.00E-02	**119385**	60272	178498	**98406**	59336	137476	**121290**	53384	275440
1.50E-02	**179078**	106252	251903	**147609**	98810	196409	**195455**	86221	442882
2.00E-02	**238770**	154178	323362				**274205**	121153	620343
2.98E-02	**355767**	251307	460228				**438411**	194135	989667

N=Normalized count value

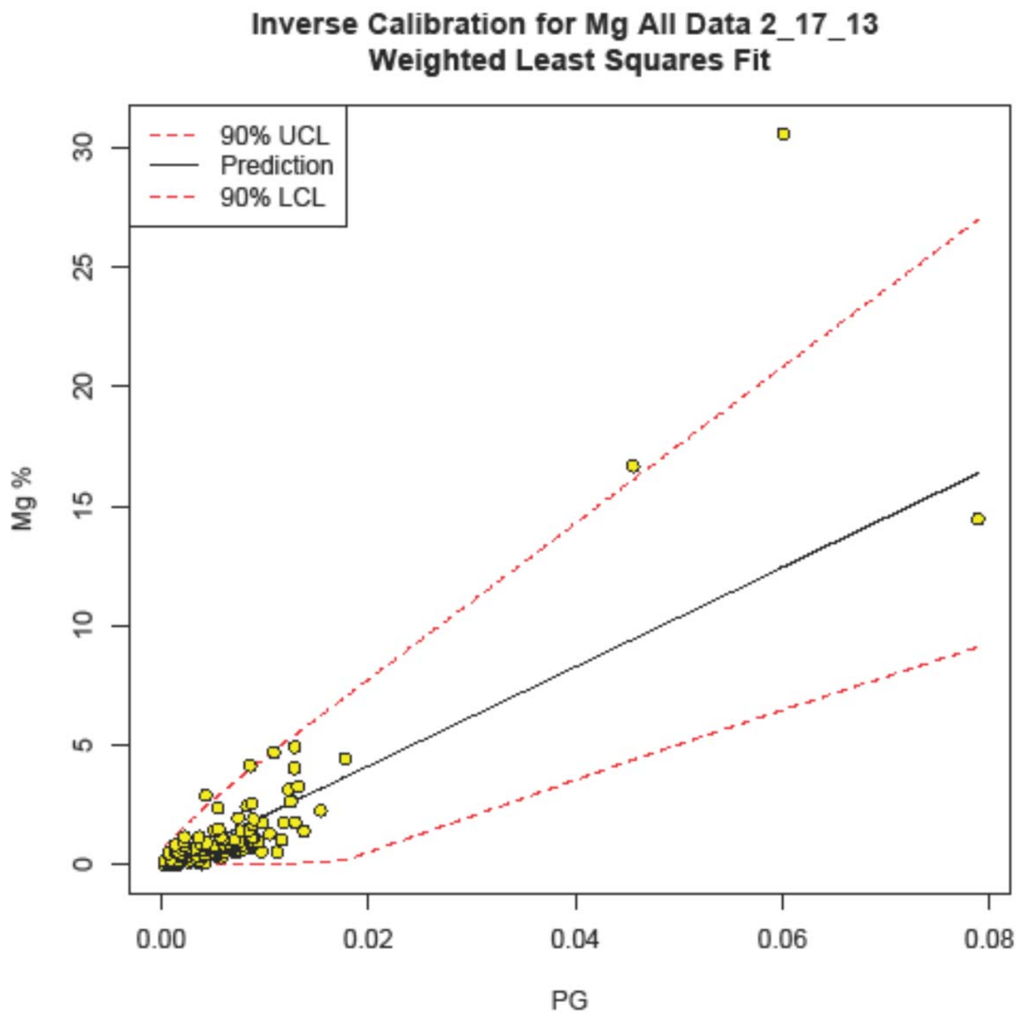
fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

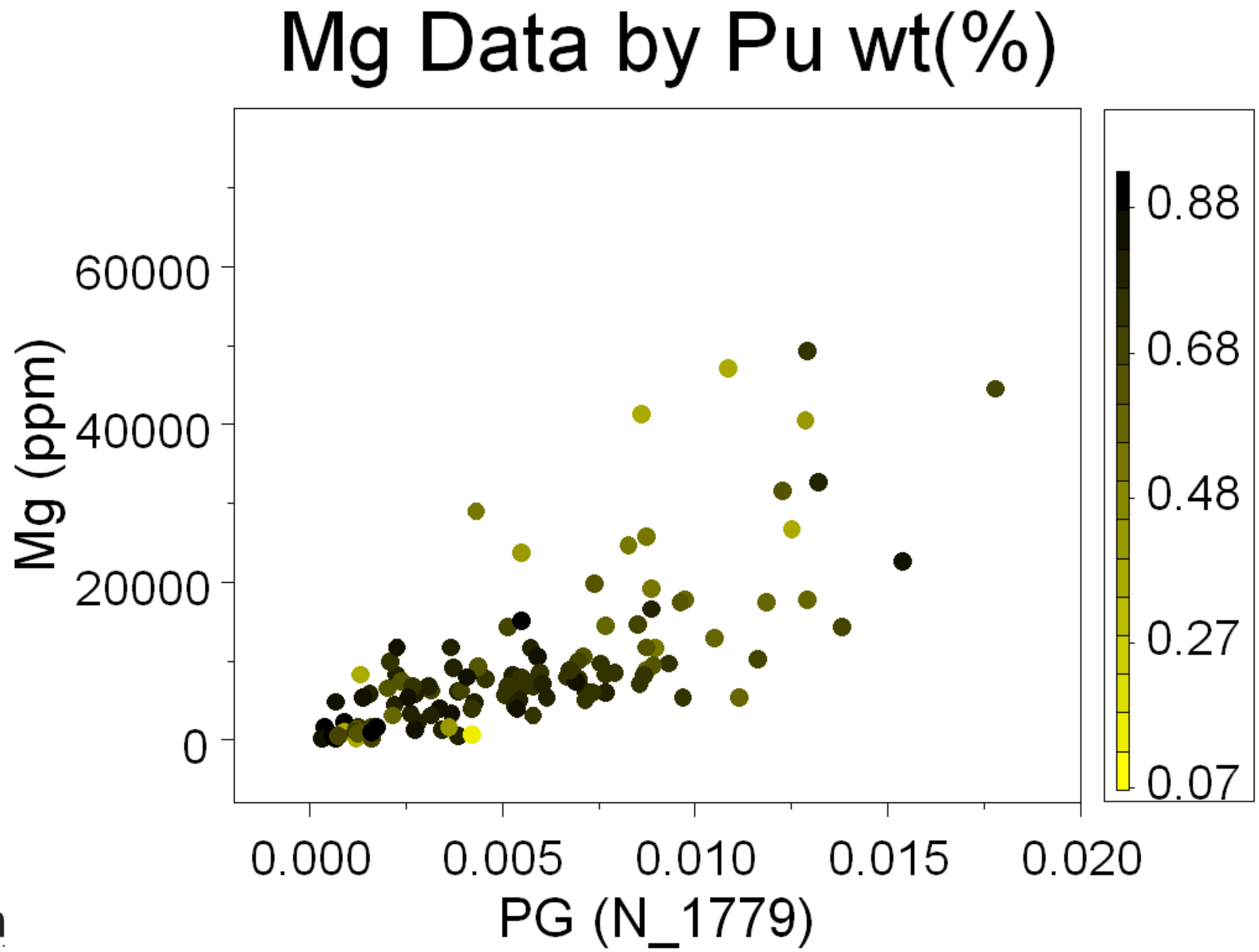
Data Coverage



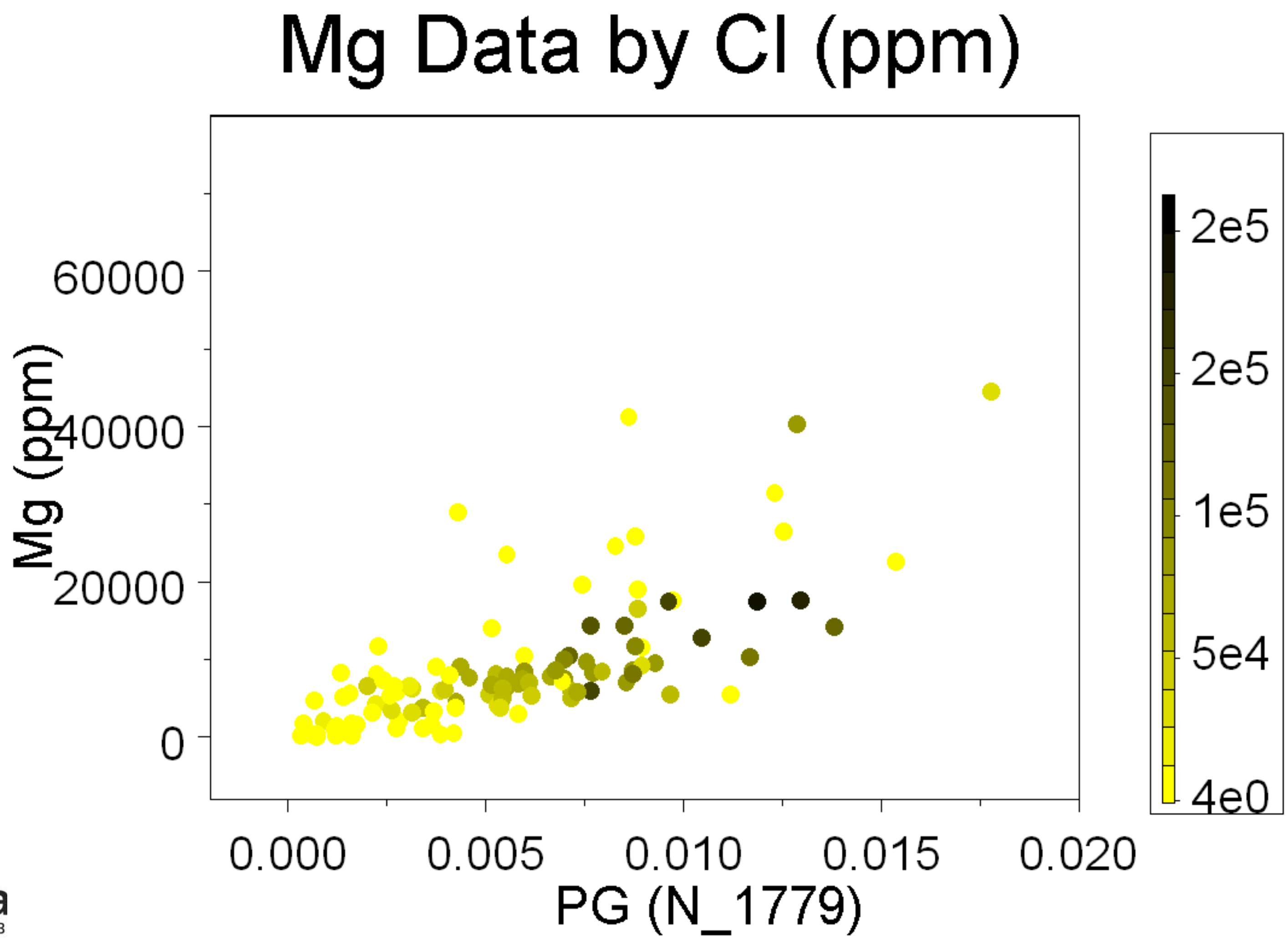
Magnesium


Inverse Calibration for Mg All Data 2_17_13
Weighted Least Squares Fit
90% UCL
Prediction
90% LCL
Mg %
PG
0
5
10
15
20
25
30
0.00
0.02
0.04
0.06
0.08

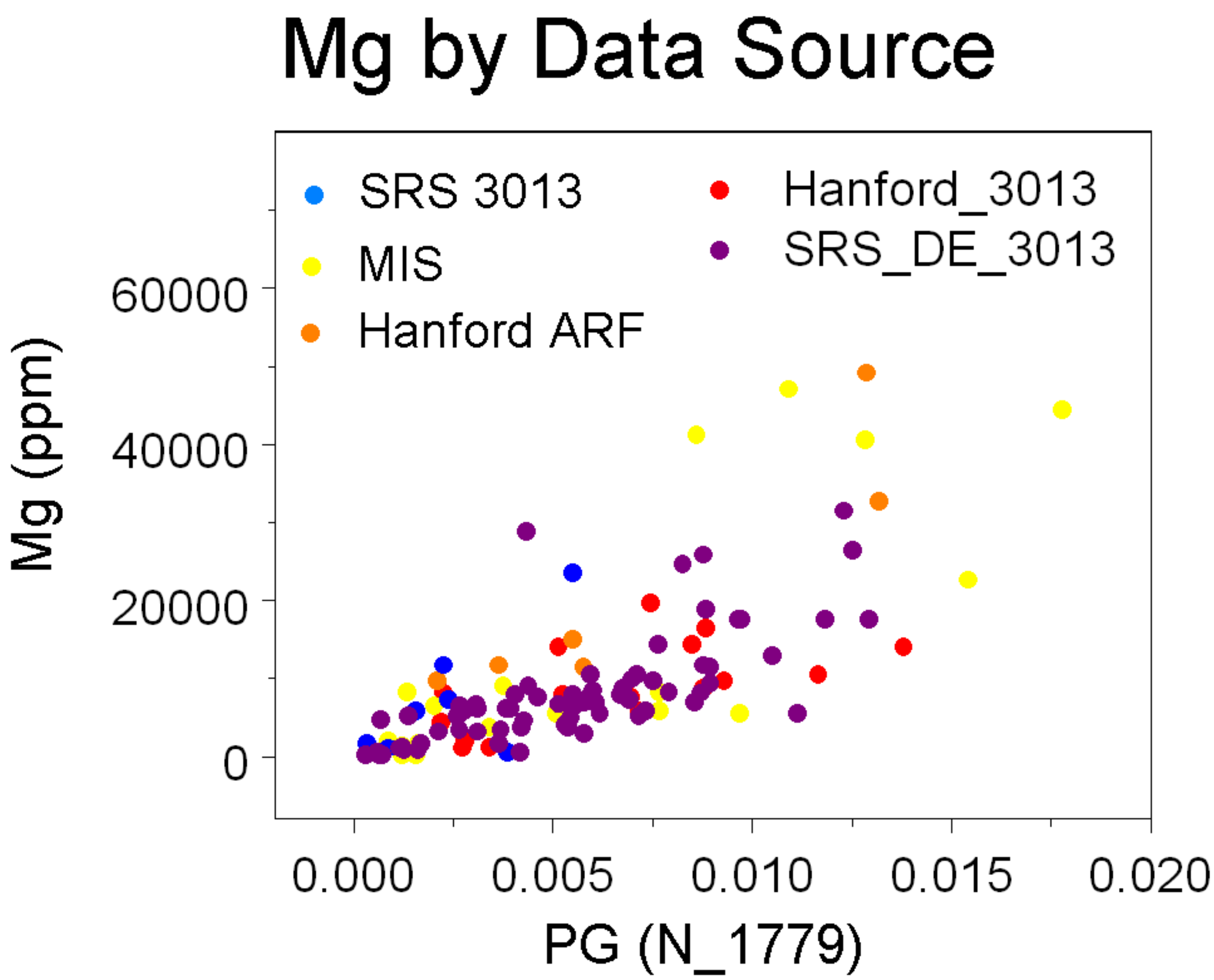
Magnesium—Sources of Variability



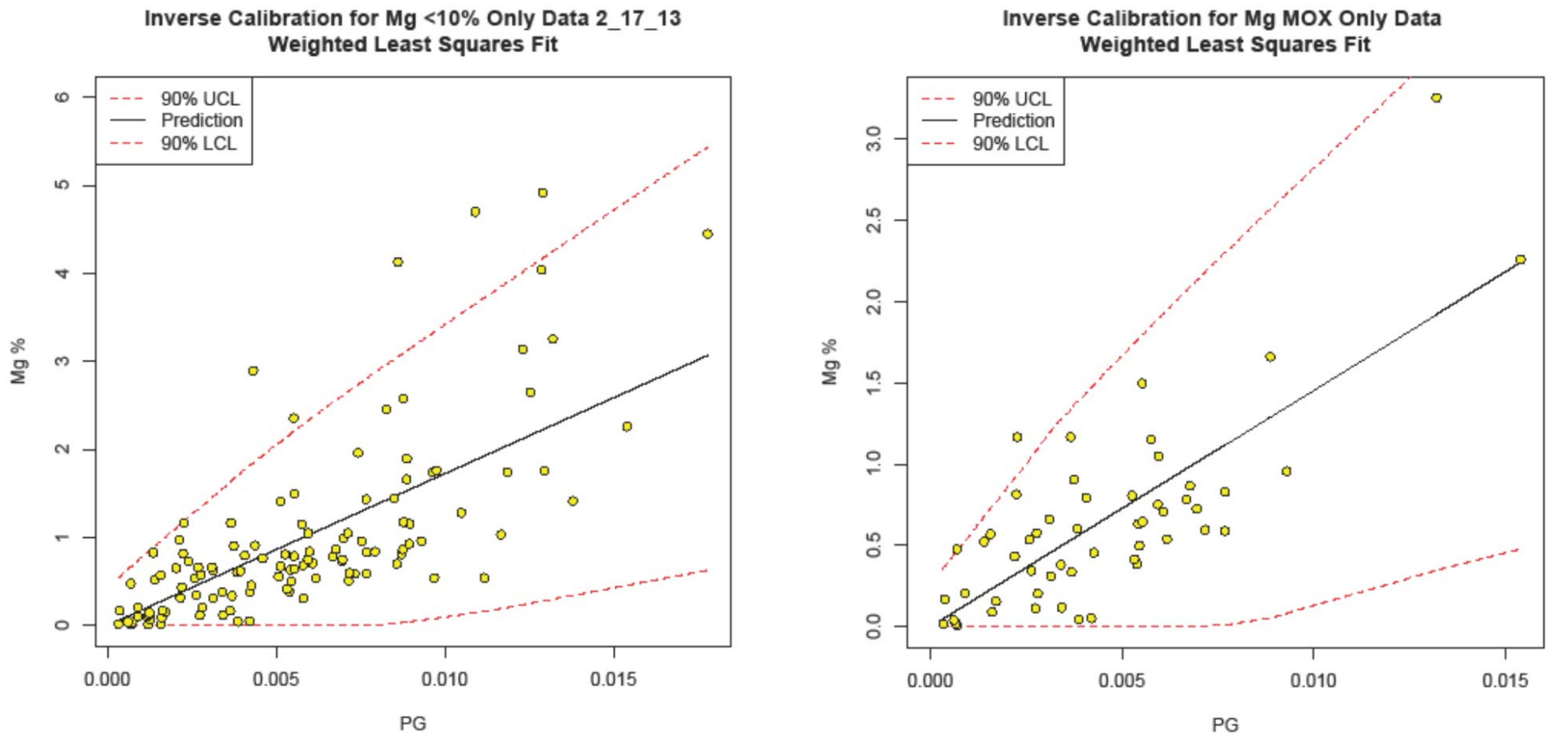
Magnesium—Sources of Variability



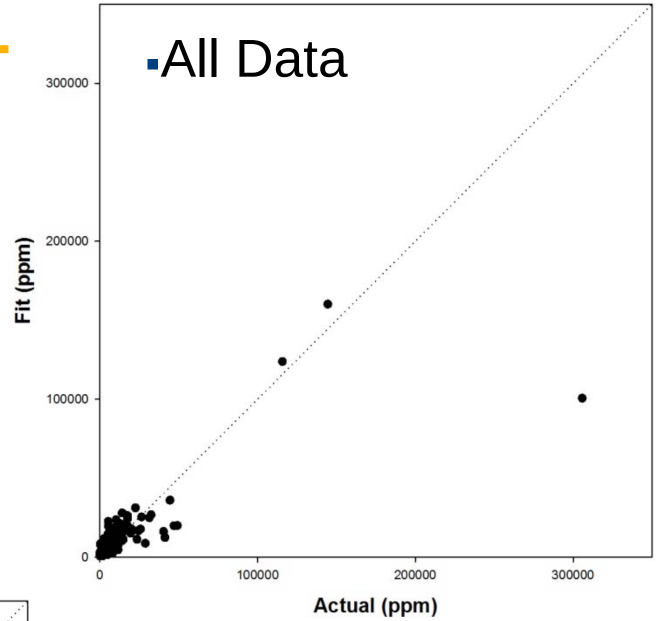
Magnesium—Sources of Variability

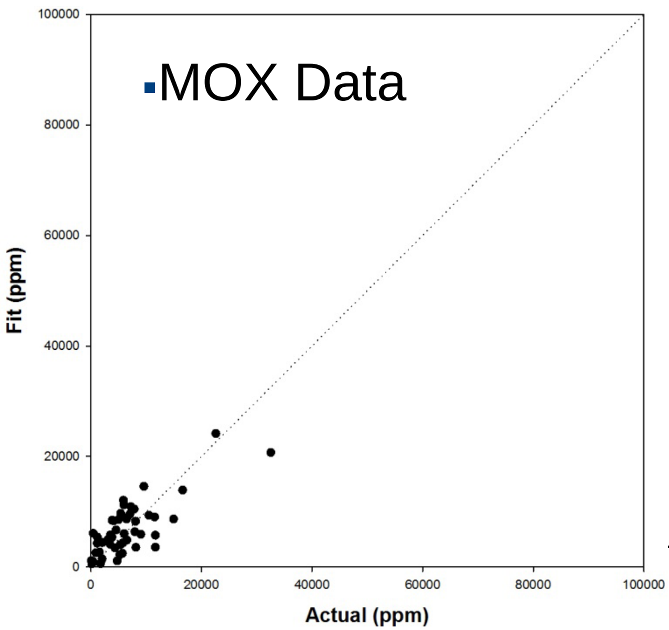


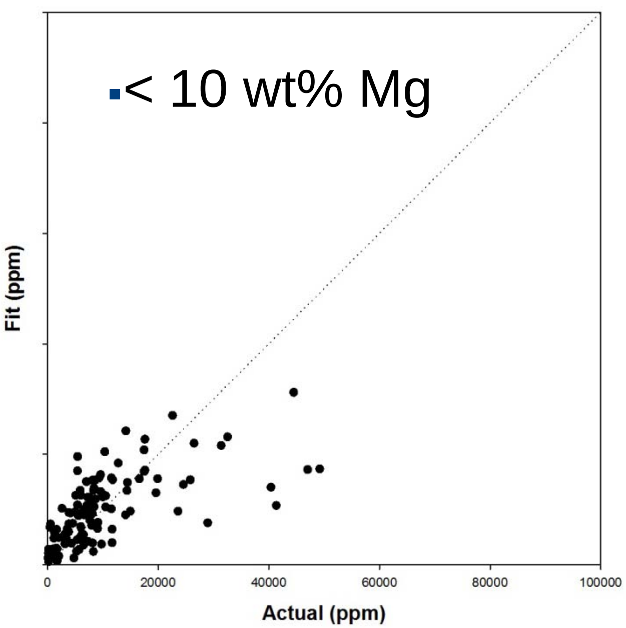
Magnesium—Reduced Variability



Diagnostic Plots







COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR Mg

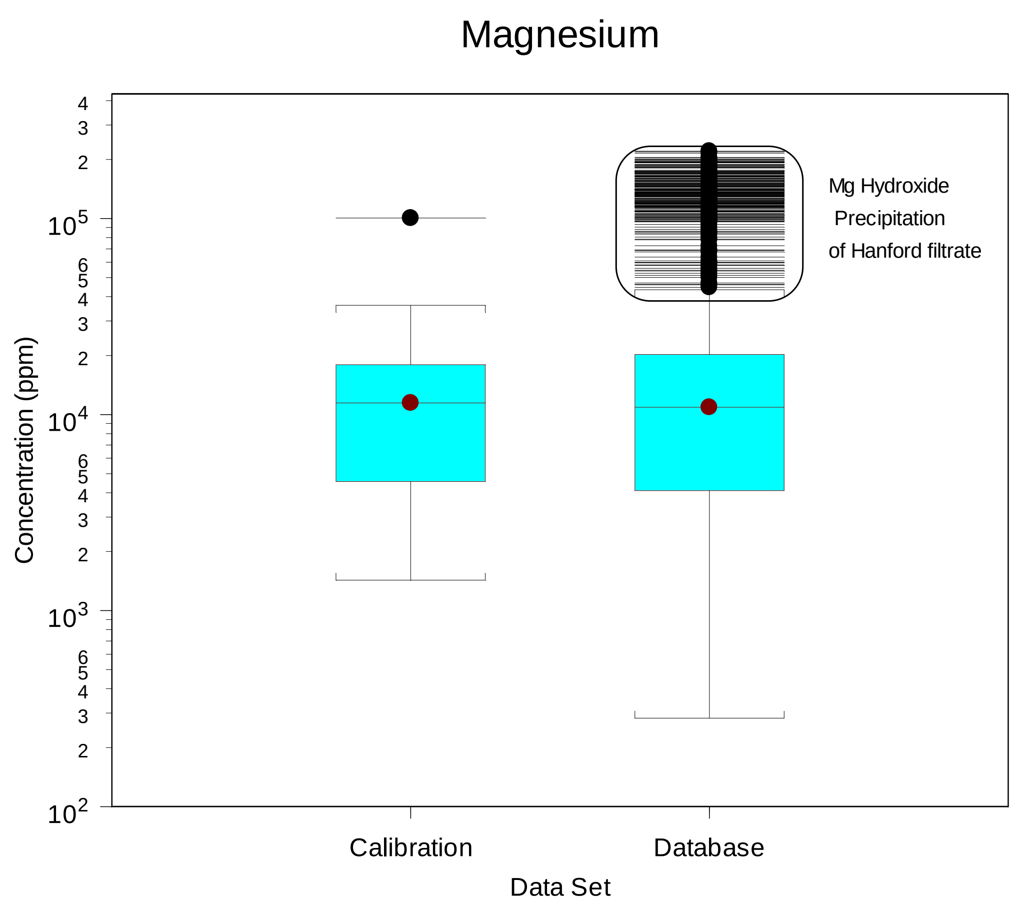
N	fit (WLS)	LCL95	UCL95	fit (WLS-MOX)	LCL95	UCL95	fit (WLS <10%)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**2030**	0	10862	**1567**	0	7468	**1754**	0	8408	**975**	134	4308
2.50E-03	**5074**	0	19000	**3918**	0	13199	**4386**	0	14872	**2915**	541	16298
5.00E-03	**10148**	0	29850	**7836**	0	20995	**8772**	0	23612	**6677**	1246	37450
7.50E-03	**15221**	0	39382	**11754**	0	27939	**13159**	0	31366	**10842**	1986	60015
1.00E-02	**20295**	0	48234	**15672**	0	34450	**17545**	0	38611	**15294**	2759	83937
2.50E-02	**50738**	6140	95335	**39179**	8606	69752	**43862**	10119	77605	**45744**	7991	252859
5.00E-02	**101476**	37391	165560	**78358**	33075	123640	**87724**	38967	136480	**104778**	18265	606005
7.50E-02	**152214**	72498	231929	**117537**	59672	175401				**170147**	29106	1000632
1.00E-01	**202952**	109505	296398							**240001**	38929	1381320
1.10E-01	**223247**	124658	321835							**268972**	42217	1517279

N=Normalized count value

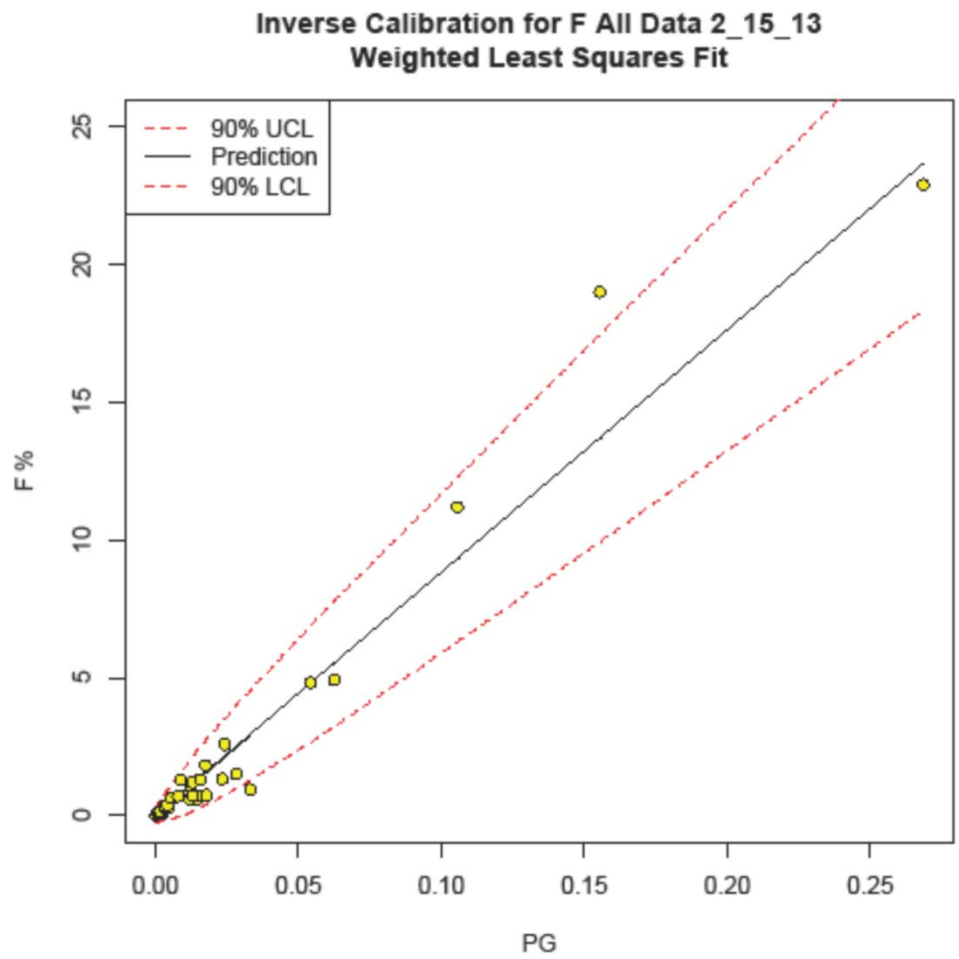
fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

Data Coverage

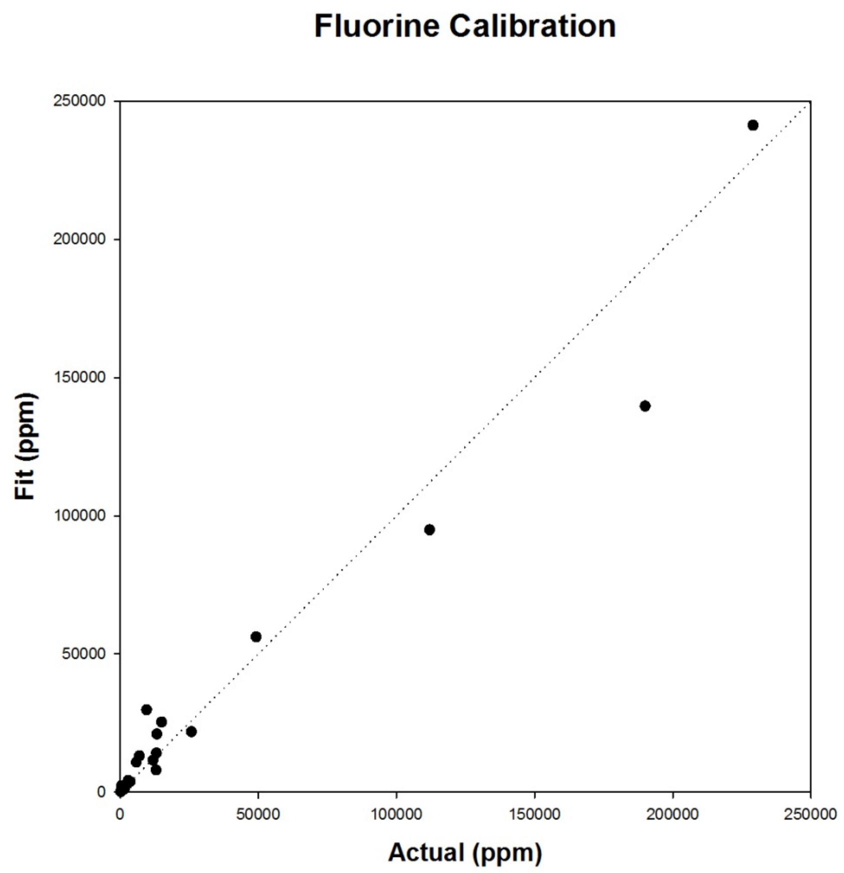


Fluorine



Inverse Calibration for F All Data 2_15_13
Weighted Least Squares Fit
90% UCL
Prediction
90% LCL
F %
PG
0
5
10
15
20
25
0.00
0.05
0.10
0.15
0.20
0.25

Diagnostic Plot



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR F

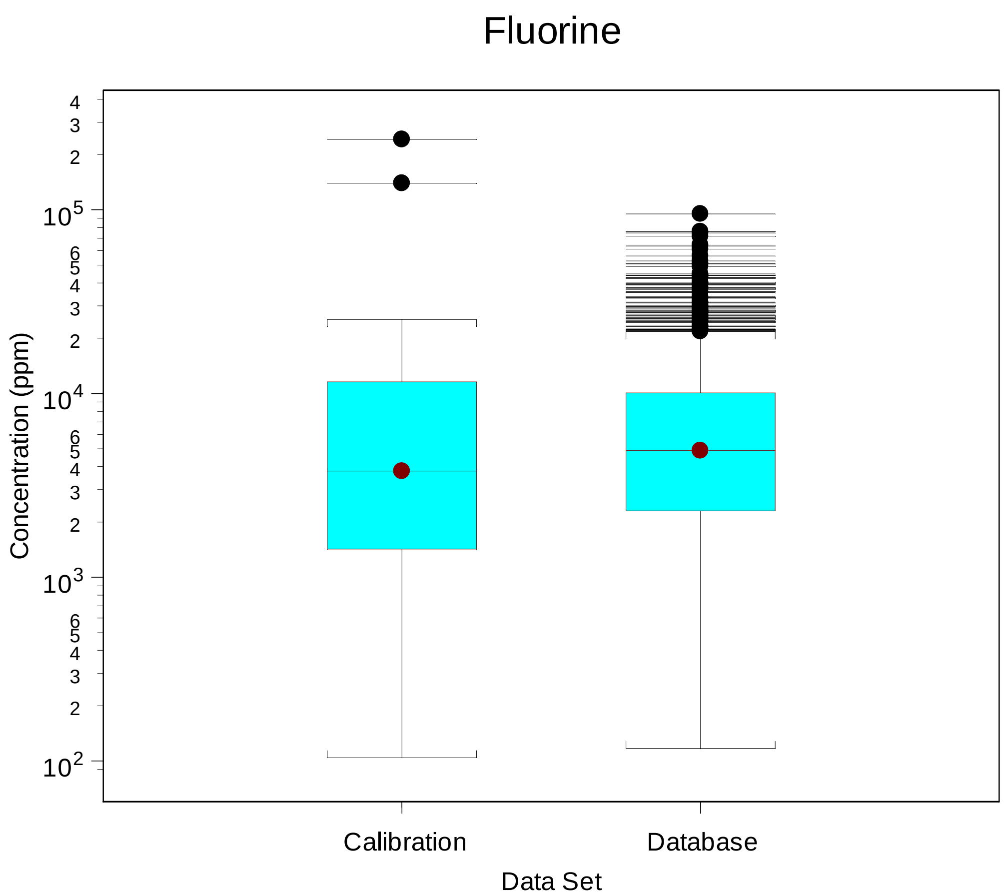
F						
N	fit (WLS)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**899**	0	4791	**686**	257	2222
2.50E-03	**2247**	0	8299	**1694**	546	5491
5.00E-03	**4494**	0	13015	**3355**	1026	10943
7.50E-03	**6741**	0	17173	**5003**	1506	16399
1.00E-02	**8988**	0	21042	**6644**	1984	21860
2.50E-02	**22469**	3258	41680	**16397**	4842	54716
5.00E-02	**44938**	17353	72524	**32474**	9544	109828
7.50E-02	**67407**	33106	101709	**48434**	14173	165381
1.00E-01	**89876**	49677	130076	**64317**	18726	221374
1.50E-01	**134815**	84159	185470	**95926**	27611	334680
2.00E-01	**179753**	119662	239844	**127383**	36198	449747
2.50E-01	**224691**	155765	293618	**158729**	44488	566576
2.69E-01	**241768**	169595	313940	**170616**	47560	611432

N=Normalized count value

fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

Data Coverage

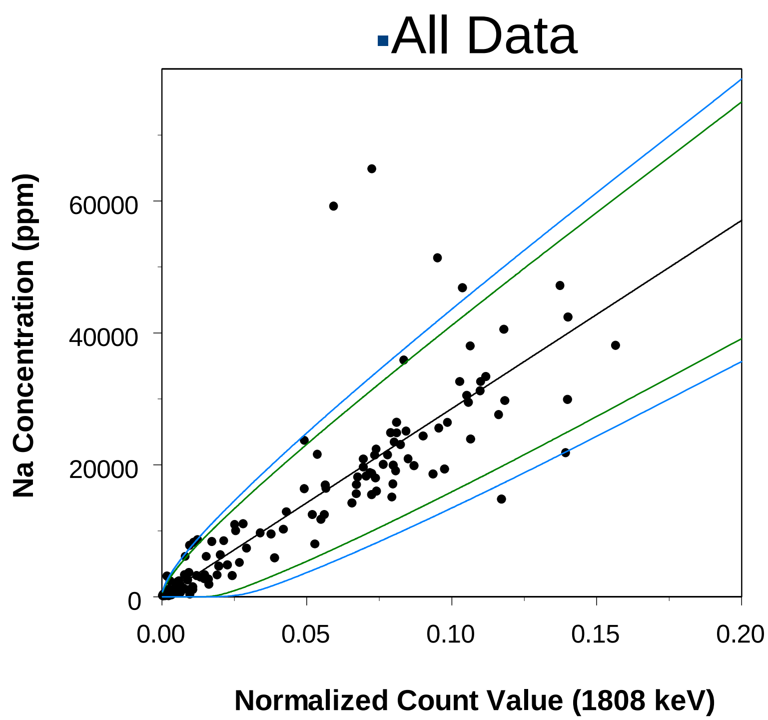


Summary

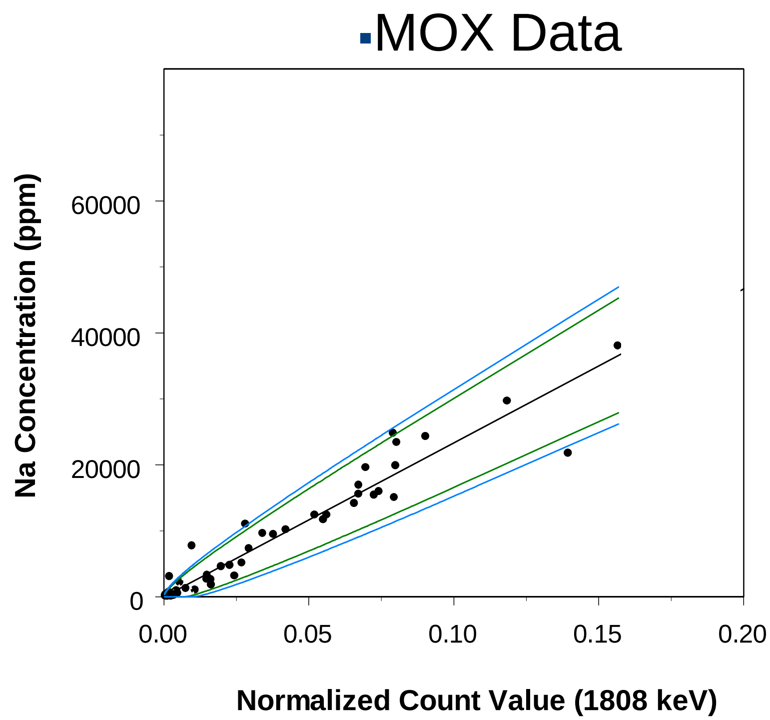
- **New calibration equations were developed using WLS**
- **New method and new data (113→ 166 data points)**
  - Includes results from FY12 DE
  - Additional data for F from 3013 DE
- **Reduced uncertainty in estimates (on the order of ~50%)**
- **Variability (scatter) is a problem in data for several elements**
- **Can reduce variability by restricting data sets; however models only valid for limited set of data**
- **Next steps**
  - Assist MOX with additional analyses
  - White paper
  - Update database

ADDITIONAL DATA

Sodium



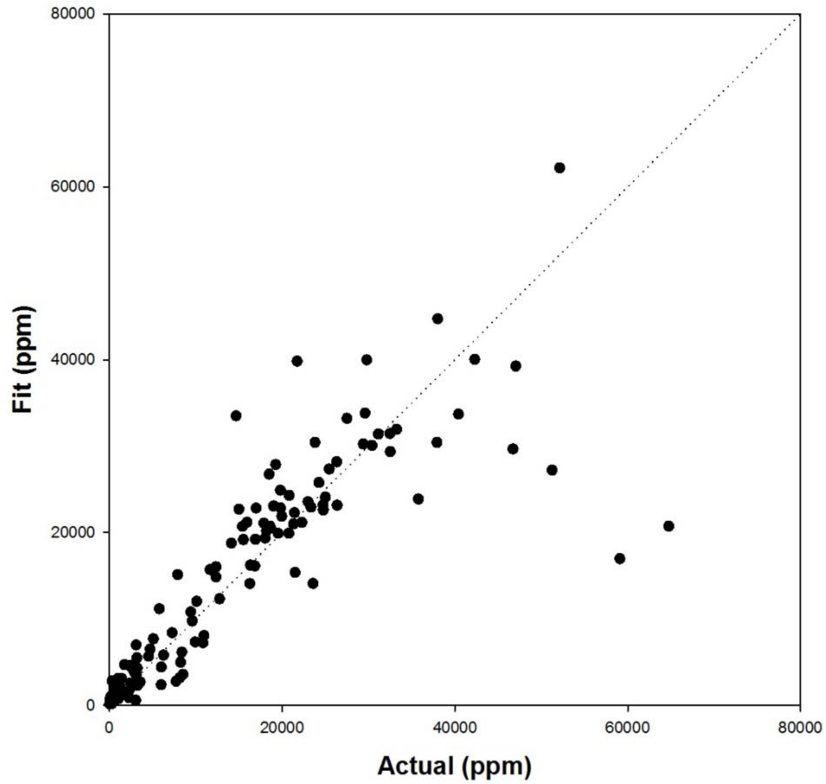
▪All Data
Na Concentration (ppm)
0
20000
40000
60000
0.00
0.05
0.10
0.15
0.20
Normalized Count Value (1808 keV)



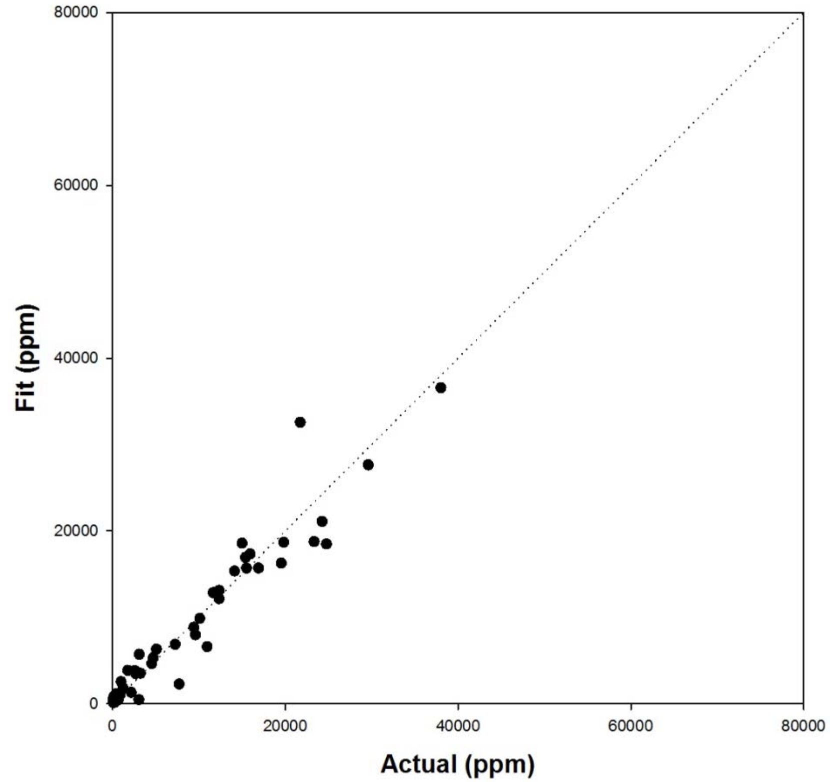
▪MOX Data
Na Concentration (ppm)
0
20000
40000
60000
0.00
0.05
0.10
0.15
0.20
Normalized Count Value (1808 keV)

Diagnostic Plots

- All Data



- MOX Data



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR Na

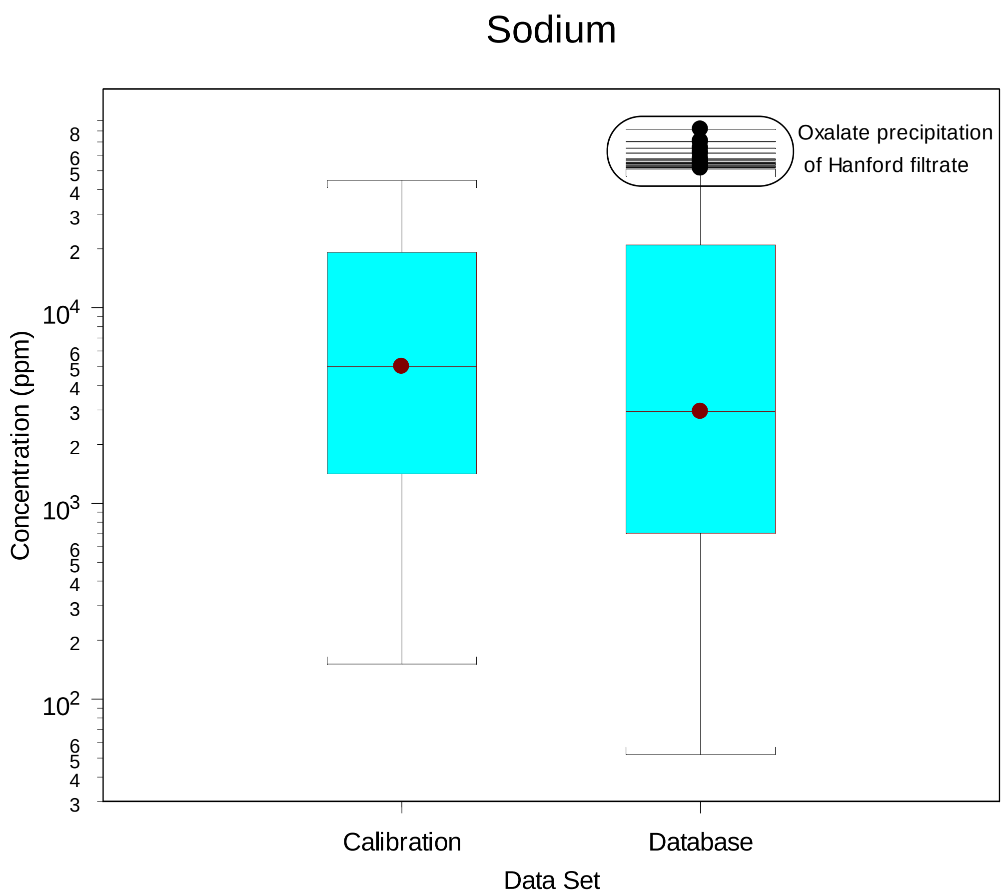
N	fit (WLS)	LCL95	UCL95	fit (WLS-MOX)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**285**	0	1790	**233**	0	1032	**120**	38	375
2.50E-03	**713**	0	3083	**583**	0	1838	**357**	114	1116
5.00E-03	**1426**	0	4774	**1166**	0	2939	**815**	261	2547
7.50E-03	**2139**	0	6238	**1749**	0	3920	**1322**	423	4126
1.00E-02	**2852**	0	7586	**2333**	0	4840	**1862**	596	5811
2.50E-02	**7131**	0	14620	**5831**	1854	9809	**5549**	1780	17296
5.00E-02	**14262**	3650	24873	**11663**	6003	17323	**12674**	4069	39469
7.50E-02	**21392**	8372	34413	**17494**	10519	24469	**20546**	6600	63952
1.00E-01	**28523**	13459	43588	**23325**	15221	31429	**28948**	9302	90067
1.50E-01	**42785**	24264	61306	**34988**	24942	45034	**46929**	15088	145937
2.00E-01	**57047**	35578	78515				**66118**	21266	205531
2.50E-01	**71308**	47214	95402				**86257**	27752	268058
2.85E-01	**81291**	55498	107085				**100833**	32448	313300

N=Normalized count value

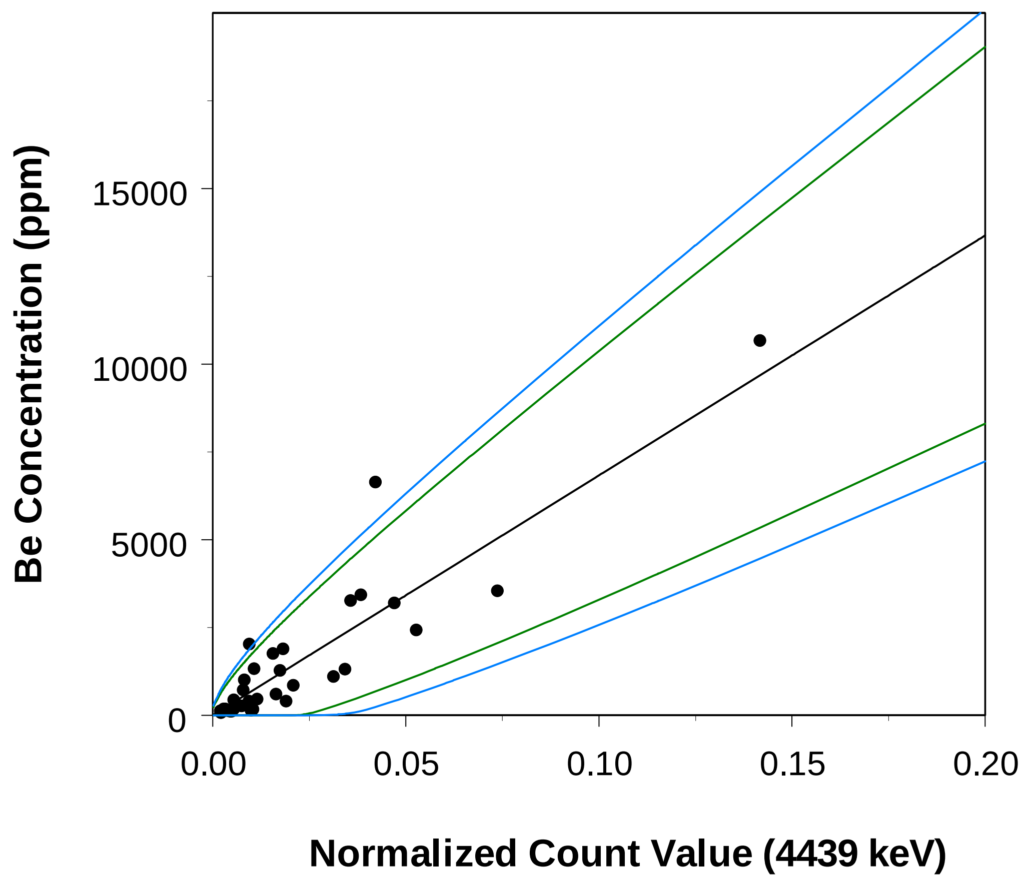
fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

Data Coverage

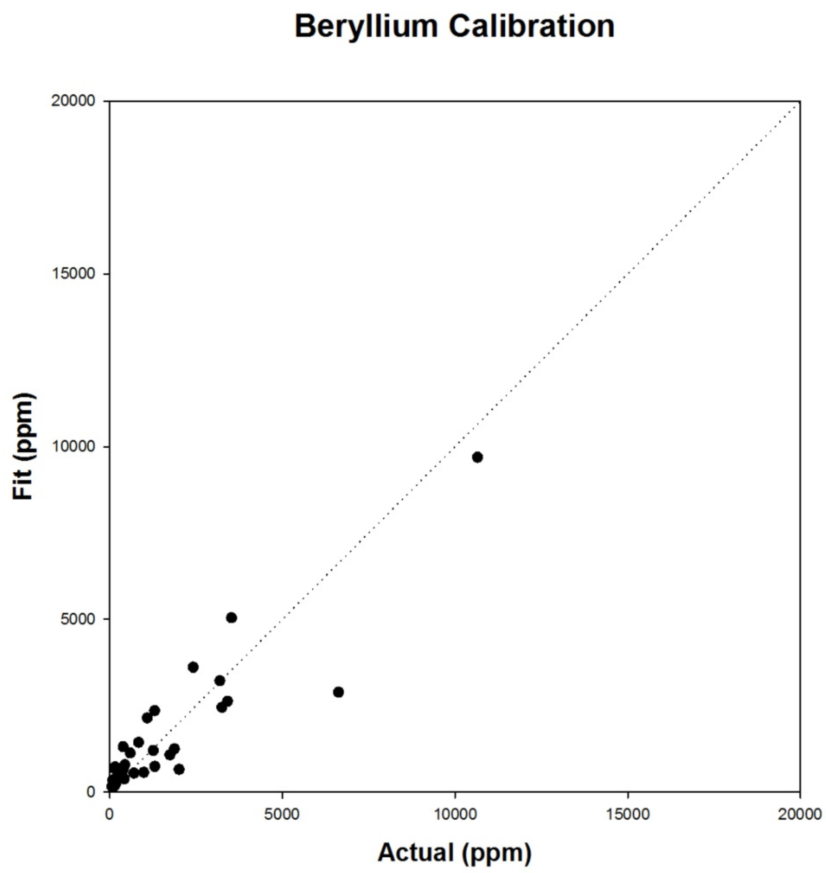


Beryllium



Be Concentration (ppm)
15000
10000
5000
0
0.00
0.05
0.10
0.15
0.20
Normalized Count Value (4439 keV)

Diagnostic Plot



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR Be

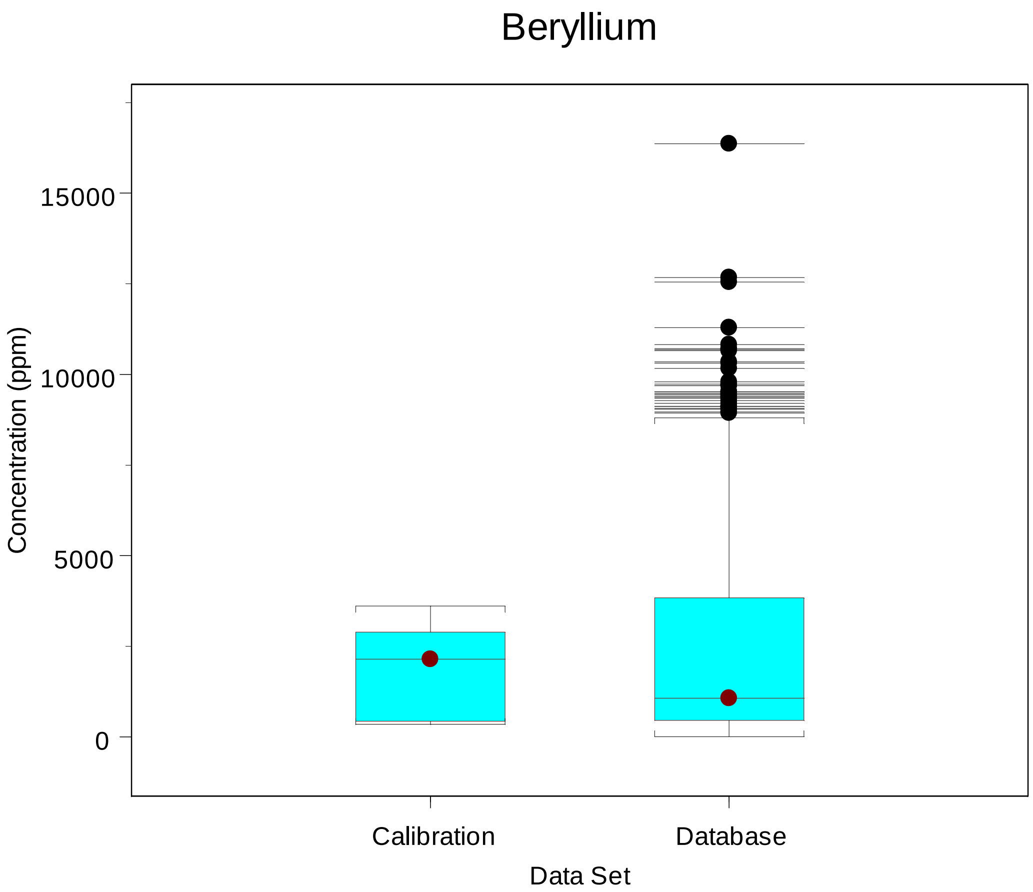
N	fit (WLS)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**68**	0	502	**31**	0	30
2.50E-03	**171**	0	820	**92**	17	326
5.00E-03	**342**	0	1243	**208**	51	835
7.50E-03	**512**	0	1611	**335**	85	1363
1.00E-02	**683**	0	1950	**470**	120	1910
2.50E-02	**1708**	0	3723	**1383**	343	5561
5.00E-02	**3416**	513	6318	**3128**	755	12887
7.50E-02	**5123**	1501	8745	**5043**	1199	21436
1.00E-01	**6831**	2571	11091	**7077**	1658	30830
1.50E-01	**10247**	4841	15652	**11408**	2543	50635

N=Normalized count value

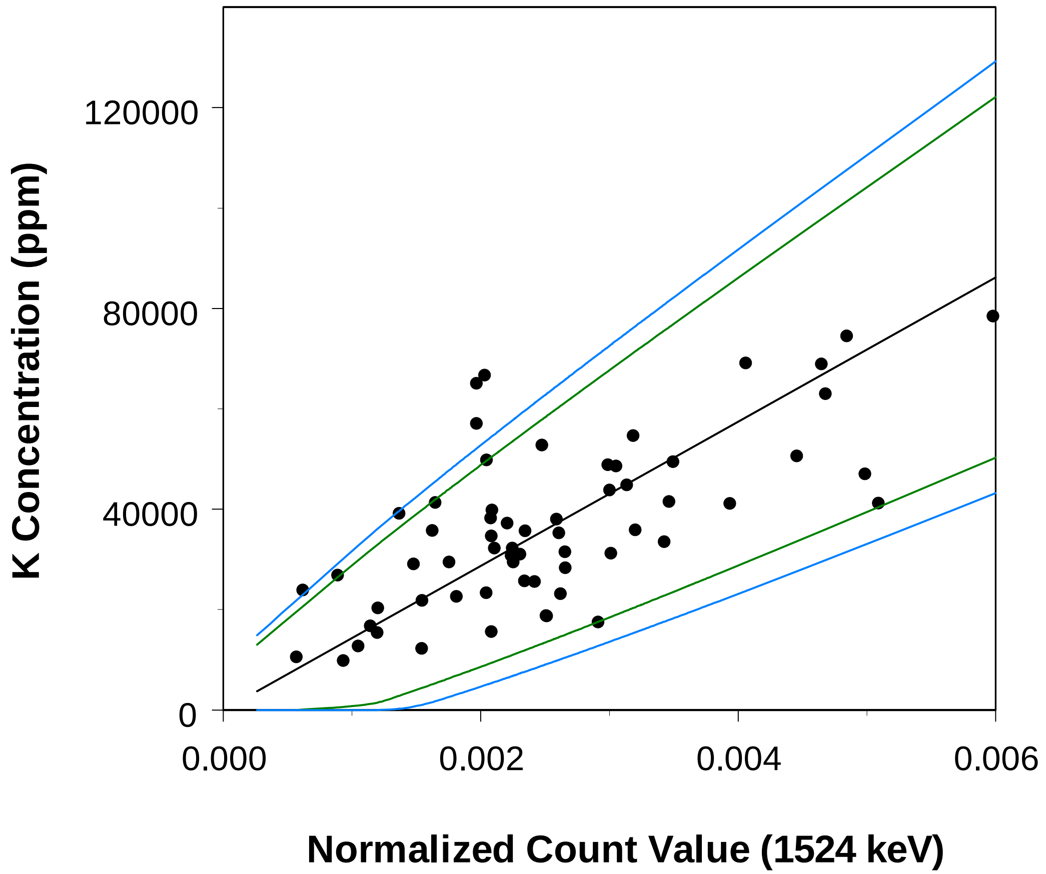
fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

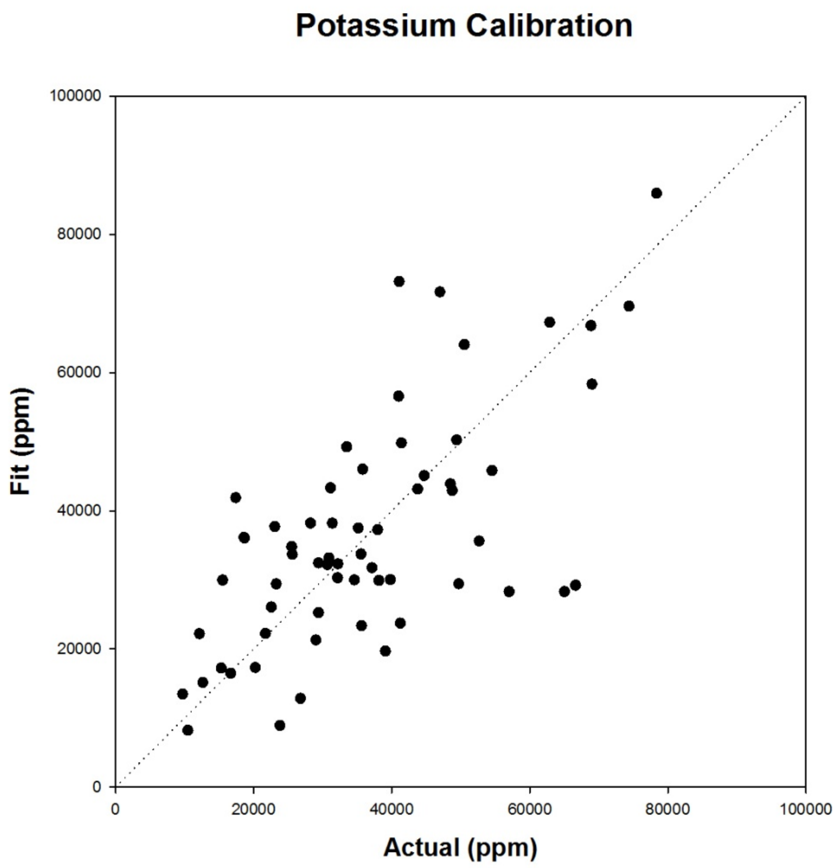
Data Coverage



Potassium


120000
80000
40000
0
0.000
0.002
0.004
0.006
K Concentration (ppm)
Normalized Count Value (1524 keV)

Diagnostic Plot



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR K

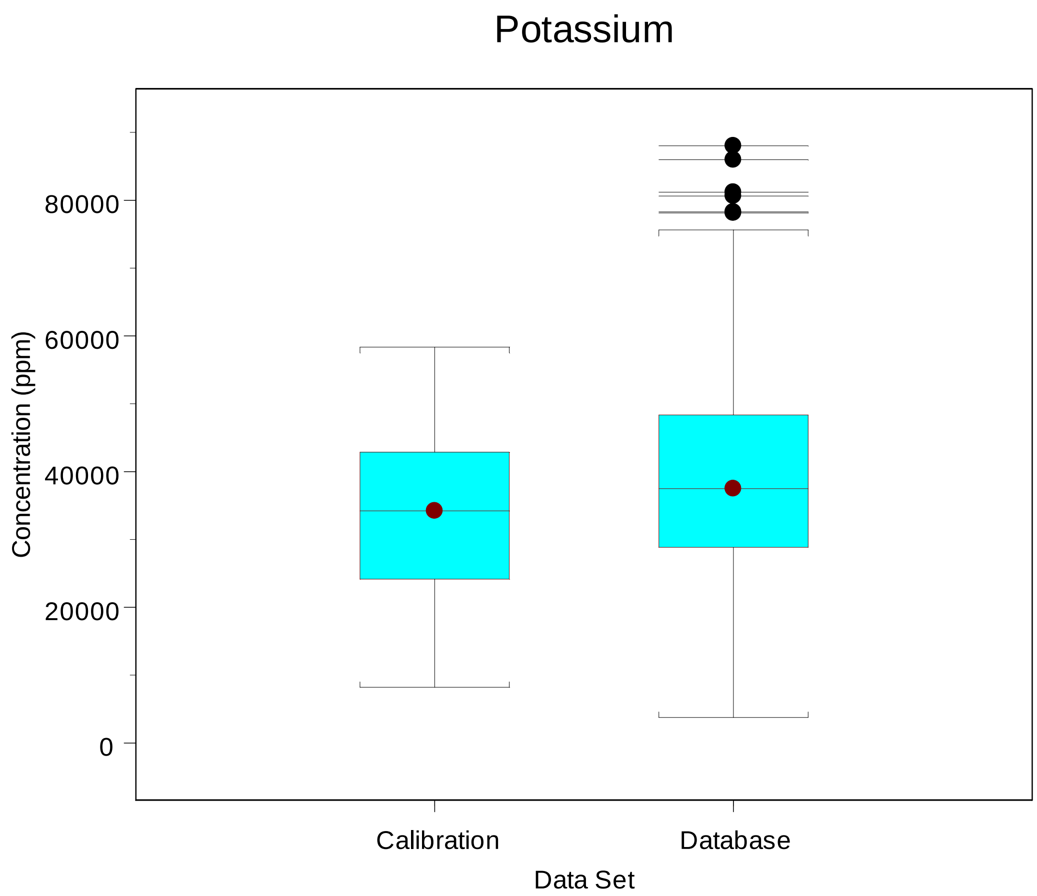
N	fit (WLS)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**14364**	0	31843	**18592**	8773	39043
2.50E-03	**35911**	9039	62782	**33880**	16352	70384
5.00E-03	**71821**	33060	110583	**53345**	25270	112119
6.13E-03	**88006**	44539	131472	**60938**	28869	130050

N=Normalized count value

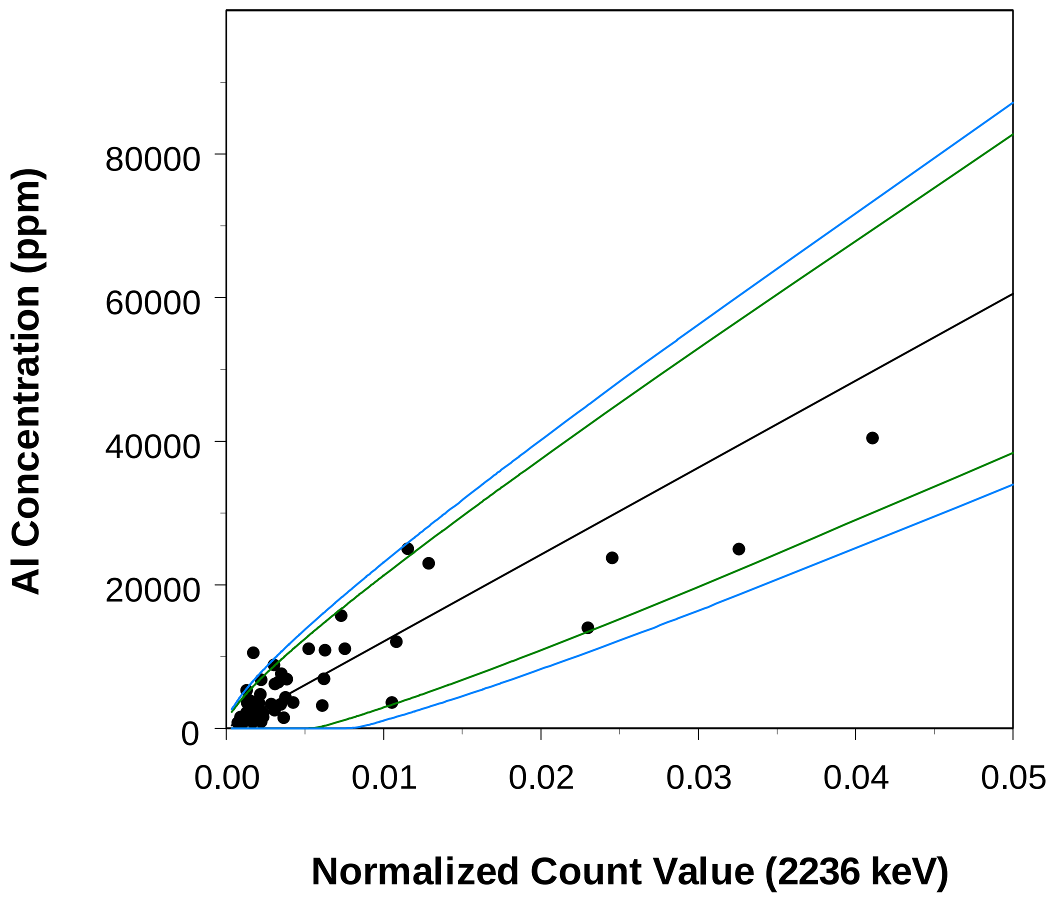
fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

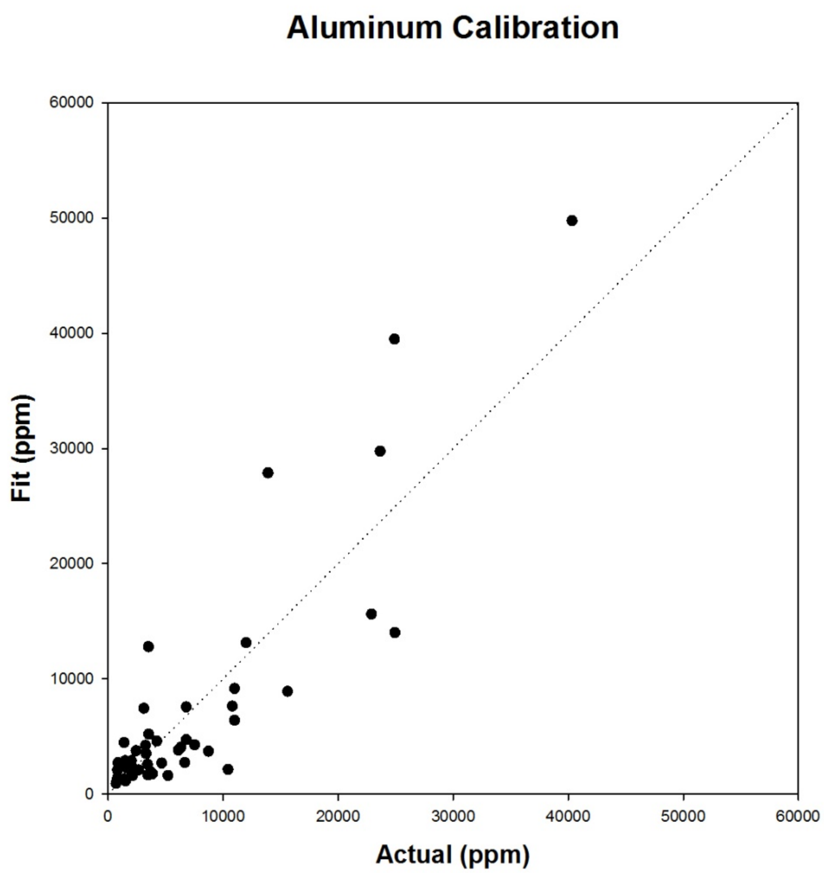
Data Coverage



Aluminum


Al Concentration (ppm)
80000
60000
40000
20000
0
0.00
0.01
0.02
0.03
0.04
0.05
Normalized Count Value (2236 keV)

Diagnostic Plot



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR Al

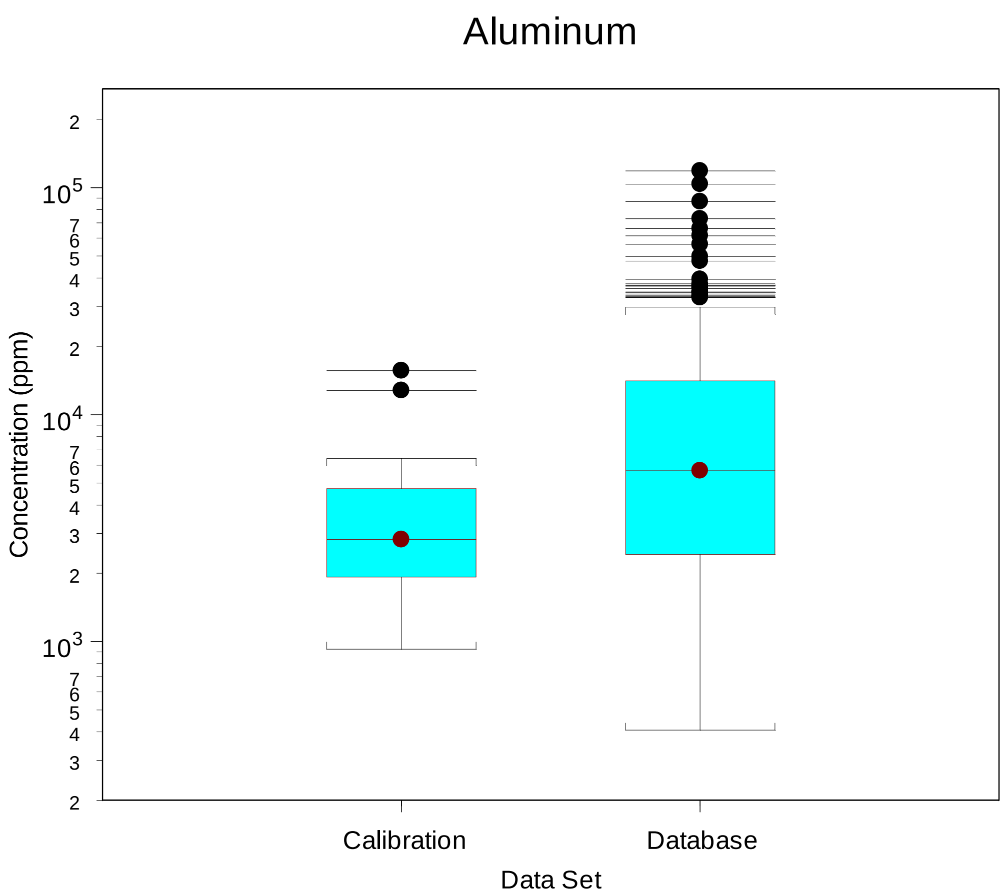
N	fit (WLS)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**1211**	0	4738	**1427**	429	5346
2.50E-03	**3027**	0	8494	**3111**	878	10737
5.00E-03	**6054**	0	13776	**5610**	1589	19462
7.50E-03	**9081**	0	18578	**7920**	2253	27891
1.00E-02	**12107**	1080	23135	**10116**	2876	36055
2.50E-02	**30269**	12176	48362	**22057**	5984	81210
5.00E-02	**60537**	33401	87674	**39776**	10716	155956

N=Normalized count value

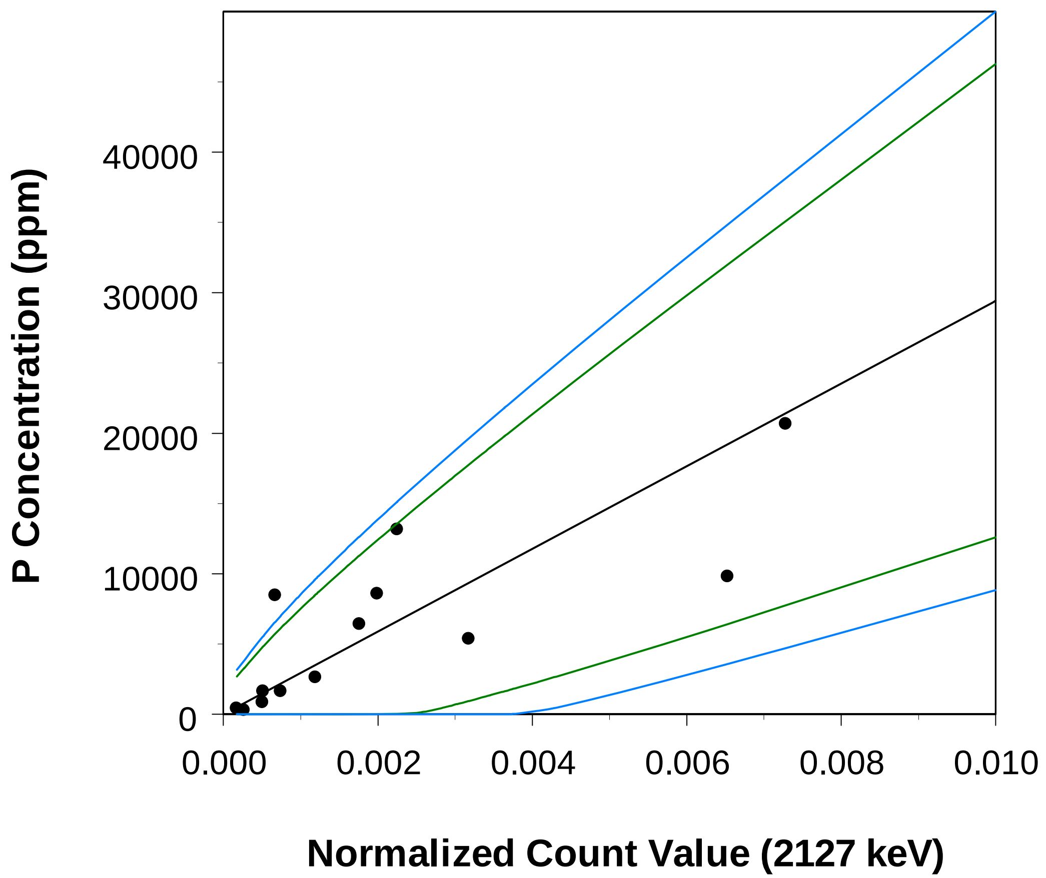
fit = concentration estimate (ppm)

LCL95 & UCL95 are upper and lower uncertainties (ppm) 95%

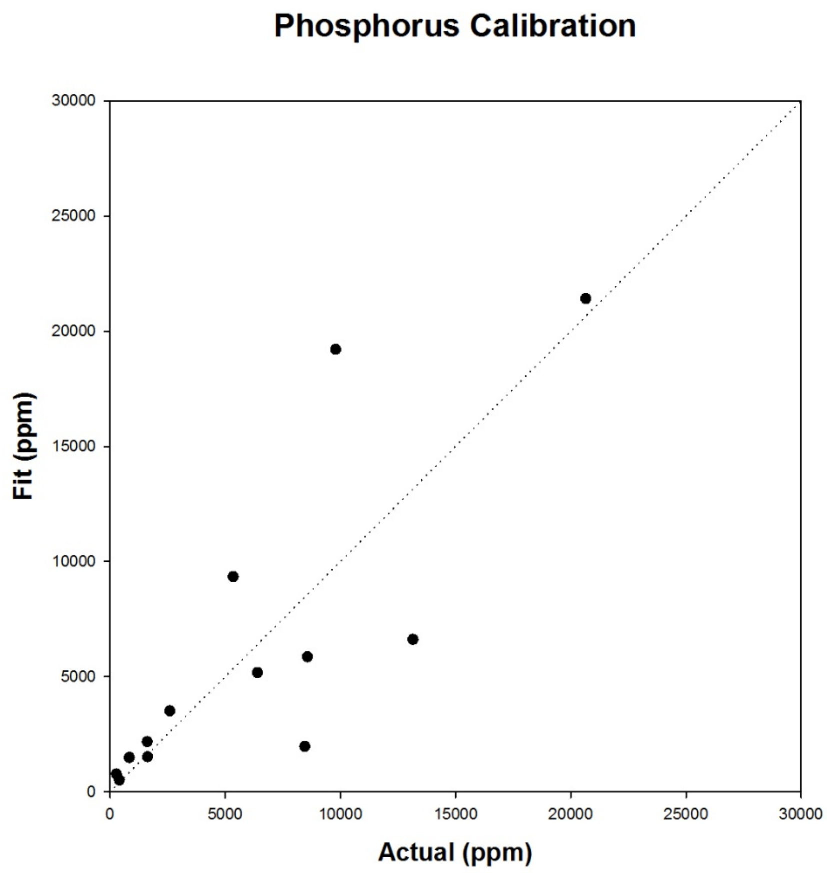
Data Coverage



Phosphorus


P Concentration (ppm)
0
10000
20000
30000
40000
0.000
0.002
0.004
0.006
0.008
0.010
Normalized Count Value (2127 keV)

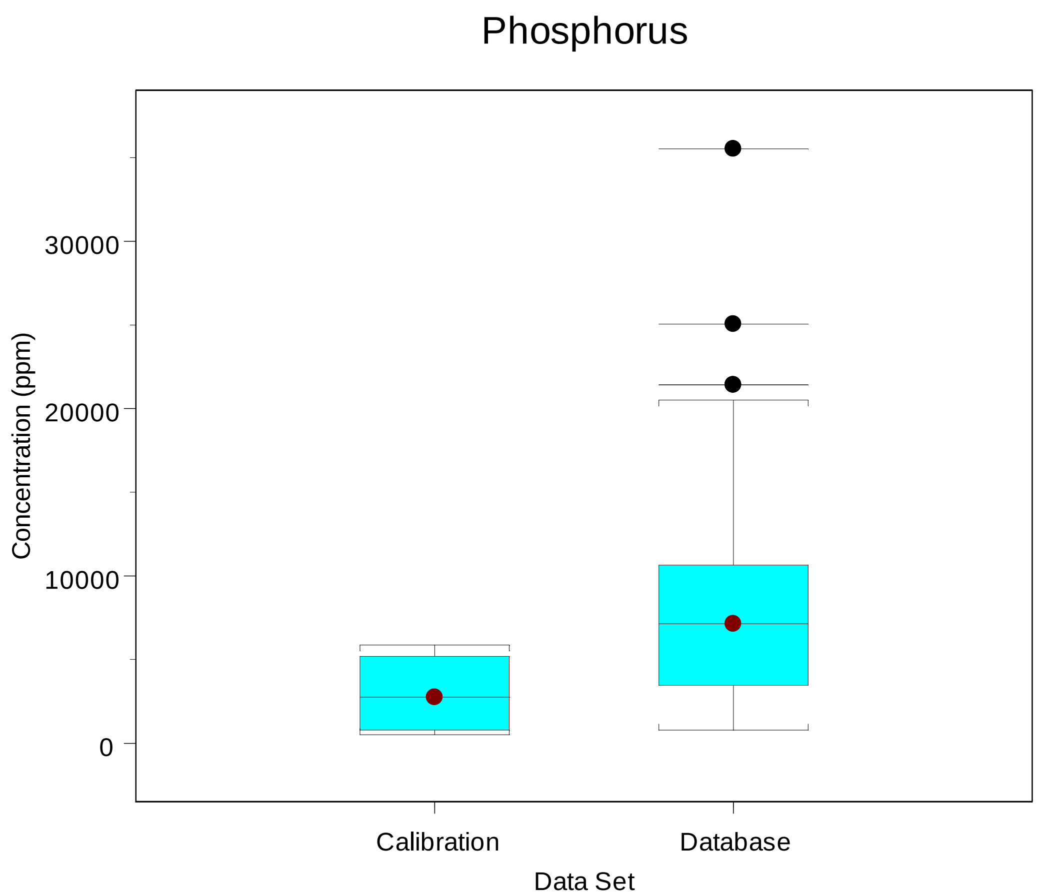
Diagnostic Plot



COMPARISON OF CALIBRATION PREDICTIONS AND UNCERTAINTES FOR P

N	fit (WLS)	LCL95	UCL95	fit (LOG-LOG)	LCL95	UCL95
1.00E-03	**2942**	0	8534	**2710**	569	13109
2.50E-03	**7356**	0	16363	**7071**	1441	34674
5.00E-03	**14711**	1353	28070	**14606**	2795	76093
7.50E-03	**22067**	4935	39198	**22327**	4023	124361
1.00E-02	**29422**	8777	50068	**30171**	5126	179478
1.50E-02	**44133**	16840	71426	**46119**	6958	310257
1.21E-02	**35530**	12079	58981	**36756**	5947	230451

Data Coverage



WLS Calibration Parameters

- Normalized counts
- (example)
- Slope (intercept=0)
- Concentration
- Estimate (ppm)
- t(n-1, 0.95)

Element	PGnew	b	se	Chem.New	wnew	wsum	sum1	sum2	wPGave	SDChem	t inverse	LCL(90%)	UCL(90%)
Be	0.1	1.46E-05	3.46E-04	6.83E+03	1.46E-04	1.18E-01	5.02E+04	34	7.25E-03	2.09E+03	1.69236	3.29E+03	1.04E+04
Al	0.02	8.26E-07	4.04E-05	2.42E+04	4.13E-05	1.81E-02	3.42E+05	48	2.57E-03	7.95E+03	1.67793	1.09E+04	3.75E+04
K	0.003	6.96E-08	4.90E-06	4.31E+04	2.32E-05	2.15E-03	2.26E+06	62	2.16E-03	1.47E+04	1.67022	1.85E+04	6.77E+04
F	0.25	1.11E-06	6.84E-05	2.25E+05	4.45E-06	2.01E-02	7.15E+05	27	2.12E-03	3.35E+04	1.7056	1.67E+05	2.82E+05
P	0.003	3.40E-07	1.57E-05	8.83E+03	1.13E-04	9.64E-03	7.97E+04	13	5.96E-04	4.57E+03	1.78229	6.80E+02	1.70E+04
Mg	0.02	4.93E-07	4.86E-05	4.06E+04	2.46E-05	6.88E-02	1.72E+06	121	2.03E-03	2.01E+04	1.65765	7.30E+03	7.39E+04
Na	0.1	3.51E-06	1.57E-04	2.85E+04	3.51E-05	2.83E-01	1.88E+06	145	2.96E-03	7.62E+03	1.65550	1.59E+04	4.11E+04
Cl	0.007	8.38E-08	7.14E-06	8.36E+04	1.20E-05	6.86E-03	5.93E+06	91	1.43E-03	2.48E+04	1.66196	4.23E+04	1.25E+05
Mg MOX	0.02	6.38E-07	4.69E-05	3.13E+04	3.19E-05	4.06E-02	4.32E+05	51	1.71E-03	1.35E+04	1.67592	8.75E+03	5.39E+04
Na MOX	0.1	4.29E-06	1.11E-04	2.33E+04	4.29E-05	2.37E-01	4.71E+05	67	1.99E-03	4.06E+03	1.66827	1.66E+04	3.01E+04
Cl MOX	0.007	1.02E-07	6.01E-06	6.89E+04	1.45E-05	4.29E-03	1.40E+06	35	1.11E-03	1.59E+04	1.69092	4.20E+04	9.58E+04
MG < 10%	0.02	5.70E-07	4.55E-05	3.51E+04	2.85E-05	6.88E-02	1.16E+06	118	2.02E-03	1.52E+04	1.65798	9.93E+03	6.02E+04

SDChem=se/b*sqrt(1/wnew+1/wsum+((PGnew-wPGave)^2*wsum)/(b^2*(wsum*sum(w*Chem.Be^2) - (sum(w*Chem.Be))^2)))

sum1 = sum(w*Chem.Be^2)
sum2 = sum(w*Chem.Be)

LCL=Chem.New-t*SDChem
UCL=Chem.New+t*SDChem

Review of Corrosion Conditions, Pitting, SCC, and Ties to 3013 Inventory

D. Kirk Veirs

LANL Corrosion Team and SRNL Corrosion Team

3013 Surveillance and Monitoring Program Review
Feb. 26 – 28, 2013
Savannah River Site

Introduction

The “Test Plan for Determining the Susceptibility of 3013 Containers to Stress Corrosion Cracking” (LA-UR-09-02953) identified four critical questions:

1. What is the RH inside the 3013 container, given its process/loading history, e.g. RH_{INT}?
2. What is the threshold RH that will support SCC, e.g. RH_{SCC}?
3. What containers have the residual stress exceeding K_{SCC}?
4. What configuration is needed for SCC initiation and propagation (i.e. does the salt need to be in direct contact with the container at an area of high stress)?

What is the RH inside the 3013 container, given its process/loading history, e.g. RH_{INT}?

Three sources of information:

1. SRS DE RH measurements at x years after loading (Nguyen).

2. LANL Large-Scale containers with RH sensors for bounding materials, i.e. with low $CaCl_2$ and low $MgCl_2$ where we expect high RH and with high $CaCl_2$ and high $MgCl_2$ where we expect low RH. Provides the decrease with time that can be coupled with SRS DE RH data to estimate initial loading value. (Narlesky)

3. LANL Small-Scale containers with RH sensors. Time data available for high-purity oxide material.(Veirs) One LANL MIS represented material to be loaded with this capability.

What is the RH inside the 3013 container, given its process/loading history, e.g. RH_{INT}? (continued)

Container	RH (%)	DE Identification	Corrosion Designation
Hanford High Moisture	22.8	HHMC	6
H003367	14.4	2010-13	3
H003650	12.9	2010-08	4
H002496	12.2	2010-02	3
H003371	11.8	2011-07	3
H002592	11.6	2011-03	0
H004111	11.3	2009-02	6

Based on LANL RH with time data, the RH could have been twice the measured RH and liquids could have been present.

What is the RH inside the 3013 container, given its process/loading history, e.g. RH_{INT}? (continued)

- RH decreases with time in both the LANL Large-Scale containers and LANL high-purity oxides. RH remains constant or slightly increases in SRS test containers.

- When deliquesced liquids are present the RH tends to remain constant.

What is the threshold RH that will support SCC, e.g. RH_{SCC}?

The working hypothesis for designing Test Plan experiments is that

1. Liquids from deliquesced salts need to be present,
2. The worst salt is $CaCl_2$ because it deliquesces (forms a liquid by adsorbing atmospheric water) at the lowest RH,
3. The potential for SCC increases as the RH decreases down to the deliquescent RH (which for $CaCl_2$ is 22% or 17% depending upon the temperature).

Studies by both SRS and LANL showed SCC at ~57% RH. In early 2012, both SRS did not observe SCC at ~35% RH and LANL did not observe SCC at ~22%RH (lower RH should have been more aggressive).

What is the threshold RH that will support SCC, e.g. RH_{SCC}? (continued)

Why SCC at 57% and not ~35% or less RH?

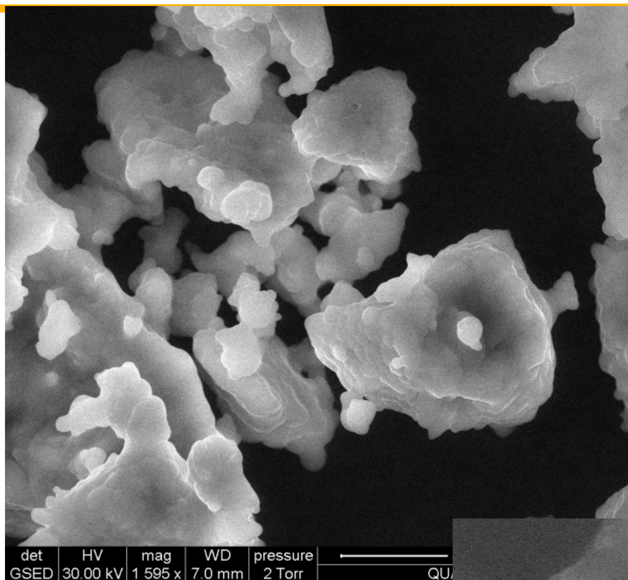
1. Did we misunderstand the literature? No, $CaCl_2$ is more aggressive at lower RHs (Duque)

2. How does the doubling of the volume associated with 57% RH compared to 35% RH for the same amount of $CaCl_2$ affect things? May limit ability to wet the metal and also may form smaller droplets.

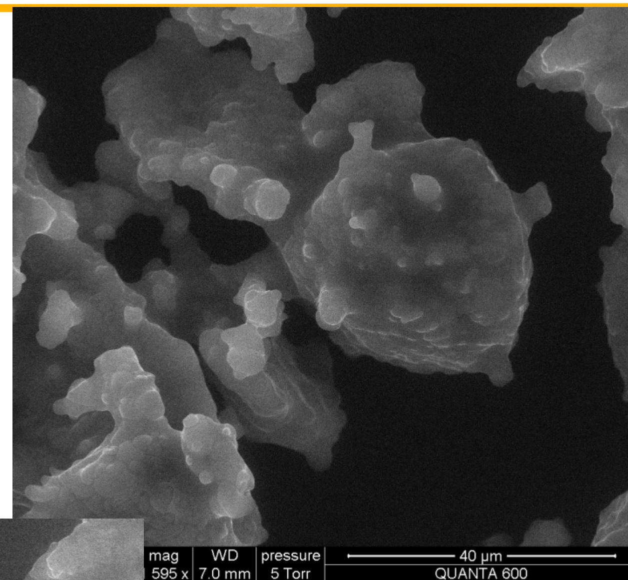
3. Is there a size dependence of the liquid droplets on the ability to cause SCC or pitting? Yes (Berg)

2010 Ca ER salt

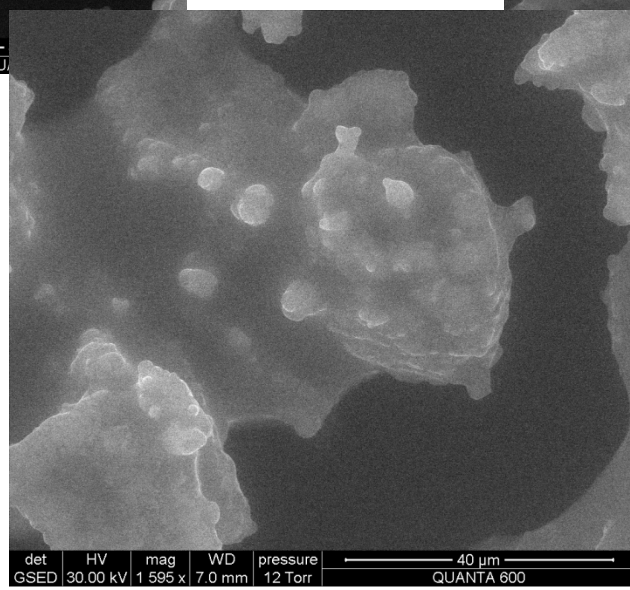
- 9%RH



- 23%RH



- 56%RH



SEM images by Steve Joyce

What is the threshold RH that will support SCC, e.g. RH_{SCC}? (continued)

The threshold RH is more complicated than originally envisioned because it appears to depend upon the geometry of the material particles and the size of the droplets formed.

Current data suggest there are fundamental reasons why the threshold RH could be higher than the deliquescent RH. Small droplets such as would be expected on the inner container wall due to deliquescence of individual particles from surface contamination would not be able to cause SCC.

The mechanism causing headspace pitting has not been considered with regard to SCC especially in the inner can lid crevice. Does this need to be considered? (Mickalonis)

What containers have the residual stress exceeding K_{SCC}?

1. Residual stresses in 3013 containers have been considered by Mickalonis and Dunn (SRNL-STI-2009-00732)

2. A stress map of the inner container lid has been reported (Lillard *Corrosion* **2009,** *65* (3), 175 - 186).

3. Stress map of the teardrop specimens has been measured (Prime in 2011) and the teardrop stresses bound the inner container lid region.

4. Measurements of K_{ISCC} using double cantilever beam specimens are being conducted in the Large-Scale containers (Narlesky)

Points 1 – 3 reviewed by Worl

What configuration is needed for SCC initiation and propagation?

See discussion of the threshold RH.

Conclusions

- RH of containers measured during DE show the only population of concern were packaged in the C-line at Hanford. The worst of these may have had liquid present.

- The Threshold RH for SCC in the contact region may be higher than 35% RH. The conditions for further tests are being evaluated. Awaiting unloading of SRNL test container 2c and evaluation of teardrops from SRNL test container 2b and 2c.

- Identifying a Threshold RH that is high enough to rule out the Hanford C-Line population may obviate the need to measure K_{ISCC}.

Pitting

- New pit depth data has been collected during SRS DE and LANL corrosion studies.

- In order to integrate all of the data, a fresh look at the statistical model was initiated.

- A new threshold model based on GEV was developed to integrate all of the data and allows comparison to maximum pit sizes identified during DE. (Kelly)

Overview SRNL Corrosion Shelf Life Studies

J. I. Mickalonis and J. M. Duffey

February 26-27, 2013

3013 Surveillance and Monitoring Program Review

Annual Meeting

Acknowledgements

Corrosion Test

Vickie Timmerman, Thaddeus Reown, Wanda Matthews and Gregg Creech

SEM Analysis

Henry Ajo and Jack Durden

Scheduling

Mark Jackson

SRNL Corrosion Test Plan - Purpose

- Phase 2 – Test Series 1: Measuring RH for conditions that caused SCC in Phase 1 testing (Zapp/Duffey data) previous tests with oxide/salt composition of 98% PuO_2 - 2% Cl^- salt with ~0.3% $CaCl_2$
- Phase 2- Test Series 2-4: Evaluating threshold RH conditions required to cause SCC for the same salt composition

SRNL Phase 1 Corrosion Test Containers

SRNL

SRNL Shelf Life Studies – Test Matrix

Series	Test	H_2O Loading (wt %)	Loading RH (%)	Container RH (%)	Temp (°C)	Storage Time (days)
1	B	0.585	54 max	53	Ambient	85
	C	0.45	54 max	57	Ambient	175
	A	0.58	54 max	49*	Ambient	320
2	A	0.18	28 max	35	Ambient	131
	B	0.16	28 max	36	Ambient	405
	C	0.175	28 max	38	Ambient	TBD
3	A,B,C	TBD	TBD	TBD	TBD	TBD
4	A,B,C	TBD	TBD	TBD	TBD	TBD

* RH probe failed at start of tests, measurement made by inserting a working probe prior to sample removal

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SRNL Shelf Life Studies – Test Configuration

- Test containers modified to fit humidity probe
- Limited volume for TD coupons only; no flat coupons (as in Phase 1 testing)
- Solid contact and headspace
- Salt composition: 98% PuO_2 - 2% Cl^- salt with ~0.3% $CaCl_2$ (same as Phase 1 testing)

Phase 2 Test Container

Phase 2 Sample Configuration

SRNL

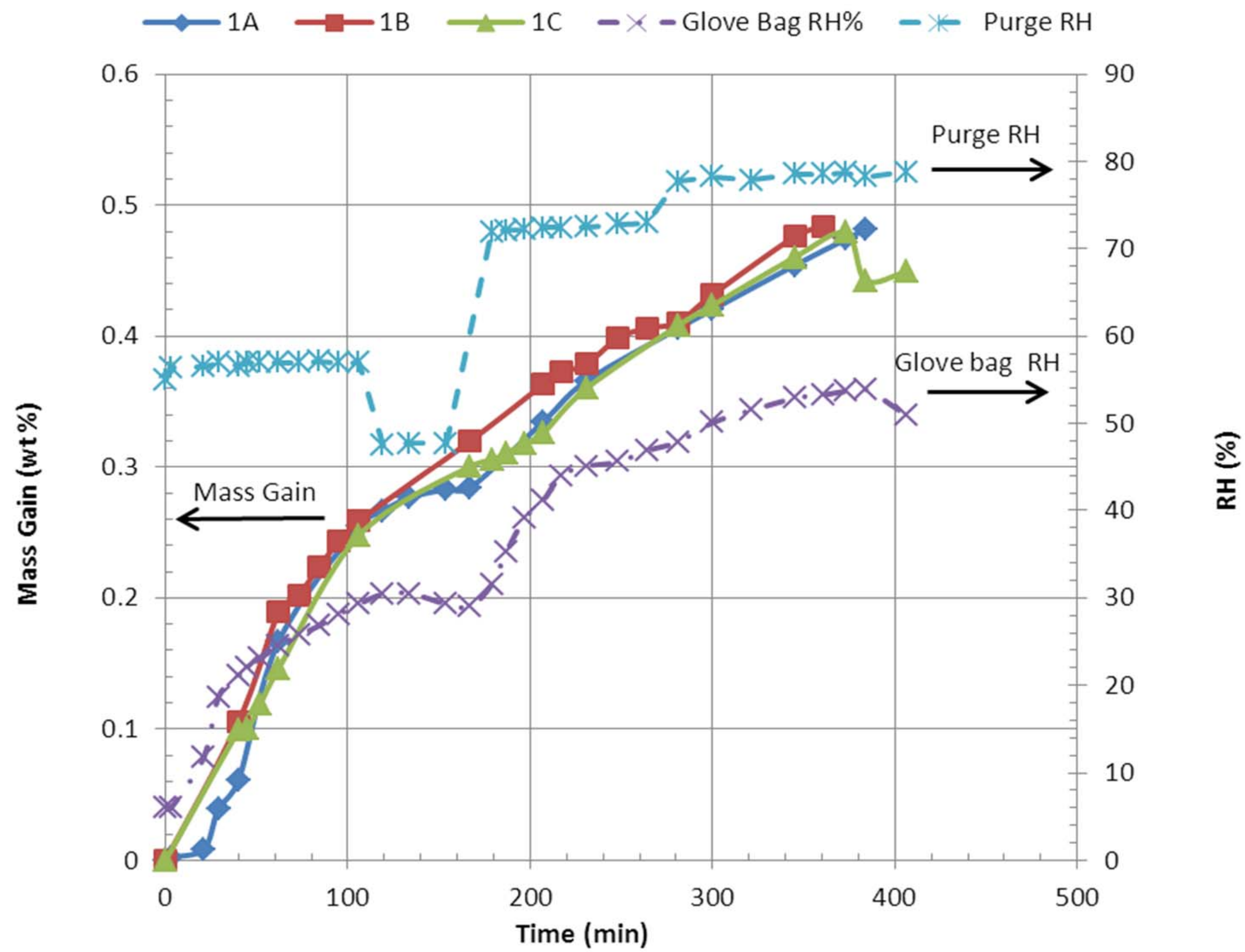
SRNL Shelf Life Studies – Test Matrix

Series	Test	H_2O Loading (wt %)	Loading RH (%)	Container RH (%)	Temp (°C)	Storage Time (days)
1	B	0.585	54 max	53	Ambient	85
	C	0.45	54 max	57	Ambient	175
	A	0.58	54 max	49*	Ambient	320
2	A	0.18	28 max	35	Ambient	131
	B	0.16	28 max	36	Ambient	405
	C	0.175	28 max	38	Ambient	TBD
3	A,B,C	TBD	TBD	TBD	TBD	TBD
4	A,B,C	TBD	TBD	TBD	TBD	TBD

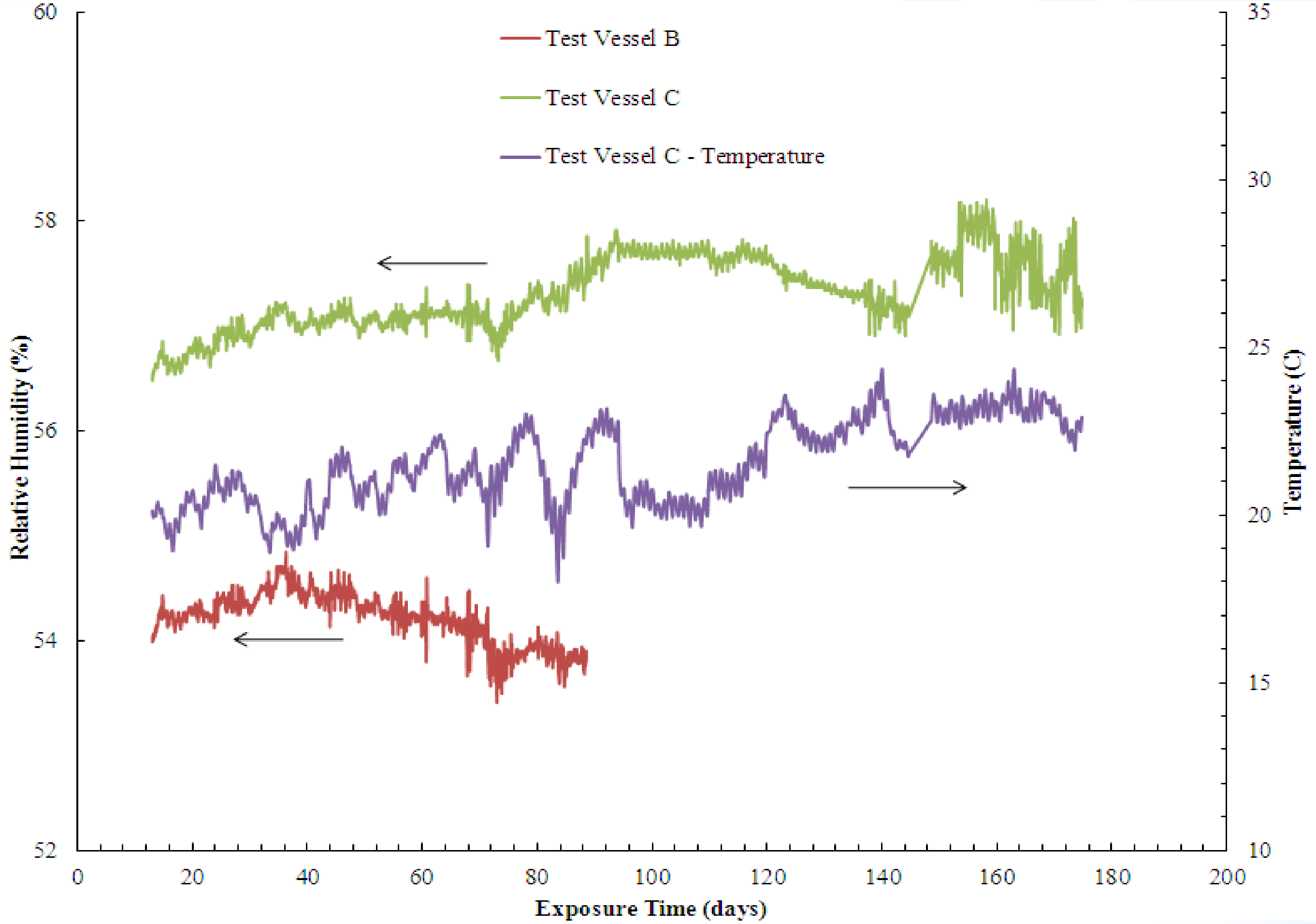
* RH probe failed at start of tests, measurement made by inserting a working probe prior to sample removal

SRNL

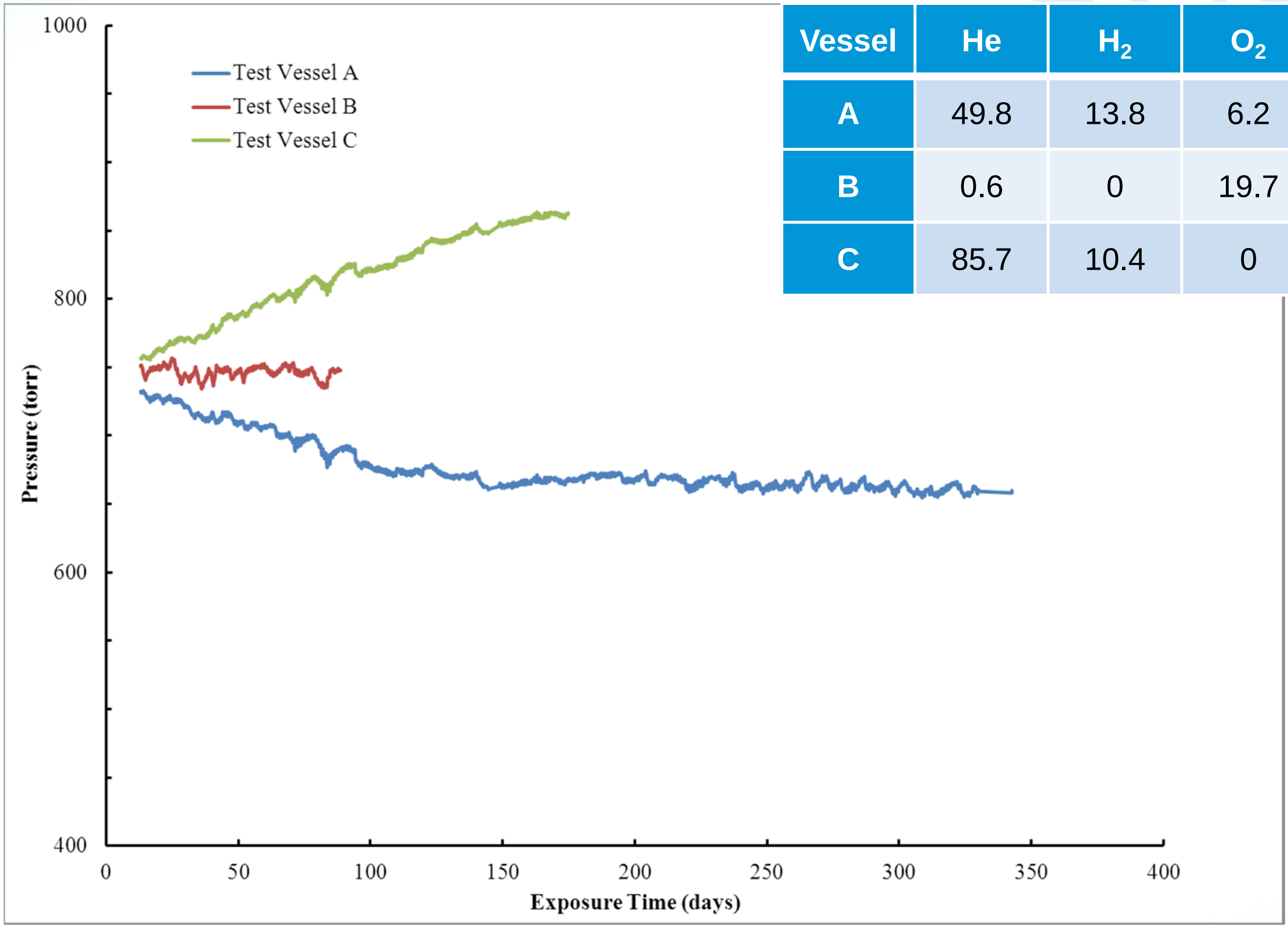
Test Series 1 - moisture uptake



Test Series 1 - RH and temperature trends



Test Series 1 - pressure trends



Vessel	He	H_2	O_2	N_2	N_2O
A	49.8	13.8	6.2	26.5	0.6
B	0.6	0	19.7	79.8	0.2
C	85.7	10.4	0	0.6	0.3

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Test Series 1 – Corrosion Summary

Cell	TD #	Exposure Condition	Water (%)	Pressure	Exposure Time (days)	Corrosion
A	30	Oxide/Salt	0.58	Decreasing	340	Pitting, SCC
	25	Vapor				Pitting
B	05	Oxide/Salt	0.585	Atmospheric	85	Pitting, SCC
	04	Vapor				None
C	03	Oxide/Salt	0.45	Increasing	175	Pitting, SCC
	09	Vapor				None

SRNL™

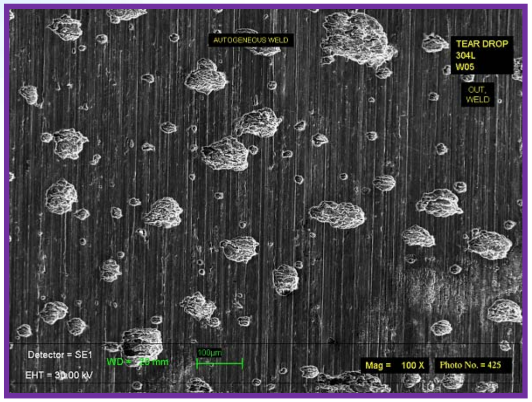
Test Series 1 – 85 Days

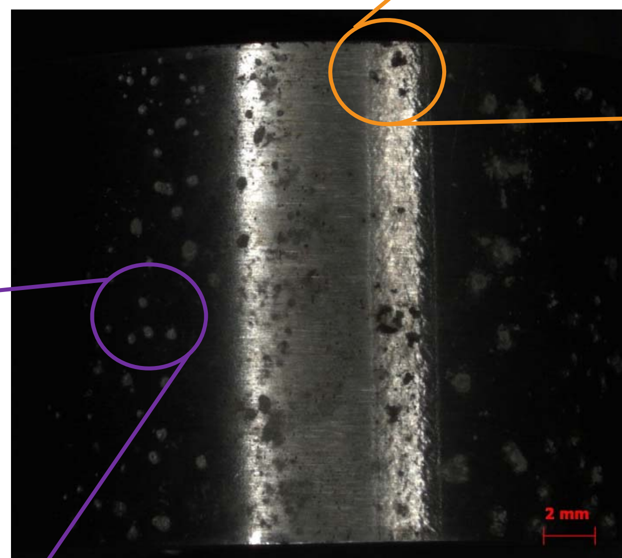
- **Conditions:** Container leaked; RH 53-55%; water loading – 0.48%
- **Oxide/ Salt Exposure:**
  - Significant corrosion on teardrop
  - Variable pit population in both base and weld metal
  - Crack-like features noted
- **Vapor Exposure:**
  - minimal spotty corrosion
  - TIG closure welds corroded

Oxide/Salt Exposure

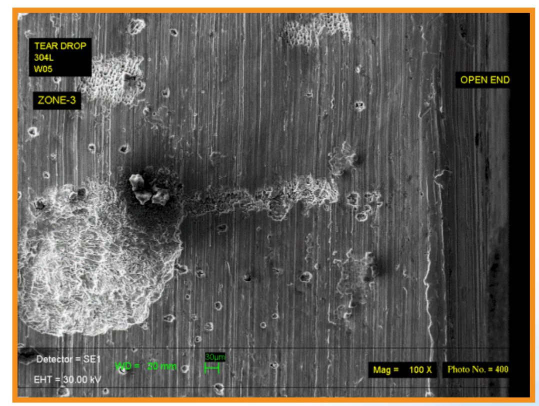
Vapor Exposure

Test Series 1 – 85 Days





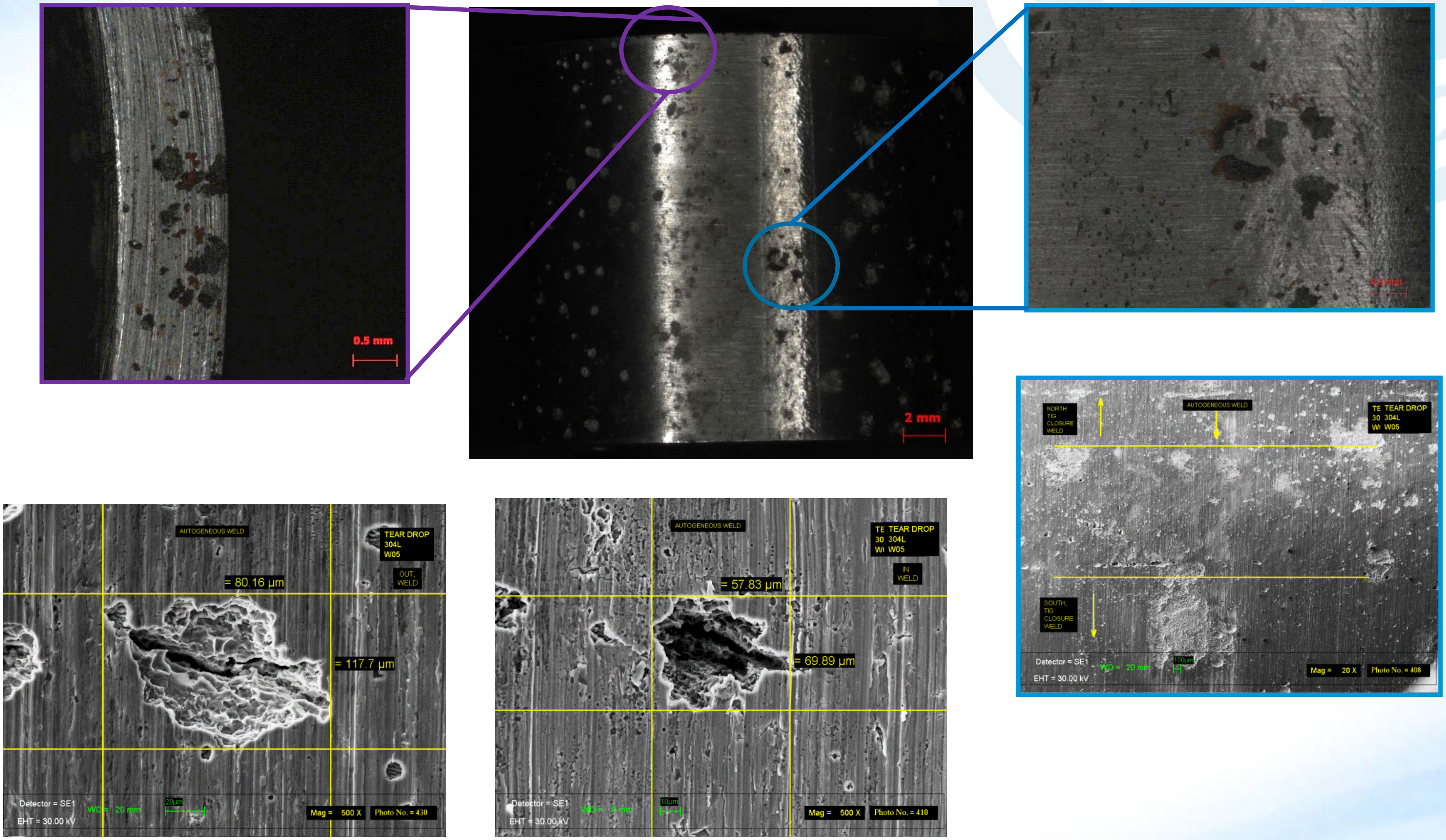
Crack like feature with pit



Variable pit size – population appears to be bi-modal

SRNL

Test Series 1 – 85 Days



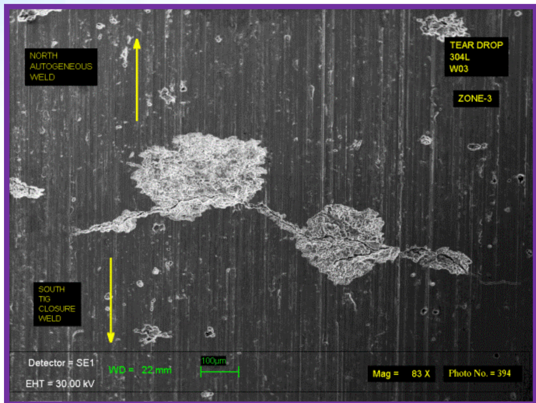
Test Series 1 – 175 Days

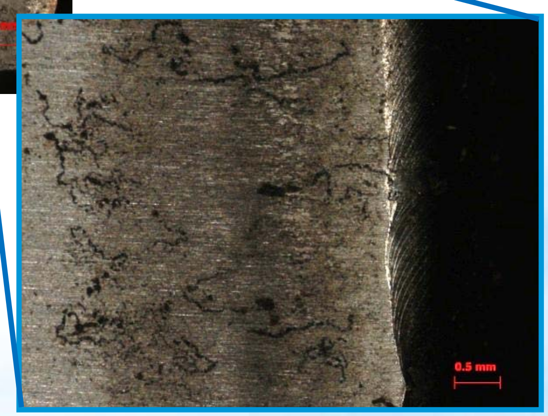
- **Conditions:** Pressure increasing; RH 56-58%; water loading - 0.45%
- **Oxide/ Salt Exposure:**
  - Significant corrosion on teardrop
  - Pitting observed in both base and weld metal; linear array
  - Small cracks located outside the weld area, not through wall
- **Vapor Exposure:**
  - some surface oxidation
  - TIG closure welds corroded


Oxide/Salt Exposure


Vapor Exposure

Test Series 1 – 175 Days

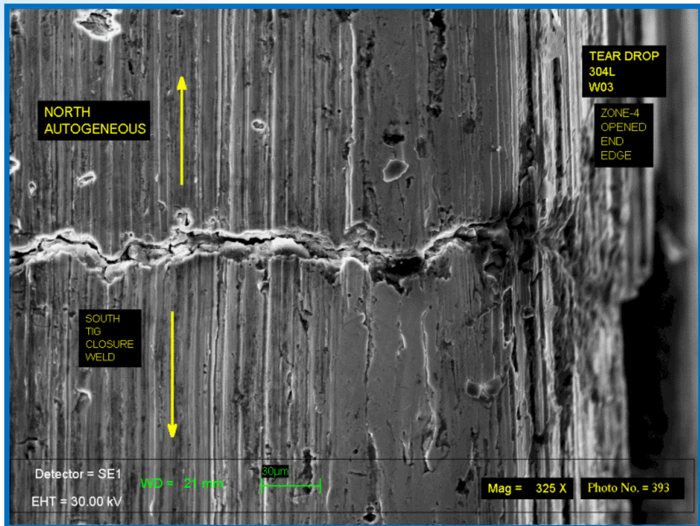


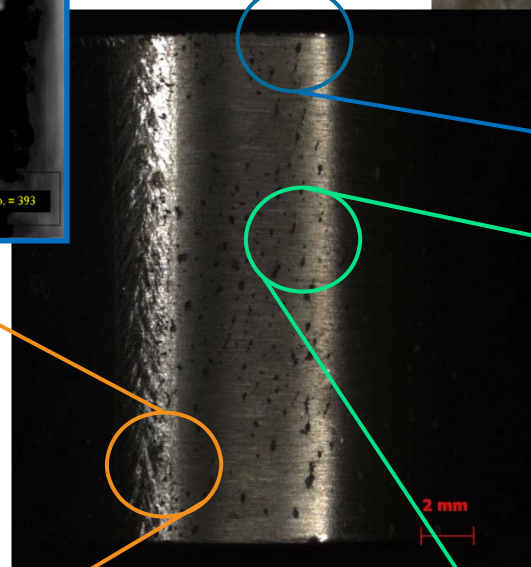


Cracks associated with array of pits

SRNL

Test Series 1 – 175 Days

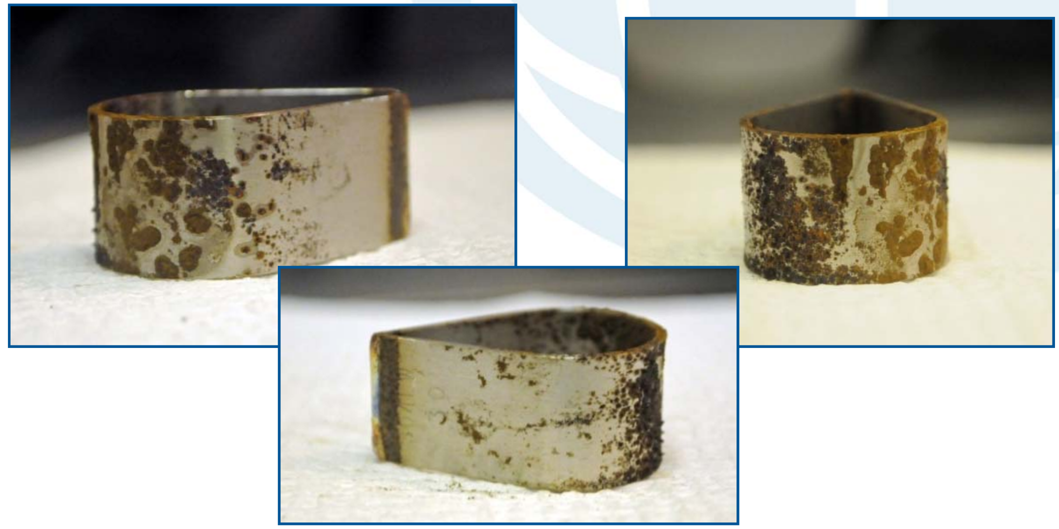




Directionality of pits near weld

Test Series 1 – 340 Days

- **Conditions:** Pressure decreasing; RH 49% (at end); water loading - 0.58%
- **Oxide/ Salt Exposure:**
  - Significant corrosion on teardrop
  - Pitting observed in both base and weld metal
  - Apparent through wall crack
- **Vapor Exposure:**
  - some pitting corrosion
  - TIG closure weld corroded

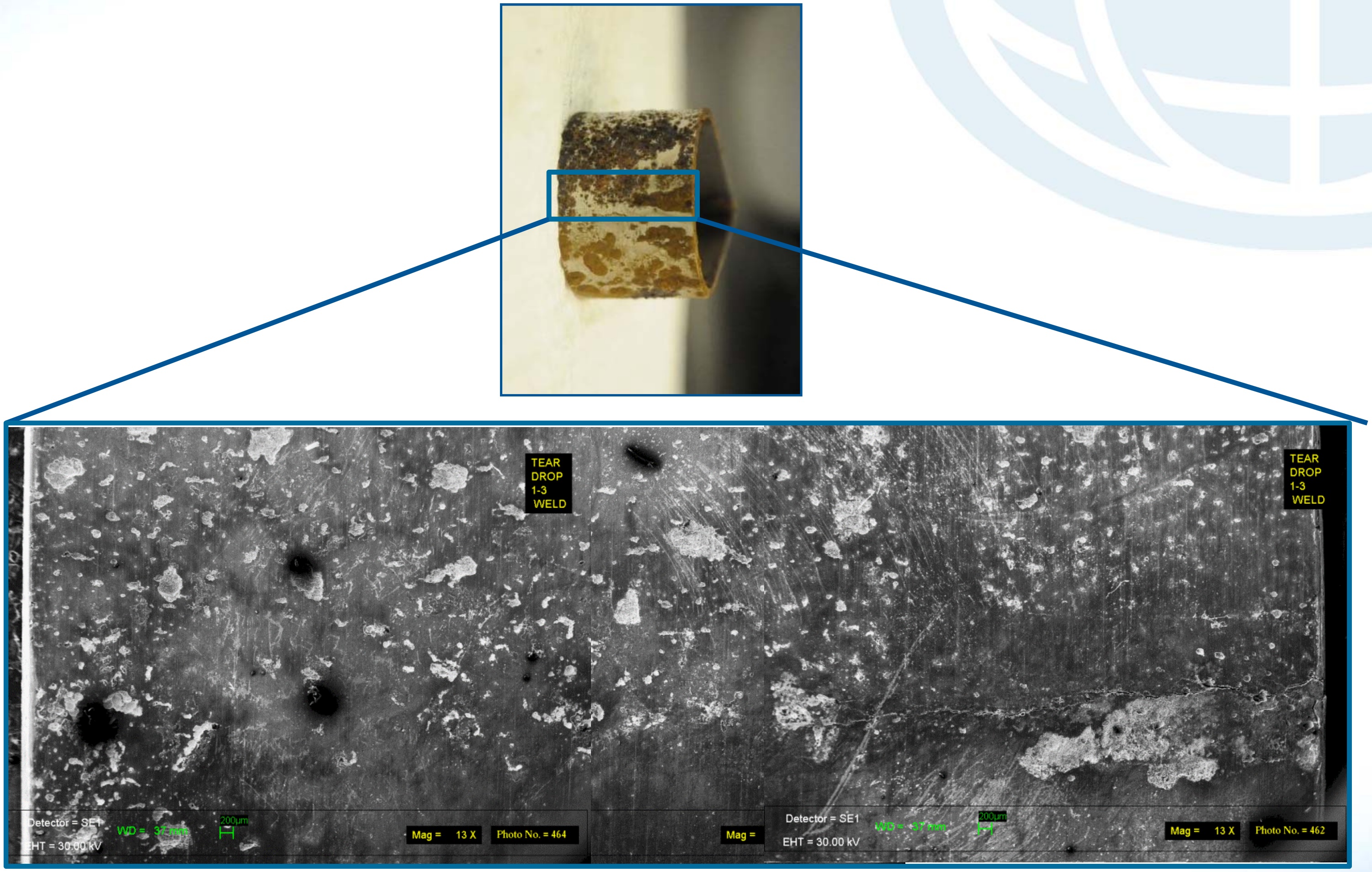


Oxide/Salt Exposure

Vapor Exposure

SRNL

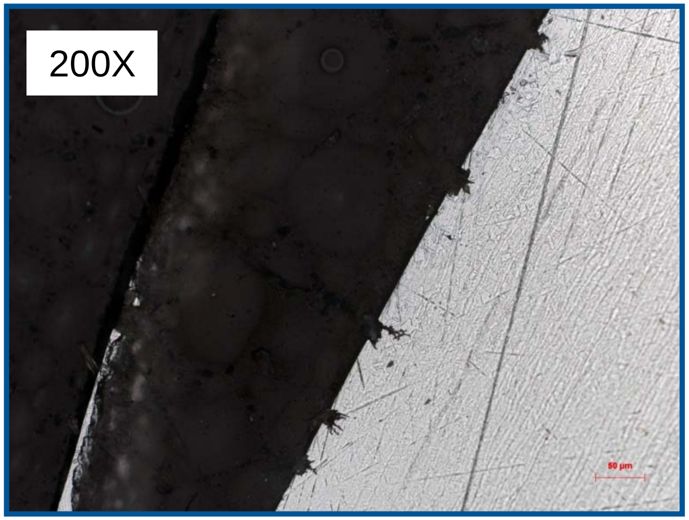
Test Series 1 – 340 Days



SRNL

Test Series 1 – Cross Sectional Metallography

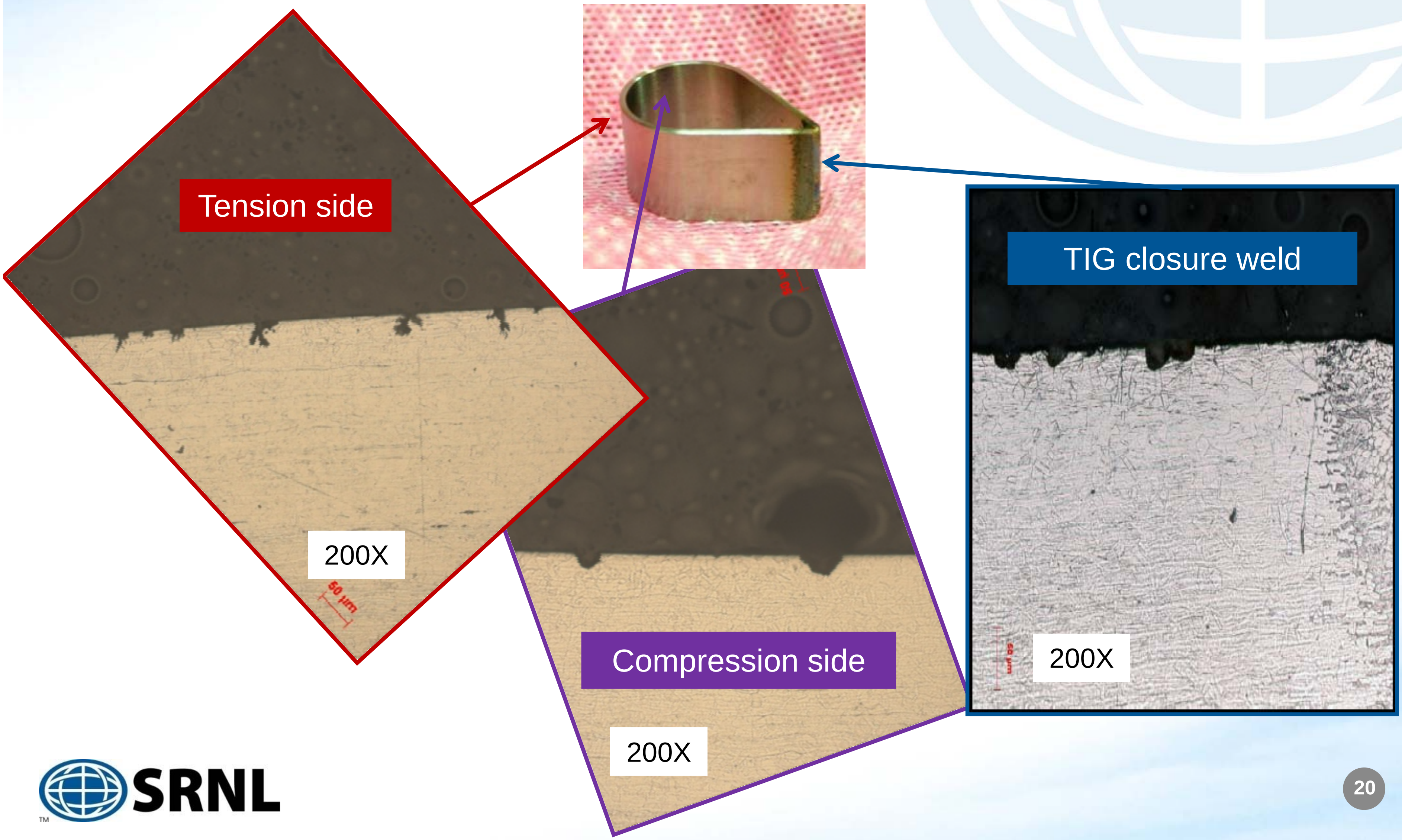
85-Day Exposure



175-Day Exposure

Test Series 1 – Cross Sectional Metallography

Teardrop exposed to salt for 85 days at 54% RH



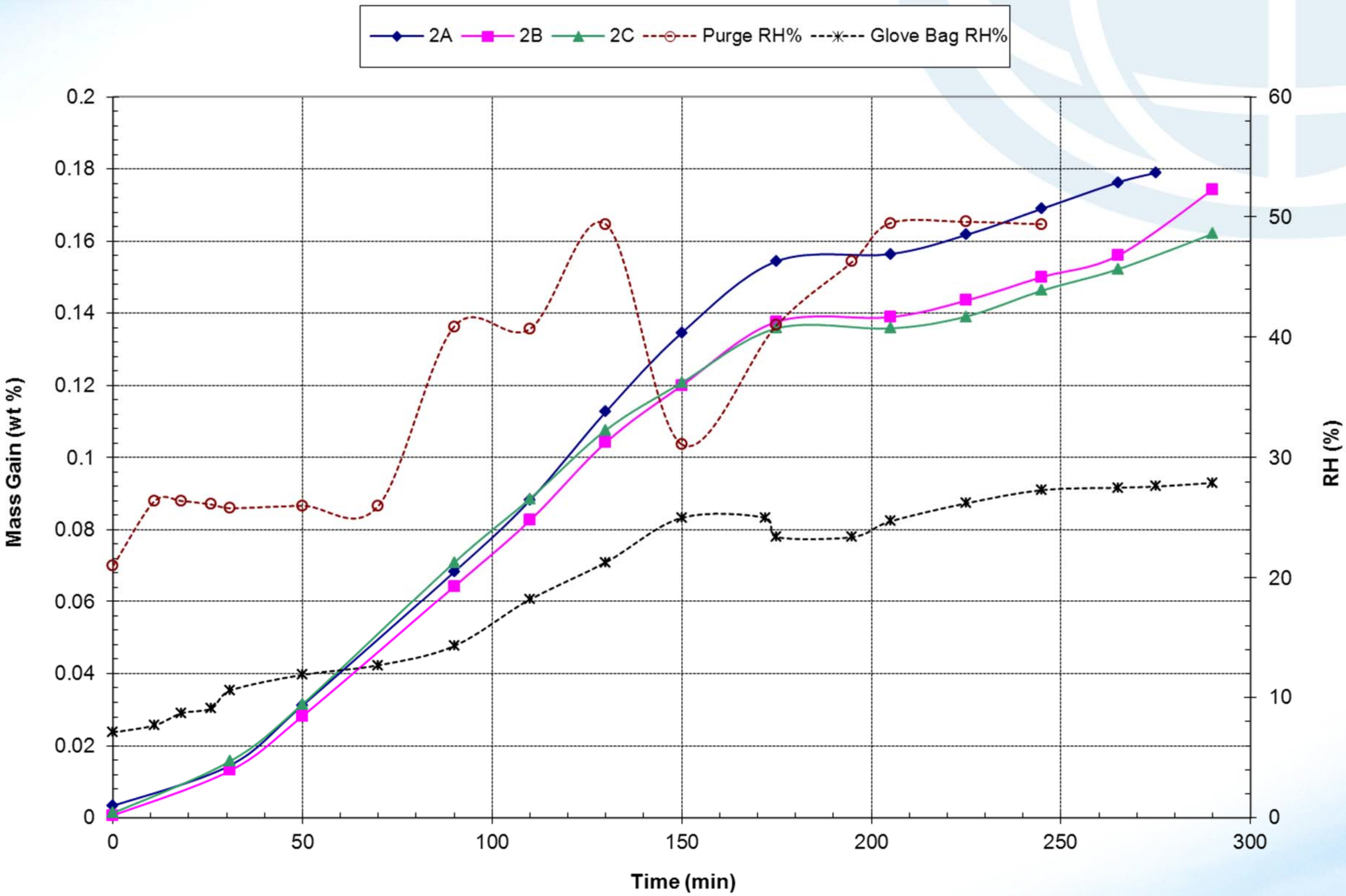
SRNL

SRNL Shelf Life Studies – Test Matrix

Series	Test	H_2O Loading (wt %)	Loading RH (%)	Container RH (%)	Temp (°C)	Storage Time (days)
1	B	0.585	54 max	53	Ambient	85
	C	0.45	54 max	57	Ambient	175
	A	0.58	54 max	49*	Ambient	320
2	A	0.18	28 max	35	Ambient	131
	B	0.16	28 max	36	Ambient	405
	C	0.175	28 max	38	Ambient	TBD
3	A,B,C	TBD	TBD	TBD	TBD	TBD
4	A,B,C	TBD	TBD	TBD	TBD	TBD

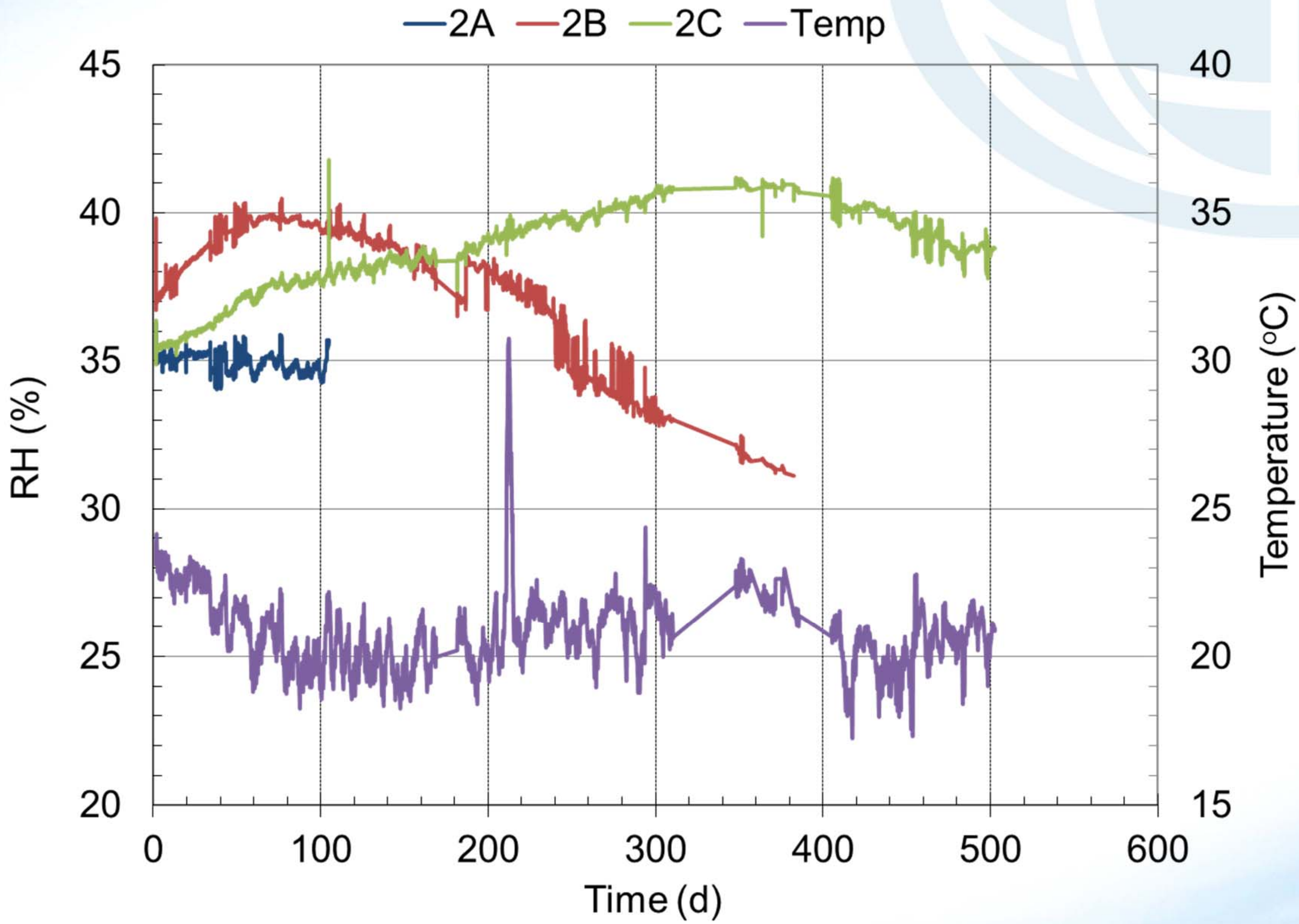
SRNL™

Test Series 2 - moisture uptake



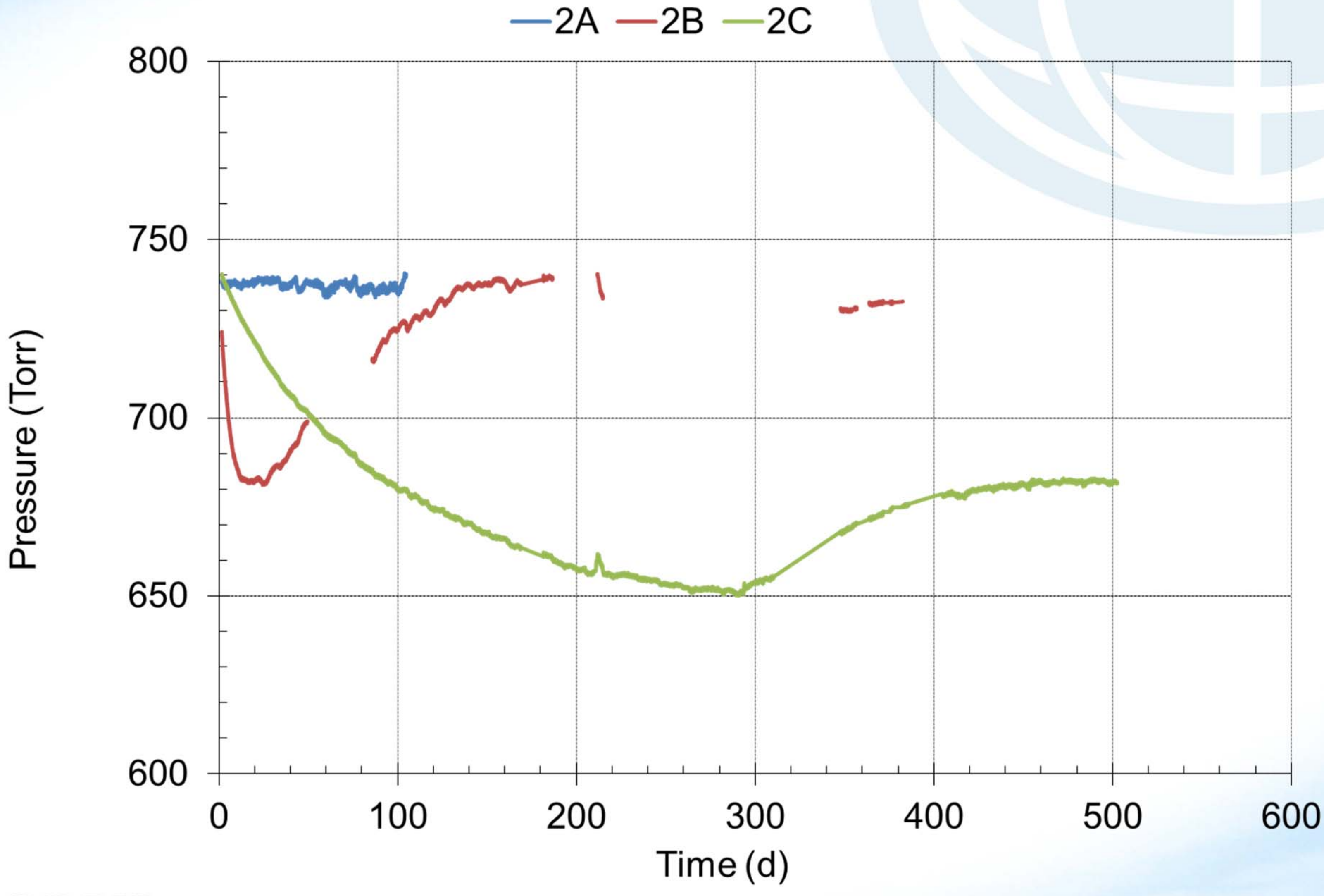
SRNL

Test Series 2 - RH and temperature trends



SRNL

Test Series 2 - pressure trends



Test Series 2 – 131 Days

- **Conditions:** Pressure constant; RH 35% (at end); water loading - 0.18%
- **Oxide/ Salt Exposure:**
  - Pitting corrosion on teardrop
  - Pitting observed in base metal
- **Vapor Exposure:**
  - surface oxidation
  - Minimal corrosion on TIG closure weld

Oxide/Salt Exposure
Uncleaned (top) and Cleaned (bottom)

Vapor Exposure

SRNL

Test Series 2 – 405 Days

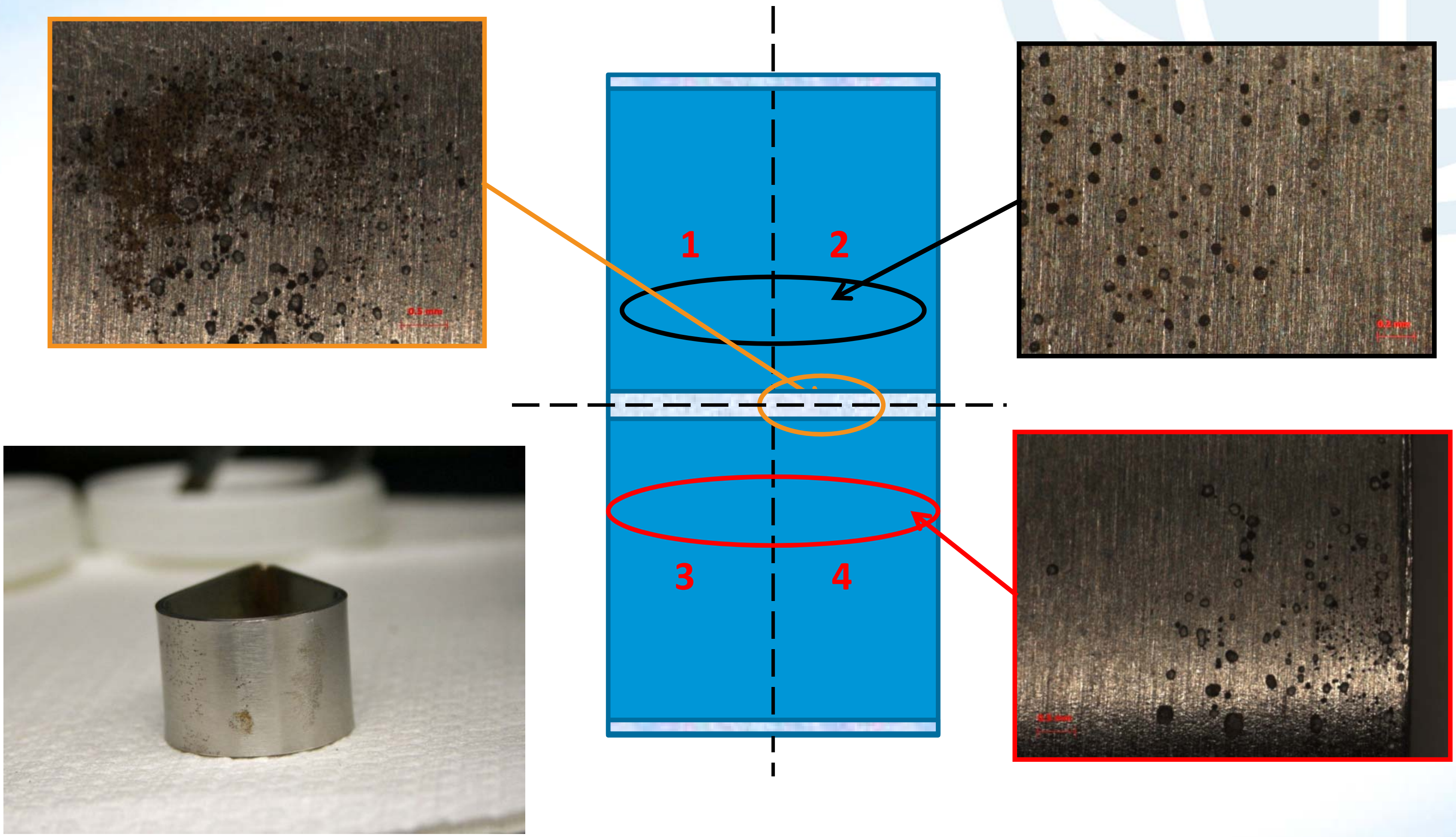
- **Conditions:** Pressure slight increase during exposure; RH 33% (at end); water loading - 0.176%
- **Oxide/ Salt Exposure:**
  - Pitting corrosion on teardrop
  - Pitting observed in base metal
- **Vapor Exposure:**
  - surface oxidation
  - Mild corrosion on TIG closure weld

Oxide/Salt Exposure
Uncleaned (top) and Cleaned (bottom)

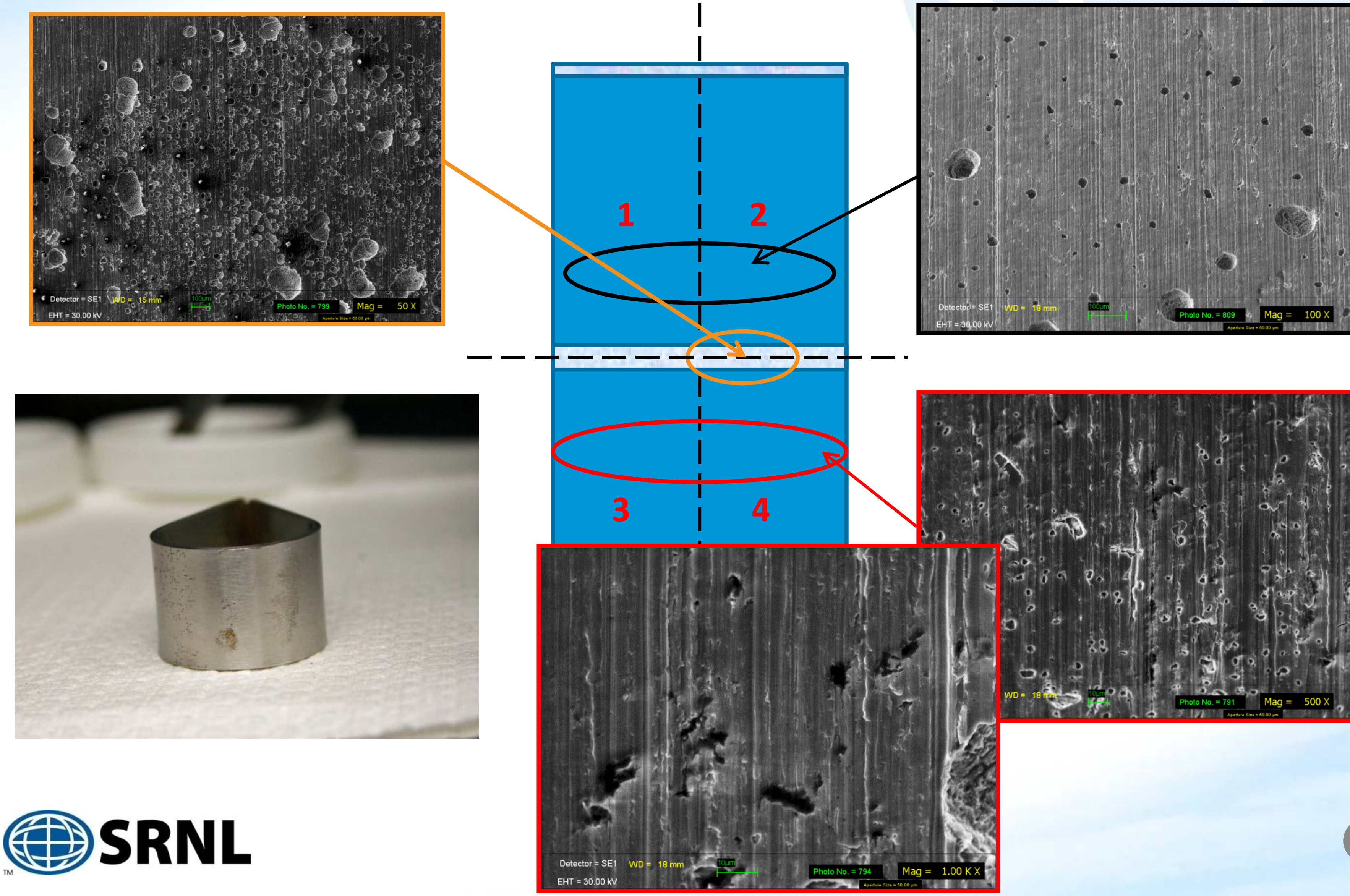
Vapor Exposure

SRNL

Test Series 2 – Teardrop Exposed to Salt – 405 days



Test Series 2 – Teardrop Exposed to Salt – 405 days



SRNL

Path Forward

- Test series 1 had similar results to the initial Zapp/Duffey results which observed SCC in 304L teardrops
  - Cracks were found to progress with time and initiate at pits 10-20 µm (observed after 85-day exposure)
- Test series 2 continues with the final test cell to be opened (summer 2013, approximately two years)
- Working to set up Test Series 3

Status of Large-Scale Corrosion Containers FY12 Update

Joshua Narlesky, John Berg, Dave Harradine, Ed Romero, Leonardo Trujillo, Kennard Wilson, Laura Worl, Kirk Veirs

Los Alamos National Laboratory

February 27, 2013

Outline

- **Large container overview**
- **Packaging conditions (review)**
- **Storage behavior update**
  - Relative Humidity
  - DCB Data
  - Gas Composition
  - Oxygen Generation
- **DE Update**
- **Discussion**
  - Future DE
  - Future loadings

- **Objectives**

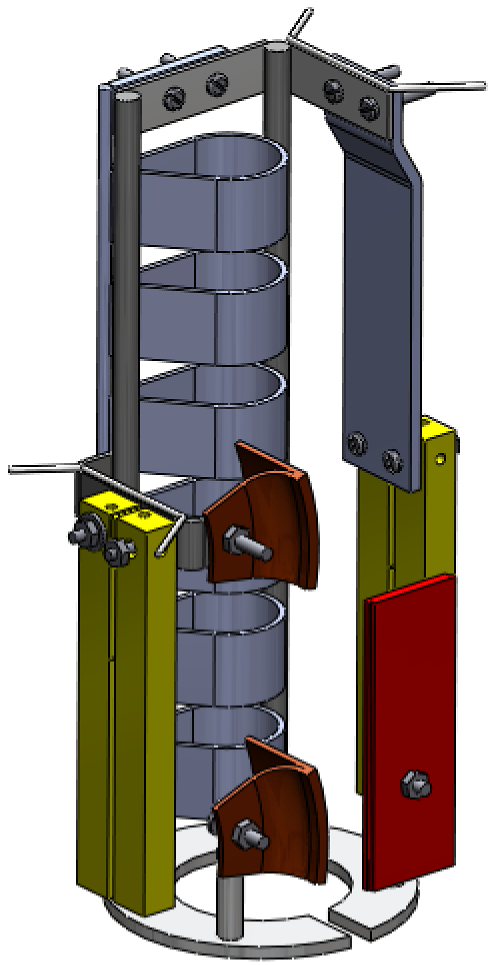
  1. *What is the RH and how does it change inside the container given its process/loading history?*
  2. *What is the threshold RH that will support SCC?*
  3. *What containers have the residual stress exceeding* K_{SCC}*?*

Status

- 6 full-scale 3013 containers loaded

Material	Material Description	Load Date
PMAXBS	12-14% Na/K Cl with 0.09 wt% added moisture at 53% RH 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 Removed for DE: September 2012
Low Ca	Base material + 0.34 wt% $KCaCl_3$ (0.28 wt% added moisture at 53% RH)	November 2009
Low Mg	Base material + 0.34 wt% $KMgCl_3$ (0.28 wt% added moisture at 52% RH)	March 2010
High Ca	Base material + 3.4 wt% $KCaCl_3$ (0.39 wt% added moisture at 30% RH)	August 2010
High Mg	Base material + 3.4 wt% $KMgCl_3$ (0.55 wt% added moisture at 8% RH)	September 2010

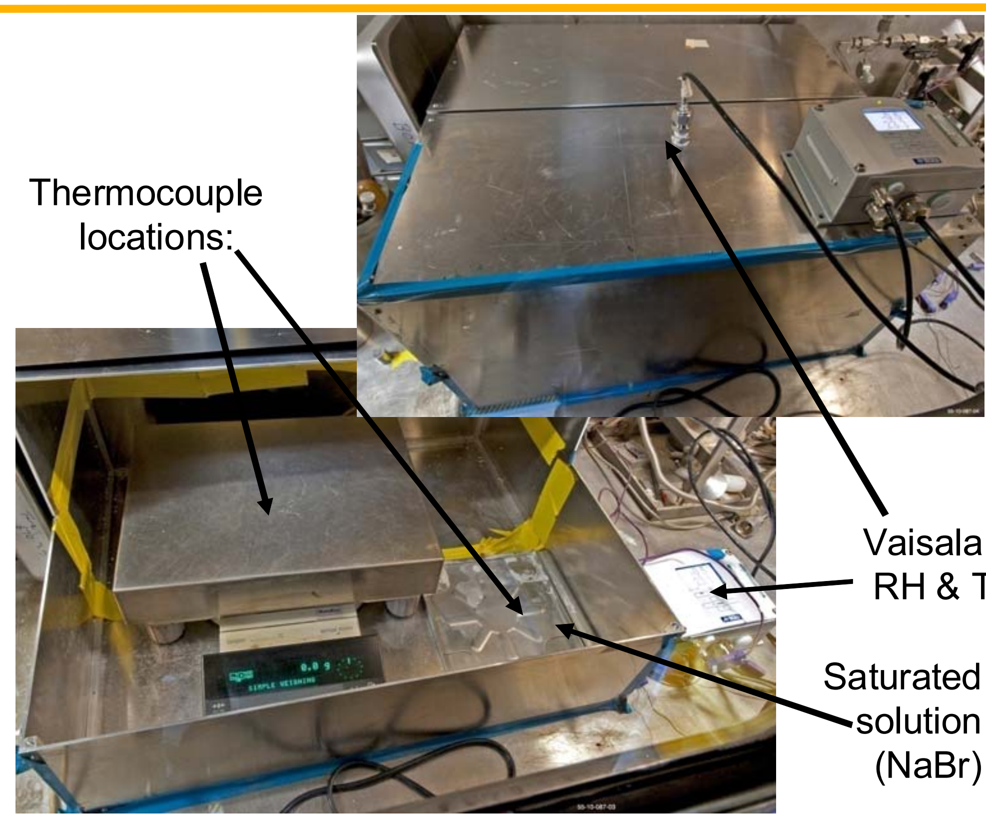
Corrosion Specimens



Simulating the 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



Species	$KCaCl_3$	$CaCl_2$-$2H_2O$	$CaCl_2$-$4H_2O$	$CaCl_2$-$6H_2O$	$MgCl_2$-$6H_2O$	$KMgCl_3$-$6H_2O$
DRH_{25C}	16	16	21	29	33	57
DRH_{50C}	19	17	--	--	31	54

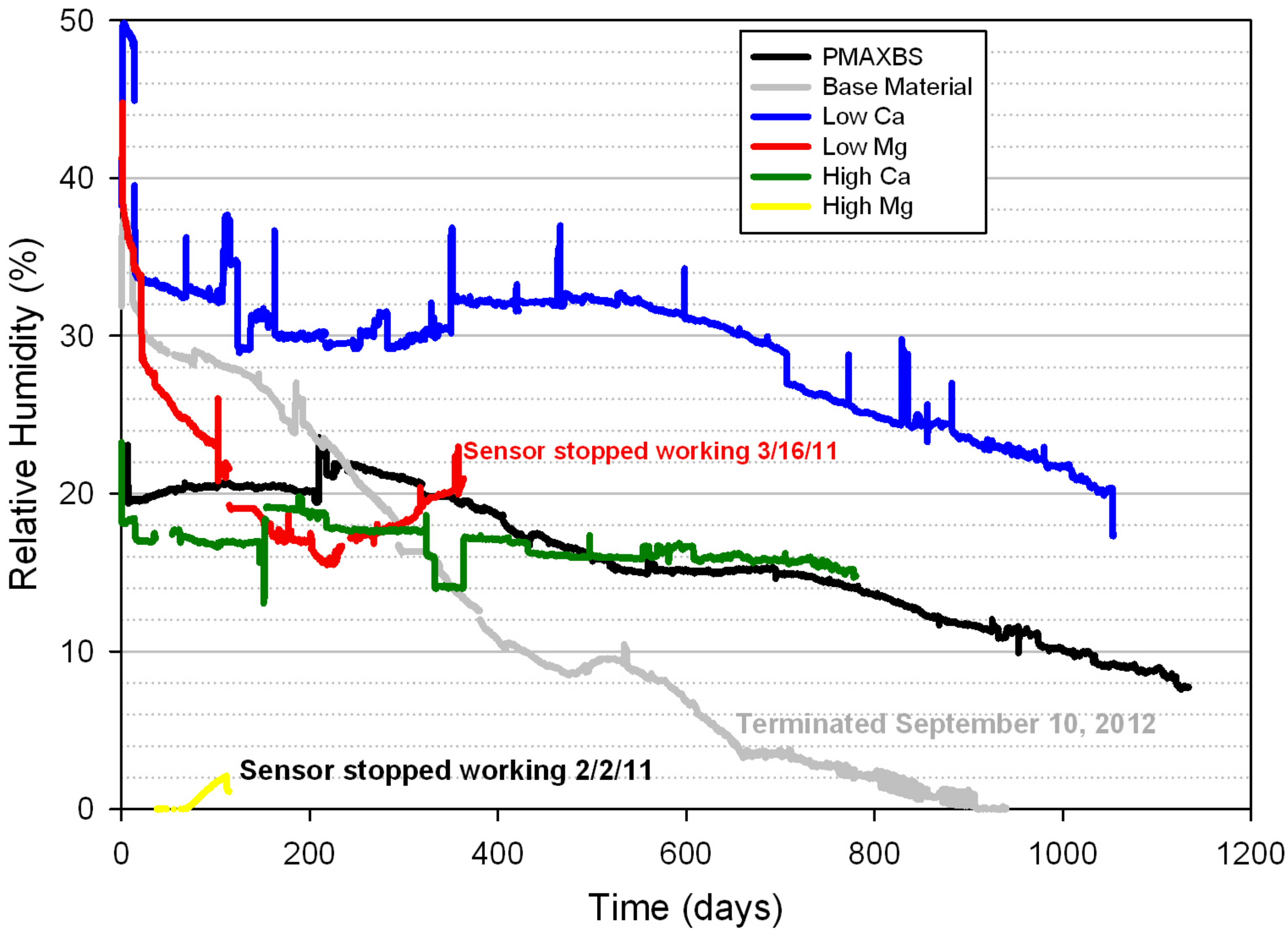
Interpretation of data

- **RH data**
  - Stable RH: MOST IMPORTANT; may indicate that the RH is controlled by a solution
  - Sharp increases / decreases: related to sudden temperature changes, BUT may lead to conditions that support corrosion.
  - Gradual increases / decreases: redistribution of moisture
- **DCB data**
  - Gradual increase in magnitude of resistance: MOST IMPORTANT; may indicate crack growth
  - Stable resistance: no change; likely no crack growth
  - Sharp increases / decreases: related to changes in current (power supply)
- **Gas generation data**
  - Oxygen generation: results from small scale studies suggest that the conditions that support oxygen generation also support the formation and persistence of liquid phases and possibly corrosion.

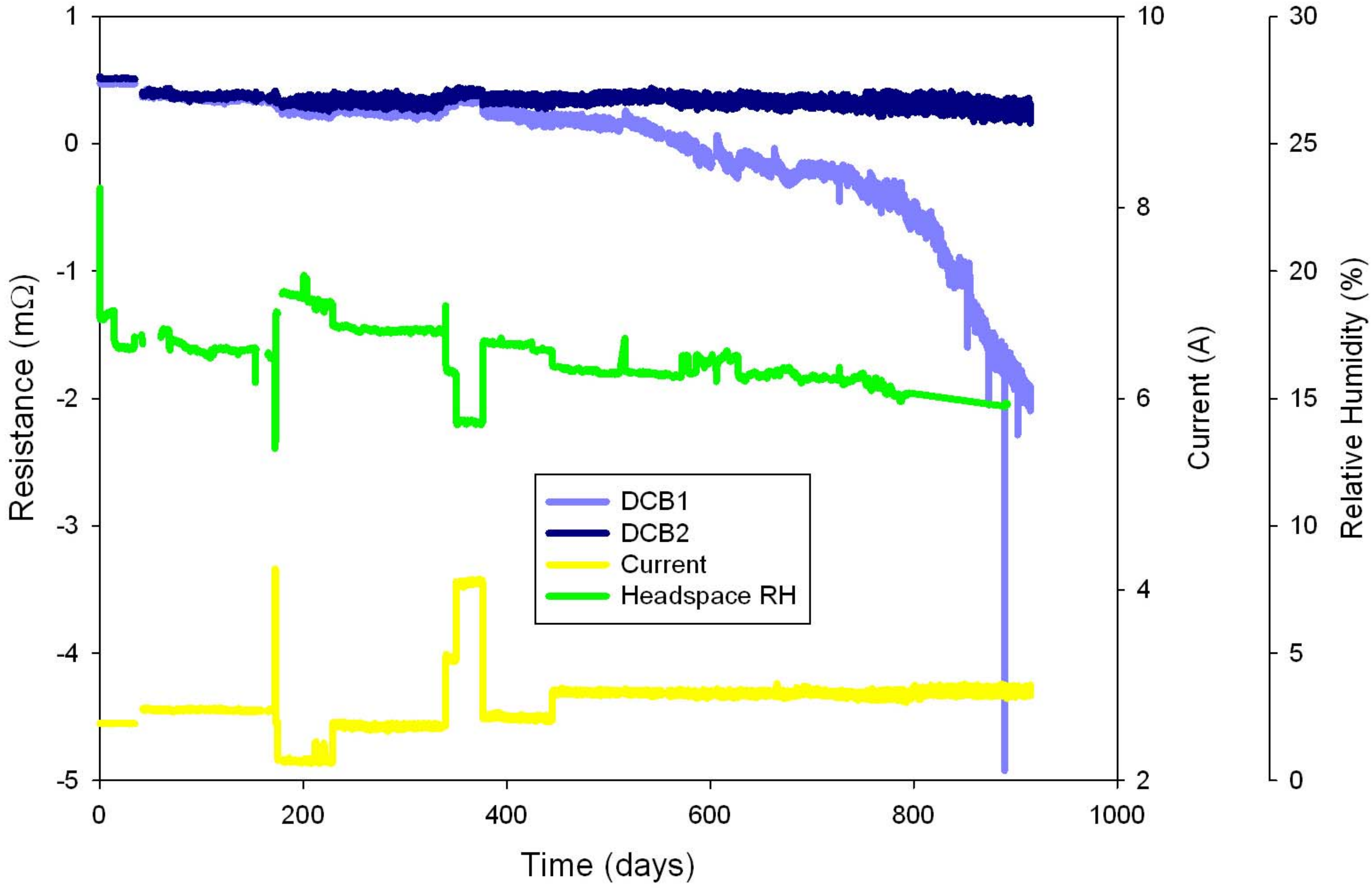
Initial Conditions

Material	wt% Moisture	Chamber RH / RH in Material	Storage Condition	Headspace Temp ºC	Headspace RH (%)
PMAXBS	0.09	53 / 26	Bare 3013	36	23
			Insulated	49	20
Base Material	0.05	56 / 27	Bare 3013	30	35
			Insulated	36	31
Low Ca	0.28	53 / 22	Bare 3013	30	**49**
			Insulated	39	**34**
Low Mg	0.28	52 / 16	Bare 3013	37	**37**
			Insulated	45	28
High Ca	0.39	30 / 9	Bare 3013	41	**18**
			Insulated	43	**17**
High Mg	0.55	8 / 3	Bare 3013	33	0
			Insulated	38	0
The measured material temperature for insulated containers ranged from 40 to 55ºC					

Relative Humidity



High Ca: DCB Data



Container DE

- **Final GC**
- **MC&A close out (weight, TID, NDA)**
- **Remove / inspect burst disk**
- **Open container with can opener**
- **Inspect / photograph container**
- **Heat material on hot plate to remove moisture**
- **Moisture measurement: 200ºC weight loss and/or TGA**
- **Analysis of corrosion samples: Teardrops, DCBs, lid sections specimens, and crevice specimens**
  - Brush
  - Photograph
  - Clean (ultrasonic bath)
  - Store in hermetically sealed container (if necessary)
  - Dye penetrant (teardrops)
  - Macroscope
  - Microscope

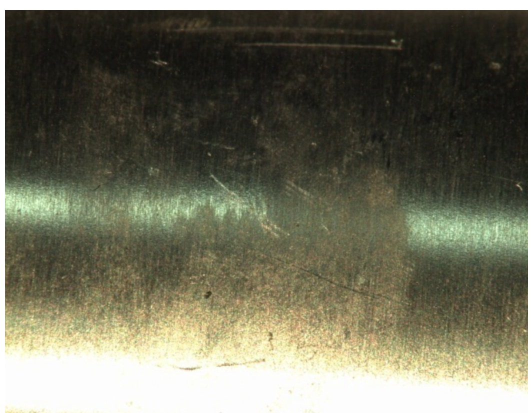
Base Material DE Results

- **Container condition: clean/shiny**
- **Burst disk condition: clean/shiny**
- **DCBs: None present**
- **Tear drops: shiny clean, slight discoloration on 05 and 07 in material phase—not removed with cleaning**
- **Lid section specimens: None present**
- **Crevice specimens: None present**
- **200ºC moisture loss: 0.0085 wt%**

Base Material Teardrops

Headspace

Material



Summary

- **Corrosion is possible where liquid phases are present**
- **Liquids phases possible even for short exposure to high RH**
- **Possibly a relationship between conditions for oxygen generation in chloride salt bearing material and corrosion**
- **Possible crack growth in high Ca material**

Material	Age (mo.)	Chamber RH_{max}	Storage RH_{max}	RH (%)	H_2 press.	O_2 Gen. / times vented	O_2 press.	Supports Corrosion Now?
PMAXBS	43	53	49	8↓	↓	N / 0	~0—	No
Base Mat.	36 **(DE'd)**	56	37	<2	↓	N / 0	~0 **(final)**	None obs.
Low Ca	40	53	49	18↓	↑	Y / 2	0—	Yes
Low Mg	36	52	41	?, 25↑	↑	Y / 1	↓	Maybe
High Ca	31	30	18	15—	↑	Y / 2	0—	Yes
High Mg	30	8	2	?, 2↑	↑	Y / **6**	↑	No

Discussion of Future Plans

- **Resume container DE (delayed due to equivalency work)**
  - Next DE's: Late FY13 and early FY14
  - Suggested priority
    - High Ca: DCB's indicate crack growth (1-5)
    - PMAXBS: (1-4)
    - Low Mg: (1-4)
- **Continue surveillance**
  - Low Ca (supports corrosion)
  - High Mg (generates O_2)
- **Replace RH sensors**
  - High Ca
  - Low Mg
  - High Mg
- **Future loading**
  - Low temperature stabilized high purity oxide from oxalate precipitation (loading conditions determined by results from small scale studies)

- **Criteria for container removal**
  1. Age: > 2 yrs in surveillance
  2. RH below DRH of added salts
  3. No longer generates O_2
  4. Conditions no longer support corrosion
  5. **Data indicate crack growth***

Status of Large-Scale Corrosion Containers

Joshua Narlesky, John Berg, Dave Harradine, Ed Romero, Leonardo Trujillo, Kennard Wilson, Laura Worl, Kirk Veirs

Los Alamos National Laboratory

February 26, 2013

Outline

- **Large container overview**
- **Packaging conditions (review)**
- **Storage behavior update**
  - Relative Humidity
  - DCB Data
  - Gas Composition
  - Oxygen Generation
- **DE Update**
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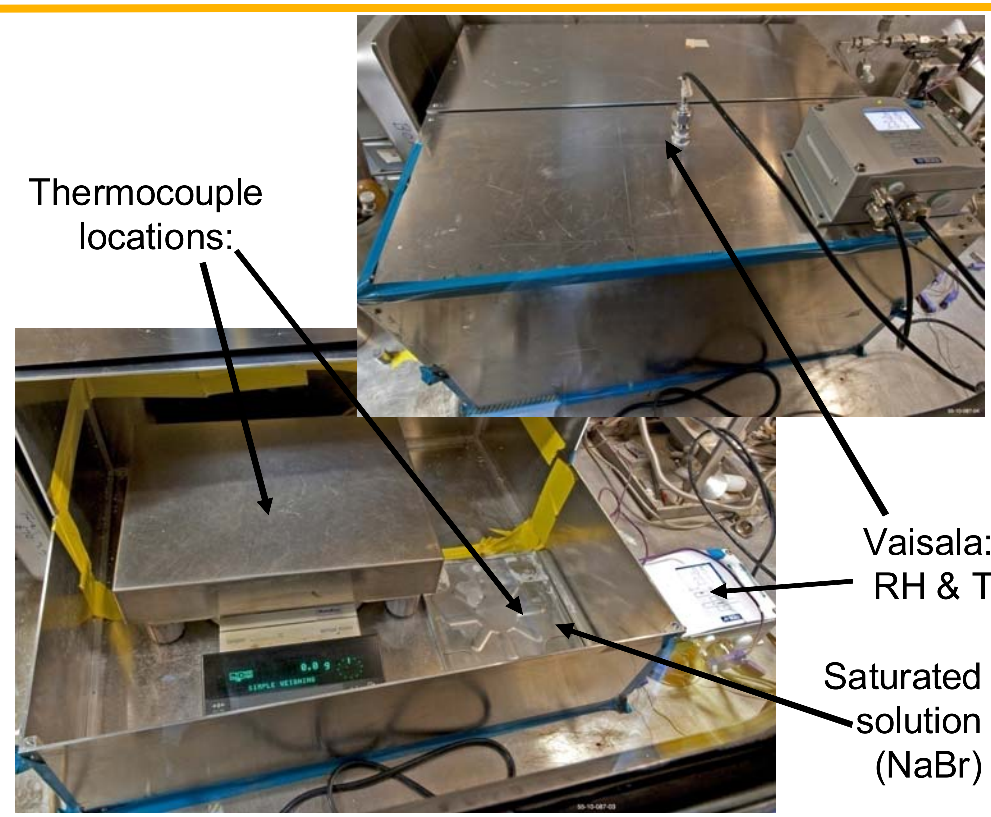

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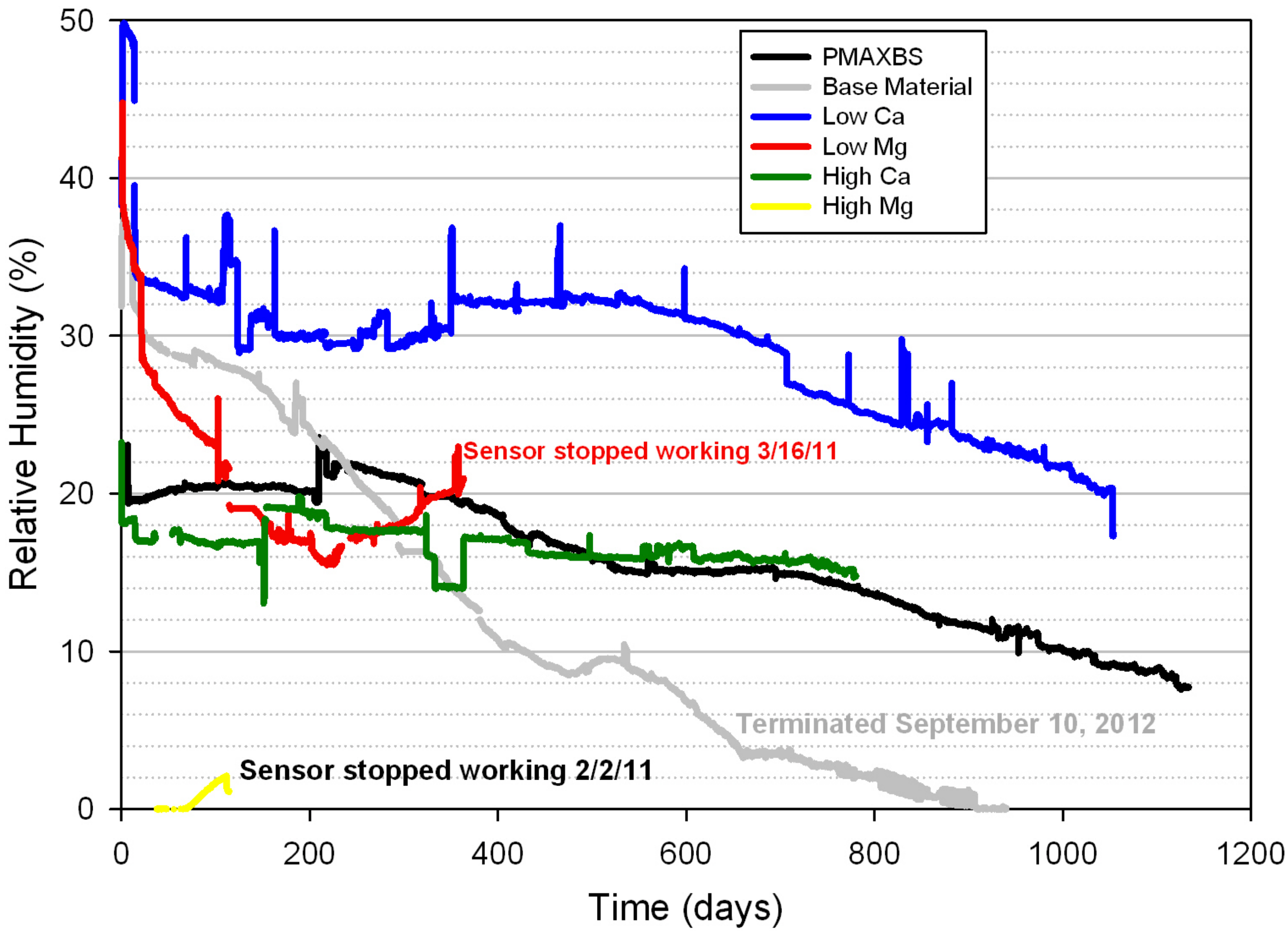
Relative Humidity

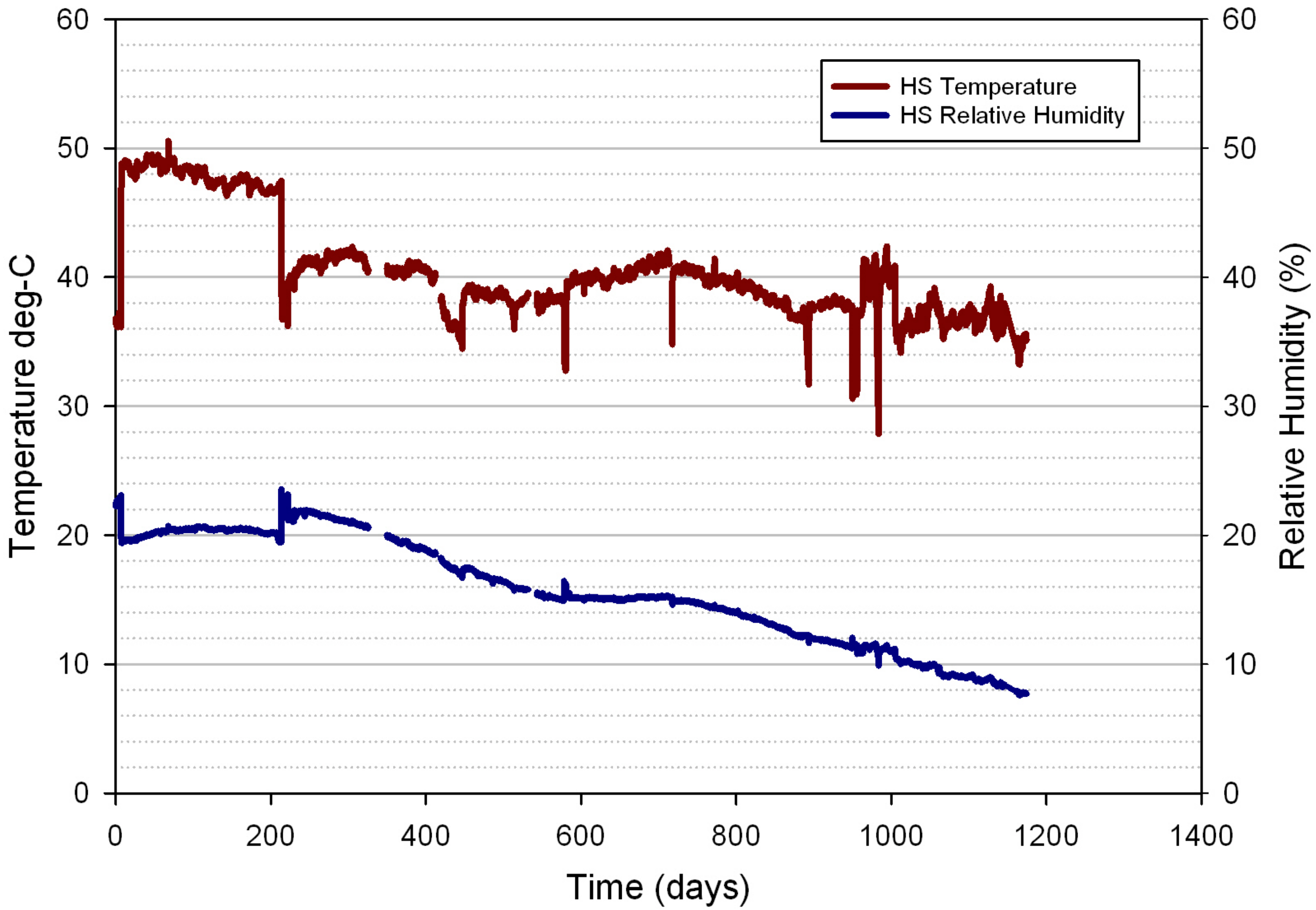


PMAXBS

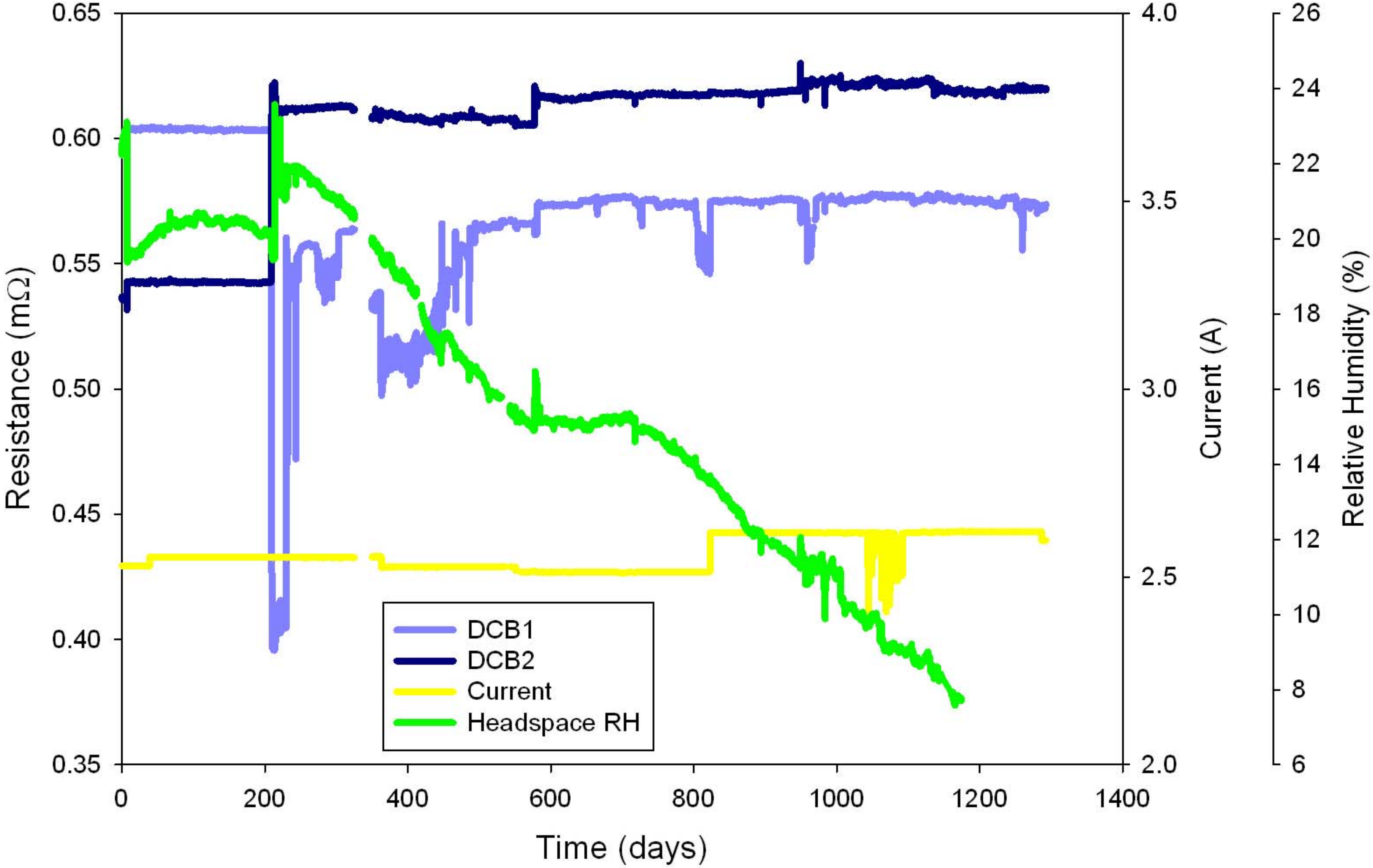
(Loaded August 2009)

Moisture: 0.09 wt%

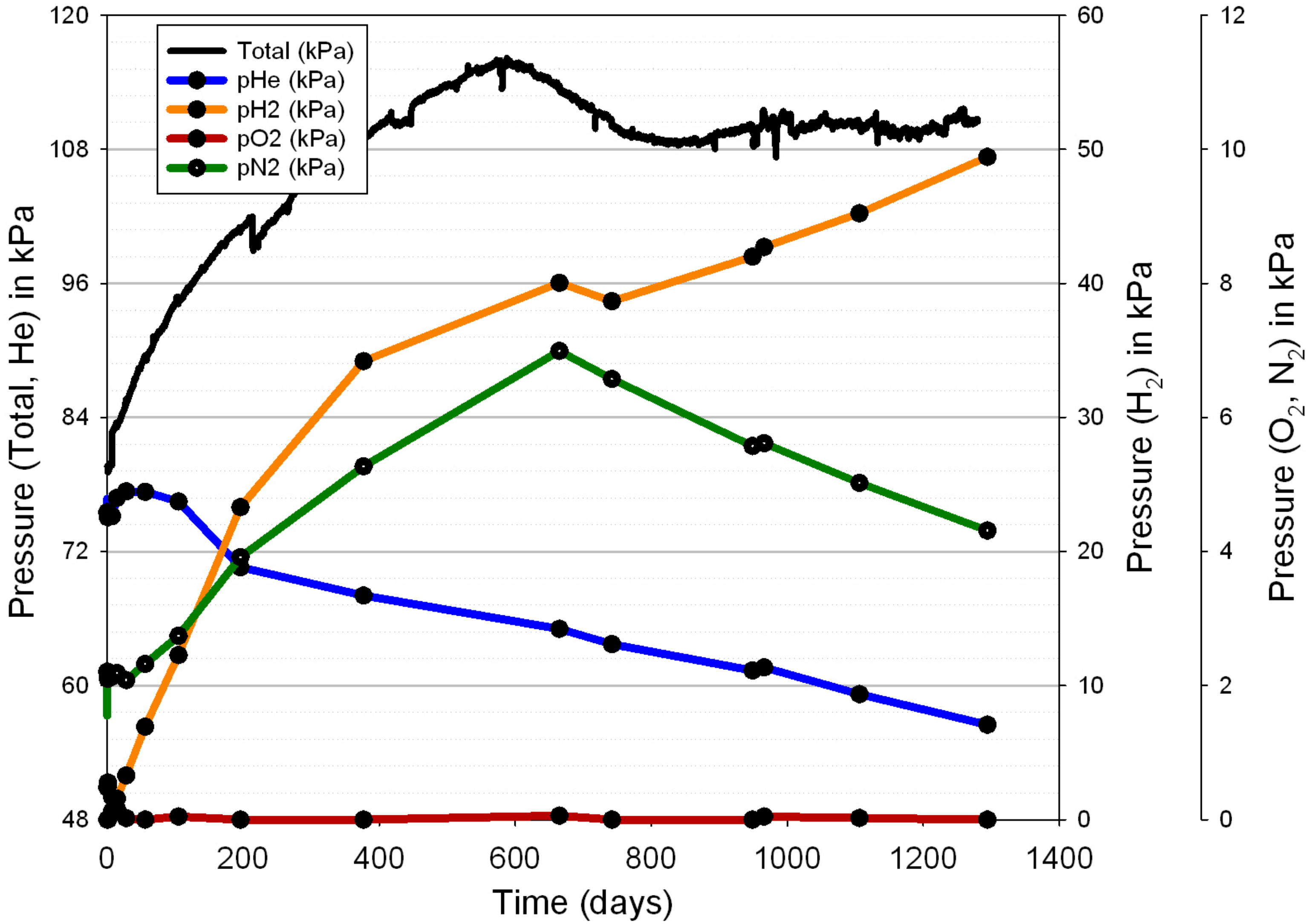
PMAXBS (0.09 wt% H_2O)



PMAXBS: DCB Data



PMAXBS: Gas Composition



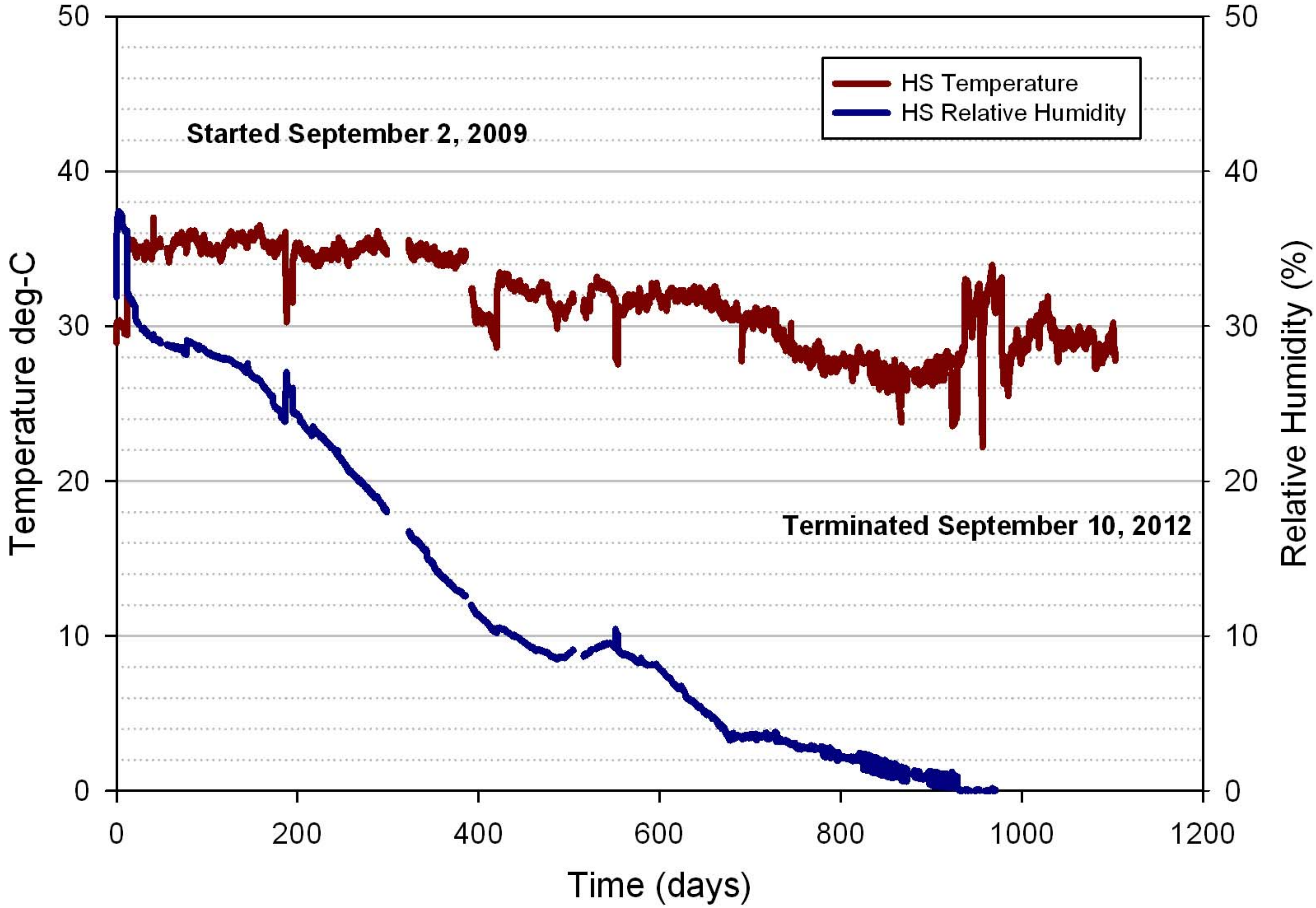
BASE MATERIAL

(Loaded September 2009)

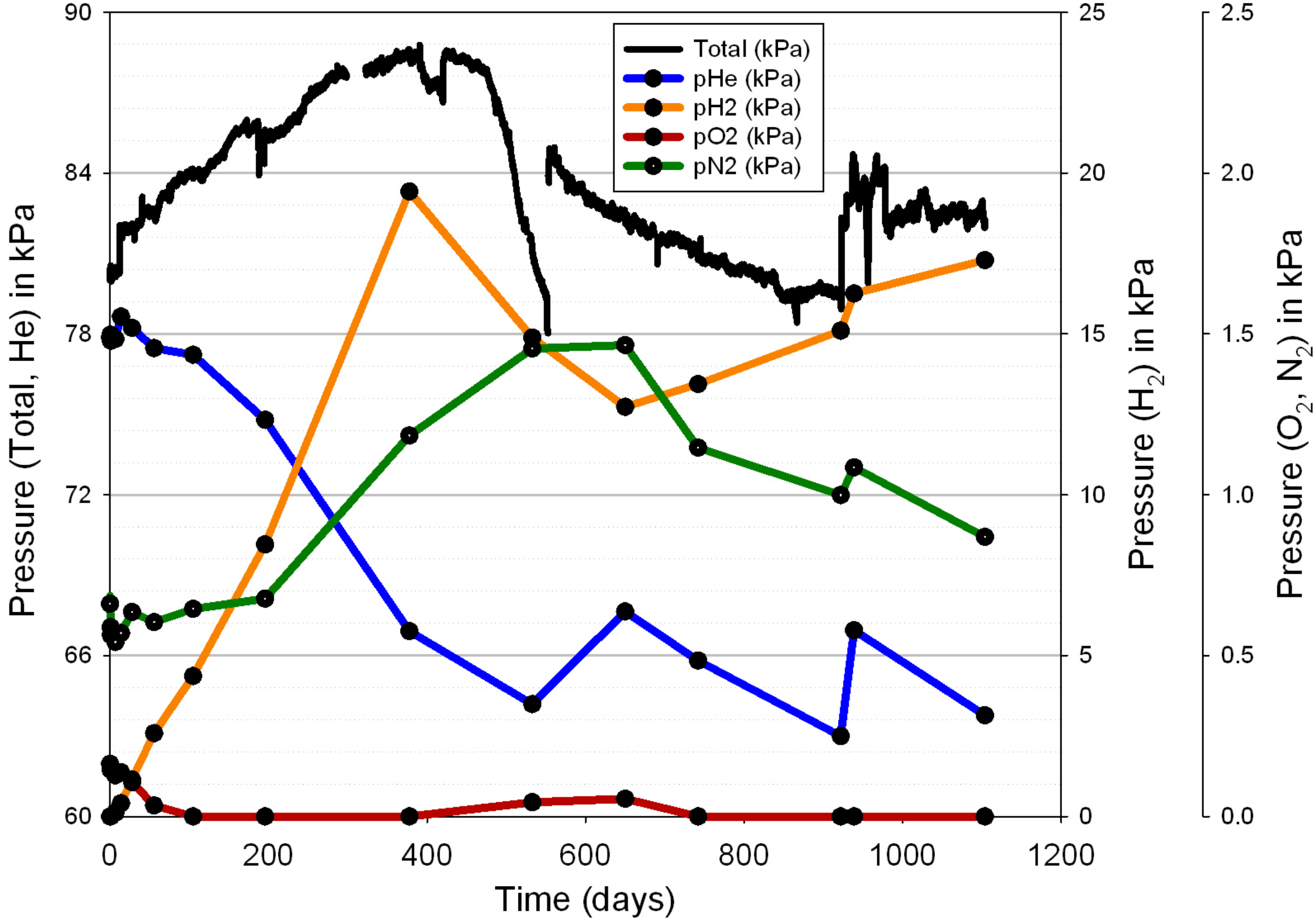
Moisture: 0.05 wt%

(DE'd September 2012)

Base Material (0.05 wt% H_2O)



Base Material Gas Composition



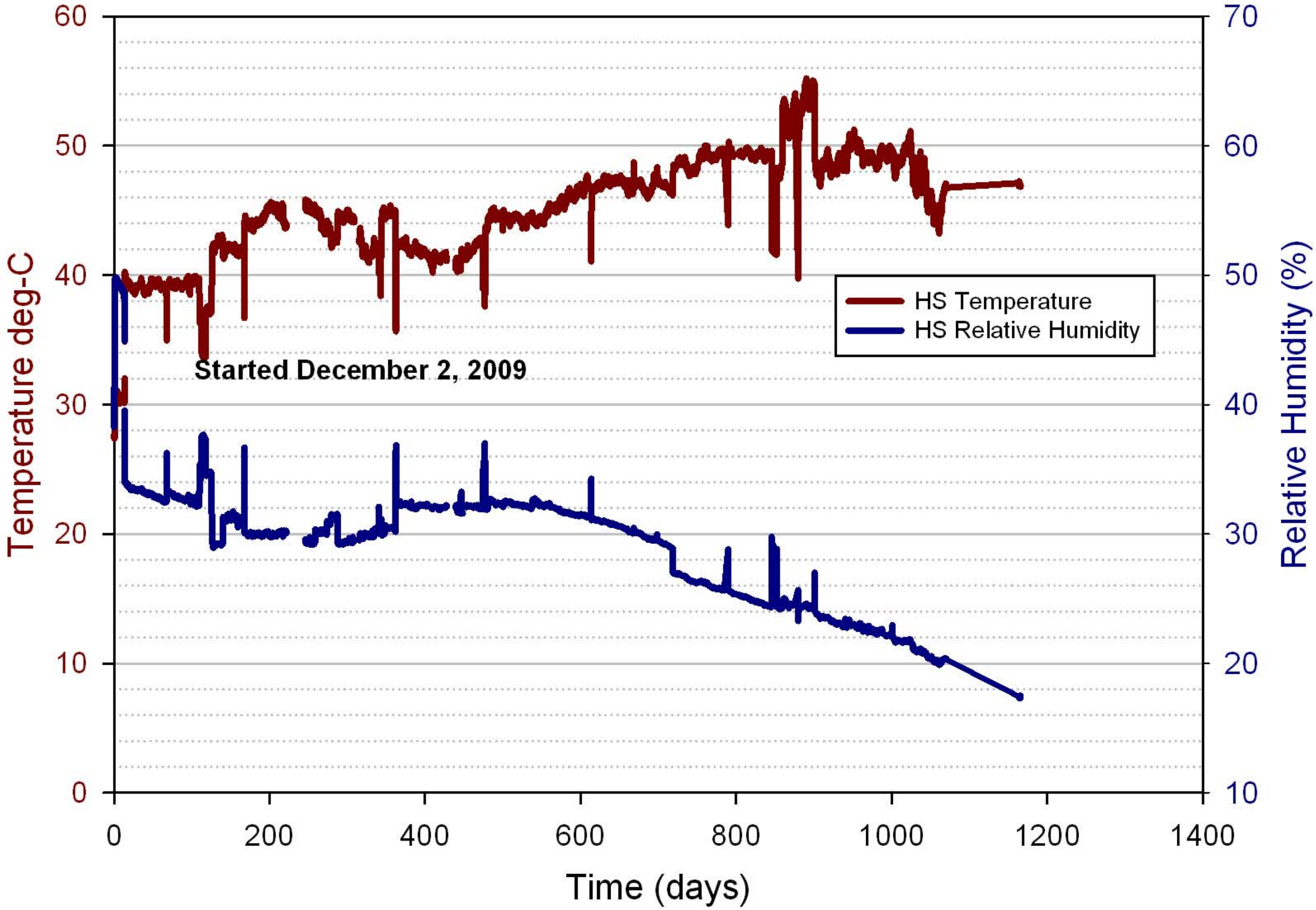
LOW CALCIUM

(Loaded November 2009)

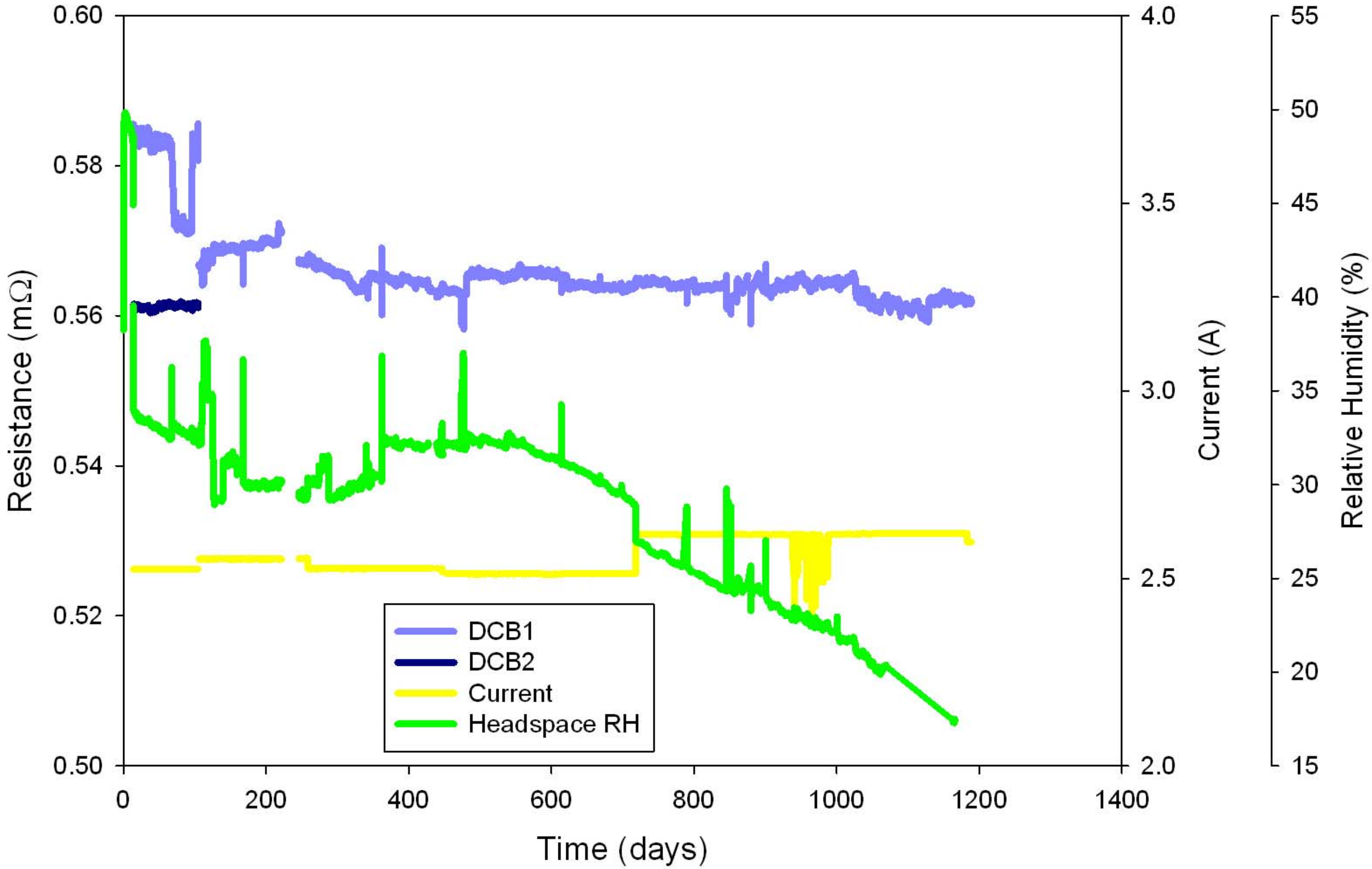
$KCaCl_3$: 0.33 wt%

Moisture: 0.28 wt%
(~7 waters of hydration)

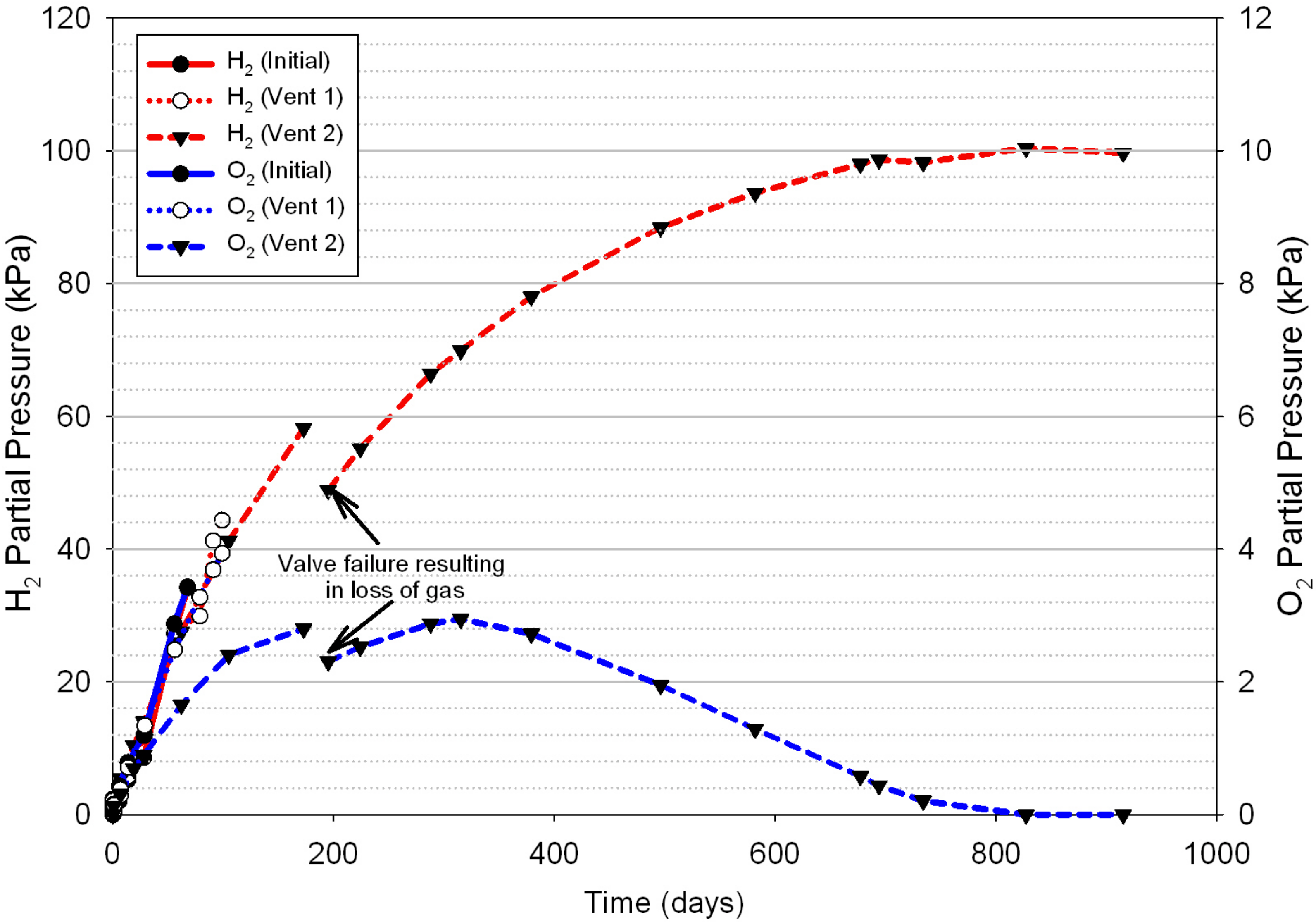
Low Ca (0.28 wt% H_2O)



Low Ca: DCB Data



Low Ca: H_2 and O_2 Pressures



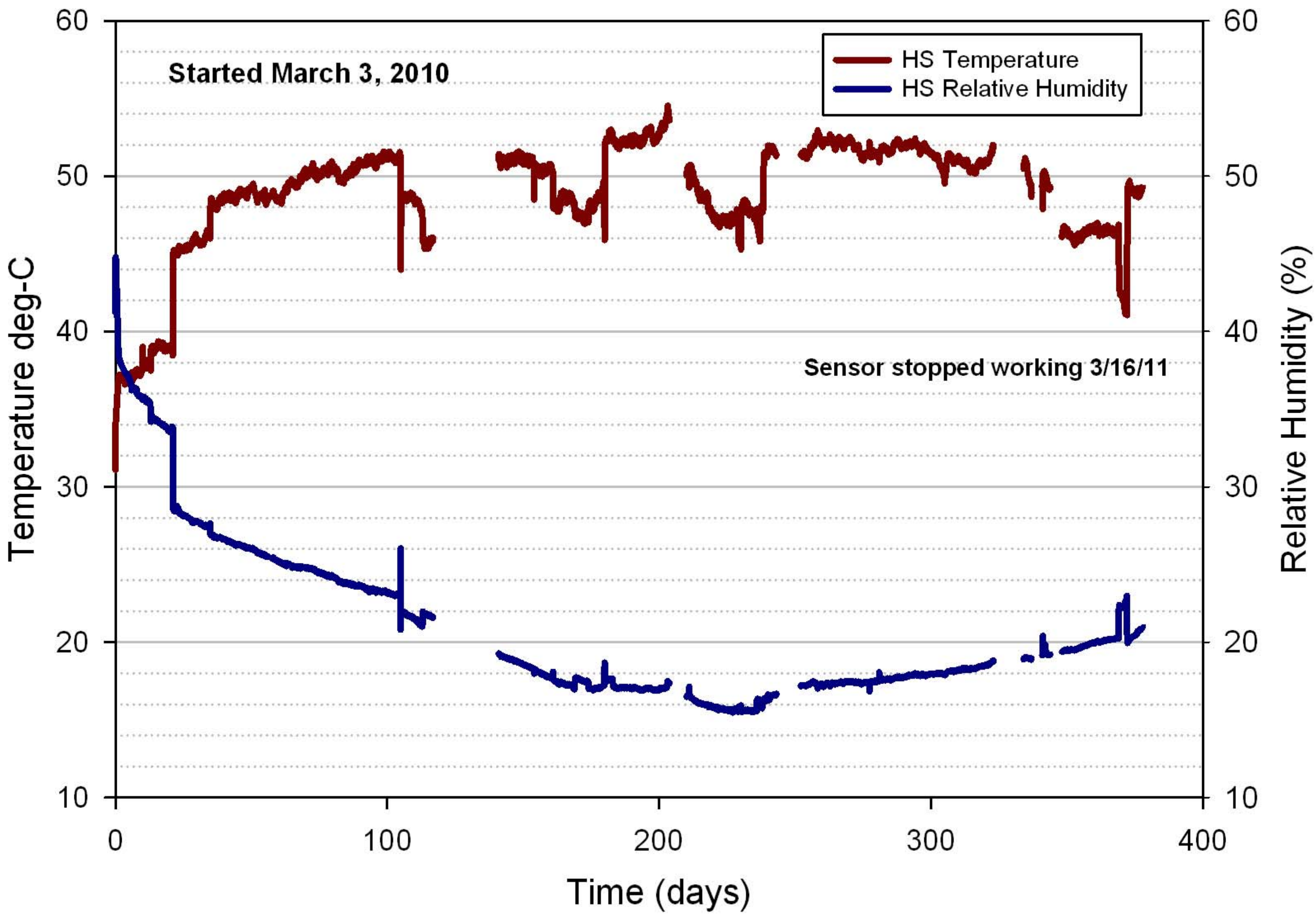
LOW MAGNESIUM

(Loaded November 2009)

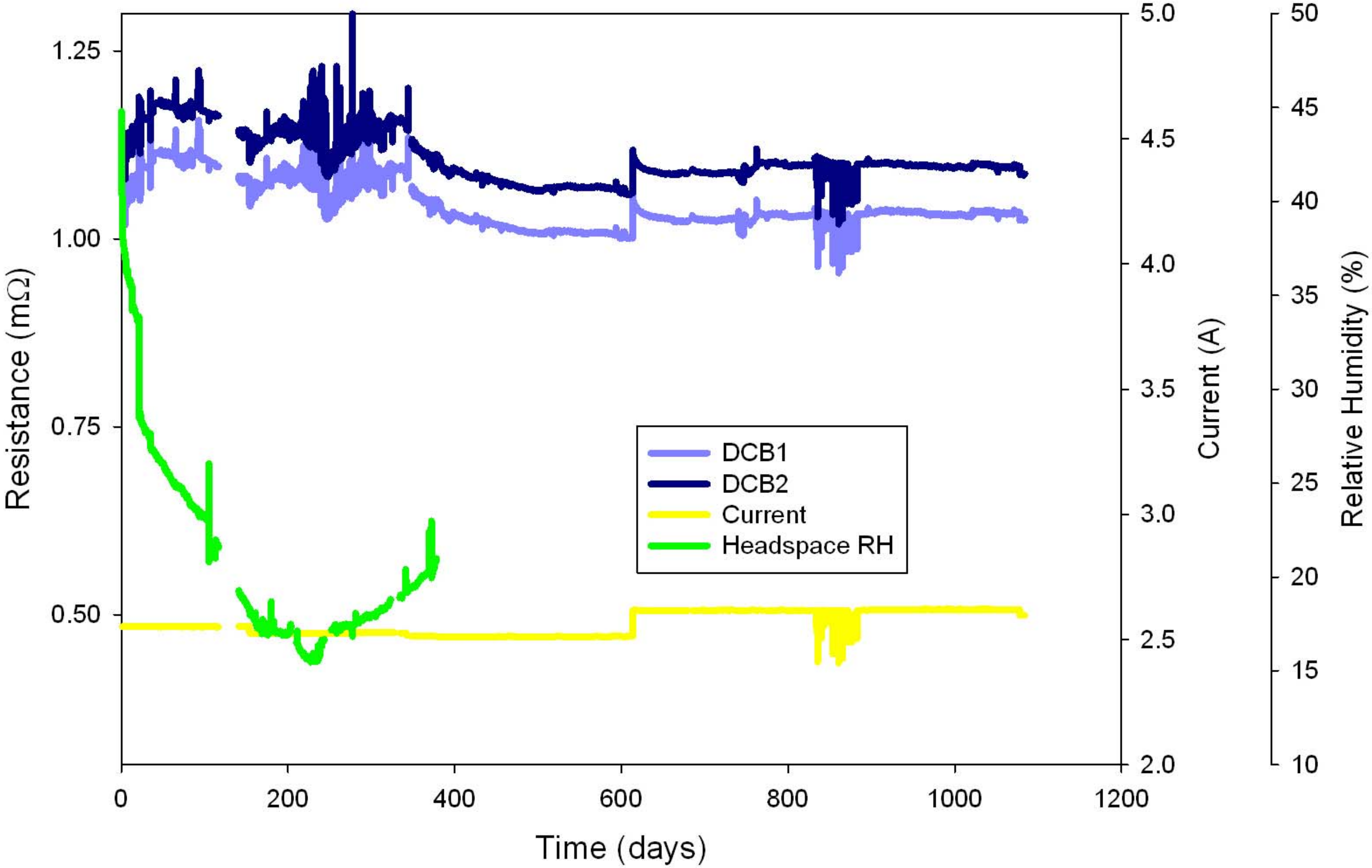
$KMgCl_3$: 0.33 wt%

Moisture: 0.28 wt%
(~7 waters of hydration)

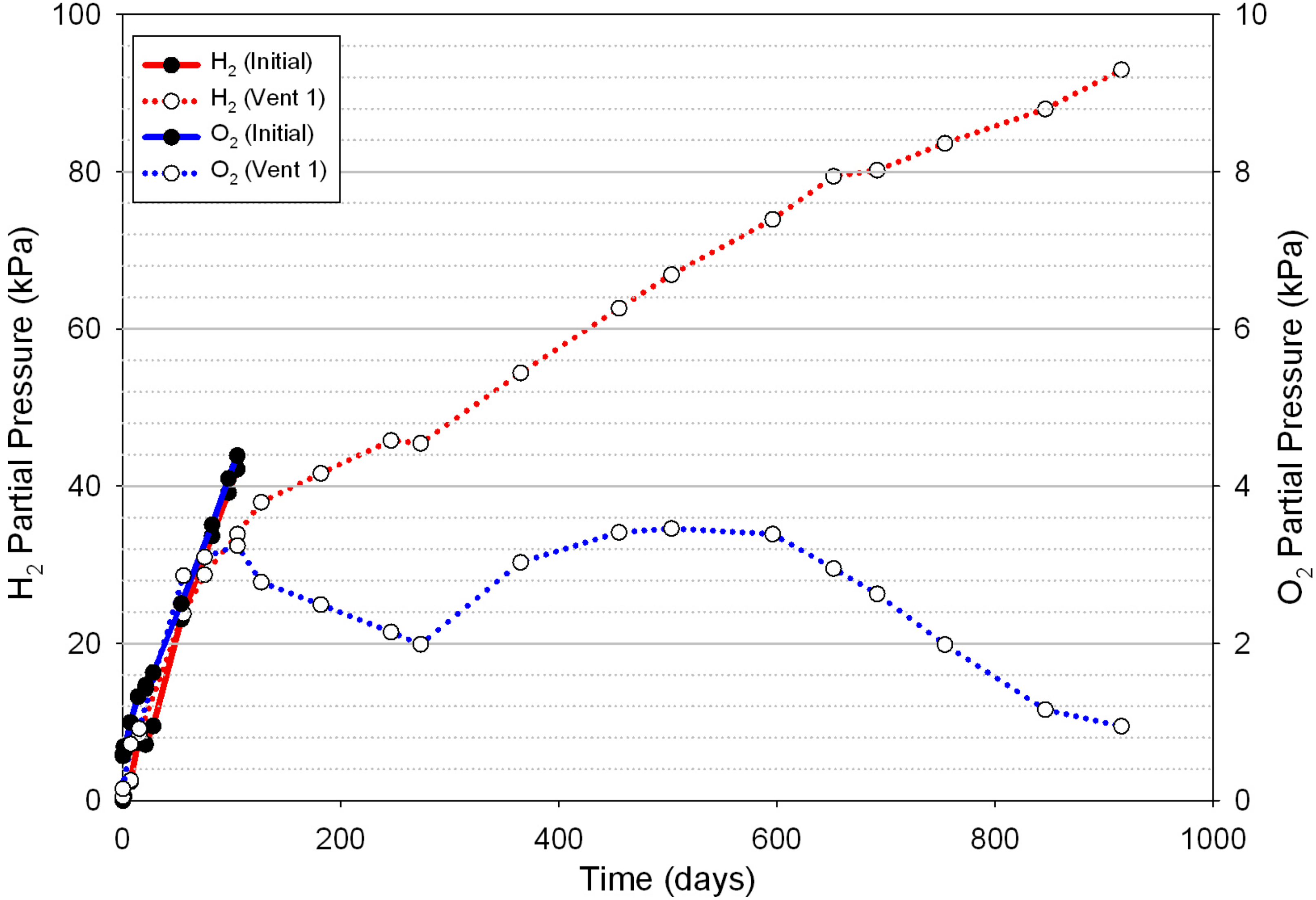
Low Mg (0.29 wt% H_2O)



Low Mg: DCB Data



Low Mg: H_2 and O_2 Pressures



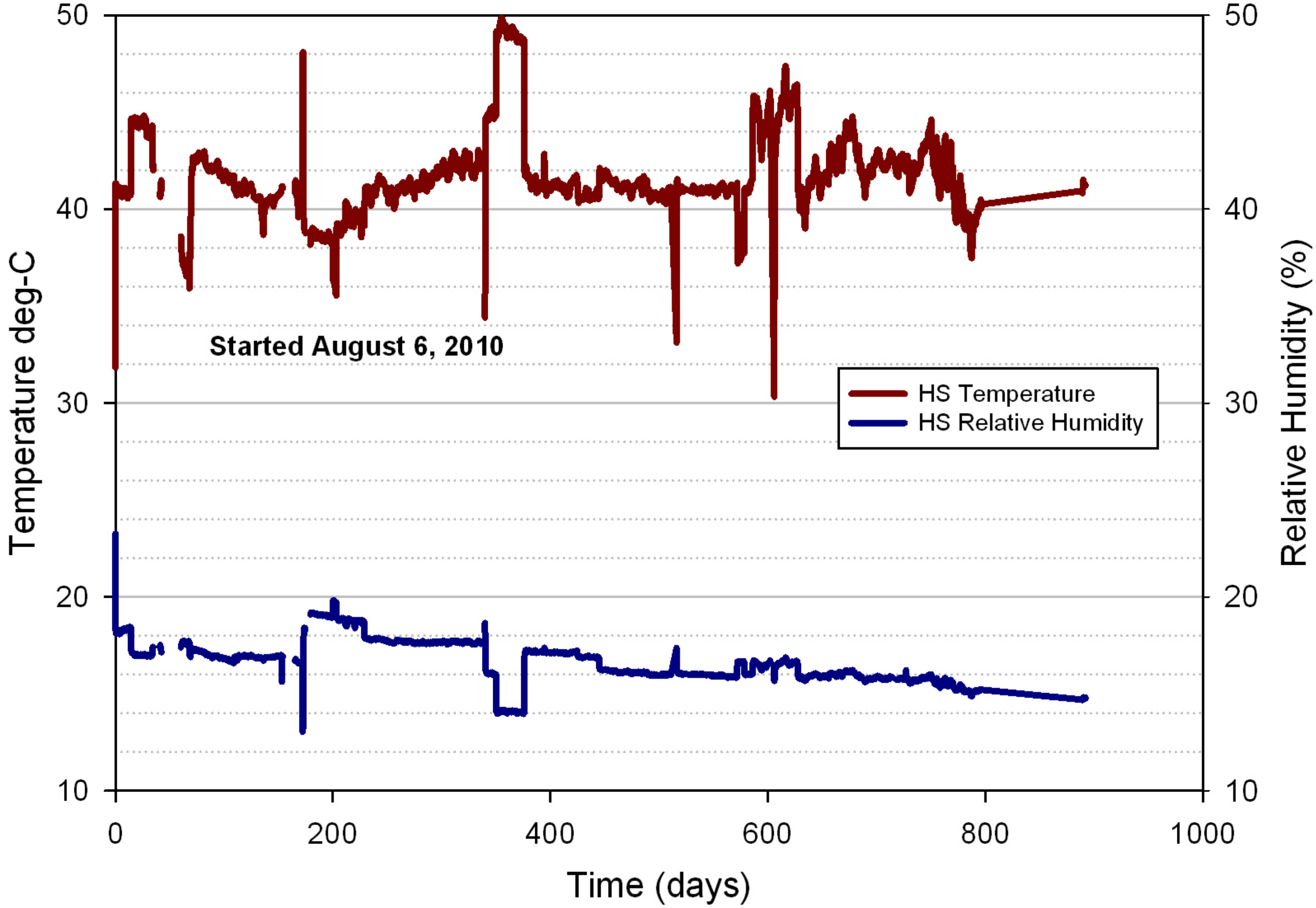
HIGH CALCIUM

(Loaded August 2010)

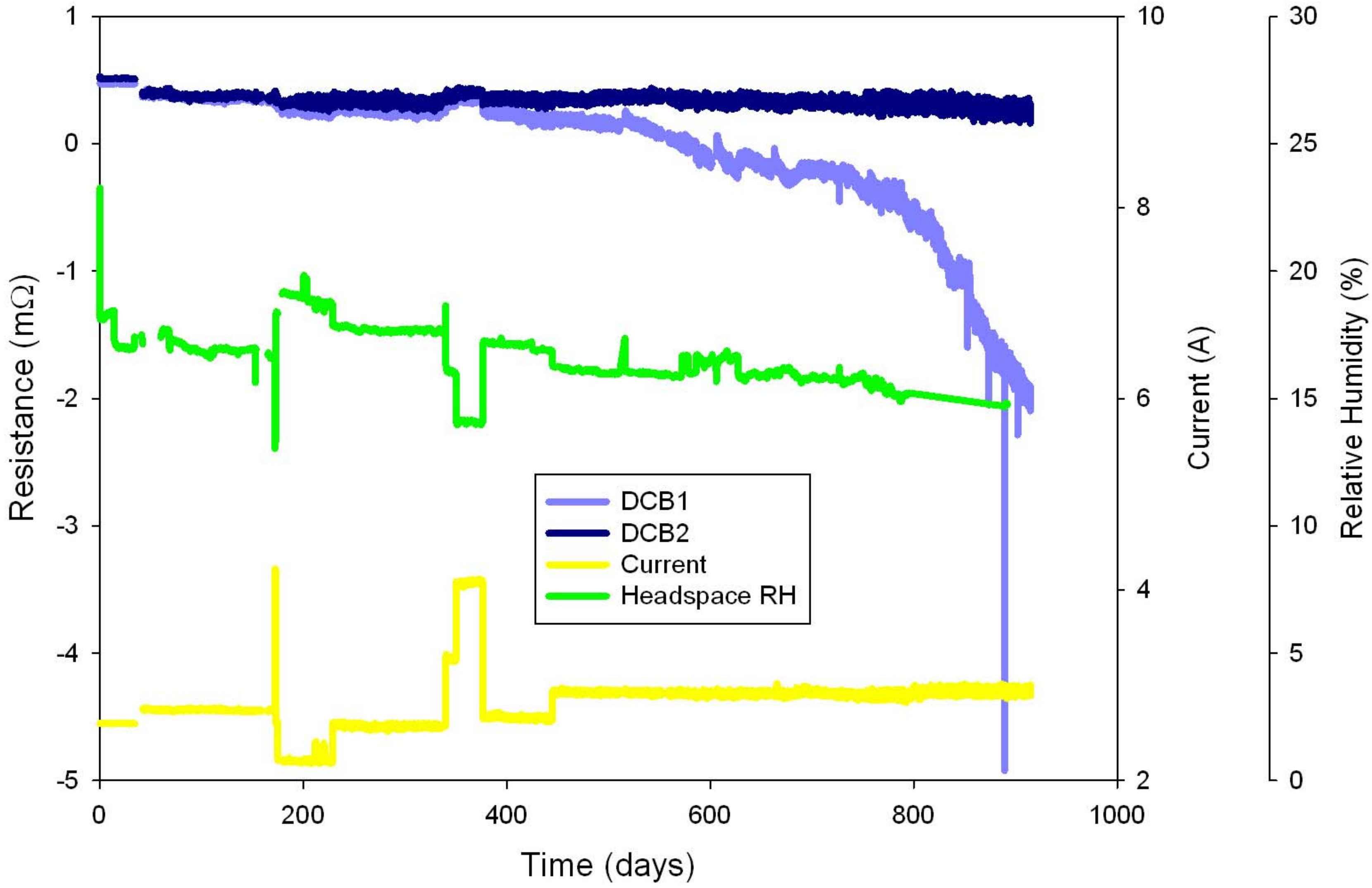
$KCaCl_3$: 3.2 wt%

Moisture: 0.39 wt%
(~1 waters of hydration)

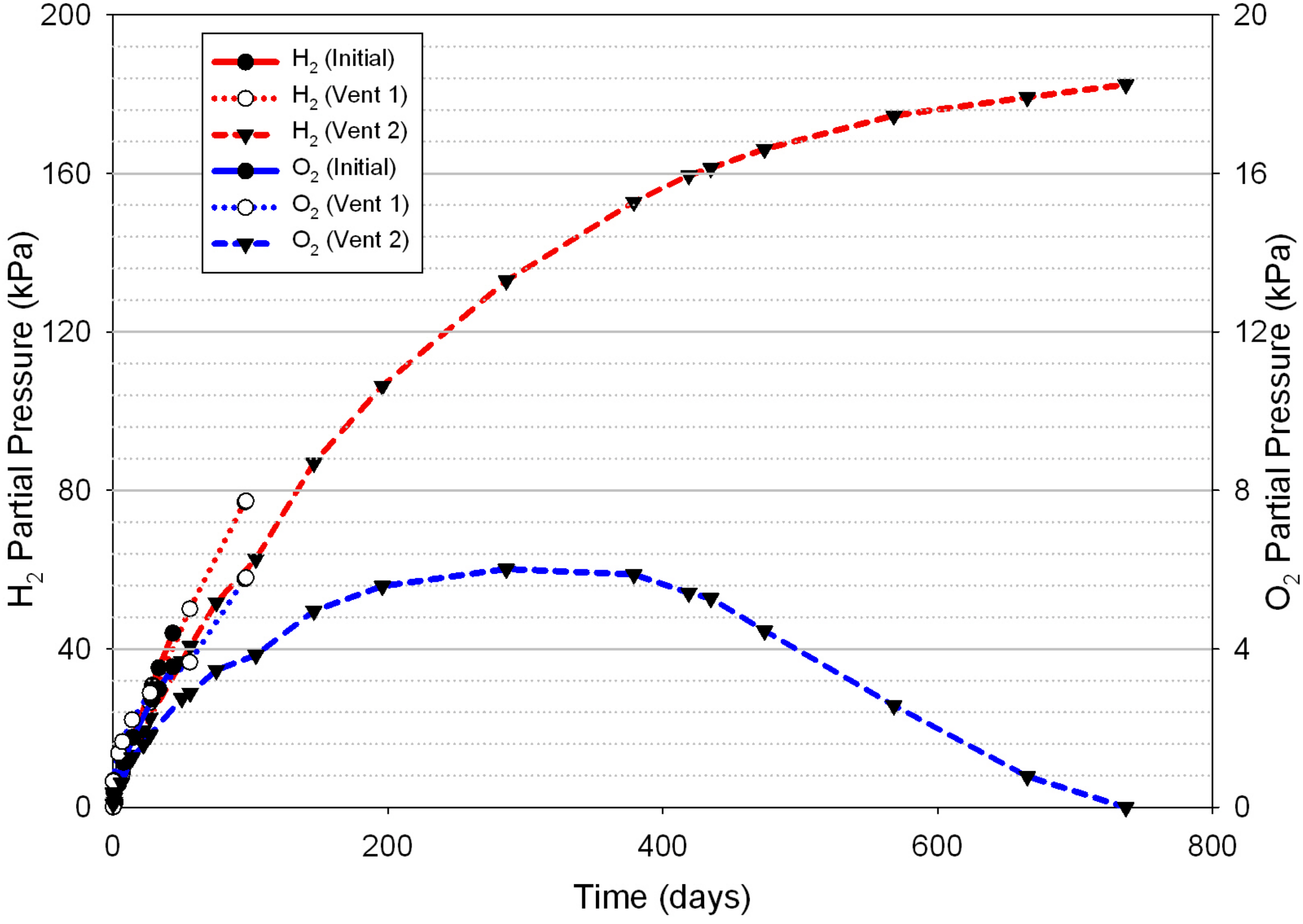
High Ca (0.40 wt% H_2O)



High Ca: DCB Data



High Ca: H_2 and O_2 Pressures



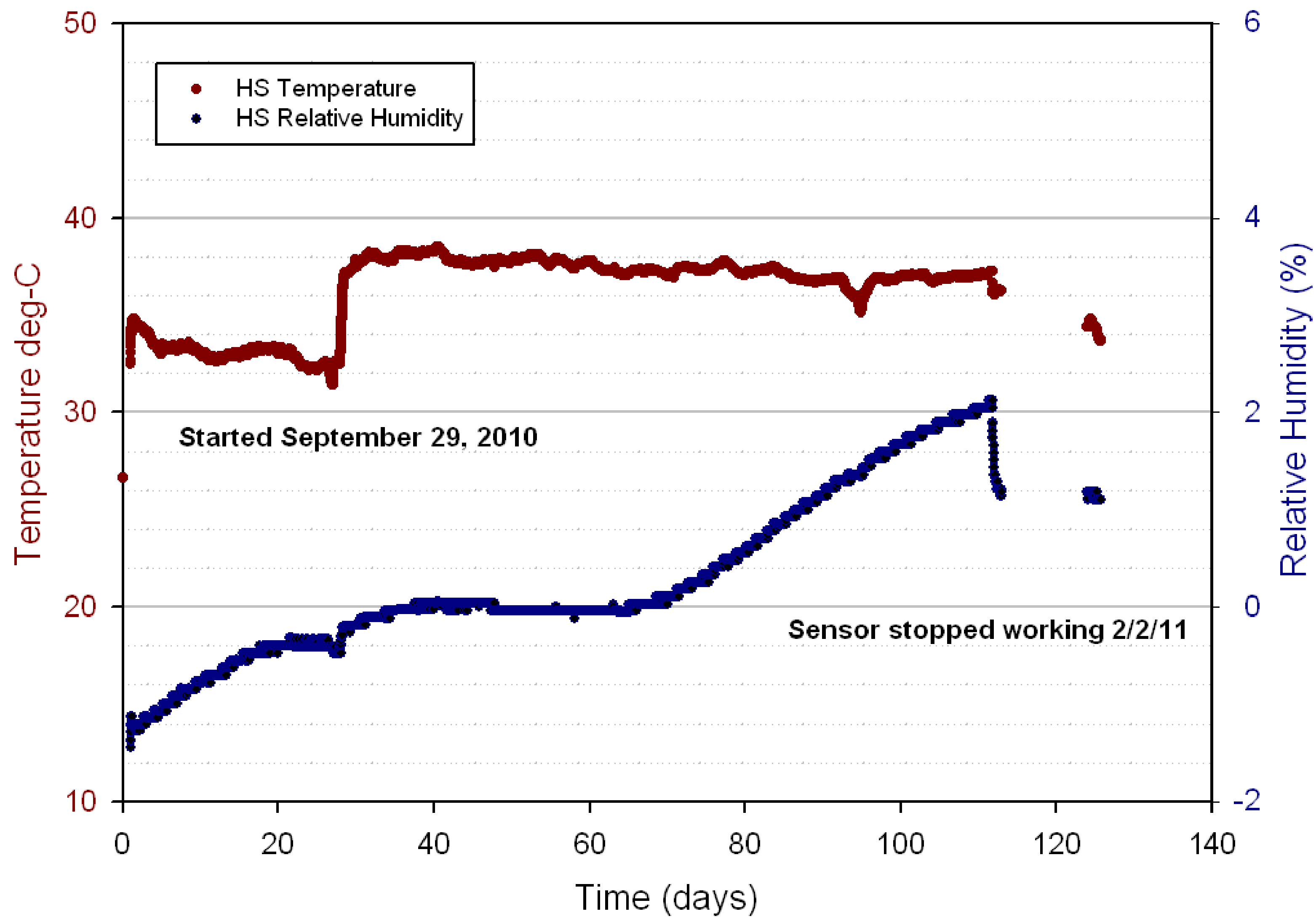
HIGH MAGNESIUM

(Loaded September 2010)

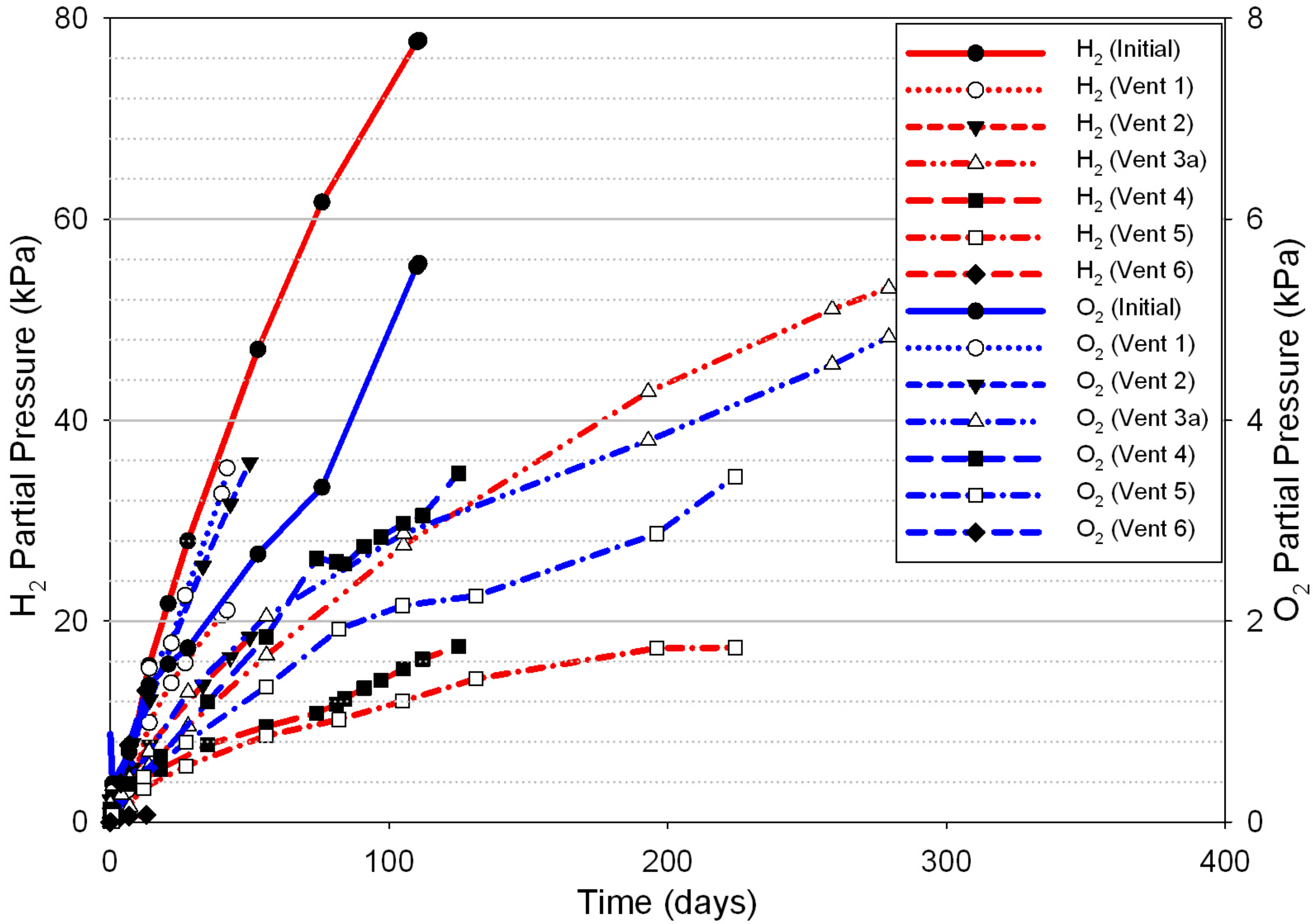
$KMgCl_3$: 3.0 wt%

Moisture: 0.55 wt%
(~1.6 waters of hydration)

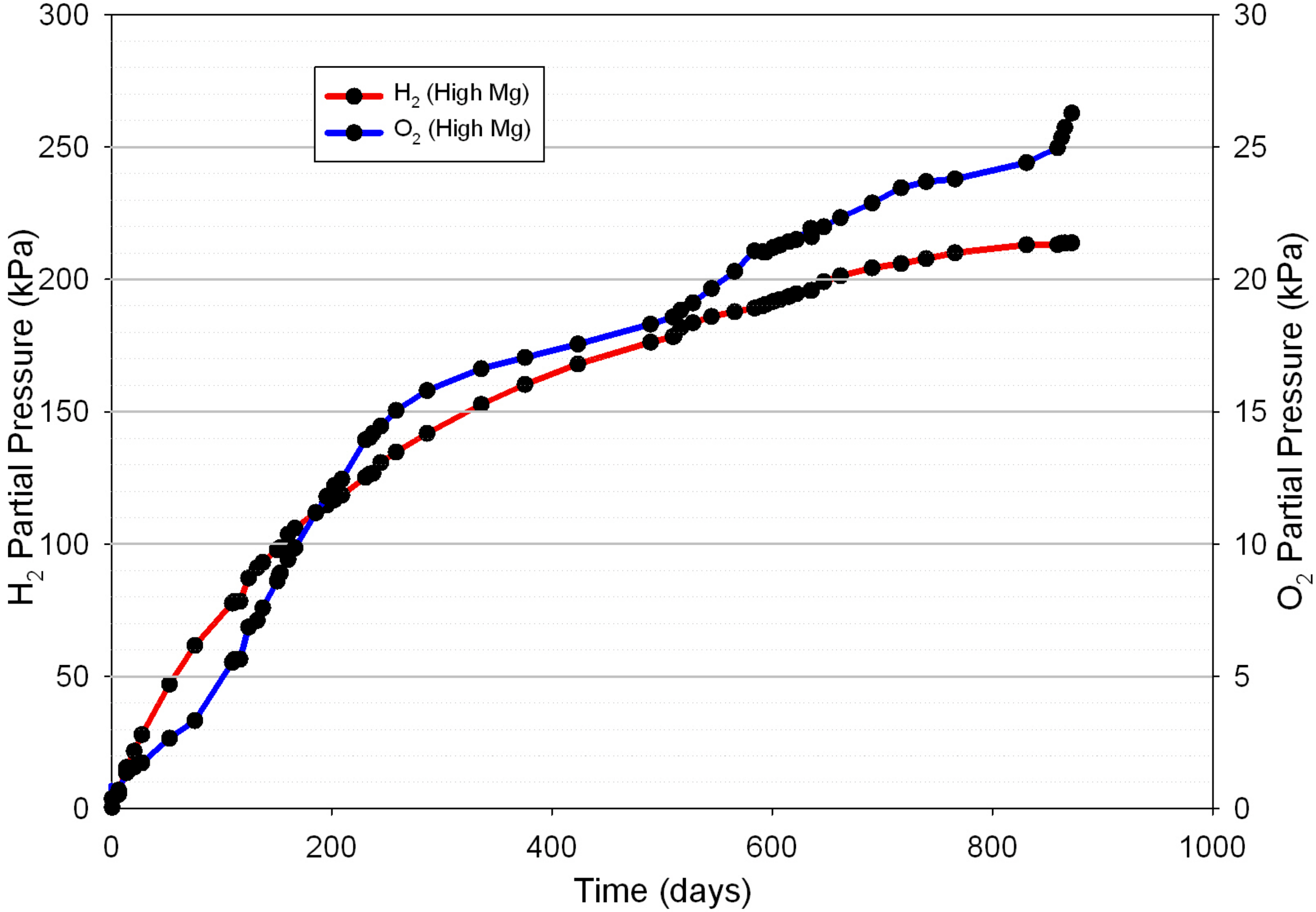
High Mg (0.56 wt% H_2O)



High Mg: H_2 and O_2 Pressures



High Mg: H_2 and O_2 Sum Pressures



Container DE

- **Final GC**
- **MC&A close out (weight, TID, NDA)**
- **Remove / inspect burst disk**
- **Open container with can opener**
- **Inspect / photograph container**
- **Heat material on hot plate to remove moisture**
- **Moisture measurement: 200ºC weight loss and/or TGA**
- **Corrosion samples preserved in hermetically sealed containers until analyzed**
- **Analysis of corrosion samples: Teardrops, DCBs, lid sections specimens, and crevice specimens**
  - Brush
  - Photograph
  - Clean (ultrasonic bath)
  - Dye penetrant (teardrops)
  - Macroscope
  - Microscope

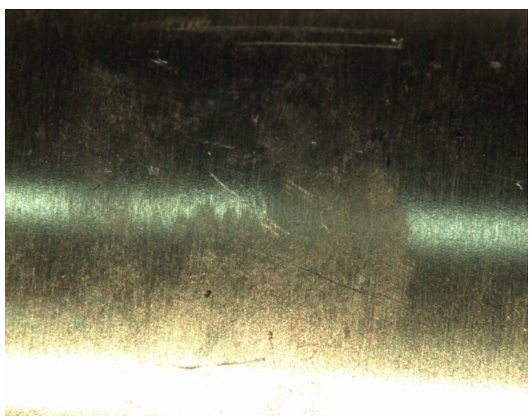
Base Material DE Results

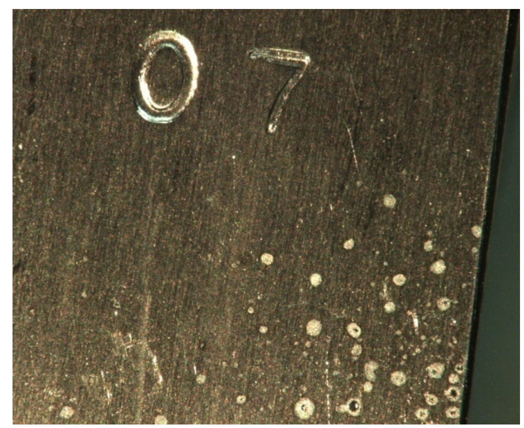
- **<u>Container condition</u>: clean/shiny**
- **<u>Burst disk condition</u>: clean/shiny**
- **<u>DCBs</u>: None present**
- **<u>Tear drops</u>: shiny clean, slight discoloration on 05 and 07 in material phase—not removed with cleaning**
- **<u>Lid section specimens</u>: None present**
- **<u>Crevice specimens</u>: None present**
- **<u>200ºC moisture loss</u>: 0.0085 wt%**

Base Material Teardrops

Headspace


Material

Summary

- **Corrosion is possible where liquid phases are present**
- **Liquids phases possible even for short exposure to high RH**
- **Possibly a relationship between conditions for oxygen generation in chloride salt bearing material and corrosion**
- **Possible crack growth in high Ca material**

Material Name	Age (mo.)	RH_{max}	RH (%)	Total P (psi)	H_2 press.	O_2 press.	Currently Supports Corrosion
PMAXBS	43	49	8↓	16—	↓	~0—	No
Base Mat.	36 (DE'd)	37	<2	12 (final)	↓	~0 (final)	None obs.
Low Ca	40	49	18↓	37—	↑	0—	Yes
Low Mg	36	41	?, 25↑	20↑	↑	↓	Maybe
High Ca	31	18	15—	54↑	↑	0—	Yes
High Mg	30	2	?, 2↑	42↑	↑	↑	No

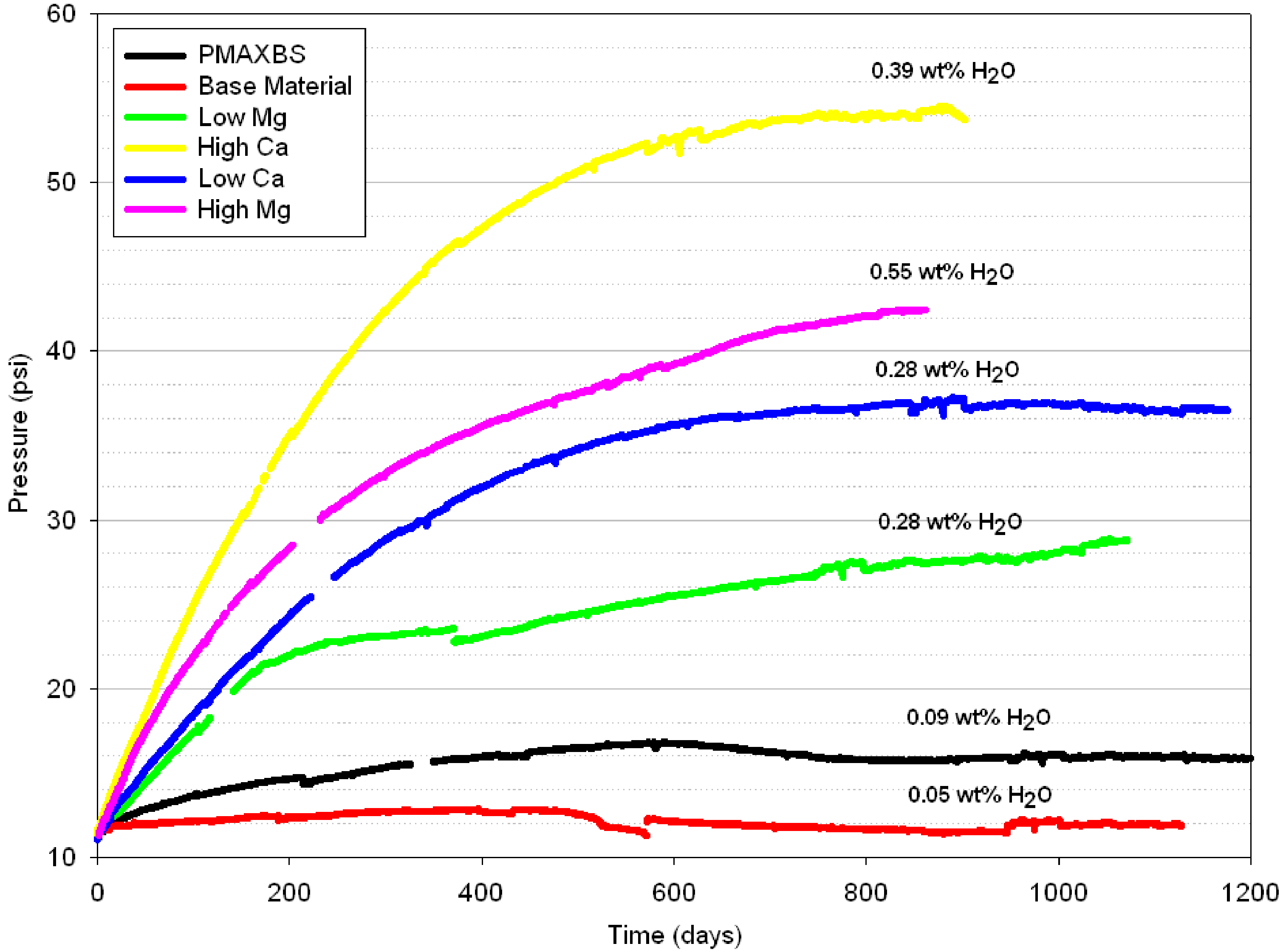
Discussion of Future Plans

- **Resume container DE (delayed due to equivalency work)**
  - Next DE's: Late FY13 and early FY14
  - Suggested priority
    - High Ca: DCB's indicate crack growth (1-5)
    - PMAXBS: (1-4)
    - Low Mg: (1-4)
- **Continue surveillance**
  - Low Ca (supports corrosion)
  - High Mg (generates O_2)
- **Replace RH sensors**
  - High Ca
  - Low Mg
  - High Mg
- **Future loading**
  - Low temperature stabilized high purity oxide from oxalate precipitation (loading conditions determined by results from small scale studies)

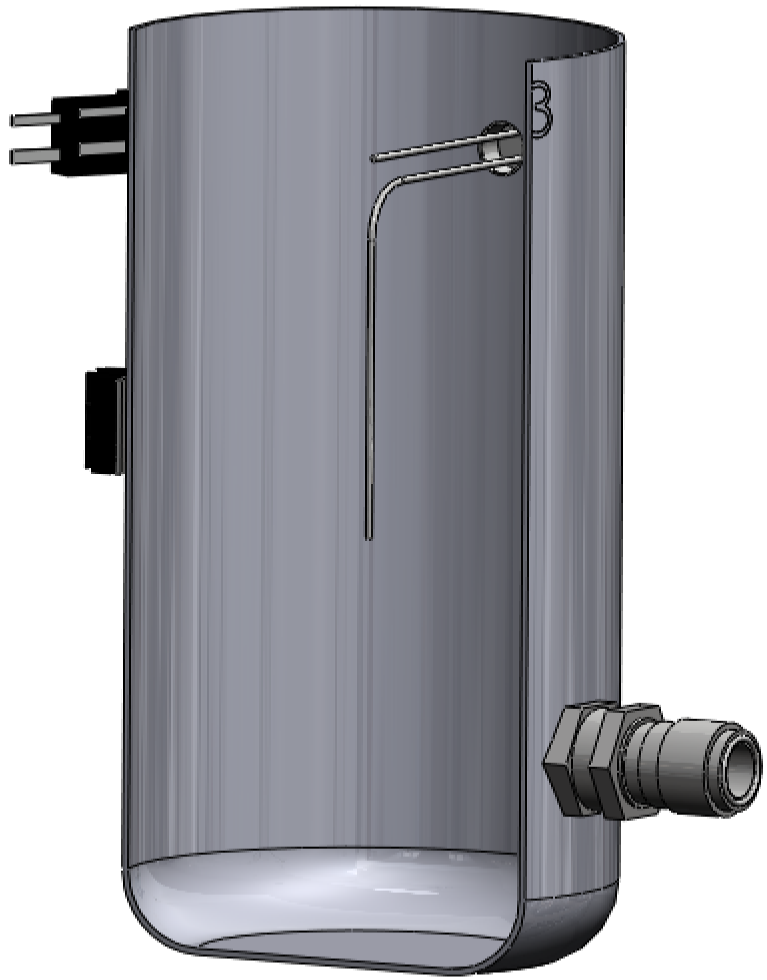
- **Criteria for container removal**
  1. Age: > 2 yrs in surveillance
  2. RH below DRH of added salts
  3. No longer generates O_2
  4. Conditions no longer support corrosion
  5. **Data indicate crack growth***

ADDITIONAL DATA

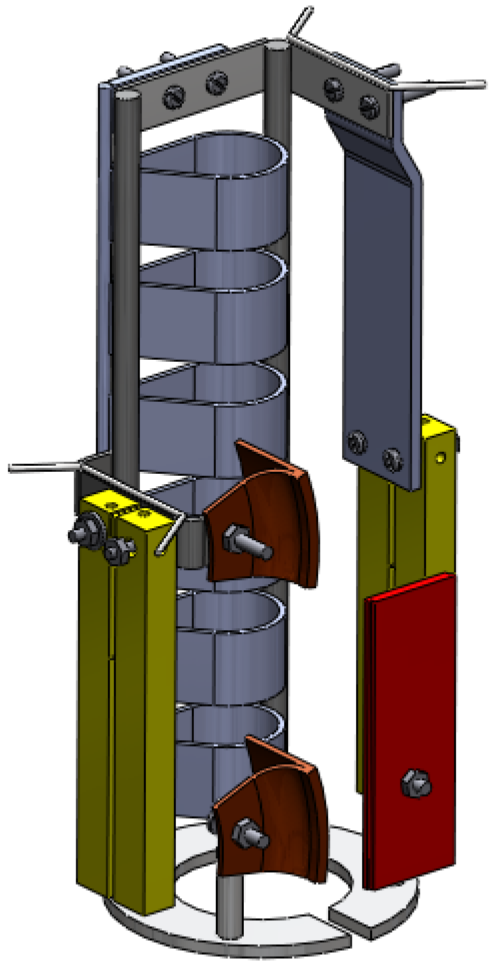
Total Pressure

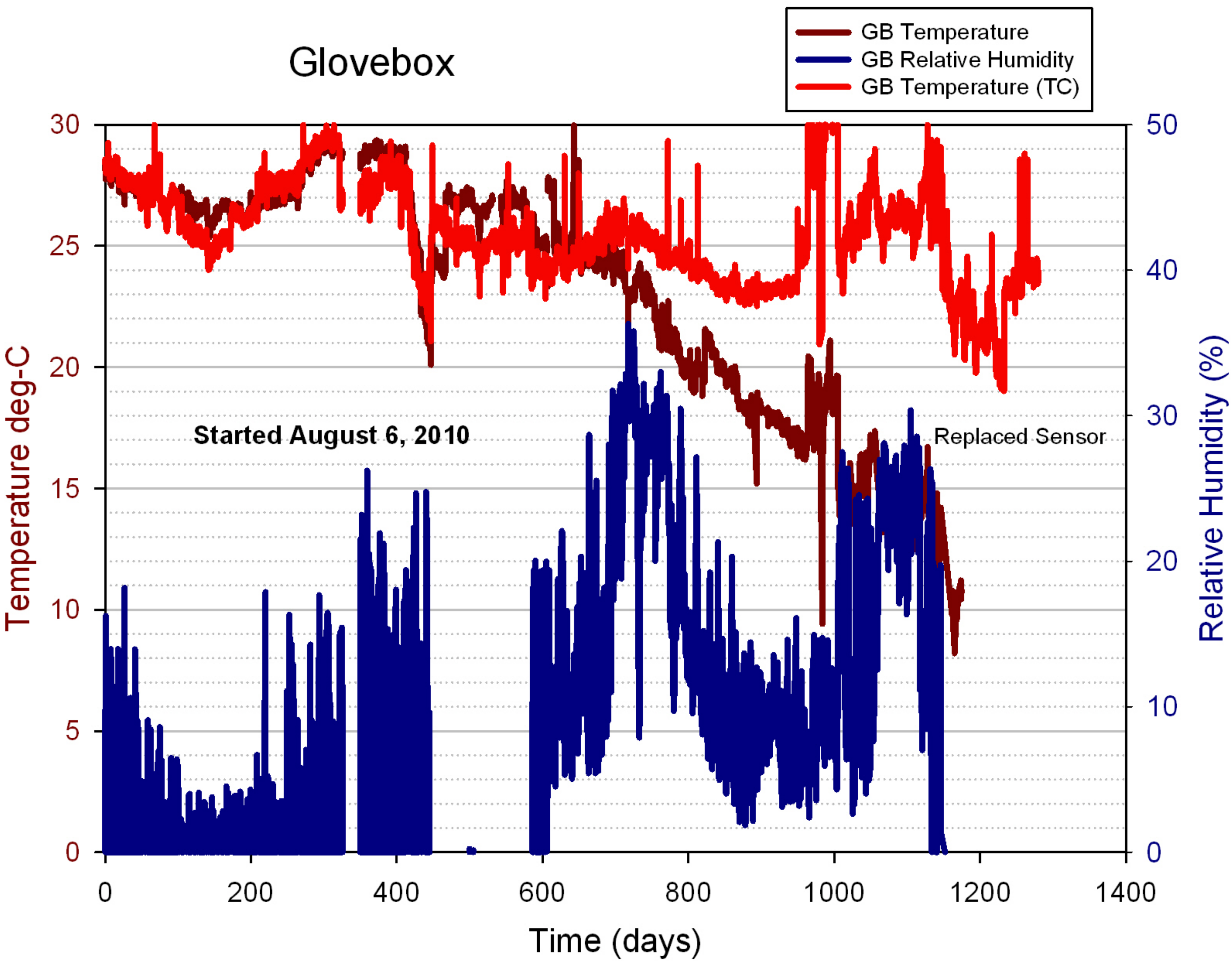


Thermocouple Locations



Corrosion Specimens

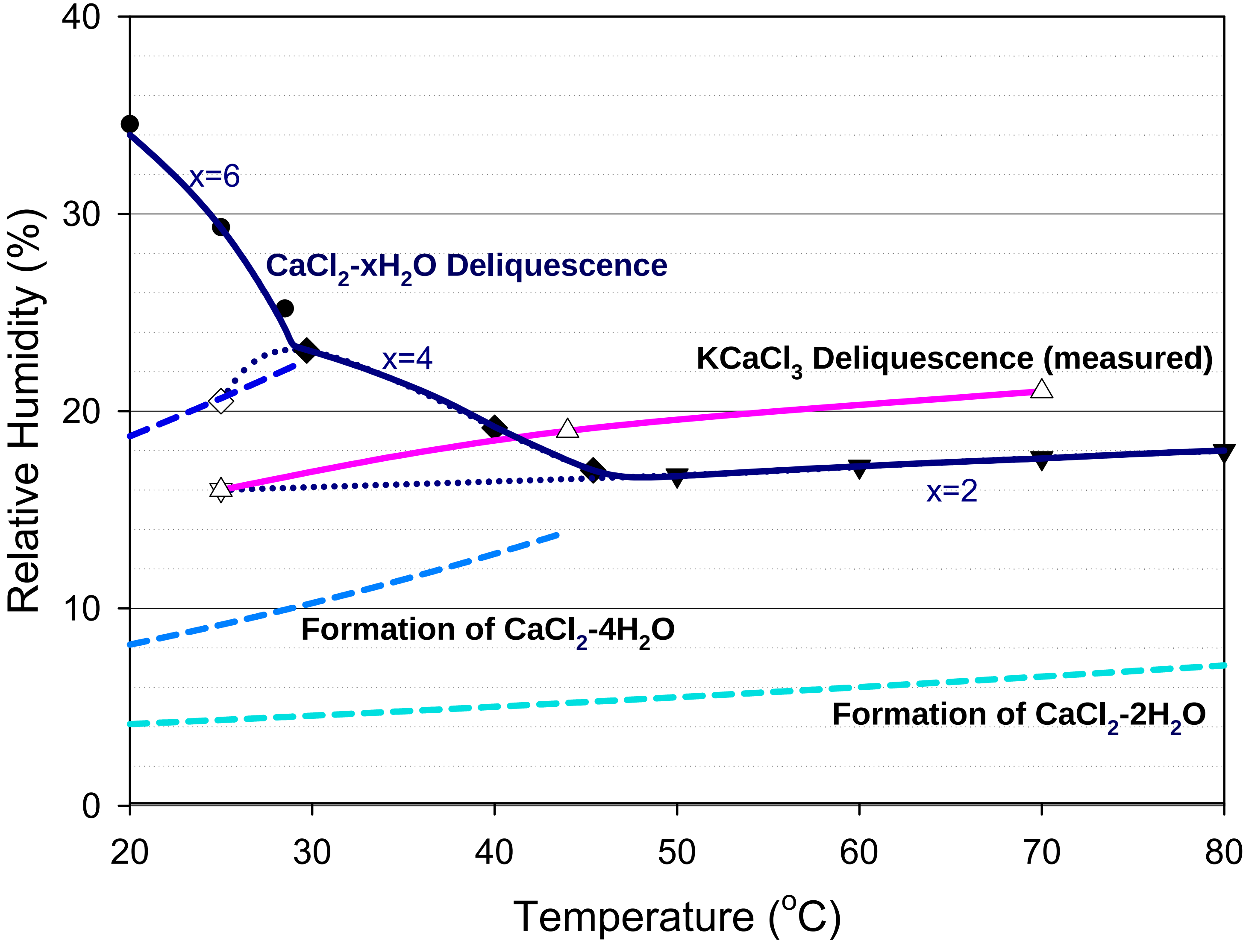



Glovebox
GB Temperature
GB Relative Humidity
GB Temperature (TC)
Started August 6, 2010
Replaced Sensor
Temperature deg-C
Relative Humidity (%)
Time (days)
0
5
10
15
20
25
30
0
10
20
30
40
50
0
200
400
600
800
1000
1200
1400

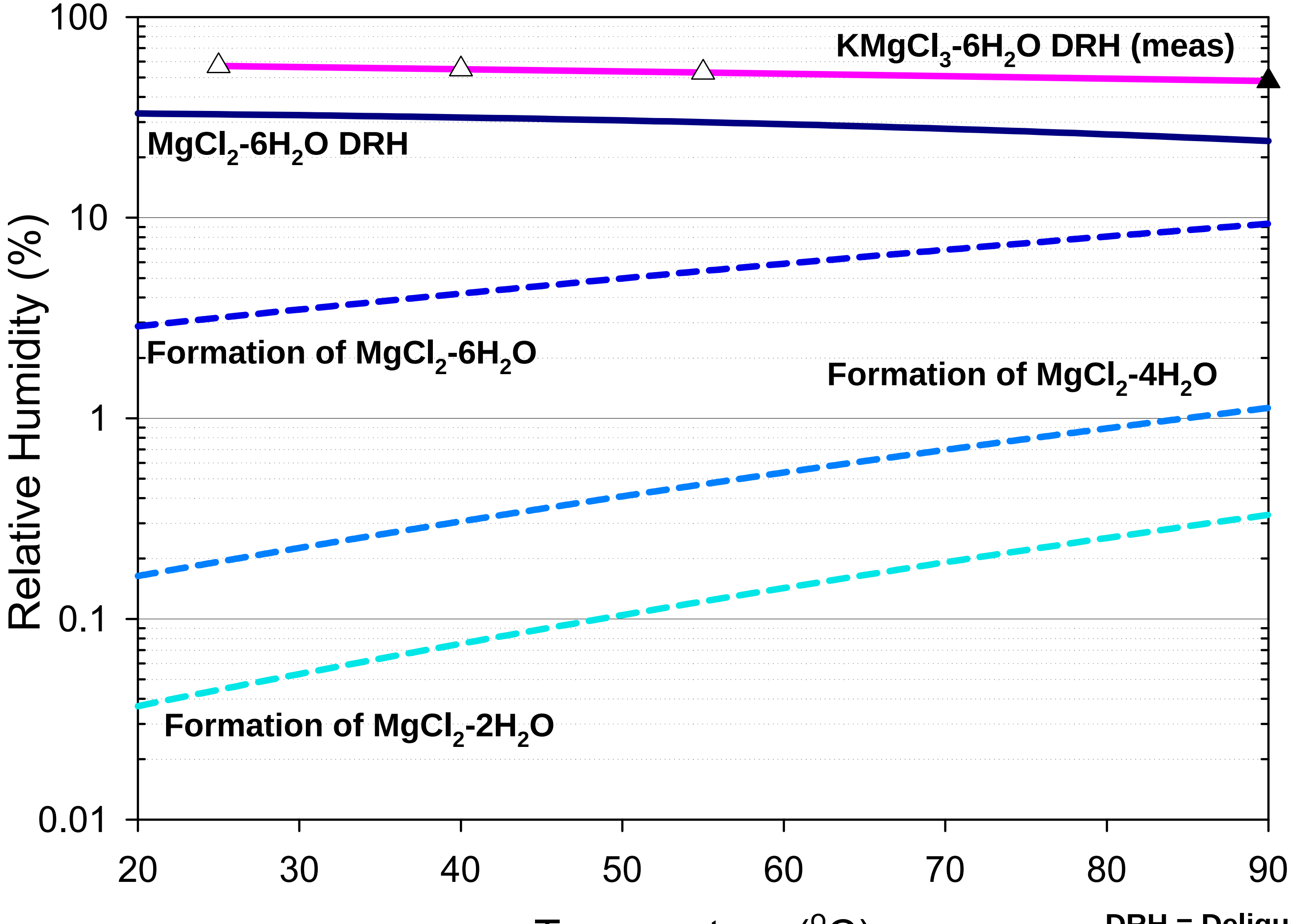
Relative Humidity for Deliquescence and Hydrate Formation

Deliquescence RH of Major Salt Components			
	%RH at 25ºC	%RH at 50ºC	% RH at 75ºC
KCl	84	81	79
NaCl	75	74	76
$KMgCl_3 \cdot 6H_2O$	57†	54†	50†
$MgCl_2 \cdot 6H_2O$	33	31	27
$CaCl_2 \cdot 6H_2O$	29		
$CaCl_2 \cdot 4H_2O$	21†	17 (at 45ºC)	
$KCaCl_3$	16†	19†	21†
$CaCl_2 \cdot 2H_2O$	16†	17	18
Minimum RH at which Various Hydrates Form			
	%RH at 25ºC	%RH at 50ºC	% RH at 75ºC
$CaCl_2 \cdot 6H_2O$	21		
$CaCl_2 \cdot 4H_2O$	9 (13†)	14 (at 44ºC)	
$MgCl_2 \cdot 6H_2O$	3	5	7
$CaCl_2 \cdot 2H_2O$	4 (2†)	5	7
$KMgCl_3 \cdot 6H_2O$	2†	2†	2†
$MgCl_2 \cdot 4H_2O$	0.2	0.4	0.8
$MgCl_2 \cdot 2H_2O$	0.04	0.1	0.2

Hydration behavior of calcium chloride salts

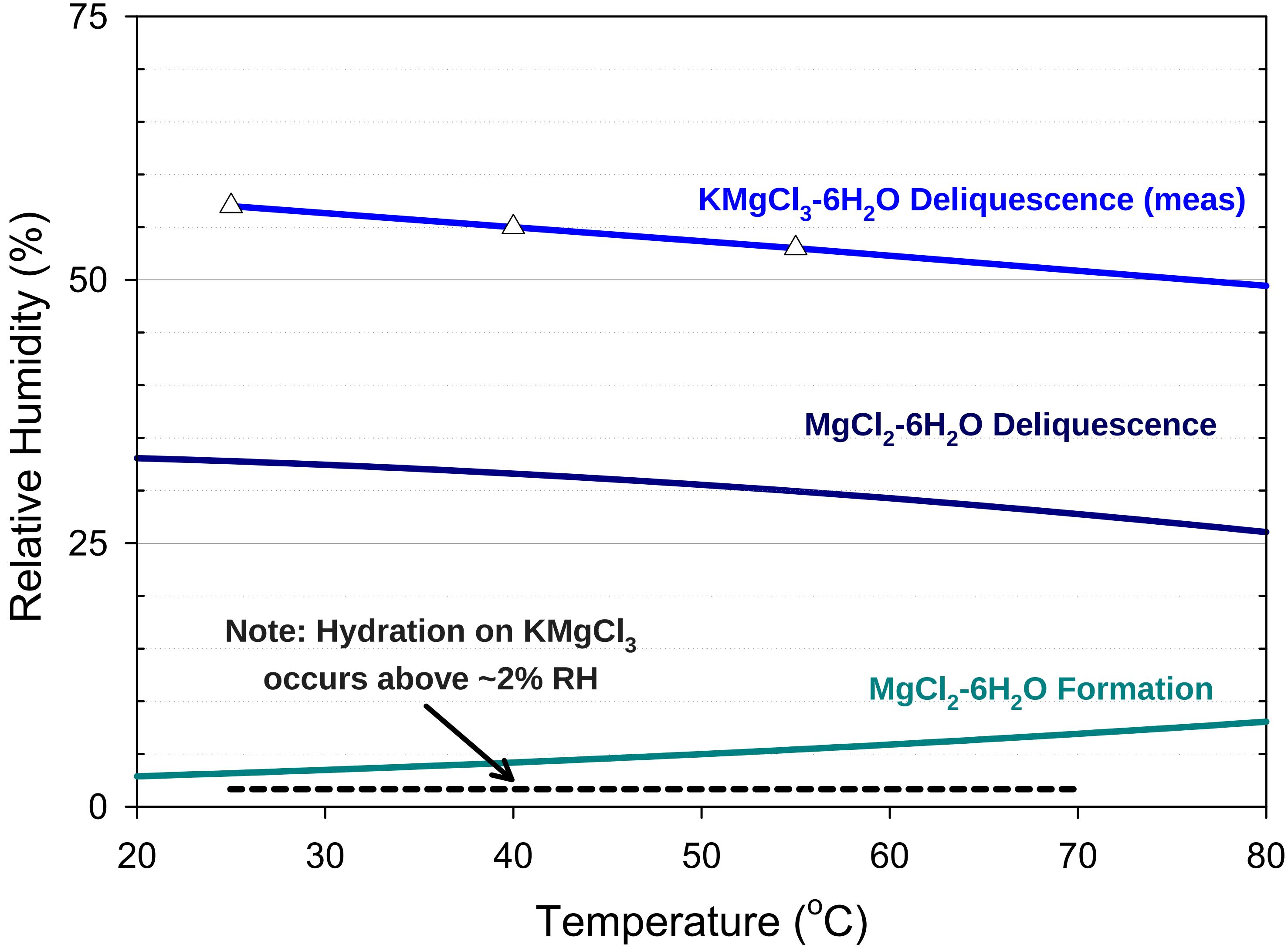


Hydration behavior of magnesium chloride salts

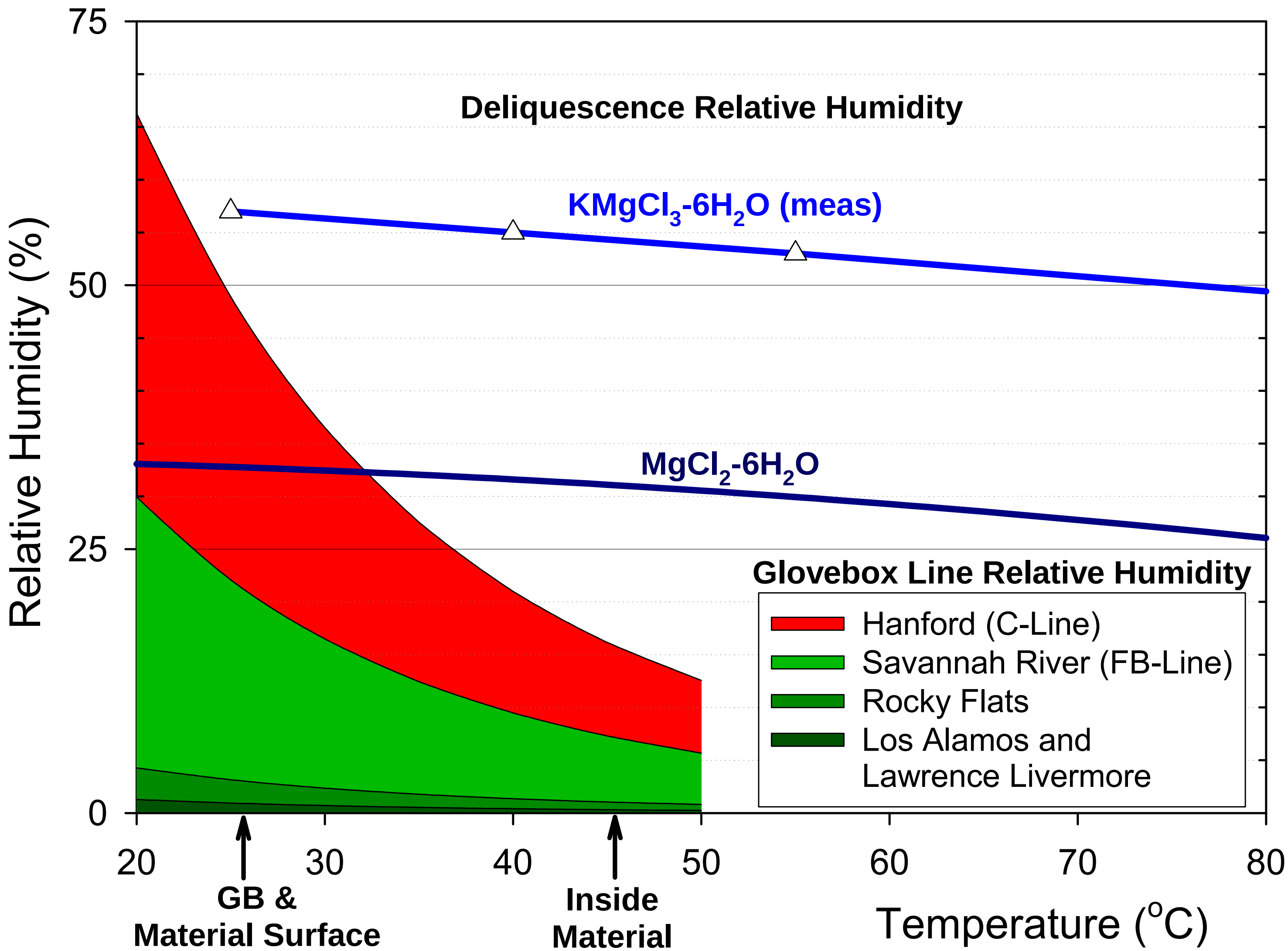


DRH = Deliquescence Relative Humidity

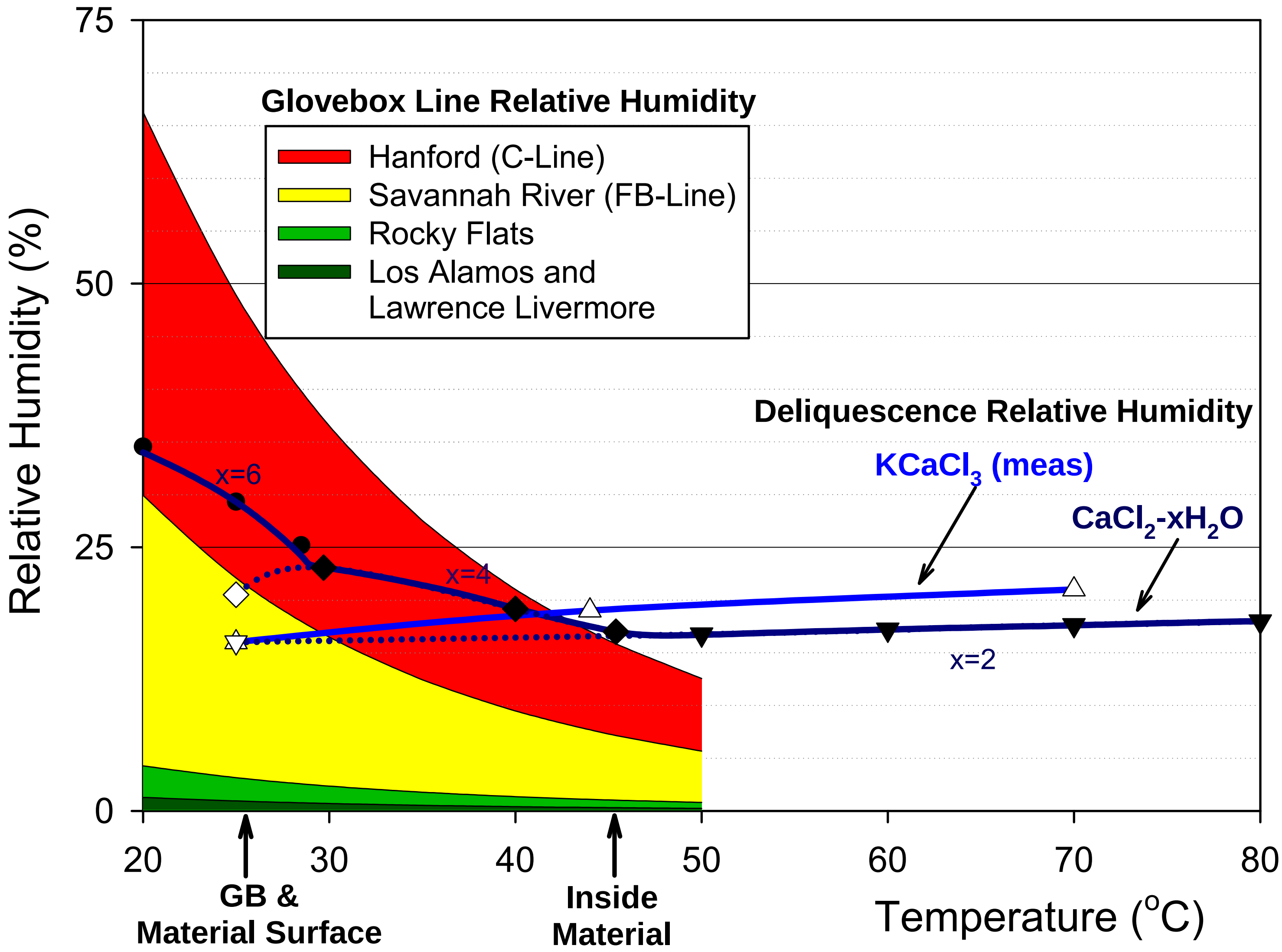
Hydration behavior of magnesium chloride salts



Magnesium Chloride Salt Behavior During Packaging



Calcium Chloride Salt Behavior During Packaging



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

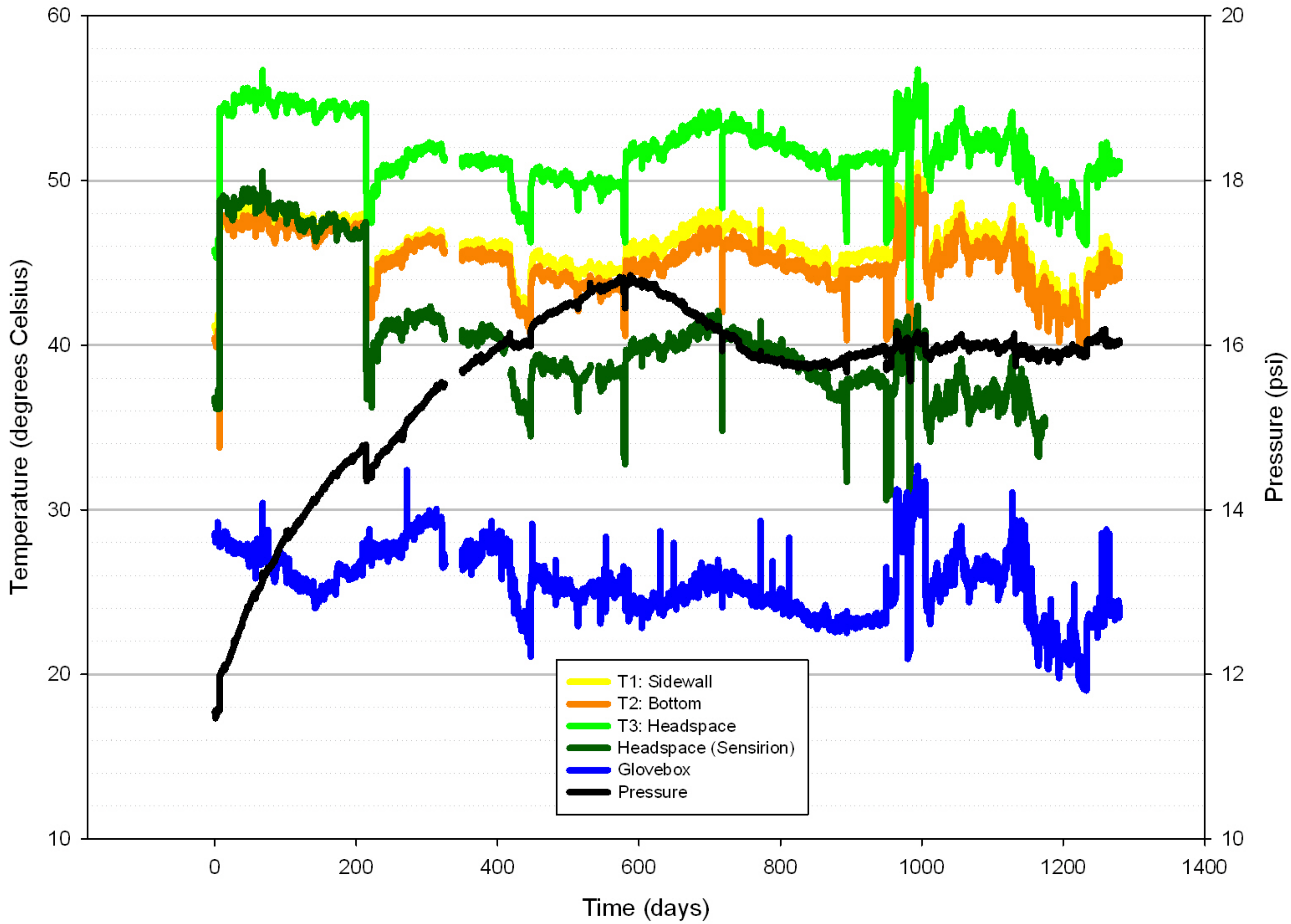
Material	wt% Moisture	Exposure Time (h)	Enclosure Temp ºC	Enclosure RH%	Material Temp C	RH% in Material (calc.)
PMAXBS	0.09	100[a]	27	53	40	26
Base Material	0.05	138[a]	26	56	39	27
Low Ca	0.28	42[a]	26	**53**	42	**22**
Low Mg	0.28	26[a]	26	**52**	48	16
High Ca	0.39	21[b]	25	**30[c]**	47	9
High Mg	0.55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

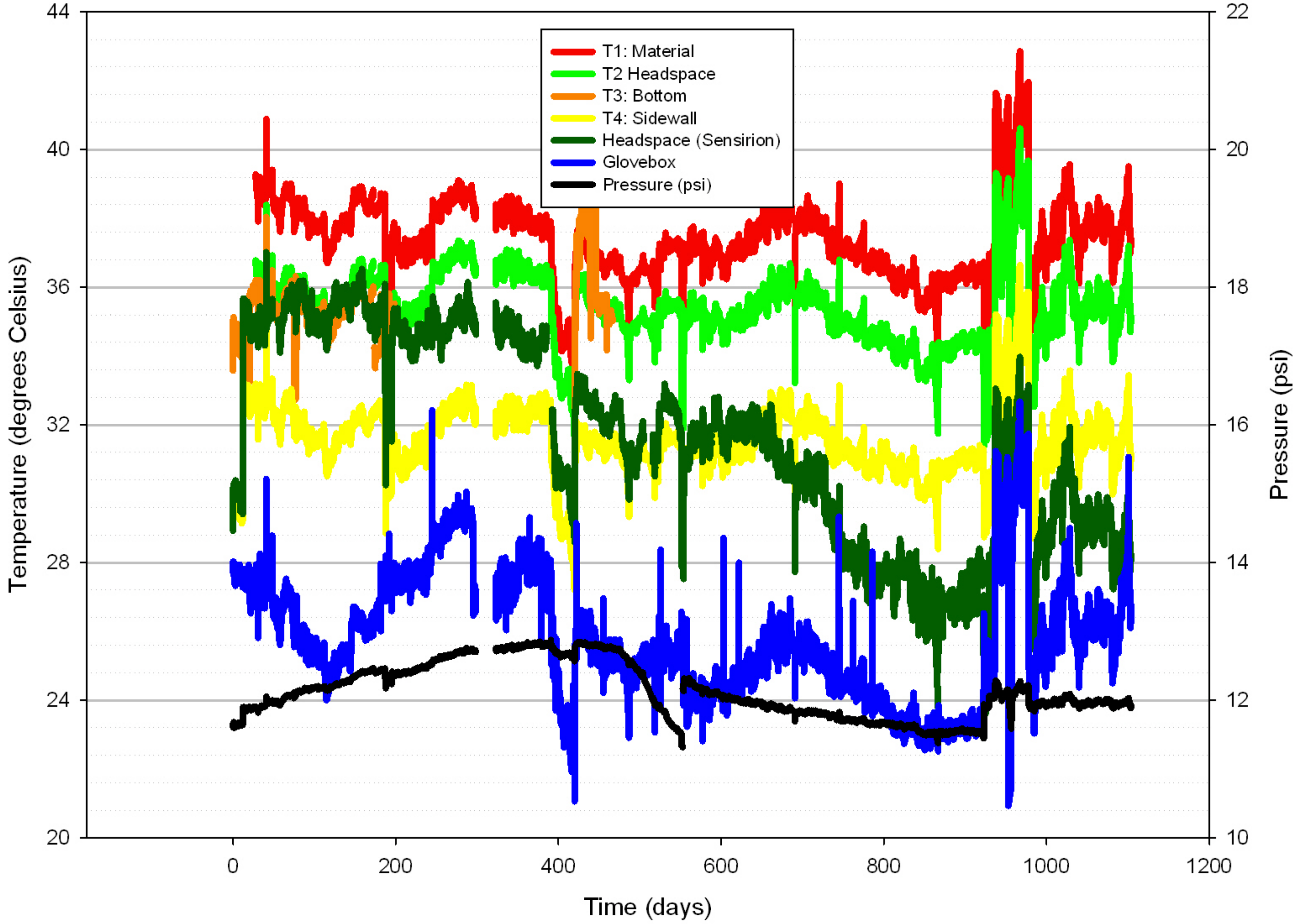
Storage Conditions (first 30 days)

Material	wt% Moisture	Condition	Headspace Temp ºC	Headspace RH (%)	Sidewall Temp ºC	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 55ºC						

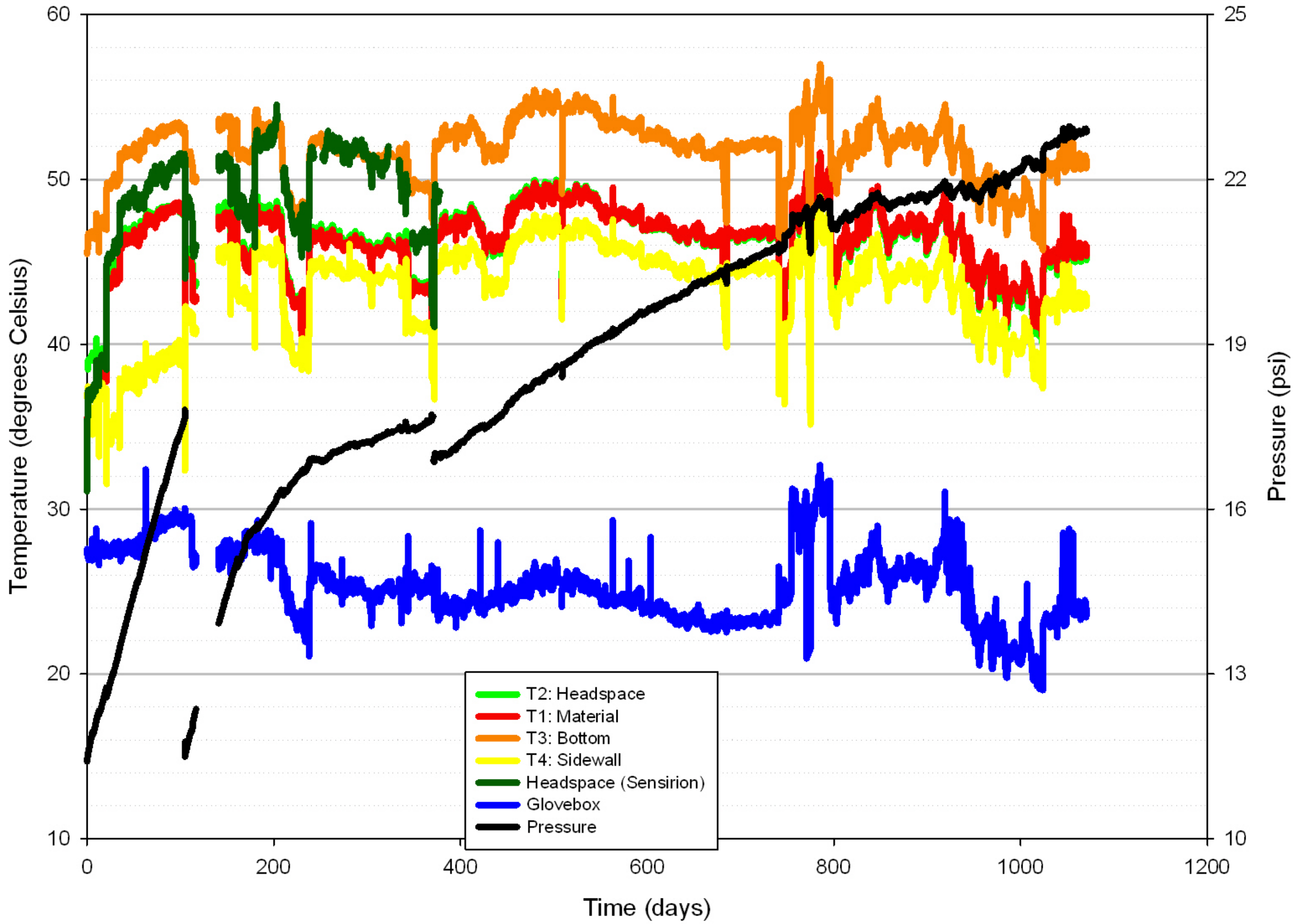
Can 2 Temperature and Pressure



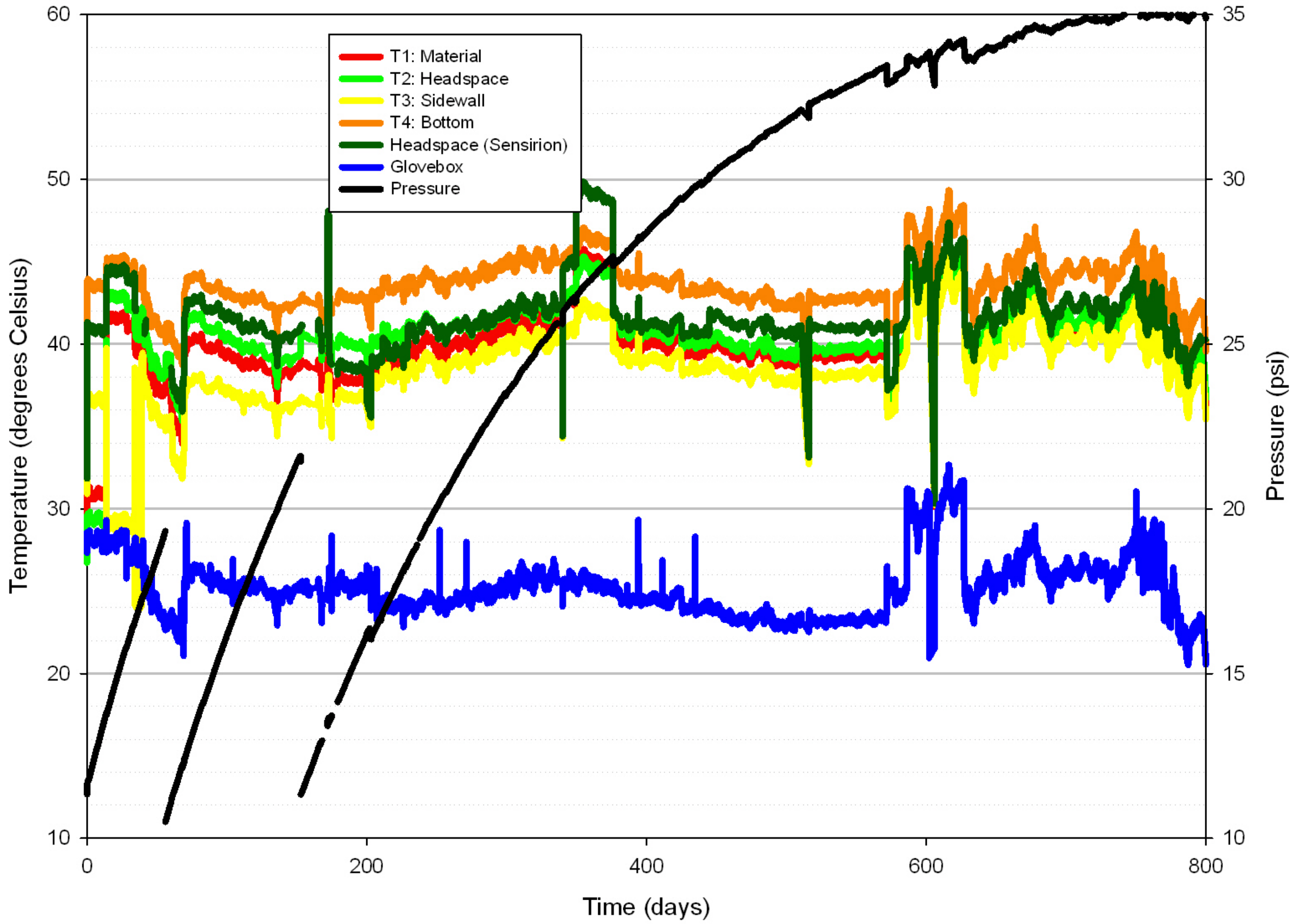
Can 3 Temperature and Pressure



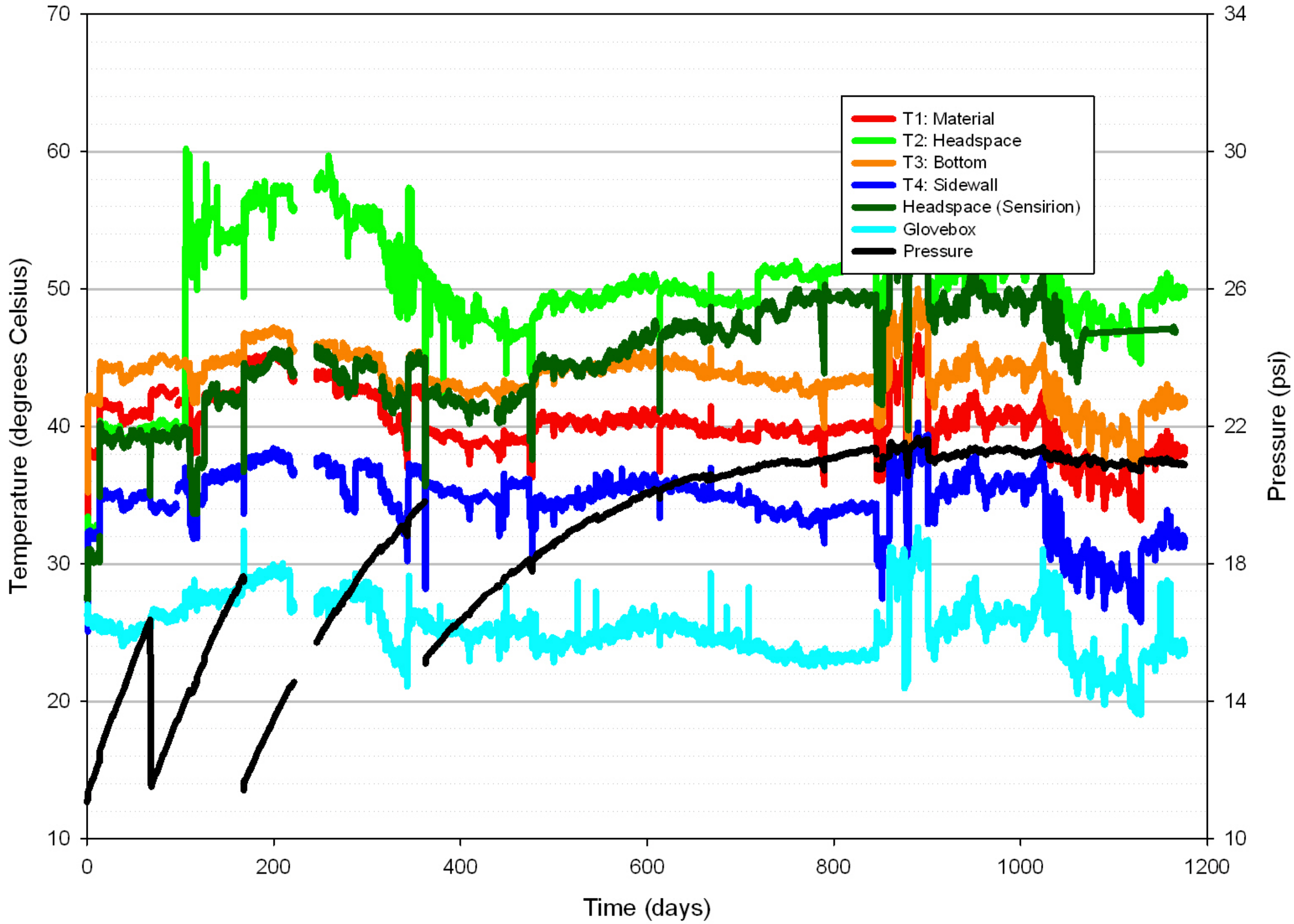
Can 5 Temperature and Pressure



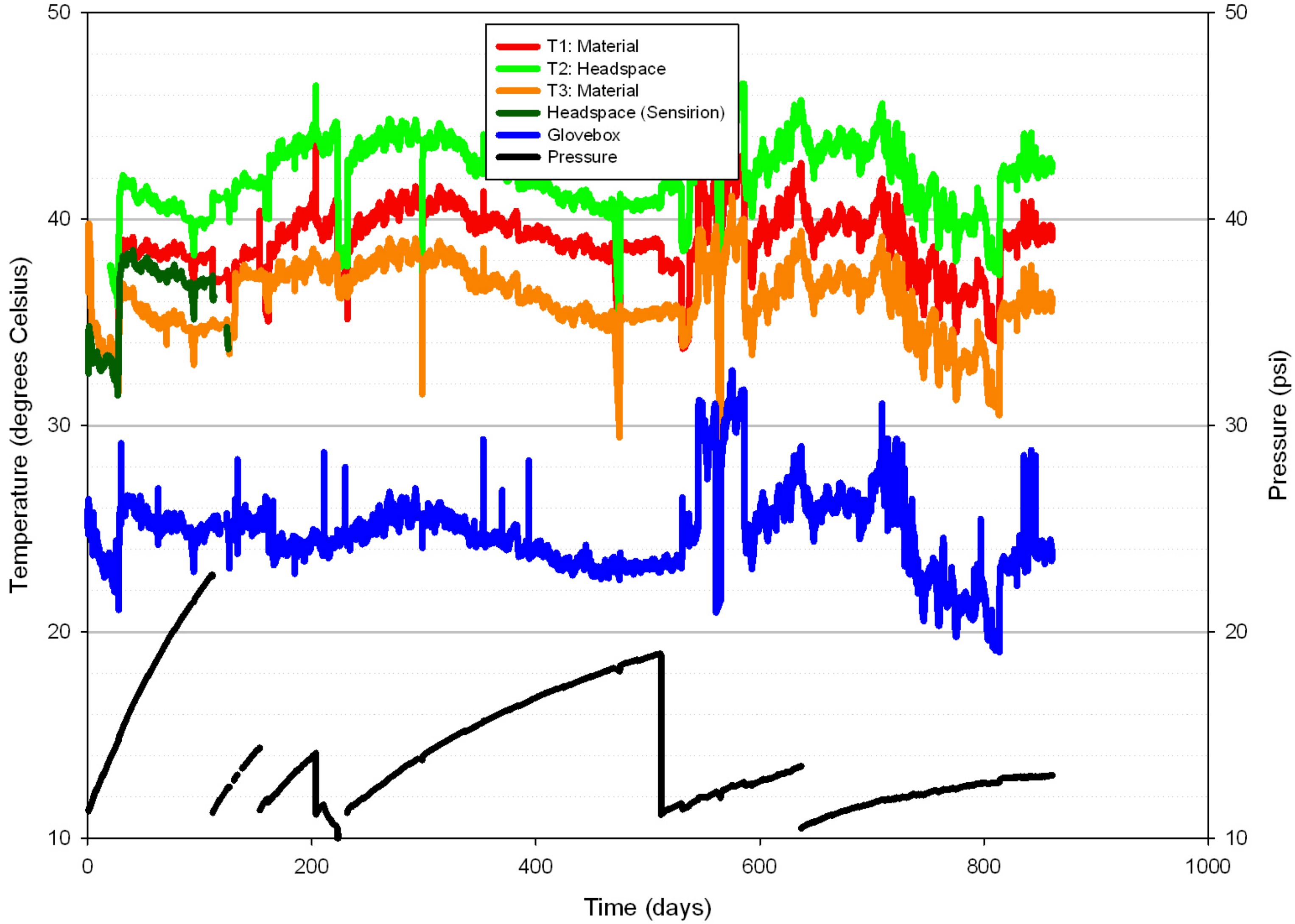
Can 6 Temperature and Pressure



Can 7 Temperature and Pressure



Can 9 Temperature and Pressure



Statistical Predictive Model for Corrosion Pit Depth Growth

Elizabeth Kelly, Los Alamos National Laboratory
Todd Graves, Berry Consulting
Kirk Veirs, Los Alamos National Laboratory
Laura Worl, Los Alamos National Laboratory

MIS Program Review
February 25-28, 2013
SRS

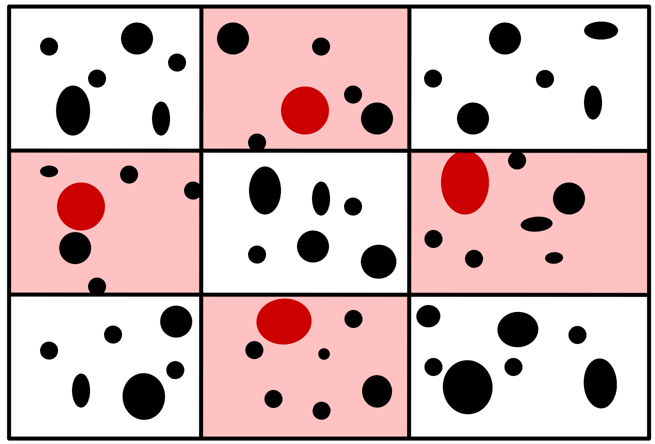
“Prediction is very difficult, especially about the future.”

Niels Bohr

View these results as providing a conservative context for assessing pit depth growth in actual 3013 containers, not as exact results.

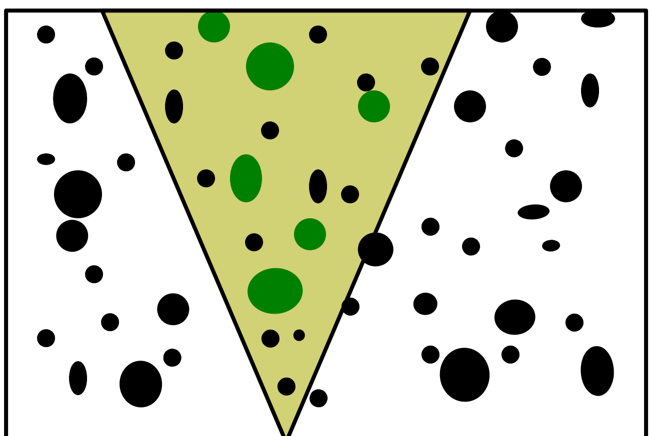
Why is a Predictive Model of Corrosion Pit Depth Data Needed

Previous analyses assumed block maxima data – sample blocks, select block maxima and measure



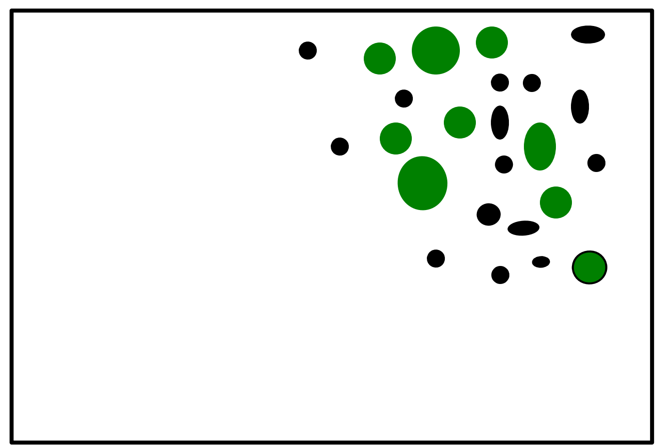
3013 data are threshold data – measure pits above a threshold size (≥ ●)

Not practical to block and select max, sample small area



Zapp Data

Corrosion blotchy, many blocks are empty



ARF Data

Cannot use block maxima approach for threshold data

Threshold Model (New Work) Provides Integrated Approach for Multiple Data Sets

- **Provides framework for comparing results from threshold pit depth data sets collected under different conditions**
  - Collected at different times/ages (e.g. months to years)
  - Collected over different areas (e.g., 2 cm^2, 4 cm^2, 11 cm^2)
  - Different thresholds
  - Different pit densities
- **Provides a context for comparing experimental results (for pitting) to field surveillance DE results**

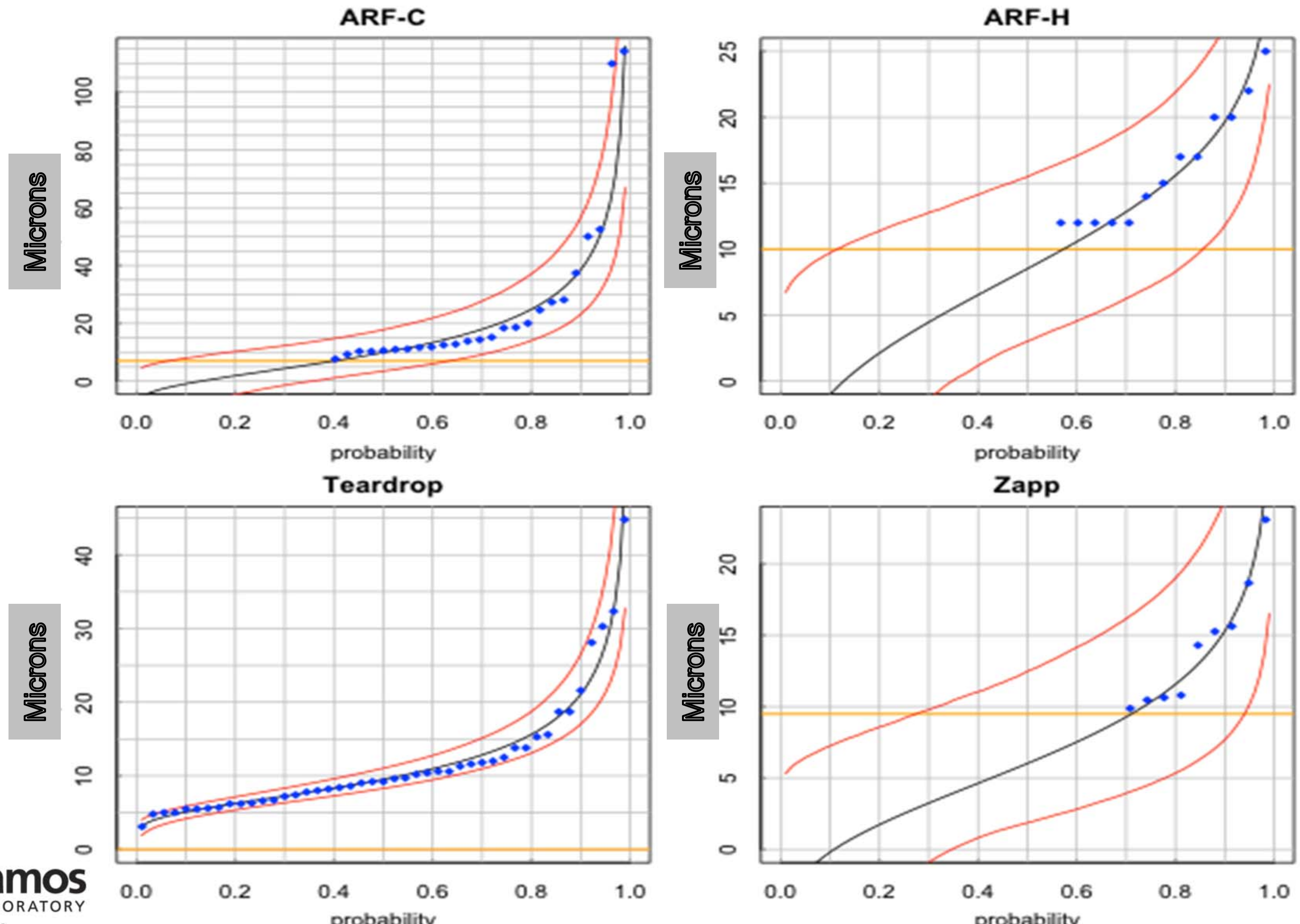
Four Threshold Data Sets

- **Three data sets from experiments engineered to produce conditions to cause corrosion**
  - ARF223-SSR111 contact region pitting (ARF-C) and ARF223-SSR11 headspace region pitting (ARF-H): loaded with 0.5 wt%
    - *Originally analyzed assuming block maxima, but close analysis of pitting images shows that these are threshold data*.
      - ARF-C threshold is 7 microns
      - ARF-H threshold is 10 microns
  - LANL teardrop data set uses material designed to have deliquescent salts, high relative humidity (RH). Contact region pitting.
    - Threshold = 0 all pits measured
- **Fourth data set from 3013 DE, inner can lid of container H004111 (Zapp data)**
  - Had one of the highest RH's after 5 years, selected based on engineering judgment. Headspace region pitting.
    - Threshold implied, approximately 9.5 microns.

Threshold Model Gives Good Fits to the Four Data Sets

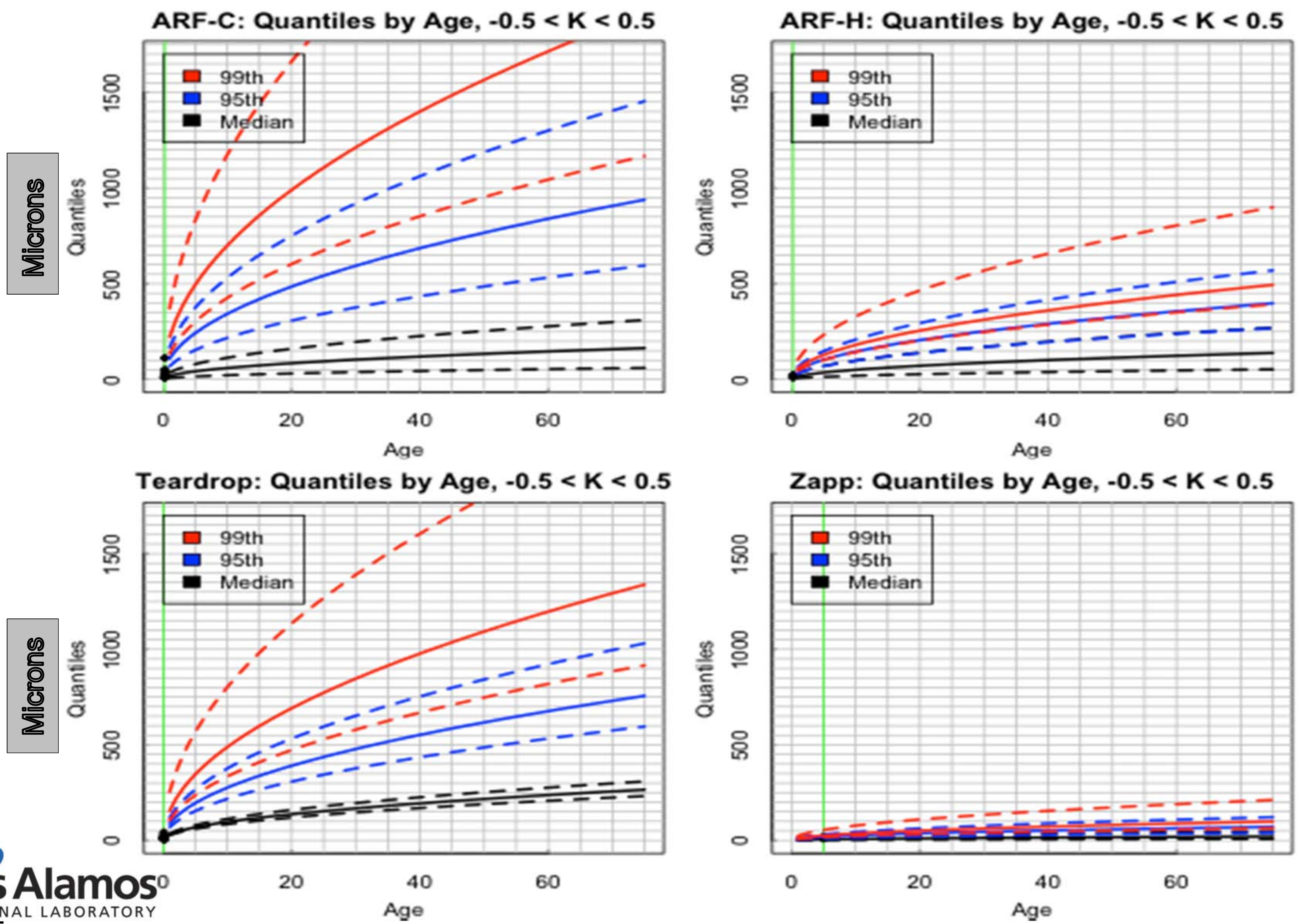
ARF-C and Teardrop have contact region pitting

ARF-H and Zapp have headspace region pitting

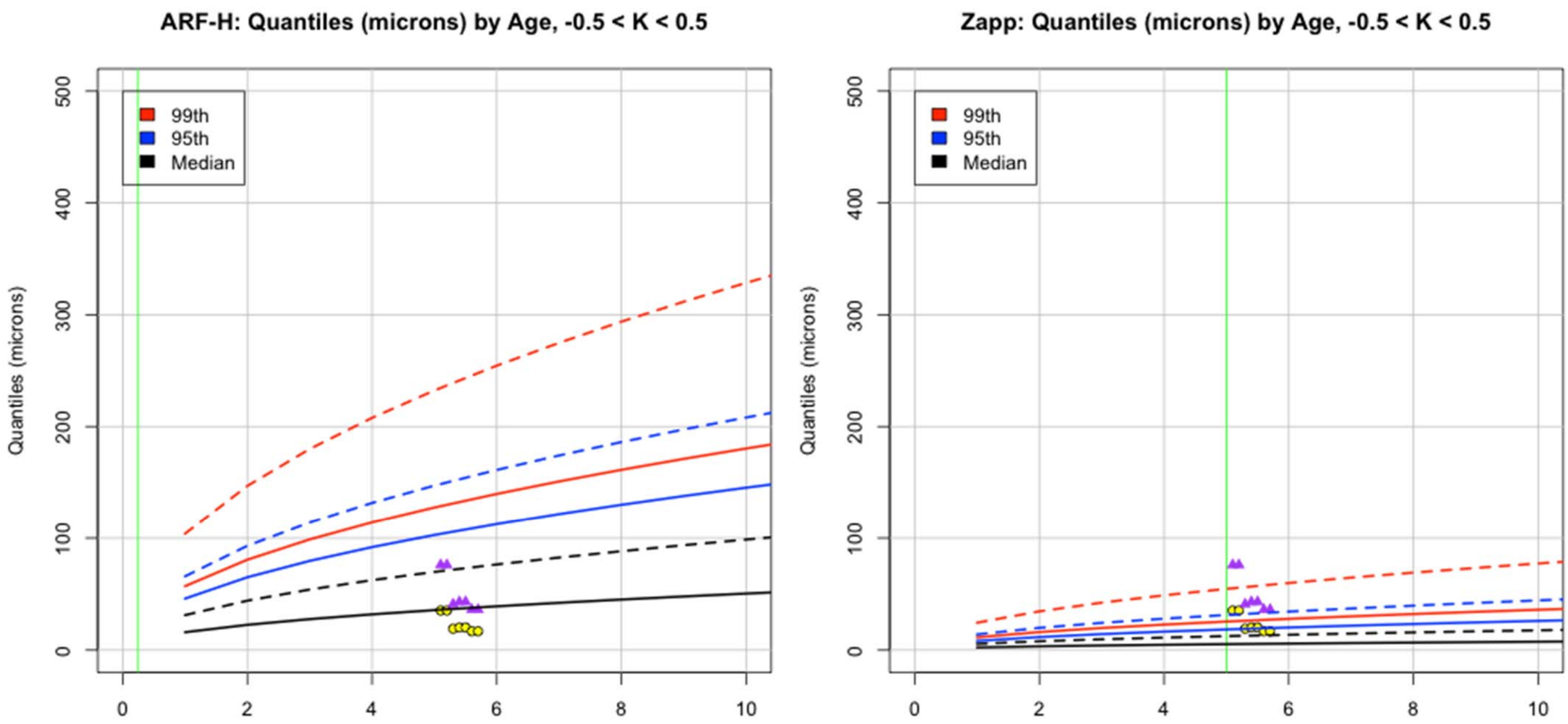


Predicting Pit Depth Growth – threshold model applied to four data sets with power law growth

ARF-C and Teardrop have contact region pitting   ARF-H and Zapp have headspace pitting

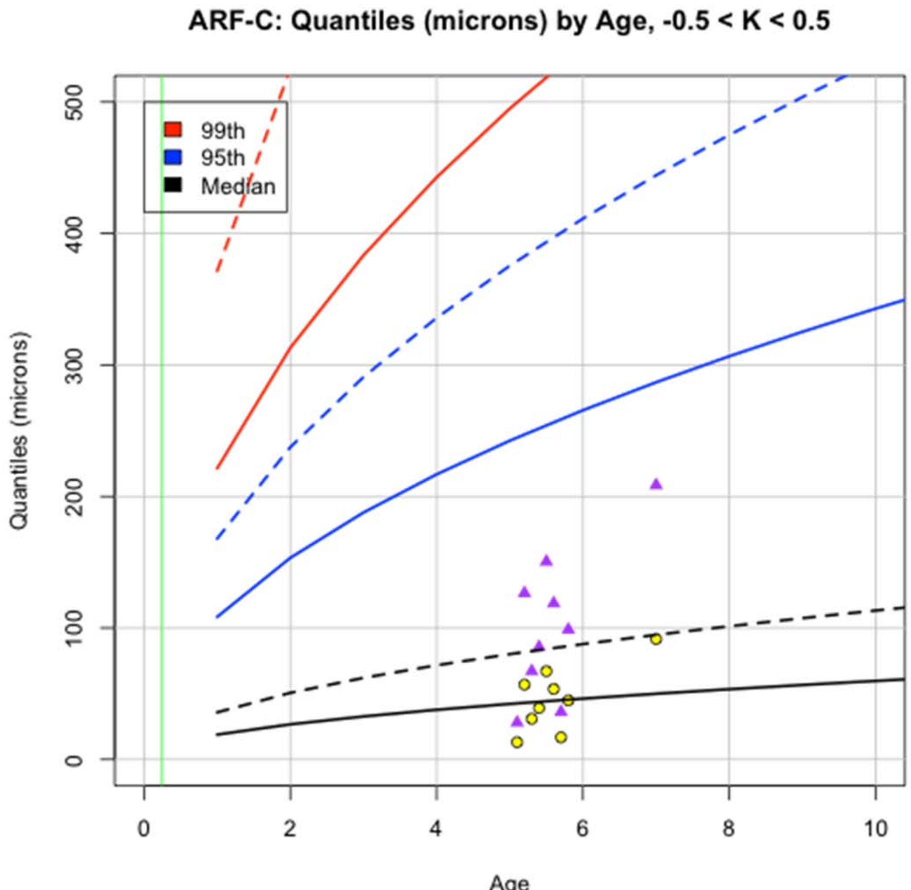


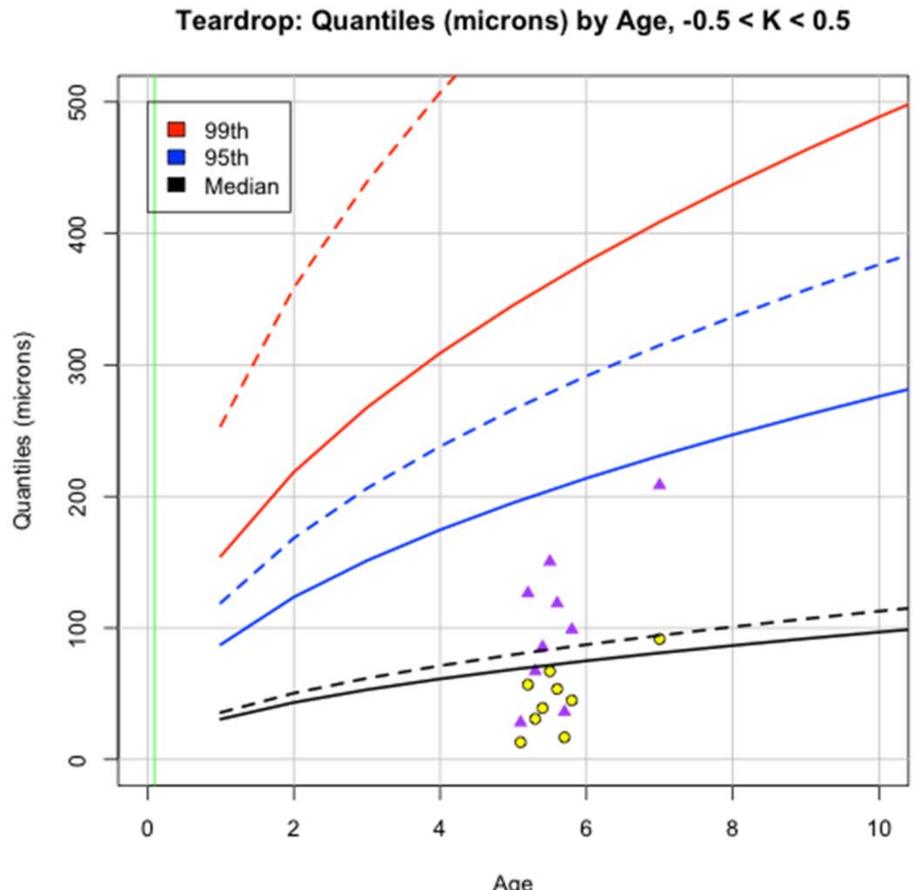
DE Field Surveillance Headspace Pit Depths (when pitting occurred) Plotted on Prediction Plots from ARF-H and Zapp Data



Green line is time when data were collected, yellow circles are DE surveillance data and purple triangles are 95% one sided prediction uncertainties based on Teardrop calibration.

DE Field Surveillance Contact Region Pit Depths (when pitting occurred) Plotted on Prediction Plots from ARF-C and Teardrop Data





Green line is time when data were collected, yellow circles are DE surveillance data and purple triangles are 95% one sided prediction uncertainties based on Teardrop calibration.

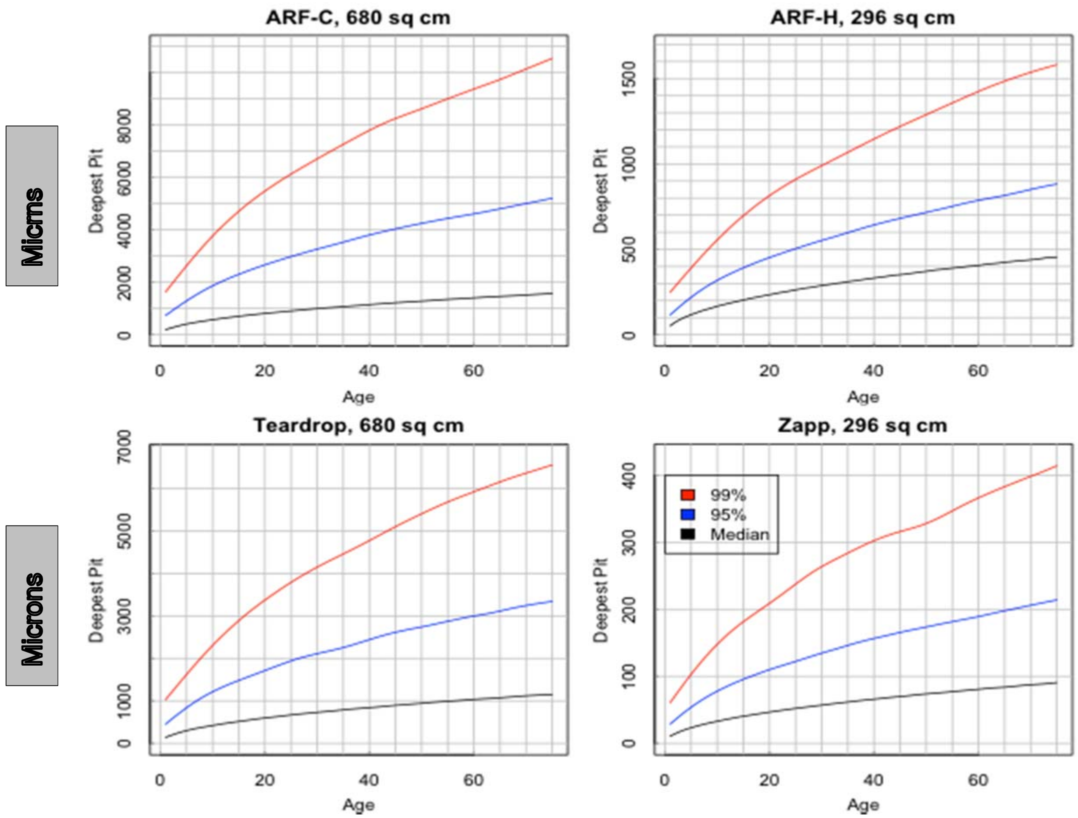
Predictied Deepest Pit Assuming Pitting Over Entire 3013 Container- based on experimental data

- 95th and 99th percentiles for deepest pits for headspace data do not exceed 400 microns after 50 years
- Expected deepest pits for contact data do not exceed1000 microns after 50 years, but 95th and 99th percentiles exceed 1600 microns before 50 years

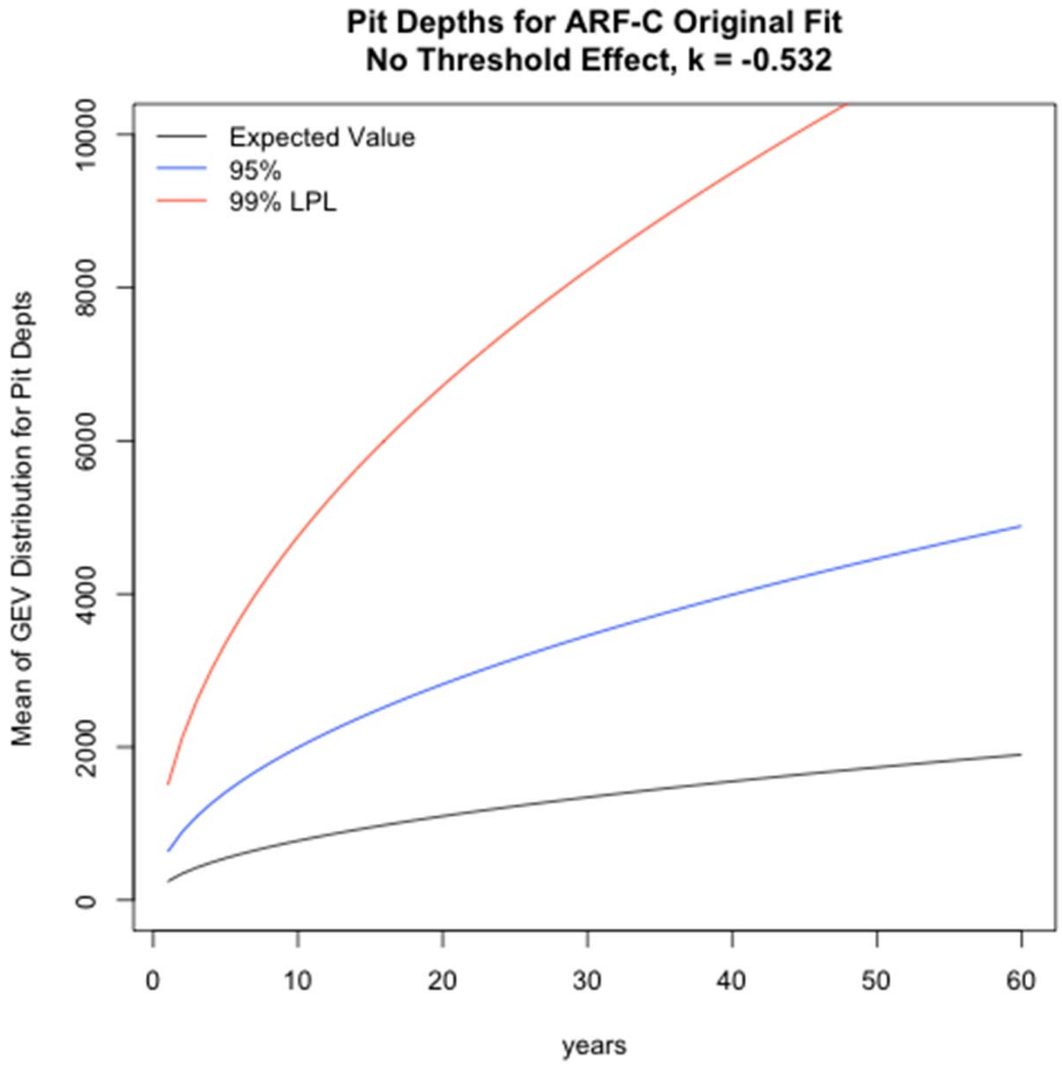
Contact region pitting

Headspace pitting

Black curve shows median values
Blue curve 95th percentile
Red curve 99th percentile



Extra Slide: Original Fit



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We Put Science To Work

3013 Equivalency for Reduced Temperature Stabilization of Oxalate-Derived PuO_2

J. M. Berg, J. M. Duffey, R. R. Livingston, and D. K. Veirs

February 27, 2013

3013 Surveillance & Monitoring Program Review

Annual Meeting

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Introduction

- **HB-Line will produce high-purity PuO_2 (<2.1 wt % total impurities) for use as feed for the Mixed Oxide Fuel Fabrication Facility (MFFF)**
- **MFFF requires packaging in conformance with DOE-STD-3013 to**
  - Meet MFFF safety basis
  - Support automated handling of PuO_2 feedstock
- **Stabilization conditions imposed by DOE-STD-3013 (≥950 °C for 2 h) cannot be met by HB-Line as currently configured**
  - Stabilization temperature limited to ~650 °C
  - PuO_2 product will have higher specific surface area (SSA) than if stabilized at 950 °C and higher capacity to adsorb water from atmosphere
- **650 °C is required for Direct Feed (MP demonstration) for MFFF**
- **3013 Equivalency needed to establish minimum operating conditions (including measurement uncertainties) to produce PuO_2 from oxalate that meets material performance requirements of the 3013 stabilization process**

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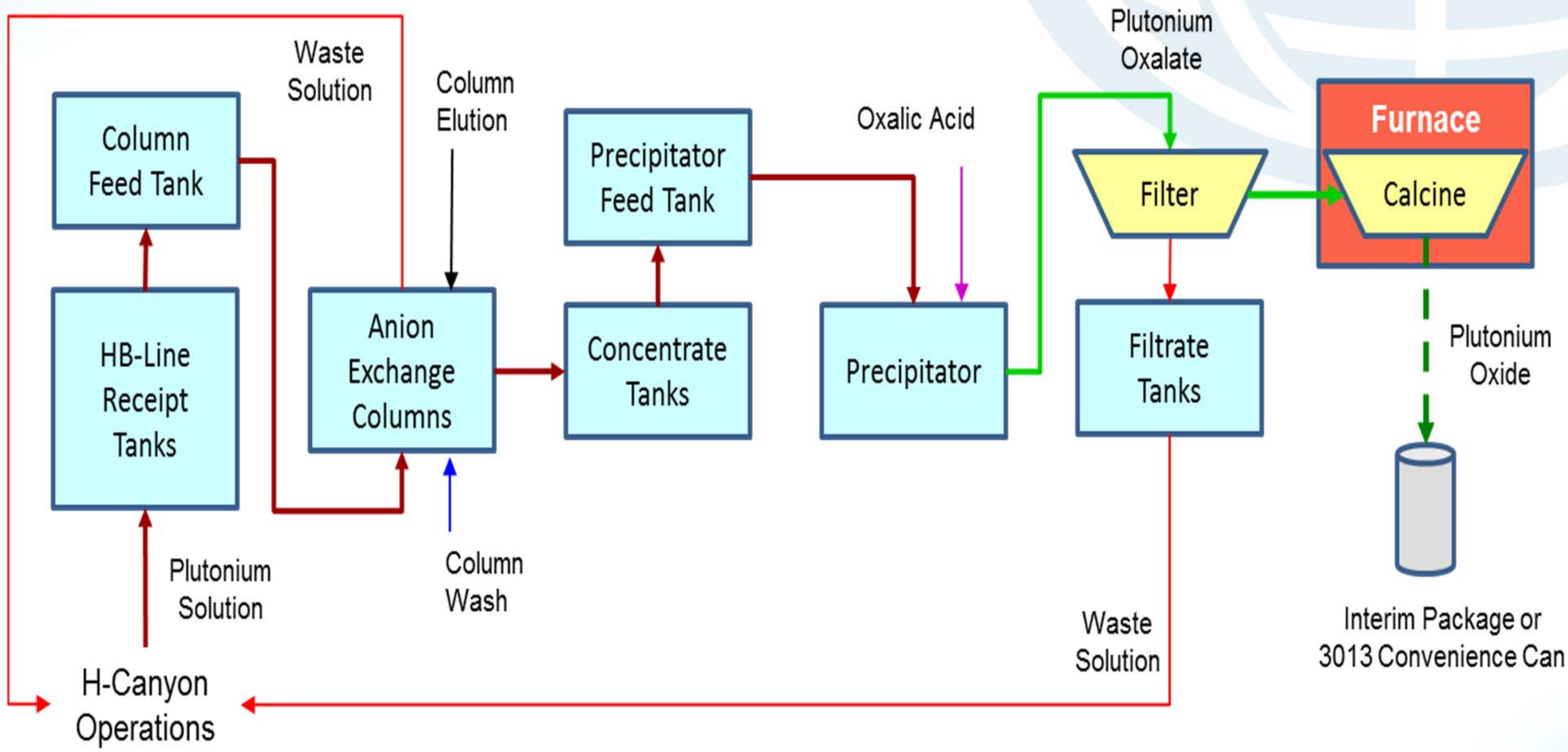
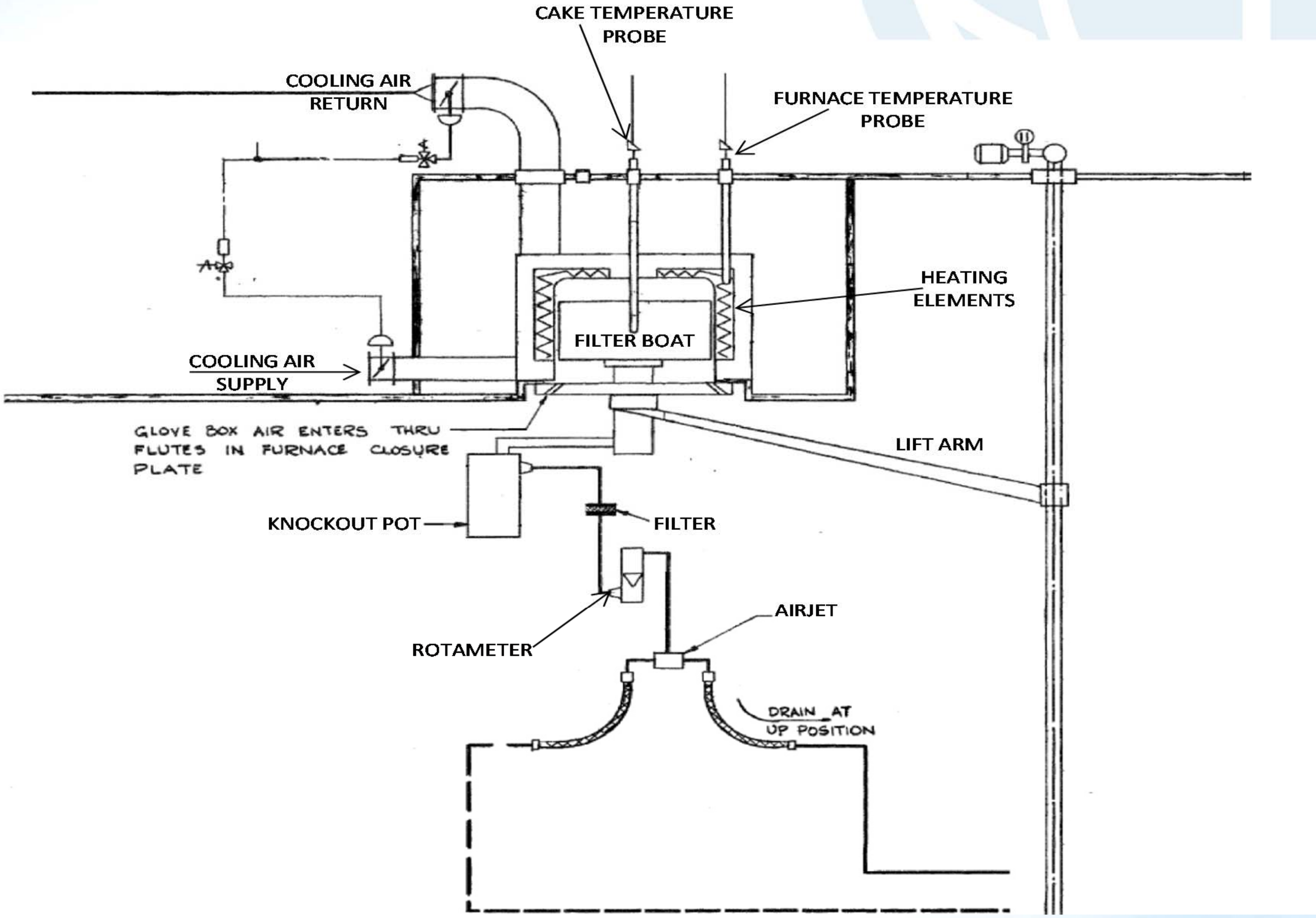
HB-Line Flowsheet

- Dissolve Pu metal in boiling 10 M HNO_3/0.1 M KF
- Purify Pu by anion exchange from 8 M HNO_3
- Precipitate Pu by adding 0.95 M oxalic acid (direct strike) at 50 °C
- Collect precipitate and air dry in filter/furnace boat with 10-μm stainless steel screen
- Stabilize at a minimum bed temperature of 625 °C (including measurement uncertainty - target is 650 °C) for at least 4 h while pulling hot air through filter cake
- Begin production with interim storage of HB-Line product in Type B packaging prior to start-up of 3013 canning system

Block Diagram of HB-Line Production Process



Schematic of HB-Line Calcination Furnace



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DOE-STD-3013 Objectives of Stabilization

- **Avoid energetic events by eliminating reactive materials**
- **Minimize potential for container pressurization and formation of flammable gas mixtures by**
  - Eliminating organic materials
  - Reducing water content to less than 0.5 wt %
  - Minimizing potential for water adsorption above 0.5 wt % threshold
  - Stabilizing any other potential gas-producing constituents
- **To achieve objectives with high confidence for a broad range of materials, DOE-STD-3013 specifies stabilization in a continuously oxidizing atmosphere at ≥950 °C for at least 2 h**
- **Evaluation of alternative stabilization conditions needed because**
  - Lower temperature might be less effective at removing gas-producing species
  - Will result in material with higher SSA (i.e., higher potential for H_2O adsorption)
  - Product may have increased potential for O_2 generation at less than 0.5 wt % moisture

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Process Evaluation Relative to Stabilization Objectives

- **Stabilization in air at no less than 625 °C for 4 h is sufficient to**
  - Oxidize residual metal if any survives aqueous chemical processes (which is unlikely)
  - Reduce water content to less than 0.5 wt %
    - Small amount (<<0.5 wt %) of strongly bound water expected to remain
    - Moisture measurement by approved method will verify <0.5 wt % water remains at time of packaging
  - Destroy or drive off organics or other potential gas-producing constituents
    - $C_2O_4^{2-}$ and NO_3^- expected to be decomposed at 625 °C
    - No credible source of sulfur in process
    - Small amounts of C, N, and S allowed pose no gas generation concern
- **These stabilization conditions are not sufficient to minimize potential for water adsorption above 0.5 wt % threshold if material is equilibrated with a high humidity atmosphere**

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Risks of Increased Potential for Water Adsorption

- **Combination of reduced stabilization temperature and high RH in HB-Line glove boxes increases potential for exceeding 0.5 wt % water and for generating flammable mixtures of H_2 and O_2**
- **The equivalency requires the facility to assure handling/packaging precludes formation of flammable gas mixture**
- **Risks must be mitigated by institution of rigorous process controls that must address, at a minimum**
  - How the material will be kept below 0.5 wt % water before packaging
  - What measurements can ensure conditions that result in flammable mixtures do not exist
  - How the measurements to support these claims are made
- **Facility Specific process controls and rework criteria will be documented by HB-Line and approved by DOE as part of the "20-Points" process and may include**
  - Relative humidity control
  - Restrictions on handling time
  - Keeping the material at elevated temperature during handling
  - Measuring equilibrium RH above material in a sealed container

Conclusions & Recommendations

- **Alternative stabilization criteria determined to be equivalent, in terms of safety, to DOE-STD-3013 criteria, if product is handled in a way that precludes formation of a flammable gas mixture within the 3013 container**
- **HB-Line process is capable of producing PuO_2 that poses no safety concern for packaging or storage in 3013 required configuration if handled according to recommended controls (next slide)**
- **Primary concerns are:**
  - HB-Line product will have greater tendency to adsorb moisture
    - Higher SSA for HB-Line product than for oxide stabilized at 950 °C for 2 h
    - Relative humidity in HB-Line facility may be as high as 70%
  - The SSA of the HB-Line product could be low enough to fall within a range that would allow multiple monolayers of water without exceeding the 0.5 wt % limit
    - Potential source for generating a flammable mixture of H_2 and O_2 during storage

SRNL

Controls for HB-Line Product

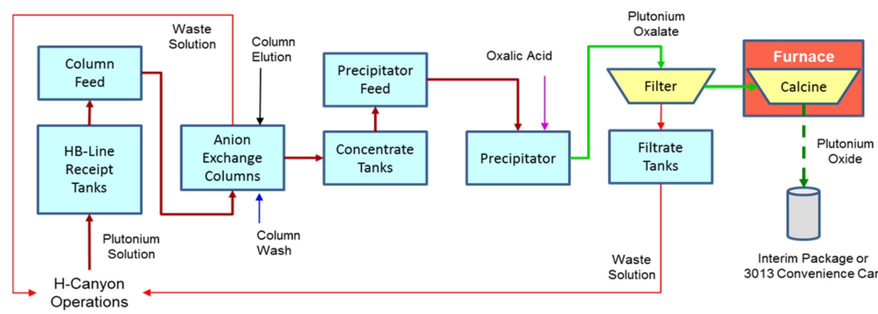
- **Stabilize Pu oxalate product in oxidizing atmosphere at no less than 625 °C (including all measurement uncertainties) for a minimum of 4 h**
- **Total product impurities must not exceed 2.1 wt %**
  - Individual metallic impurities may exceed defined maximum MFFF chemical impurity limits provided total impurities remain less than 2.1 wt %
  - Non-metallic impurities should be constrained to MFFF chemical impurity maximum exceptional limits
- **Product shall be packaged in a way that precludes formation of a flammable gas mixture in the 3013 container**
  - Controls for packaging must be documented as part of "20-Points" process (i.e., facility specific implementation document)
- **"20-Points" document review shall ensure HB-Line procedures provide conservative measurements of key parameters**
  - Moisture content of product at time of 3013 packaging is less than 0.5 wt %
  - Relative humidity or alternate controls identified to preclude formation of a flammable gas mixture in the 3013 container
- **"20-Points" documents are approved by same authority as the 3013 Standard and Equivalencies**

Independent Review of HB-line Equivalency

Ted Venetz

Review Team Lead

Washington River Protection Solutions



Independent MIS Review Team

- Established by DOE/SR in July 2012
  - By Chairman of the Integrated Surveillance Program
- Members
  - Chip McClard, Savannah River Nuclear Solutions
  - Laura Worl, Los Alamos National Laboratory
  - David Riley, Lawrence Livermore National Laboratory
  - Ted Venetz, Washington River Protective Solutions
- All long time MIS Working Group Members with extensive experience with DOE-STD-3013.

Initial Revision

- Received SRNL-STI-2012-00256, Rev 0 on 7/31/2102
- No Involvement in document preparation
- Submitted 67 comments to the authors and the facility in August and formally to DOE/SR in November 2012
- 3 essential comments
  - Concern about packaging RH and acceptance of formation of a flammable mixture
  - Unclear which data gaps threaten Safety or standard compliance
  - Controls that affect safety not clearly indentified

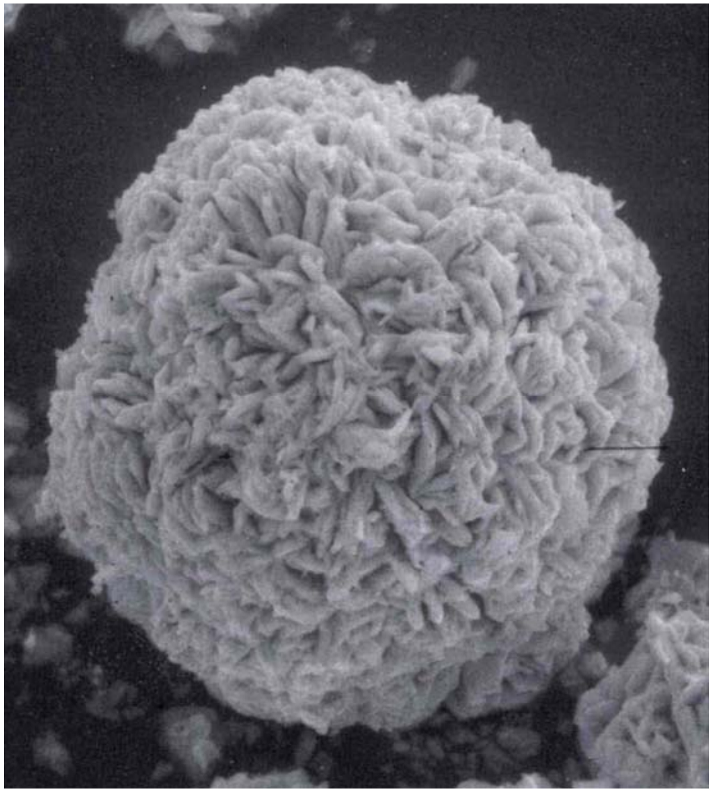
Second Revision

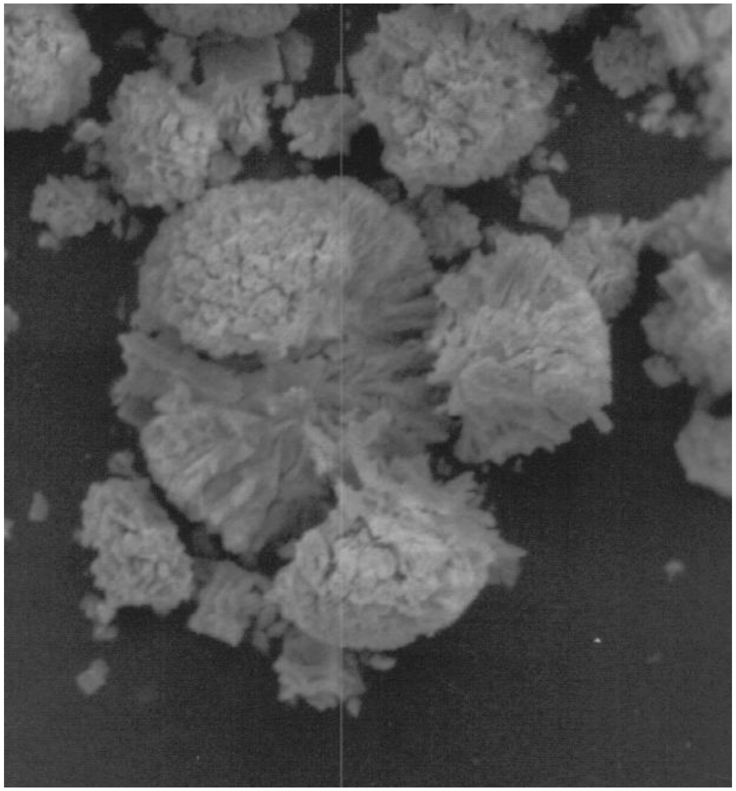
- Iterative process with authors to address issues
- Test Plan proposed to better understand impact of packaging RH
- Second revision formally submitted to team on 2/13/2013
- Letter with Recommendation to Approve issued 2/21/2013
- All Rev 0 comment satisfactory addressed
- Two greatest concerns must be addressed in "20-points" documents
  - Packaging high surface area oxide in high RH atmosphere
    - Prevent flammable mixture, Meet moisture limits
  - Representative moisture measurement
- Encourage continued dialogue on testing of the high surface specific area oxides and the conditions required for formation of flammable atmospheres with the storage containers.

Concluding Remarks

Team confident HB line produced oxide can be packaged and handled in way to ensure safe, compliant storage

Thanks to team members, Pam Dominguez, document authors, and DOE/SR.





Experimental Results – Effect of RH on O_2 Generation

D. Kirk Veirs

LANL Team: John Berg, Dave Harradine, Dallas Hill, Rhonda McInroy, Josh Narlesky, Ed Romero, Leonard Trujillo, Kirk Veirs, Laura Worl

3013 Surveillance and Monitoring Program Review
Feb. 26 – 28, 2013
Savannah River Site

Introduction

Implementation of the *Reduced Temperature Stabilization of Oxalate-Derived Plutonium Dioxide* in HB-Line at SRS will result in unique-to-3013-packaging high specific surface area (SSA) PuO_2. This material *if in equilibrium* with high RH atmospheric conditions will generate both H_2 and O_2. This talk will:

•Provide a framework to understand why high SSA and high RH result in unique gas generation behavior.

•Present experimental results of gas generation from high SSA PuO2 exposed to high RH atmospheres.

Where is all that surface area???

As they say in Physics, lets assume all particles are spheres. Then the SSA is the ratio of the surface of a sphere to the mass of the material in the sphere:

$$A = 4\pi r^2$$

$$m = V\rho$$

$$V = \frac{4}{3}\pi r^3$$

$$SSA = \frac{A}{m} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3 \rho} = \frac{3}{r\rho}$$

For r = 3 microns (average particle diameter of 6 microns) and ρ = 11 g cm^{-3}, SSA = 0.1 m^2 g^{-1}.

For material with a SSA of 10 m^2 g^{-1}, the ratio of the area on the outside of the particle to the area on the inside of the particle is 100. Even assuming that the outside of the particle has 10 times the sphere's area, 90% of the area is inside the particle.

How far apart can the surfaces within a particle be?

The total surface area is 100 x the particle surface area and 90% is within the particle. The number of planes within the sphere assuming all to be of radius r:

$$0.9 \cdot 100 \cdot 4\pi r^2 = n \pi r^2$$

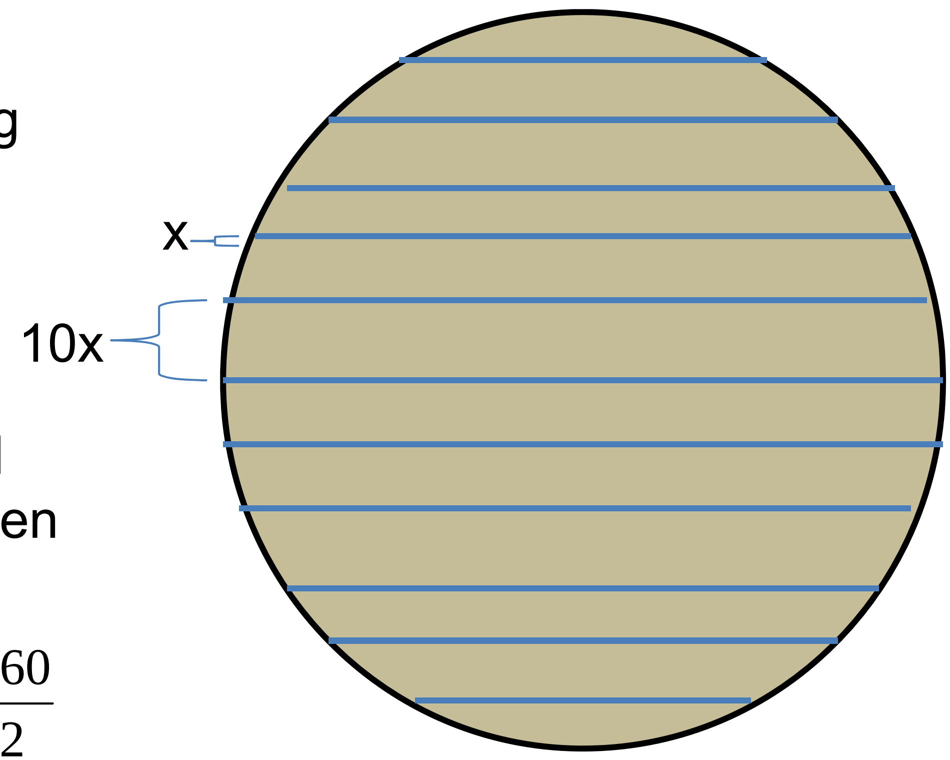
$$n = 360$$

If a pair of surfaces is x apart and assuming that the material between pairs of surfaces is 10x, then:

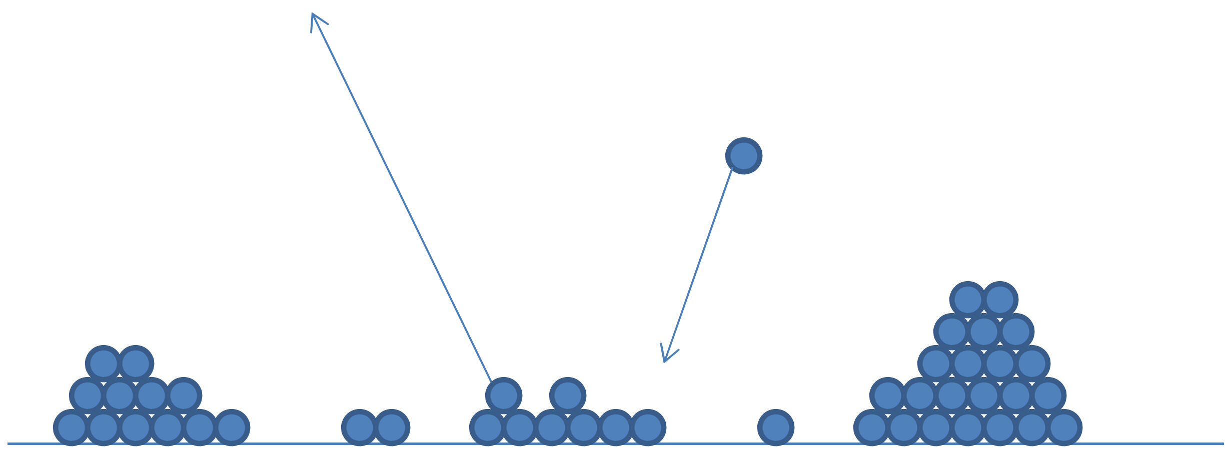
$$6000\,\mathrm{nm} = x\frac{360}{2} + 10x\frac{360}{2}$$

$$33\,\mathrm{nm} = 11x$$

$$x = 3\,\mathrm{nm}$$



How does BET theory view molecules adsorbing onto a surface

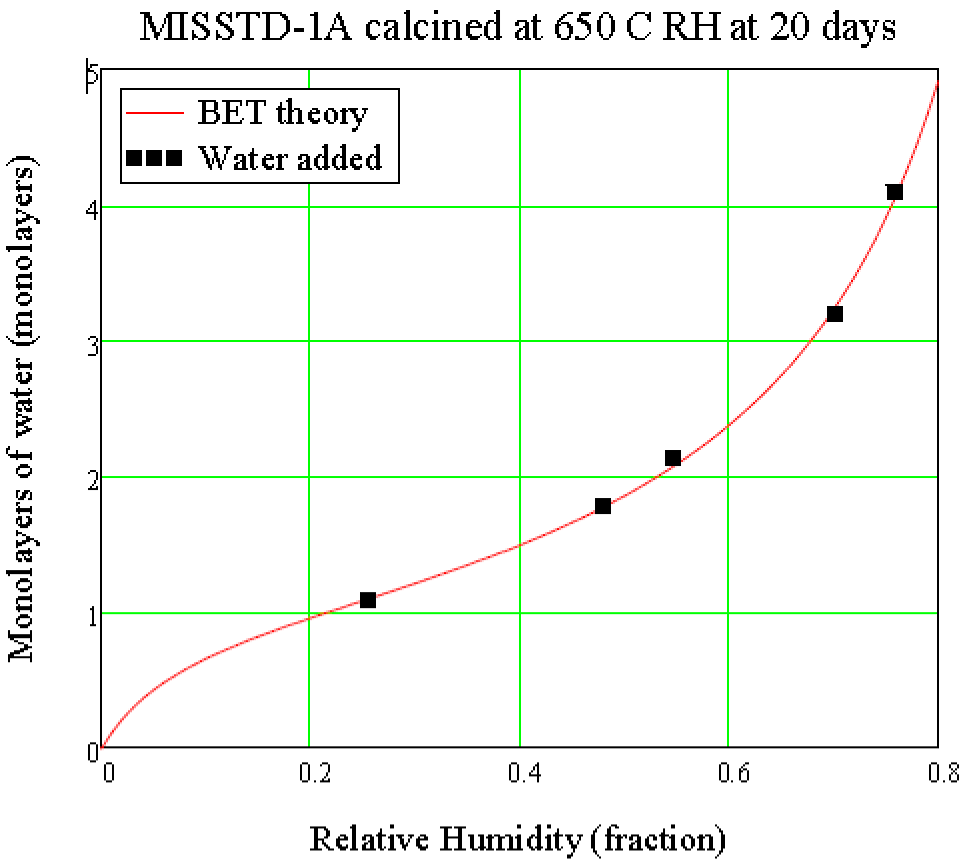


1. Surface is not quiescent – average lifetime is ~10^{-6} s

2. Adsorbents are clustered with a higher adsorption energy for the first layer only.

3. A "monolayer" is composed an average of clusters and does not cover the surface.

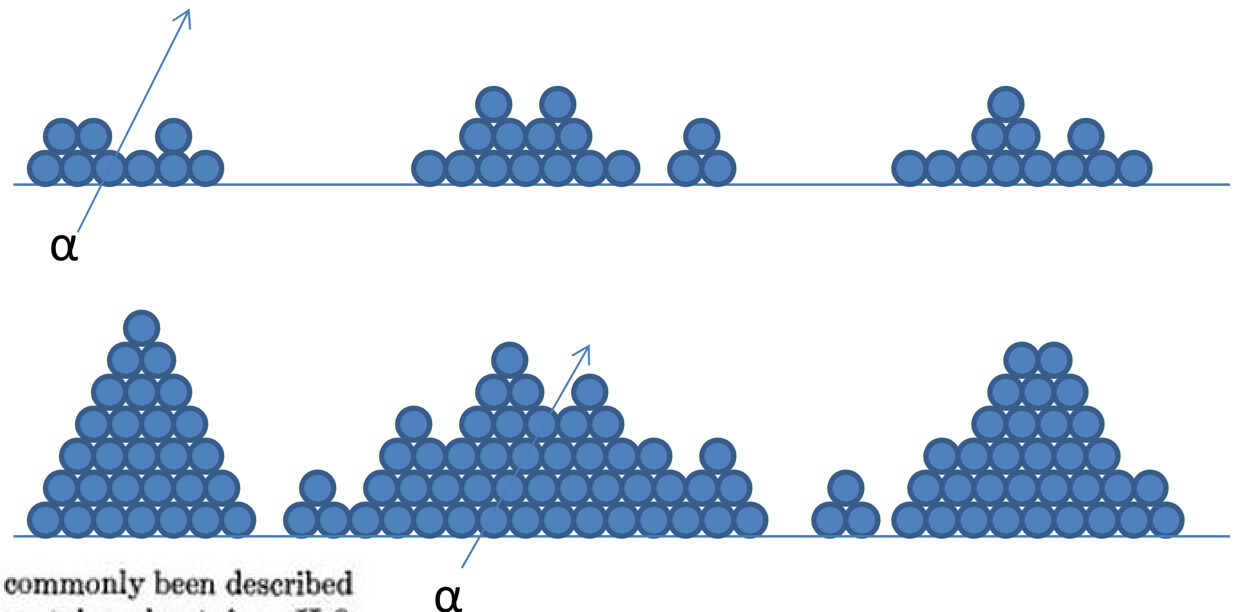
How does the number of monolayers very with RH?



How does radiolysis proceed?

1 monolayer

3 monolayer



The radiolysis of water has commonly been described in terms of the spur which contains about four H_2O decomposed in clusters within a radius of 20 Å to give e_{aq}^-, OH, and H_3O^+. The reactions which give the primary products may include

$$e_{aq}^- + e_{aq}^- = H_2 \quad (1)$$

$$e_{aq}^- + H_3O^+ = H \quad (2)$$

$$e_{aq}^- + H = H_2 \quad (3)$$

$$e_{aq}^- + OH = OH^- \quad (4)$$

$$H + H = H_2 \quad (5)$$

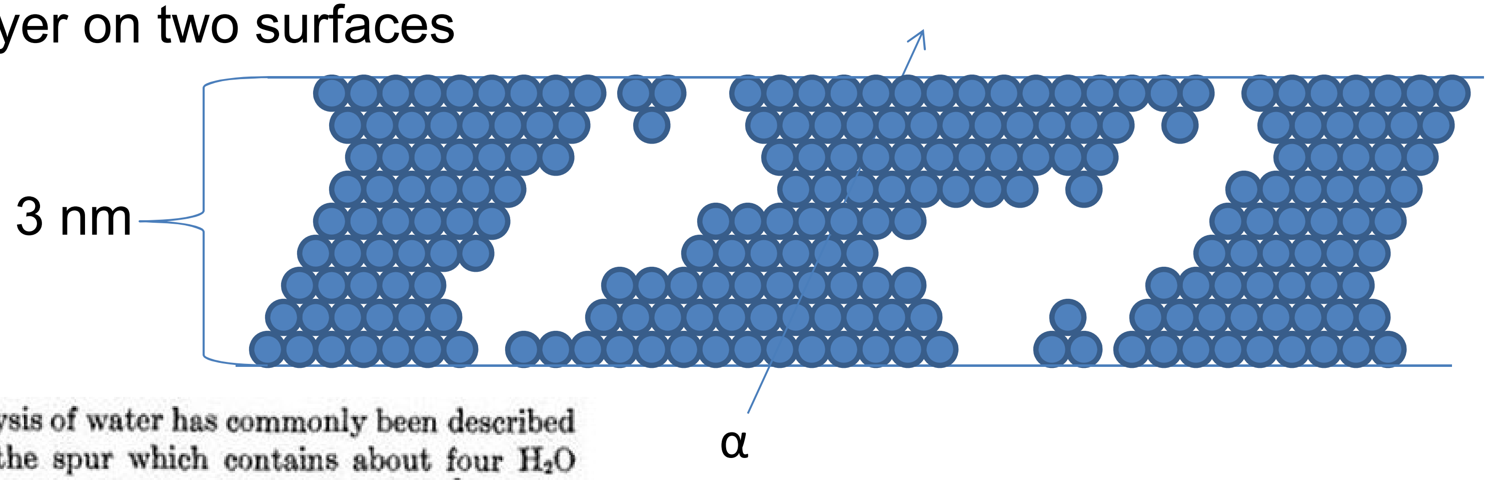
$$OH + OH = H_2O_2 \quad (6)$$

$$H + OH = H_2O \quad (7)$$

Conditions are not present for radiolysis to proceed according to classic mechanisms on a monolayer.

How does radiolysis proceed?

3 monolayer on two surfaces



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$$e_{aq}^- + OH = OH^- \quad (4)$$

$$H + H = H_2 \quad (5)$$

$$OH + OH = H_2O_2 \quad (6)$$

$$H + OH = H_2O \quad (7)$$

At high RH for internal surfaces the conditions approach those required for classical radiolysis.

Experimental results

Material: MISSTD1

Two calcination temperatures: 650 ºC and 750 ºC

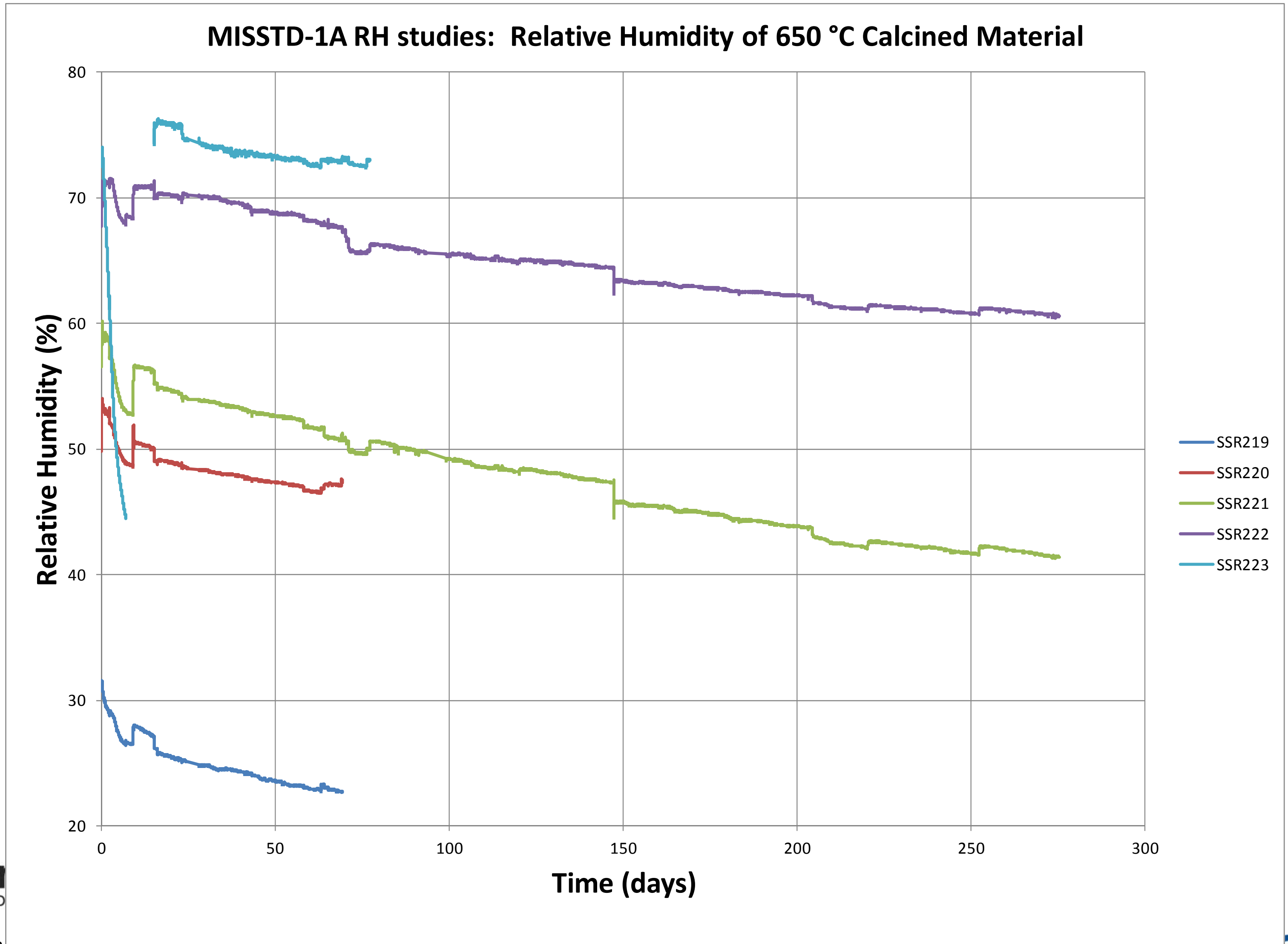
Material	Water content		SSA (m^2 g^{-1})	
650 Calcined	0.18%	0.21%	11.14	11.06
750 Calcined	0.29%	0.29%	7.41	7.70

Five RHs: 32.8, 52.9, 57.6, 71.5, and 78.6

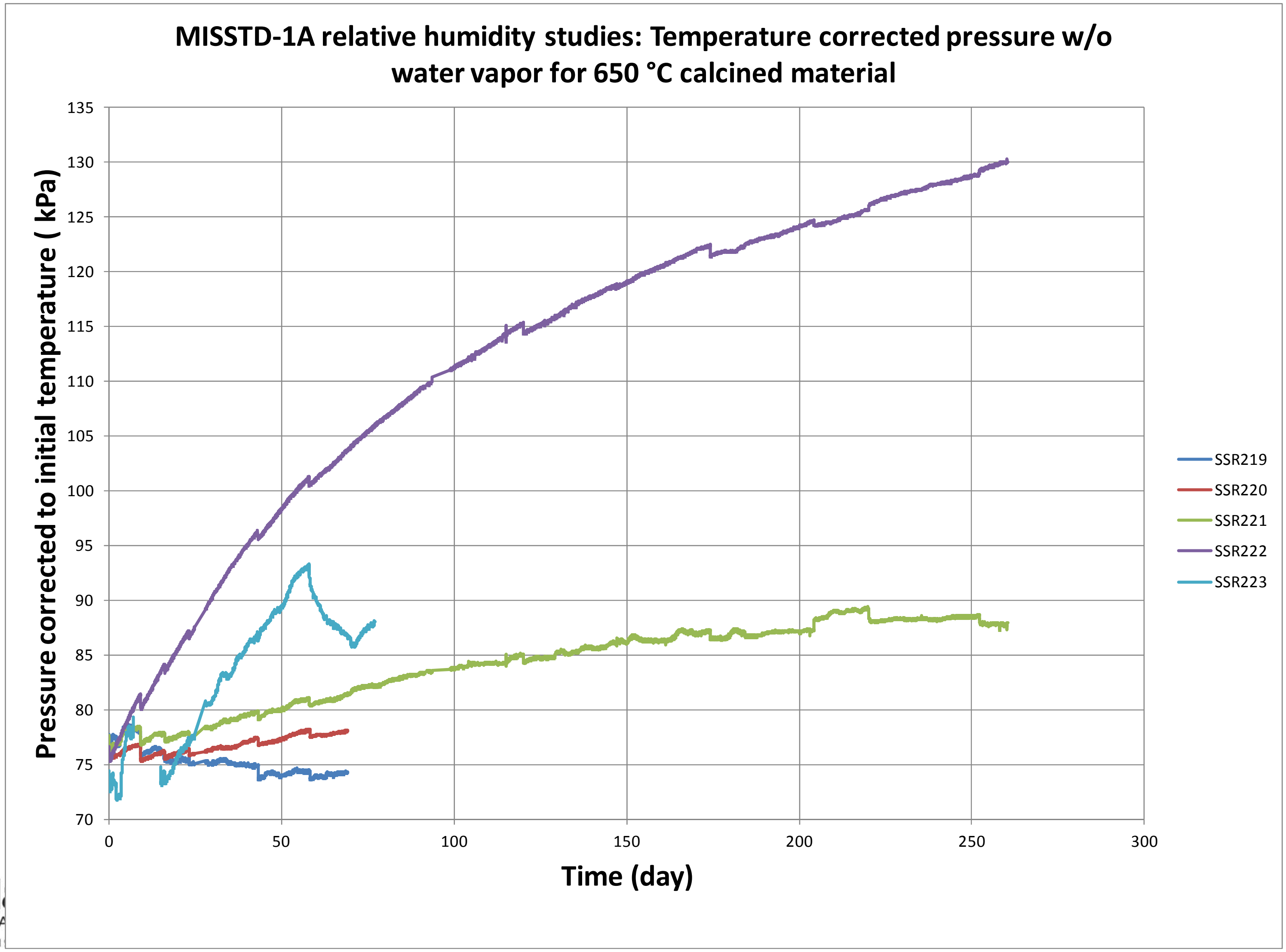
Material calcined at 650 ºC

Reactor	Saturated solution	RH at 25 °C (%)	Mass (g)	CHC closed	CHC open	Transfer Time	Mass gain (g)	Mass gain
SSR219	$MgCl_2$	32.8	4.31076	5/10/12 3:30 pm	5/15/12 9:06 am	50 s	0.02050	0.476%
SSR220	$Mg(NO_3)_2$	52.9	4.84865	5/10/12 3:30 pm	5/15/12 9:25 am	55 s	0.02980	0.615%
SSR221	NaBr	57.6	4.29351	5/10/12 3:35 pm	5/15/12 9:41 am	65 s	0.02934	0.683%
SSR222	NaCl/KCl	71.5	5.94845	5/10/12 3:40 pm	5/15/12 9:51 am	65 s	0.05320	0.894%
SSR223	NH_4Cl	78.6	4.39027	5/10/12 3:45 pm	5/15/12 10:02 am	80 s	0.04423	1.007%
SSR223	NH_4Cl	78.6	4.39027	5/29/12	5/30/12 11:12 am	87 s	0.04727	1.076%

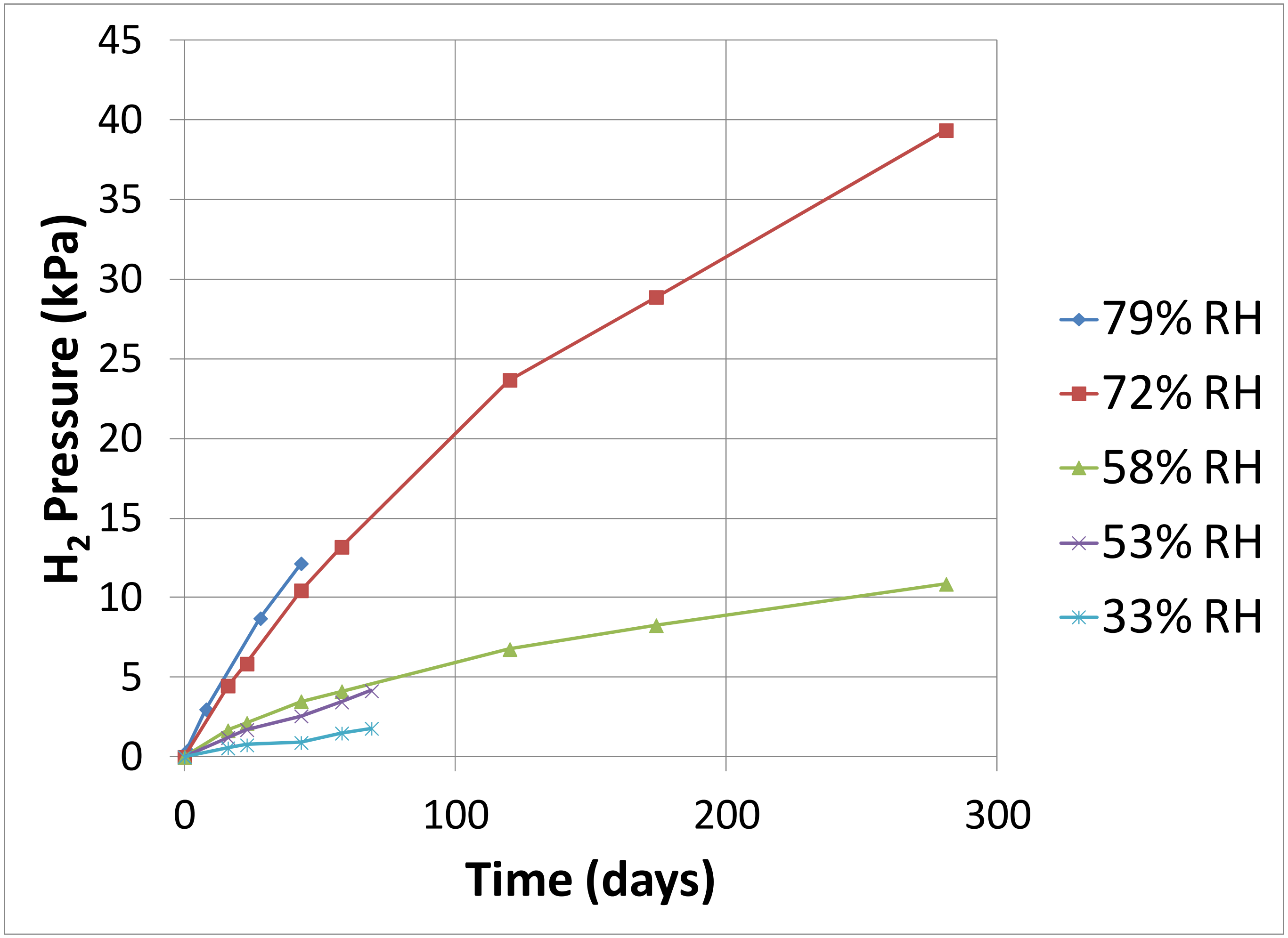
Relative humidity 650 ºC material



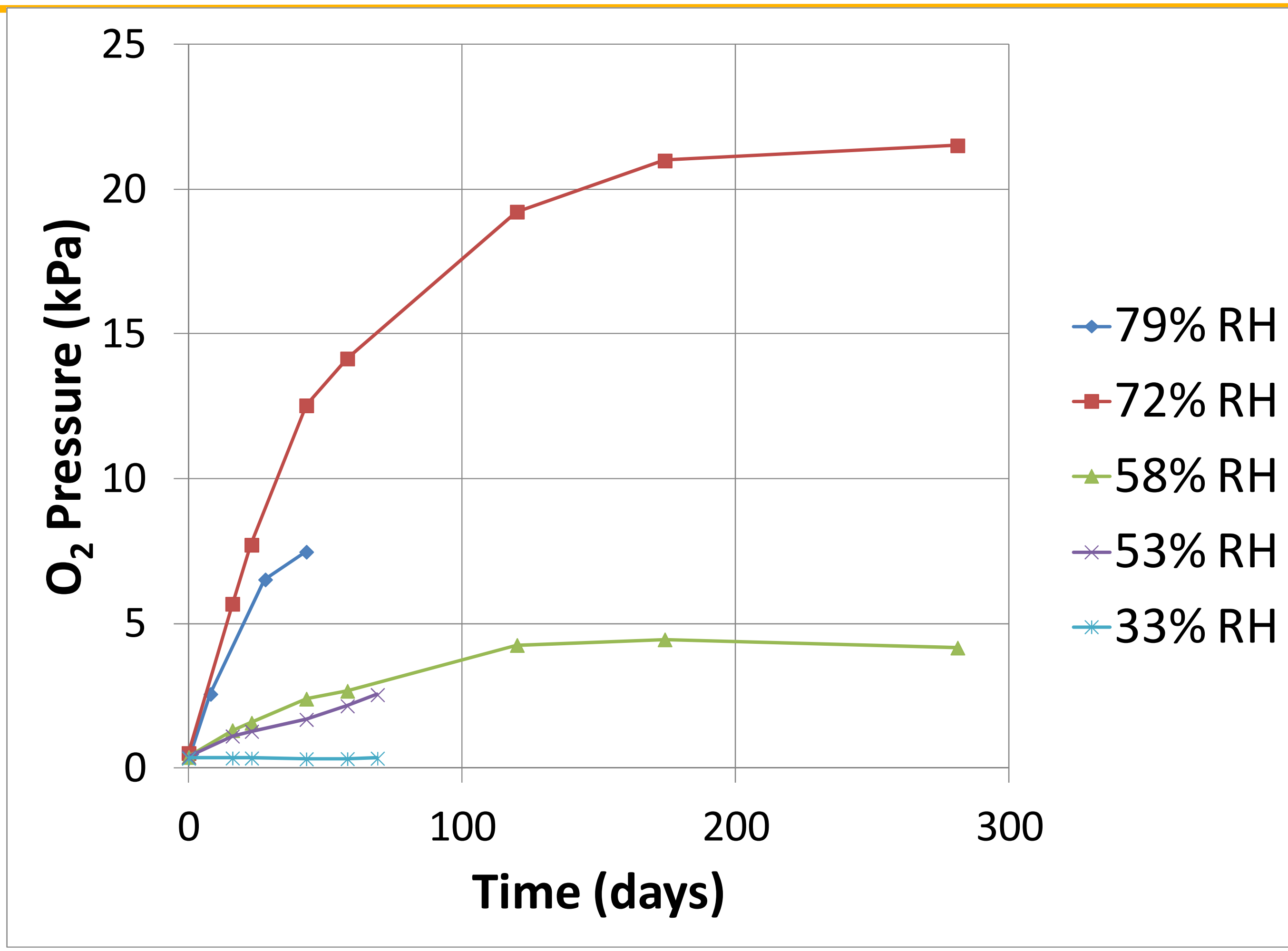
Pressure 650 ºC material



Hydrogen 650 ^oC material



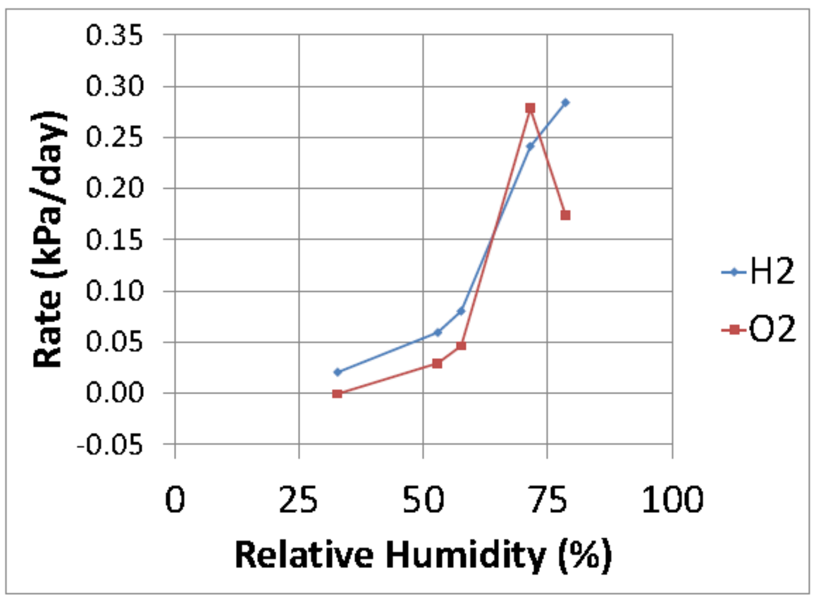
Oxygen 650 ºC material



Initial rates of H_2 and O_2 generation

Table 14. The rate of O_2 and H_2 formation form material calcined at 750 °C.

	Rate of O_2 formation (kPa/day)	
Relative Humidity	O_2	H_2
33% RH	-0.002	0.005
72% RH	0.017	0.030



Test Plan to Evaluate Initial Rates of H_2 and O_2 Generation in Sealed Containers of High-purity, High Surface Area PuO_2 as a Function of Relative Humidity in Packaging Atmospheres

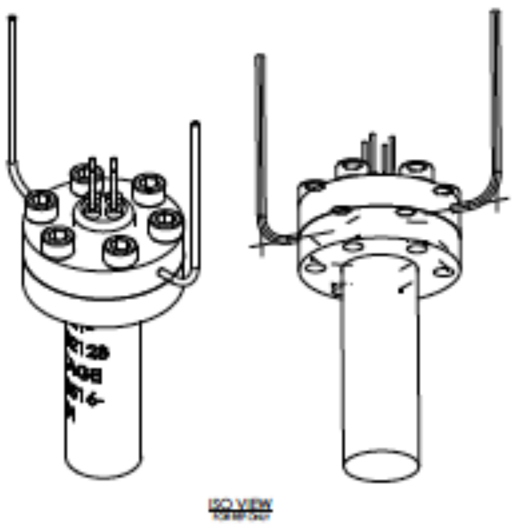
John Berg, Kirk Veirs, Joshua Narlesky (LANL)

MIS Program Review, February 2013

Issues addressed by planned tests

- HB-Line requires 625 °C stabilization to produce PuO_2
- Lower T stabilization will give higher specific surface area (SSA) and greater H_2O adsorption capacity.
- When exposed to high relative humidity for sufficient time:
  - H_2O can adsorb in excess of 0.5 wt % limit.
  - Simultaneous generation of H_2 and O_2 can occur and exceed flammability limit.
- Tests will determine lower RH threshold for O_2 gen.

Use small-scale shelf life containers with modifications



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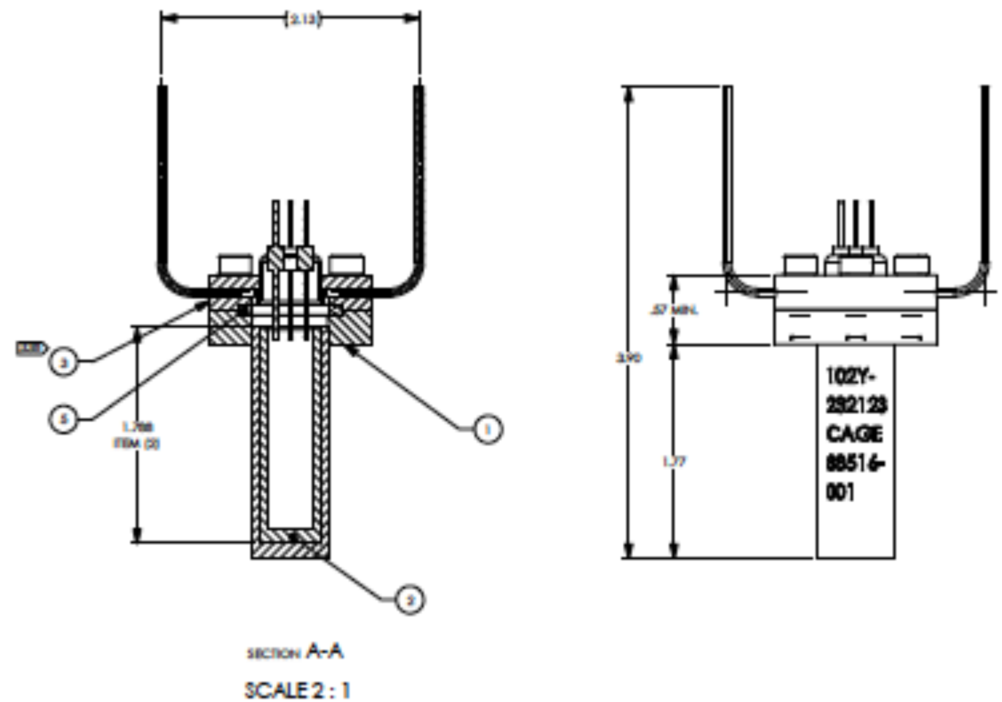


Test design

- Start with freshly-calcined (600 °C) PuO_2 from oxalate.
- Calcine again at 640 °C or higher to adjust SSA.
- Expose to controlled RH, seal, and monitor gas generation for total of ~150 days.
- Parameters to be varied across multiple trials:
  - Temperature of second calcination (vary SSA).
  - Relative humidity of exposure before sealing.
  - Initial headspace gas composition in test container.

Test container	Stabilization T (°C) [(a)]	Expected SSA (m^2/gram) [(b)]	Pre-test RH exposure (%)	Anticipated moisture uptake (wt%)	Duration (days) [(c)]
1	640	10	50	0.58	150
2	640	10	60	0.71	150
3	640	10	40	0.53	150
4	750 [(d)]	7	50	0.31	150
5	750 [(d)]	7	60	0.38	150
6	750 [(d)]	7	40	0.28	150
7 [(e)]	640	10	50	0.58	30
8	640	10	60	0.50 [(f)]	30
9	~600 [(g)]	13-17	40	>0.50	120
10	~600 [(g)]	13-17	50	>0.50	120

Monthly changes in gas composition to get accelerated data on O_2 and H_2 consumption reactions.

Table 1: Initial gas fill compositions targeted for the start of each of five month-long time segments of testing on containers 1 - 6. Container 7 will have only one gas fill and it will include H_2. Container 8 will have one time segment using only gas fill 1. Containers 9 and 10 are provisionally planned to include gas fills 1-4.

Gas Fill	N_2 fraction	O_2 fraction	H_2 fraction
1	96%	4%	0%
2	100%	0%	0%
3	98%	2%	0%
4	97%	3%	0%
5	TBD	TBD	0%
Container 7 only	91%	4%	5%

Anticipated Results

- Net increase in O_2 will be observed at highest RH.
- Decrease in O_2 will be observed at lowest RH.
- O_2 changes will be most rapid for high SSA material if there is no restriction on the amount of adsorbed H_2O.
- O_2 generation will be slow as its concentration increases.
- O_2 generation will be inhibited by initial partial pressure of O_2.

Low-temperature Stabilization of Direct Metal Oxidation (DMO) Product: 3013 Equivalency Tests and Recommendations

John Berg, David Wayne, Stephen Willson, Kirk Veirs,
Paul Deburgomaster,
Mark Saba, Steve McKee, Larry Peppers… (LANL)

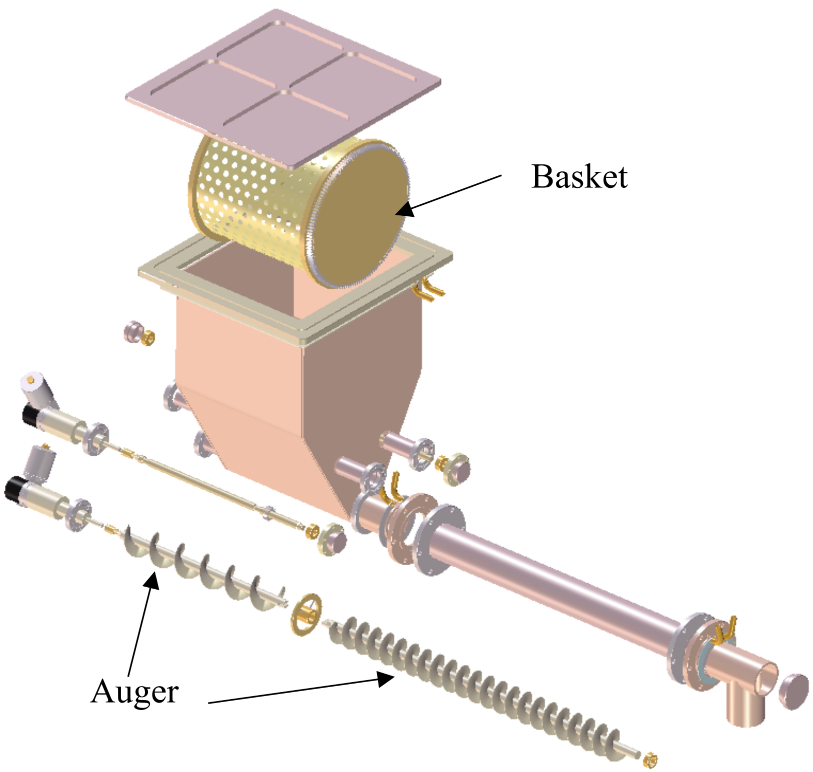
Ron Livingston (SRS)

MIS Program Review, SRS, February 2013

Office of Fissile Material Disposition (NA-26) and Office of Environmental Management (DOE-SR)

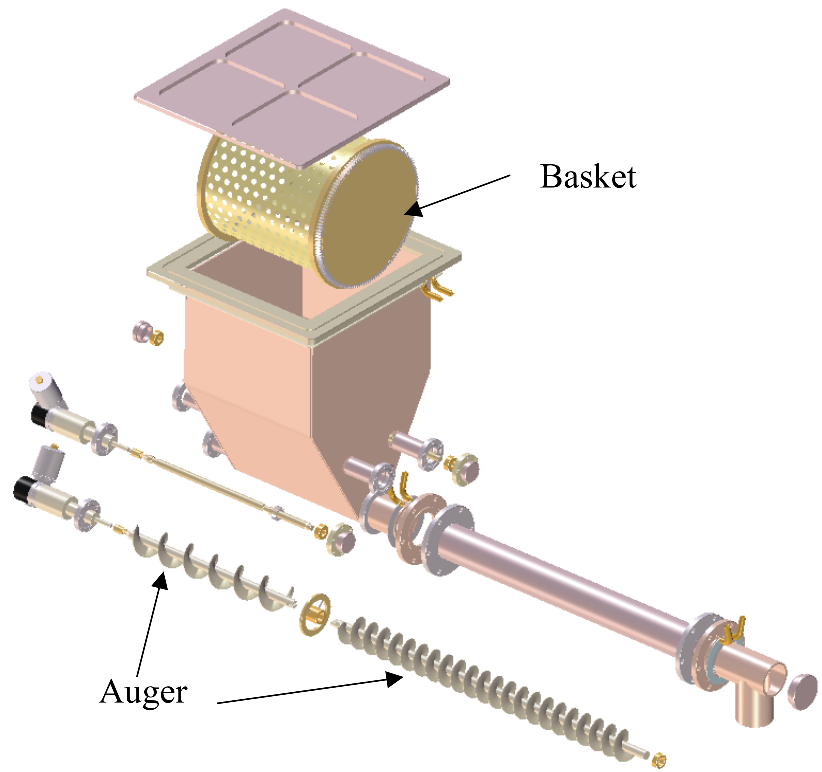
LANL ARIES Direct Metal Oxidation System (DMO-2)

- First stage: oxidation of metal pieces in rotating basket.
- Oxidizer is 70% O_2 gas flowing counter to material.
- First-stage product fed into calcination (stabilization) stage with auger.
- Second, calcination stage auger slowly moves oxide through stabilization furnace to achieve two hours at >950 °C.



Direct Metal Oxidation (DMO) Stabilization Conditions

- Lower temperature or reduced residence time would increase throughput and decrease maintenance cost and delays for DMO screw calciner.
- Can 3013 stabilization objectives be reliably achieved at lower temperature?
    - Principal objective for DMO: Eliminate reactive materials such as finely divided metal or sub-stoichiometric Pu oxide



Test Plan Tasks

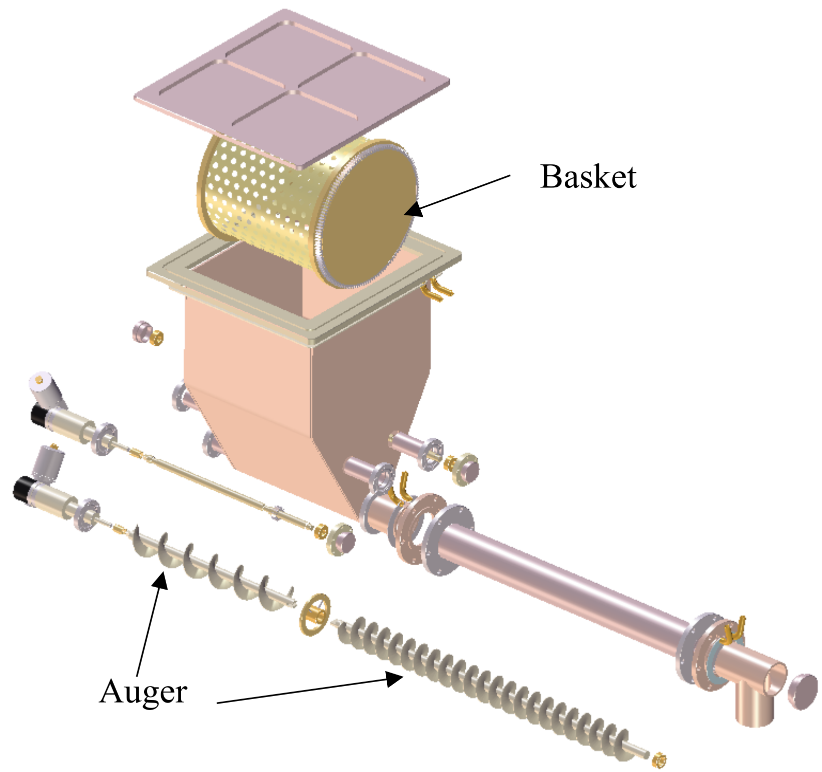
- **Run DMO-2 first stage to make oxide without stabilizing.**
- **Riffle to split samples.**
- **Stabilize samples at 650, 750, 850 and 950 °C for two hours and 650 °C for one hour. Replicate.**
- **Analyze for:**
  - Residual capacity for oxidation
  - Impurity concentrations
  - Specific surface area
- **Write and issue data report.**
- **Draft equivalency document for external review.**
- **Resolve comments and obtain approval.**

Test Plan

- Produce one batch of oxide from typical metal feed using the ARIES DMO-2 furnace with the calcination furnace and auger off.
- Sample from kg-scale batch of product oxide using rotary rifflers.
- Calcine representative samples at various temperatures.
  - Two hours at 650, 750 and 850 °C.
  - Two hours at 950 °C control.
  - One hour at temperature to be determined by two-hour results.
- Measure the degree of oxidation by controlled atmosphere LOI.
  - ASTM technique for measuring the stoichiometry of Pu and U oxides in fuel pellets and powders.
  - Heat in flowing stream of $Ar/H_2O/H_2$
  - Δ mass gives deviation of sample stoichiometry from PuO_2.
- Characterize samples of uncalcined and calcined material.
  - TGA-MS, specific surface area, particle size, trace impurities
- Sample a calcined batch of DMO product from similar feed material and measure average stoichiometry by controlled-atmosphere LOI.

Production of test material in DMO 1st stage

- Ran DMO-2 with normal operating parameters in the oxidation stage, including oxidant gas flow, heating and basket rotation.
- Screw calciner and auger were both off.
- Material removed by pulling auger out manually after cool down.
- Product was mostly granular, with a distinct finer powder fraction.



DMO Product Oxide vs. Test Material

- unmilled DMO product
  - 30-80% greater than 200 μm
  - Typical surface area < 0.4 m^2/g
- TGA-MS of blend lots
  - Typical moisture = 0.01 wt%
  - Total volatiles < 0.05 wt%

- uncalcined DMO product
  - 25 % greater than 200 μm
  - surface area 0.38 m^2/gram
  - moisture = 0.007 wt% (by TGA-MS)
  - Total volatiles ≈ 0.05 wt % by TGA

Summary of results

Measured fractional mass increases of the DMO oxidation-stage product samples during stabilization tests.

Stabilization Conditions	Mass Increase	
	Crucible 1	Crucible 2
950 °C / 2 hr.	0.42%	*
850 °C / 2 hr.	0.31%	0.64%
750 °C / 2 hr.	0.35%	0.22%
650 °C / 2 hr.	0.30%	0.77%
650 °C / 1 hr.	0.43%	0.50%

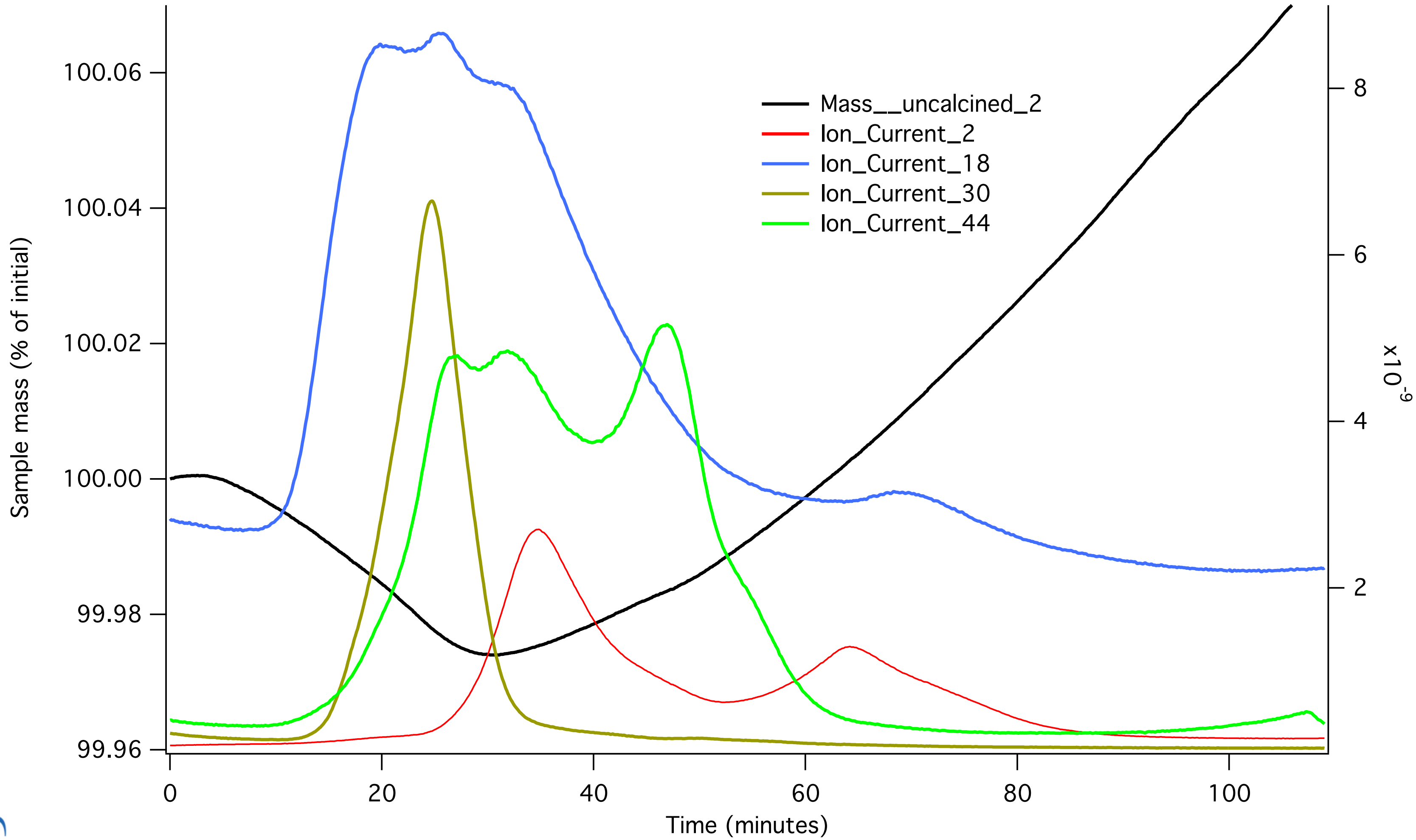
* Sample spilled before weighing.

Summary of results

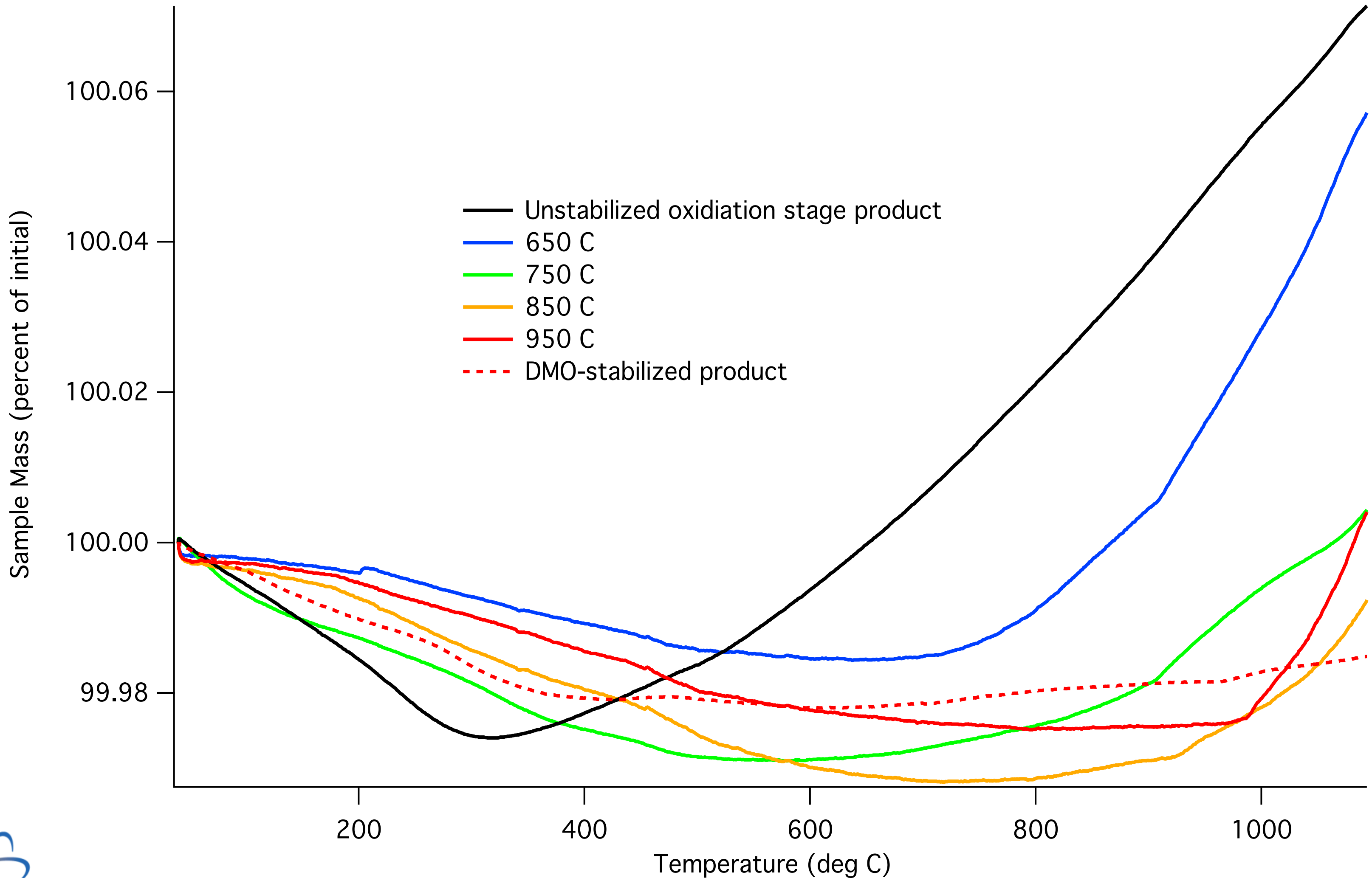
Stabilization conditions	Mass changes during stabilization		Controlled-atmosphere LOI mass changes		Ignoring impurities, average PuO_x stoichiometry	
	Crucible 1	Crucible 2	Sample 1	Sample 2	Sample 1	Sample 2
DMO product (unstabilized)	N/A	N/A	+0.391%	+0.194%	1.934	1.967
950 / 2 hr.	+0.42%	*	+0.009%	-0.006%	1.999	2.001
850 / 2 hr.	+0.31%	+0.64%	+0.001%	-0.016%	2.000	2.003
750 / 2 hr.	+0.35%	+0.22%	+0.033%	+0.034%	1.994	1.994
650 / 2 hr.	+0.30%	+0.77%	+0.048%	+0.032%	1.992	1.995
650 / 1 hr.	+0.43%	+0.50%	+0.048%	+0.043%	1.992	1.993
DMO-2 stabilized oxide product			-0.070%	-0.069%	2.012	2.012

* No data. Sample handling error.

TGA-MS of unstabilized DMO product



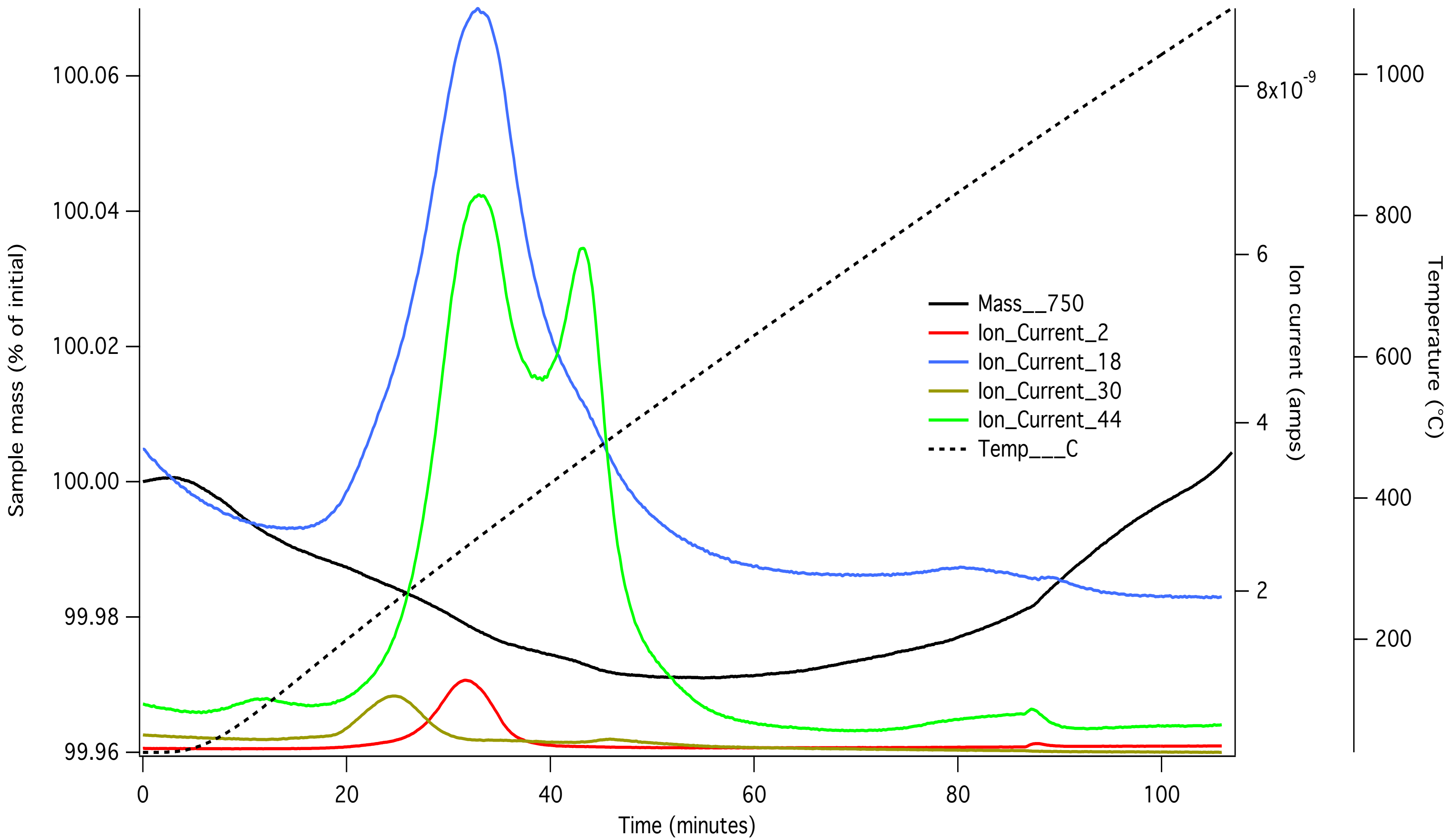
High T mass gains in TGA of all samples



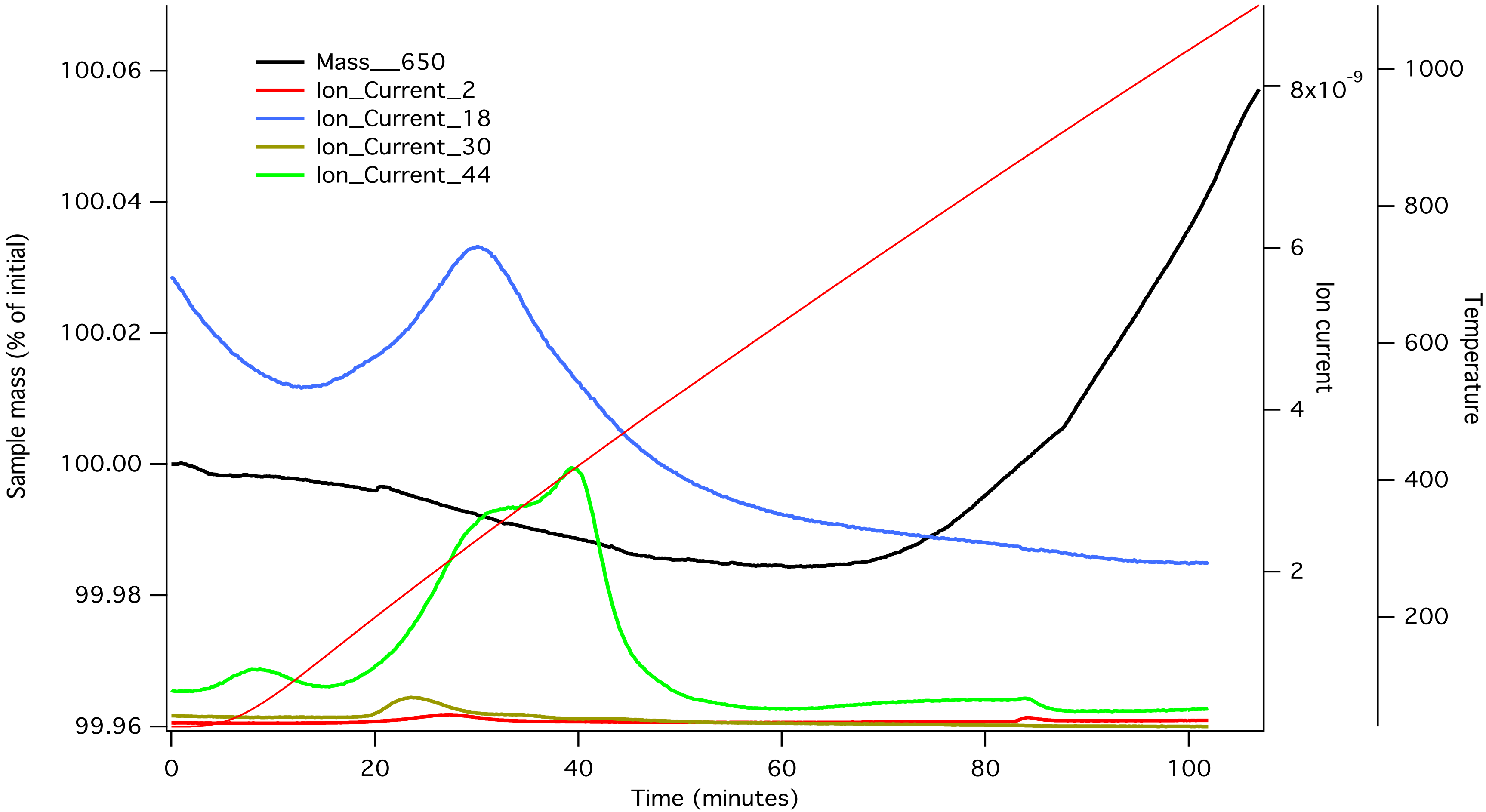
Elemental impurity analysis

	DMO oxidation stage product	650 °C stabilized	Method	Uncertainty (%)
Cr	95 ppm	84 ppm	ICP-MS	15
Ni	350 ppm	330 ppm	ICP-AES	15
Pb	10 ppm	10 ppm	ICP-MS	15
Al	130ppm	110 ppm	ICP-AES	15
Ca	4.2 ppm	6.2 ppm	ICP-AES	15
Fe	390 ppm	360 ppm	ICP-AES	15
Si	210 ppm	97 ppm	ICP-AES	15
Ga	7900ppm	7500 ppm	XRF	5

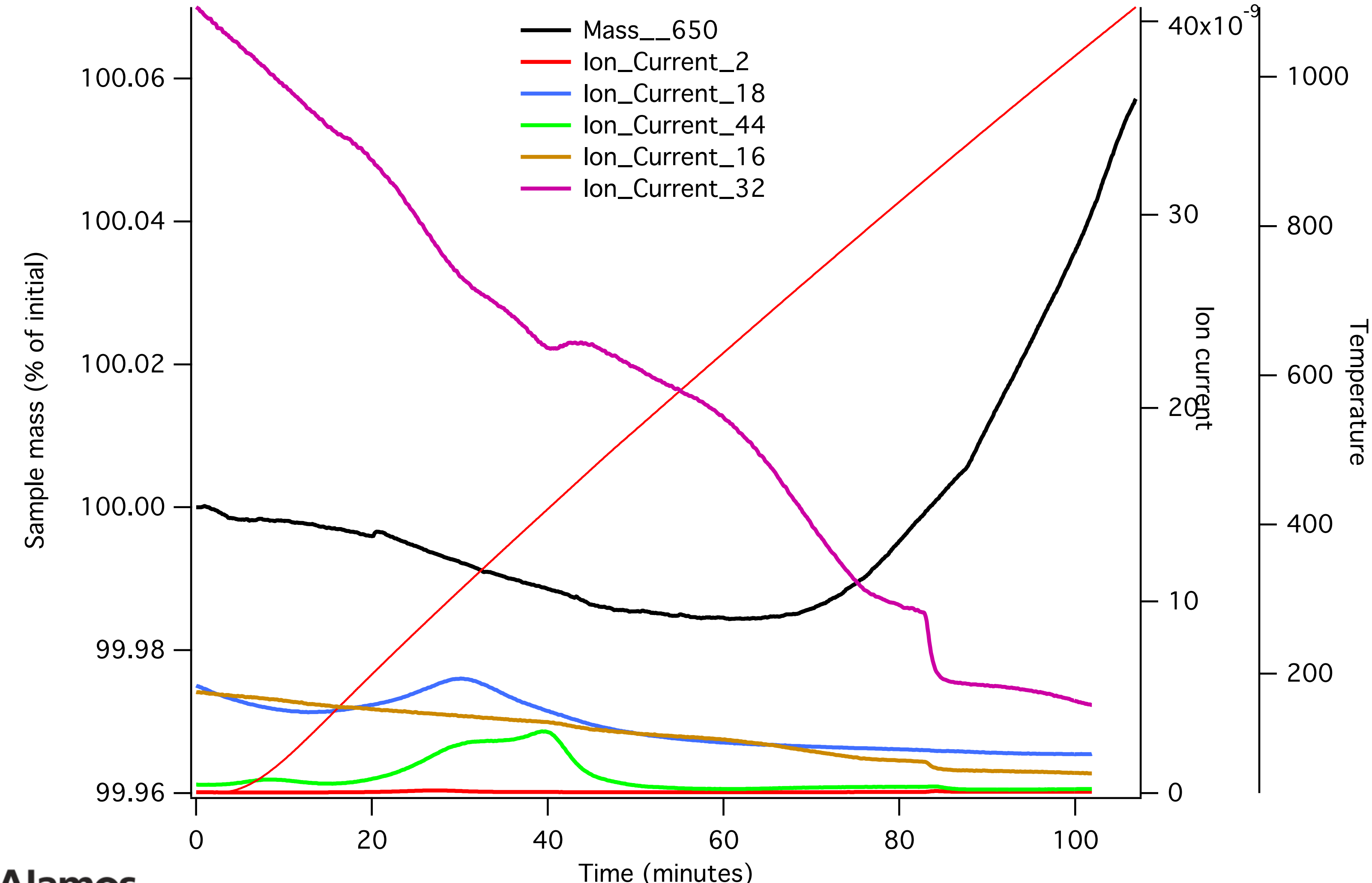
TGA-MS of 750 °C stabilized DMO product



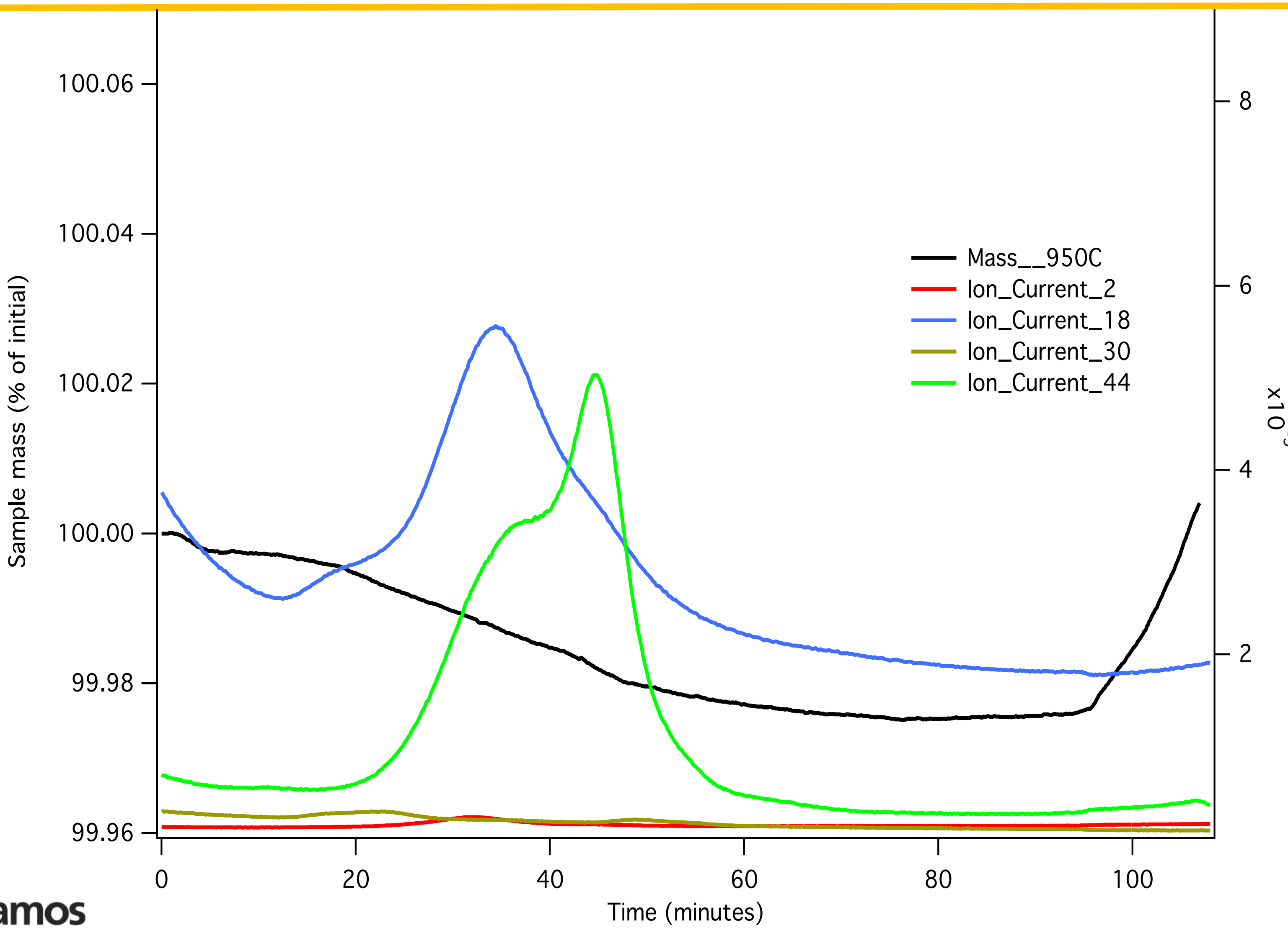
TGA-MS of 650 °C stabilized DMO product



TGA-MS of 650 °C stabilized DMO product



TGA-MS of 950 °C stabilized DMO product



Conclusions

- The product of the DMO oxidation stage has a residual capacity for oxidation of about 4% of the original feed.
- Stabilization tests as low as 650 °C for 1 hour produced oxide with an average stoichiometry greater $PuO_{1.99}$
- Post-stabilization tests indicate that the residual capacity to be oxidized is restricted to high temperature.
- DMO oxidation stage and all stabilization tests produced product with low capacity for adsorbed gases consistent with low specific surface.

Residual reactivity

- After stabilization, the DMO product is unreactive to oxygen unless it is heated above the stabilization temperature.
- Trace remaining oxidation, making the conservative assumption that it is due to Pu metal and that it could react in a few minuts, would raise the oxide temperature by less than 40 °C. Reaction over hours to weeks is more realistic and would lead to no discernable temperature rise.

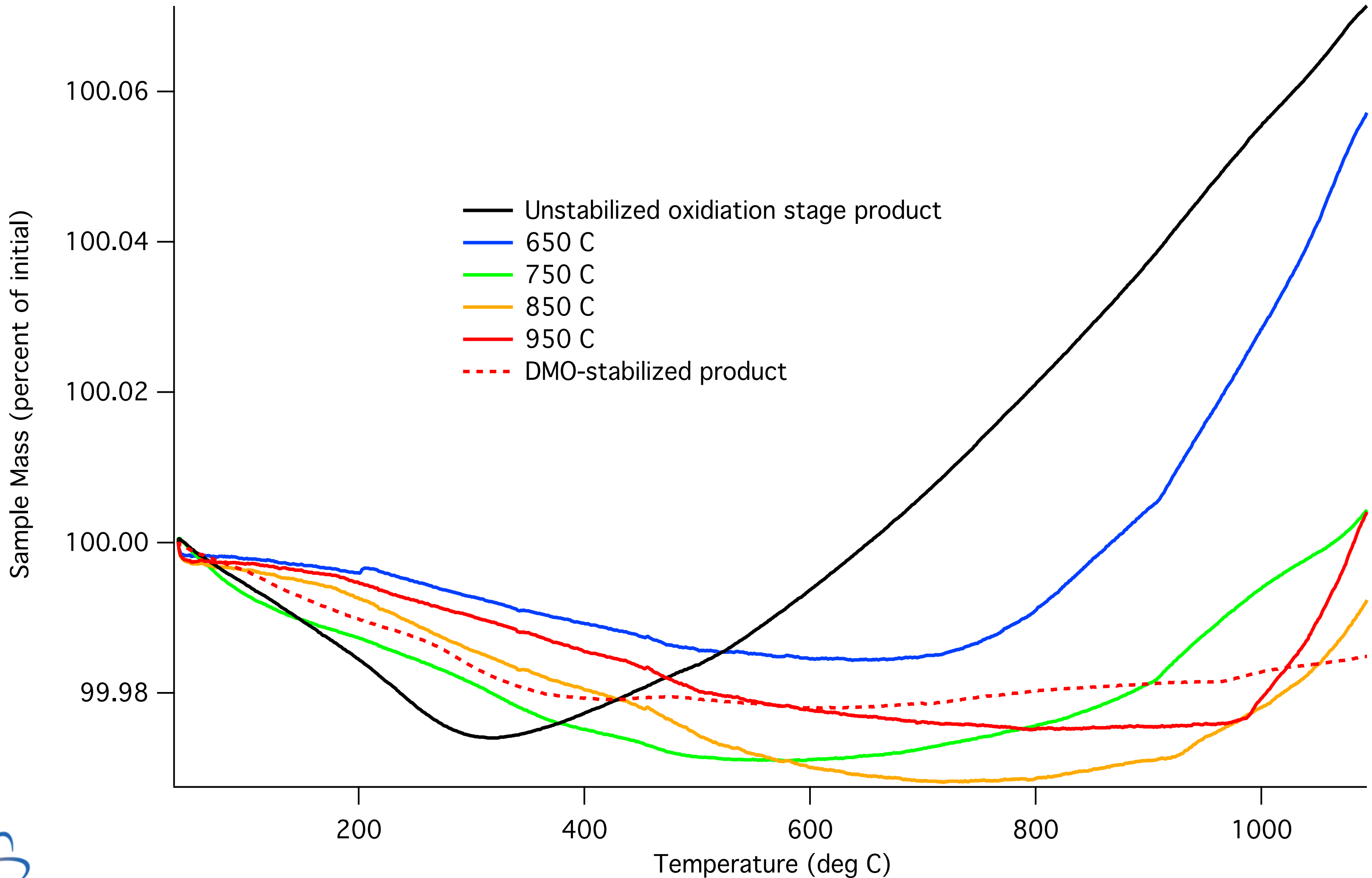
Recommendation for Equivalency

- **Stabilization at or above 650 °C for 2 hours will produce a product that is stable in air .**
  - No residual reactivity to air at temperatures below 600 °C.
  - Slight capacity to incorporate more oxygen above 600 °C is probably due to oxidation of impurity phases.
  - This is clearly not a storage or handling safety concern.

Residual reactivity bounding energy release

- ΔH for conversion of sub-stoichiometric oxides to PuO_2 is less than ΔH for the oxidation of Pu metal: 1056 kJ per mole of O_2 consumed. For example, oxidation of one mole of $PuO_{1.5}$ to PuO_2 consumes ¼ mole of O_2 has a heat of reaction of no more than 1056/4 = 226 kJ/mole.
- The heat released by oxidizing $PuO_{1.995}$ to $PuO_{2.000}$ would be less than 0.005/2.000 or 0.25% of 1056 kJ/mole = 2.6 kJ/mole. The heat capacity of PuO_2 at 50 °C is 70 J/mol K. If residual oxidation were instantaneous, the temperature would rise by 2.6 kJ/mole / (70 J/mol K) = 38 °C.
- Instantaneous oxidation is an extremely conservative assumption given the observed slow reaction even at elevated T in an oxidizing atmosphere.

High T mass gains in TGA of all samples



White, solid phase formed in TGA crucible

- History of this 2 gram sample:
  - From DMO, not calcined
  - Stabilized 15g to 950°C
  - Photo after TGA of 2g to 1100 °C

- Characteristics of white matl.
  - Low bulk density, easily broken up and sometimes hollow deposit.
  - Commonly observed after TGA of calcined oxide as well.

Evidence white solid is Ga_2O_3

- Ga_2O_3 is the stable oxide phase of gallium.
- Ga_2O is volatile at temperatures reached in TGA but would form Ga2O3 in slightly oxidizing carrier gas.
- Microprobe and EDXRF analyses indicate that the white material is a gallium oxide, probably Ga_2O_3.

Examples of literature on gallium / oxygen reactions

S. Penner et al. / Thin Solid Films 516 (2008) 4742–4749

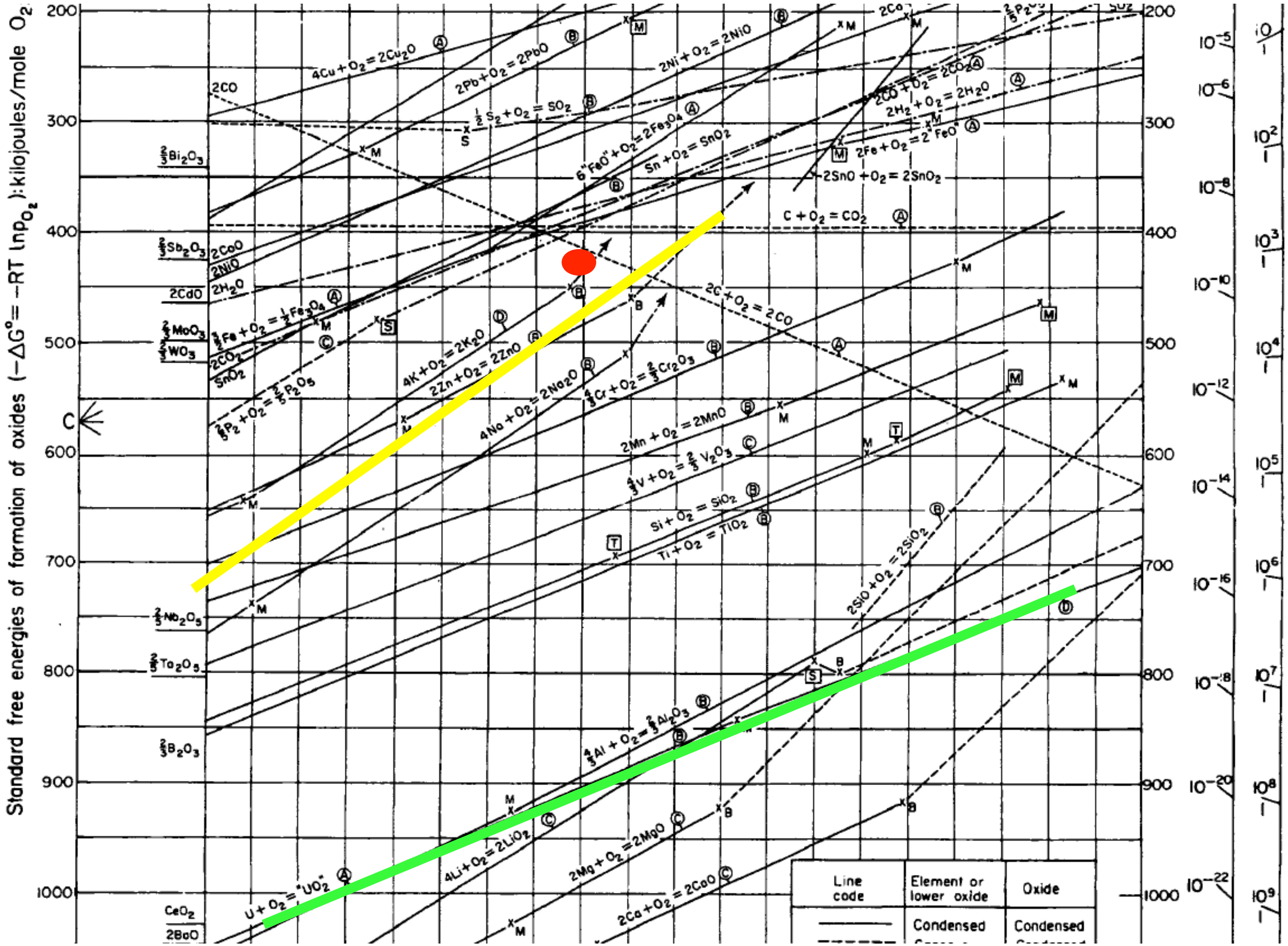
We propose a qualitative dynamic model of Ga-oxide deposition and growth based on the following reactions, assuming mass transport via the well-established volatile Ga_2O sub-oxide species [25]:

$$Ga_2O_3(s) \leftrightarrow Ga_2O(g) + O_2\uparrow (\text{crucible}, \sim 1300\text{K}) \quad (1)$$

$$Ga_2O(g) \overset{k_1/k_{-1}}{\longleftrightarrow} Ga_2O(ads) \quad (2)$$

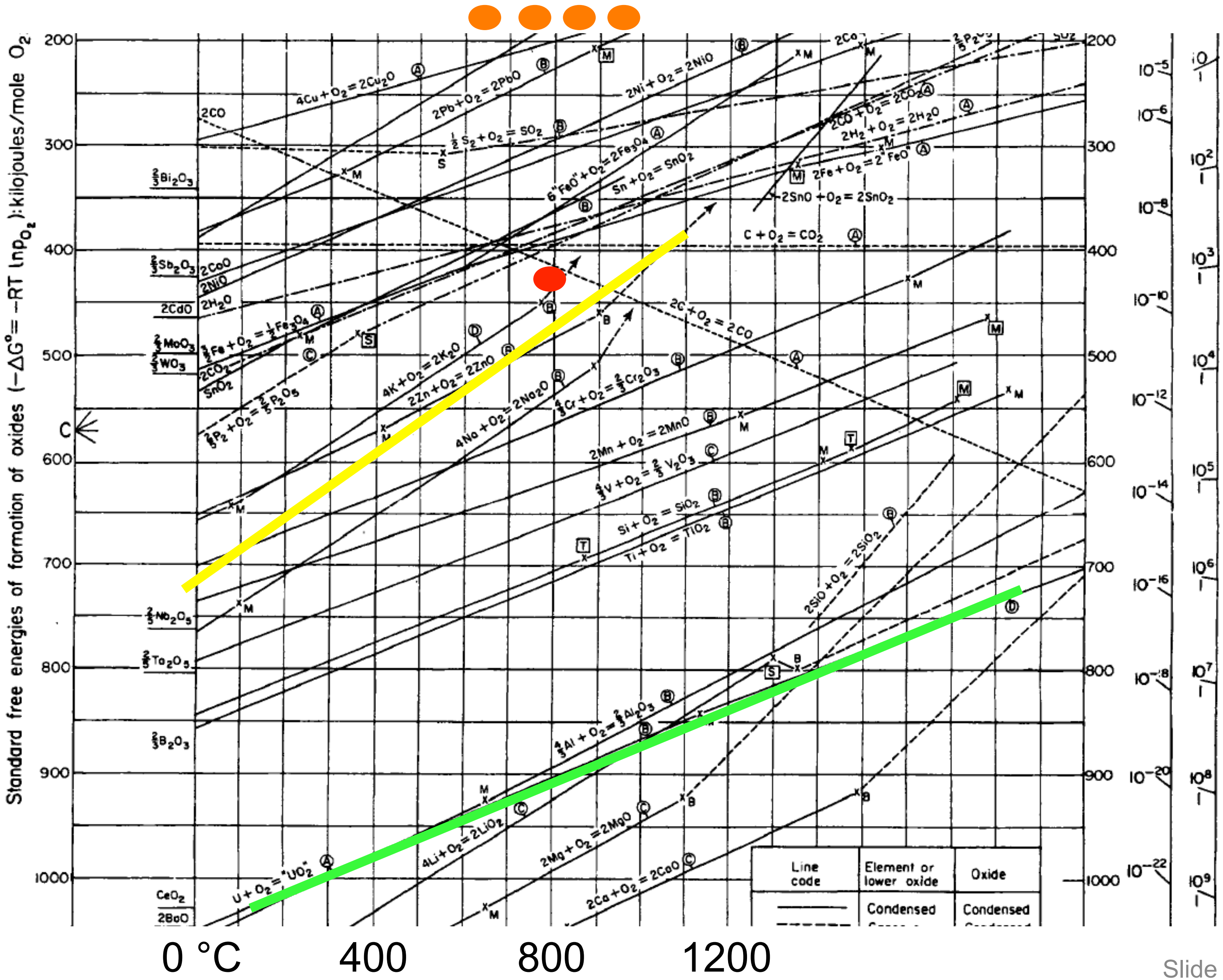
$$Ga_2O(ads) + O_2 \overset{k_2}{\rightarrow} Ga_2O_3(ads) \quad (3)$$

Ellingham Diagram of Oxide Formation Energies



0 °C 400 800 1200

Ellingham Diagram of Oxide Formation Energies



Gallium / oxygen reactions

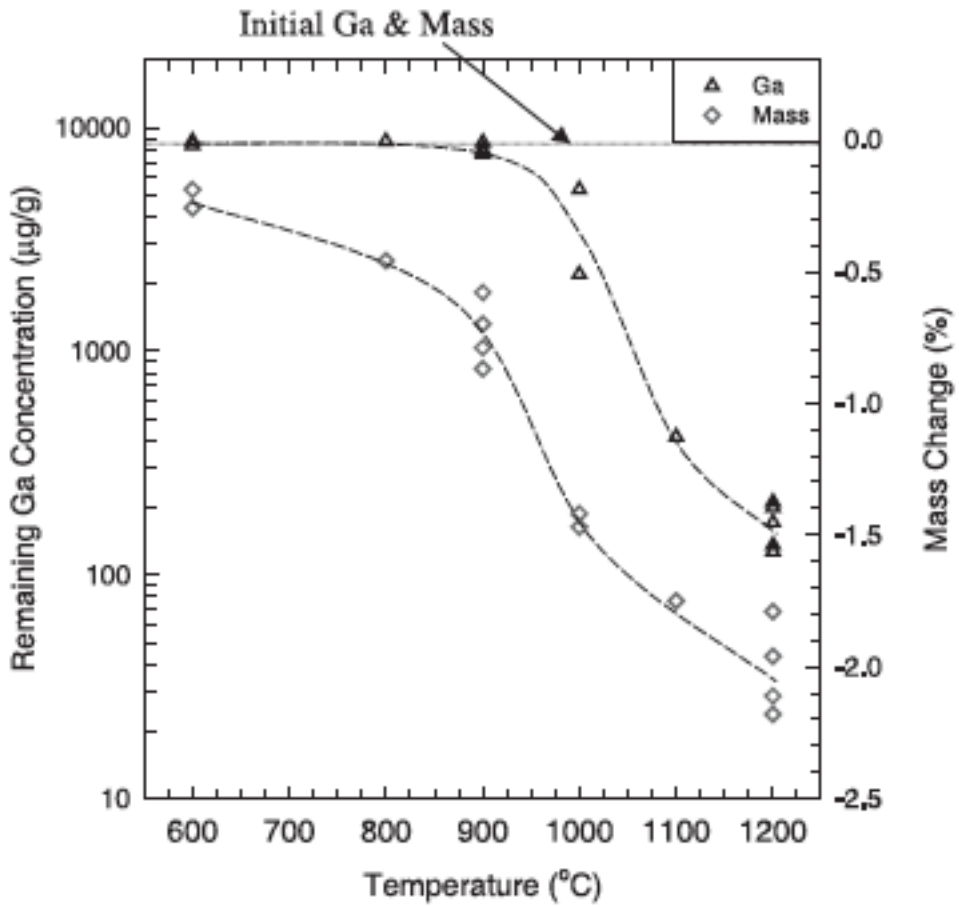


Fig. 4. Remaining Ga concentration in, and mass loss from, three-step powder as a function of exposure temperature in flowing Ar–6% H_2. Test duration: 0.5 h; sample mass: 2.5 g; flow velocity: 1.5 cm/s.

Equivalency of Lower-T DMO Stabilization

- Stabilization of DMO oxide in air at 650 °C for two hours produces a product that is stable with respect to further oxidation during storage or subsequent handling.
- The stoichiometry of the resulting plutonium oxide is $PuO_{2.00}$ to within the error introduced by the chemistry of ubiquitous impurities.
- We recommend authorizing use of stabilization at

Tasks and status

- **Run DMO-2 first stage to make oxide without stabilizing.**
- **Riffle to split samples.**
- **Stabilize samples at 650, 750, 850 and 950 °C for two hours and 650 °C for one hour. Replicate.**
- **Analyze for:**
  - Residual capacity for oxidation
  - Impurity concentrations
  - Specific surface area
- **Write and issue data report.**
- **Draft equivalency document for external review.**
- **Resolve comments and obtain approval.**

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- Write and issue data report.
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- Resolve comments and obtain approval.

Small-Scale Update

D. Kirk Veirs

LANL Team: John Berg, Dave Harradine, Dallas Hill, Chris Liebman, David Martinez, Rhonda McInroy, Josh Narlesky, Ed Romero, Leonard Trujillo, Kirk Veirs, Laura Worl

3013 Surveillance and Monitoring Program Review
Feb. 26 – 28, 2013
Savannah River Site

Summary

1. Small-Scale equipment modified to conduct studies on high specific surface area material exposed to high RH.
2. Added ability to obtain RH versus time.
3. A new column was installed to improve the quantitative analysis especially of H_2 and He.
4. Eight MIS represented materials removed.

Conducting studies of high SSA oxide at high RH

The issue is minimizing the temperature gradients within the reactor.

Within the heated array, temperature gradients are approximately 20 ºC.

Solution: Place a new Al block outside the tray holding the heated blocks. Attach the reactor to the original manifold within the tray using an extended line from the lid to the first valve.

Valve at ~35 ^{0}C

Heated to 55 ^{0}C

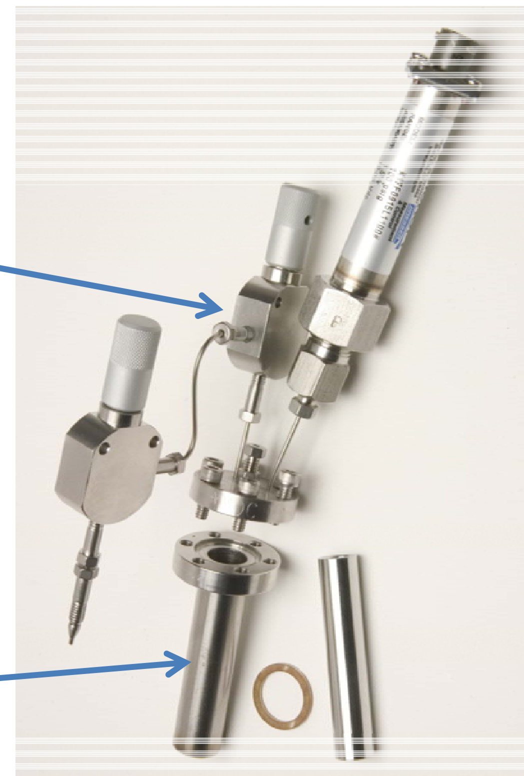
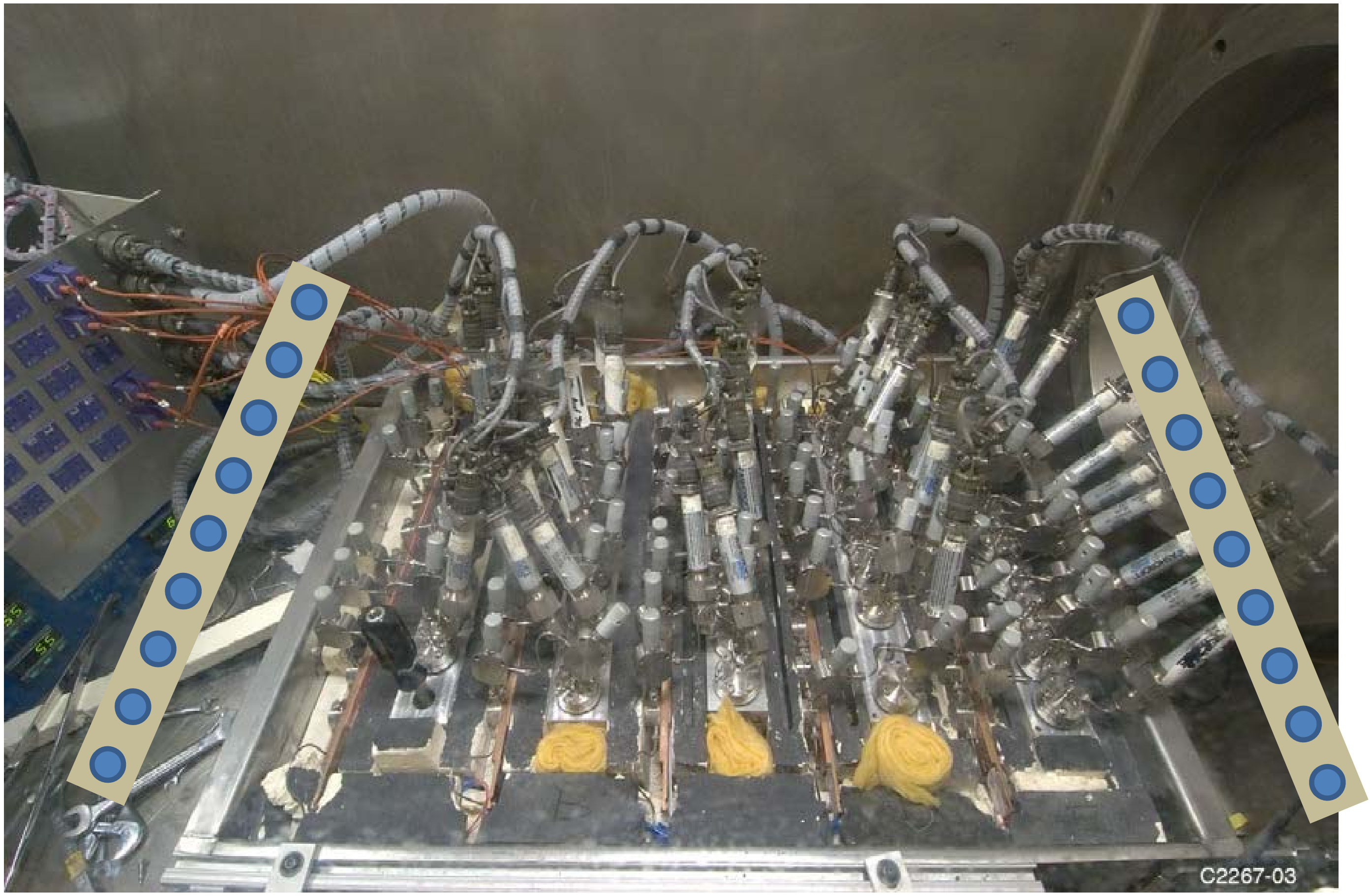


Illustration of new configuration

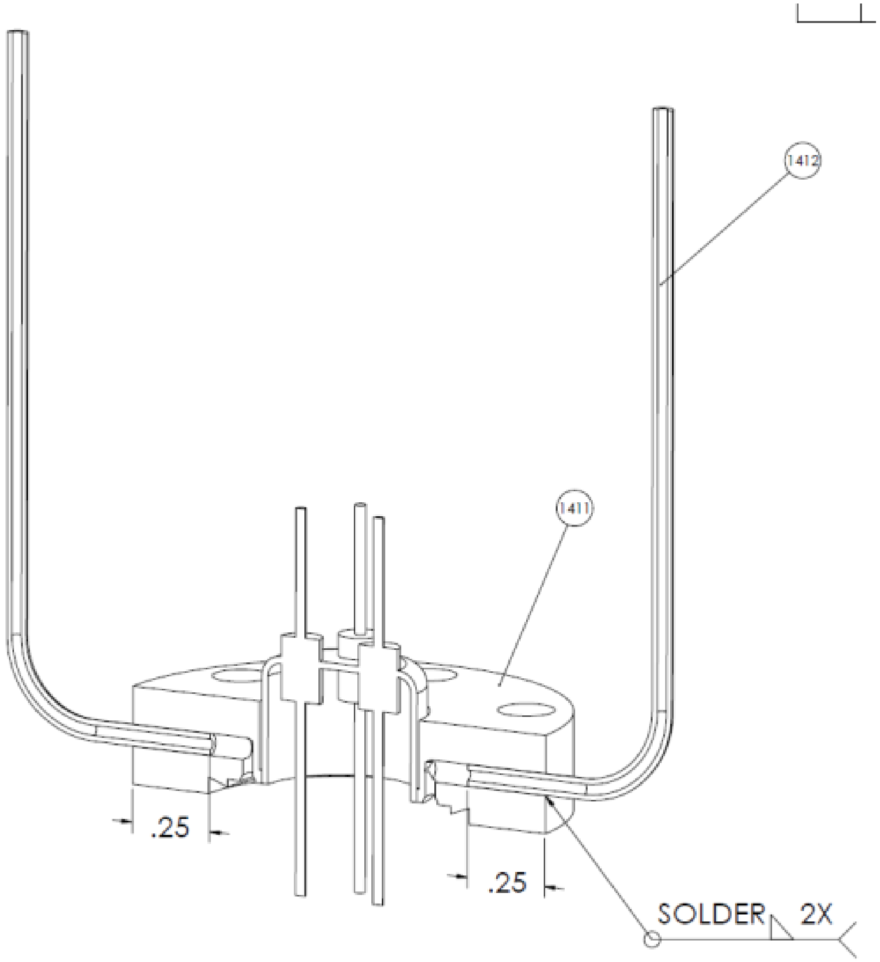


Small-Scale re-designed lid with RH sensor

Features and modifications:

1. RH sensor at top of material.
2. Container shortened to keep 5 ml internal volume.
3. New pressure transducer with better accuracy and 50 psi full scale (older one 125 psi full scale).

Last two ensure new loadings of MIS representative materials are consistent. They can be used for H_2/O_2 studies.



RH sensor

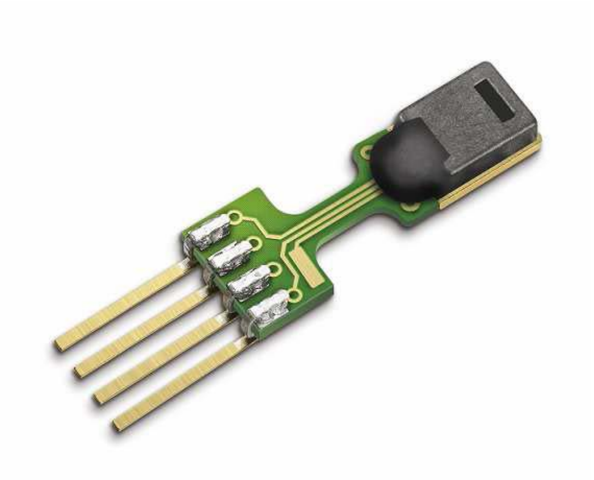
The RH sensor interface box will allow 20 sensors.

Data collection program modified to collect data from RH sensors: temperature and relative humidity. Allows vapor pressure of water to be calculated.

Twenty lids, inner buckets, and outer containers have been fabricated.

Twenty new pressure transducers have been acquired.

Modifications of electrical connectors is currently underway.



Restek Shincarbon GC column

A micropacked carbon molecular sieve column.

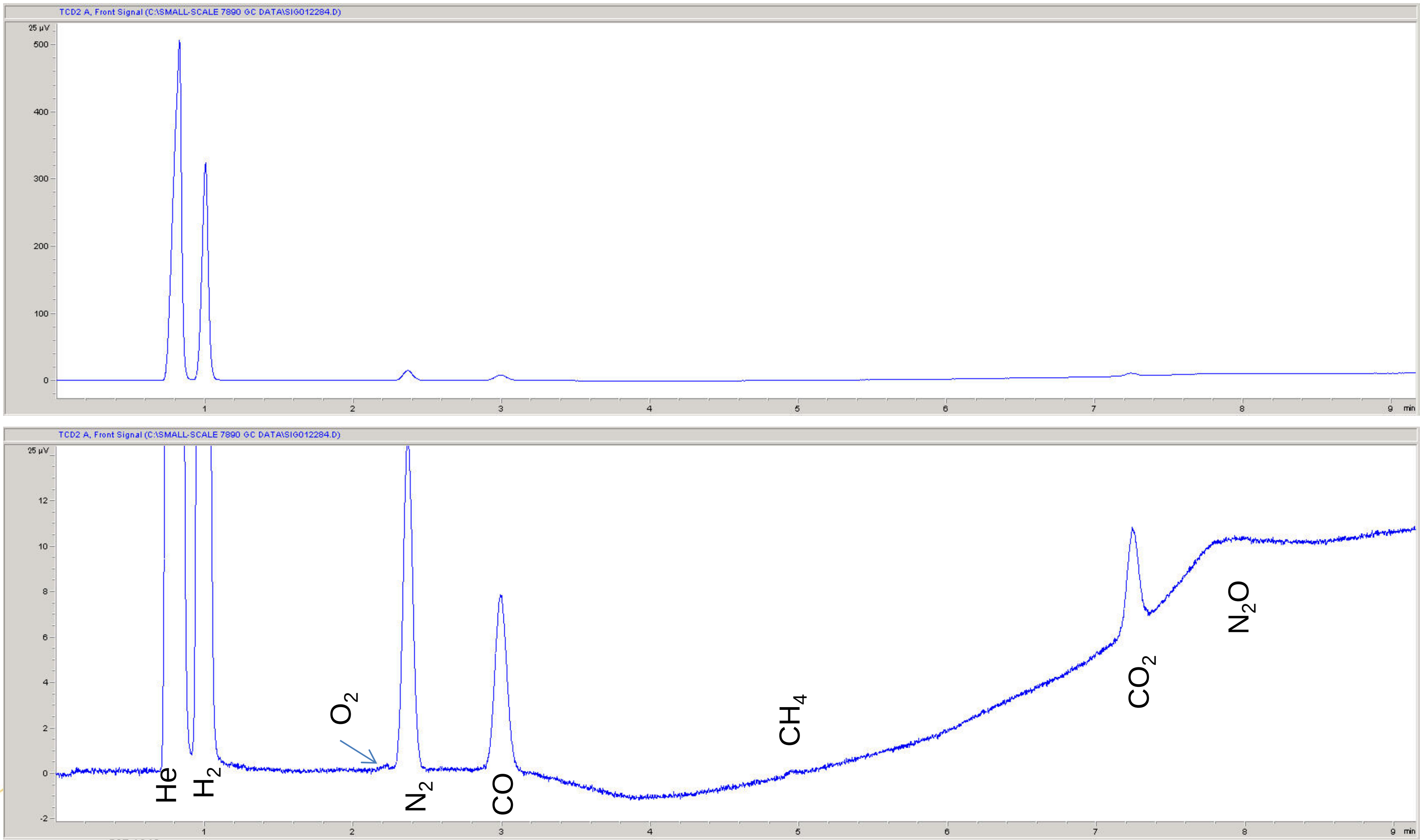
Separates permanent gases without cooling. Our method runs at 40 ºC.

Improves time from over 30 minutes to about 10 minutes.

Narrow peaks improve signal:noise ratio and sensitivity.

He and H_2 peaks are resolved and do not influence each other.

GC chromatogram of SSR207 04272-CC-220-AS ("Thorium sample")



Shincarbon reproducibility

	He	H_2	O_2
Gas content	85.3%	9.6%	5.0%
SIG12242	85.4%	10.2%	4.4%
SIG12243	85.2%	9.9%	4.9%
SIG12244	85.2%	10.1%	4.7%
SIG12245	85.2%	10.1%	4.7%
SIG12246	85.3%	10.1%	4.6%
Average	85.3%	10.1%	4.6%
2 sigma	0.2%	0.2%	0.3%

Shincarbon quantification

	He		H_2		O_2	
File	Cal gas	meas	Cal gas	meas	Cal gas	meas
SIG12247	97.0%	97.3%	1.0%	1.3%	2.0%	1.5%
SIG12248	89.6%	90.1%	6.9%	6.7%	3.6%	3.2%
SIG12249	93.9%	93.9%	4.0%	4.4%	2.1%	1.8%
SIG12250	96.0%	96.0%	2.0%	2.4%	2.0%	1.6%

Removal of MIS represented materials

SSR Number	MIS SAMPLE ITEM	Date Started	Date Removed	Cut	Pu/U	Anal P-γ	Cl	Source Site	Mass MT	Calcine Date	Sample Split Date	Sample History	Bulk Density (g/cc)	Sample mass	Wattage W/kg net	SSA (m2/g)	Pyconometer Density (g/cc)
SSR125	MT-1490	1/8/2004	2/20/2013	1	86/0	Y/Y		RFETS	52 / 82	2/23/99	12/9/03	800, 950°C 50/50 Mix, 12g vault split	6.1	9.98	2.18	0.8 (800)	10.96
SSR128	7242201	1/8/2004	2/20/2013	1	63.5/0	Y/Y		RFETS	52	3/3/98	12/9/03	950°C 12g vault split	3.3	10.01	1.58	3.70	7.97
SSR132A	BLO-39-11-14-004	6/10/2008	2/20/2013	1	87.5/0	Y/Y		HANFORD	56	6/19/97	9/23/98	950°C 10g GB stored	2.7	2.54	14.70	3.48	10.77
SSR139	520610020	4/6/2004	2/20/2013	2	33.7/0	Y/N	1	RFETS	52	1/1/04	5/7/98	750°C newly calcined	2.2	4.95	0.95	0.40	4.68
SSR150	TS707013	3/13/2007	2/20/2013	3	69.7/0	Y/N	1	RFETS	52	600 - 2/28/98 950 - 5/1/98	7/19/99	mix 600/950°C GB stored	3.6	10.01	1.71	1.62	7.45
SSR151A	7032282	6/4/2008	2/20/2013	3	69.4/0	Y/Y		RFETS	52	2/9/98	2/9/98	950°C newly calcined	3.7	10.01	1.73	2.93	7.63
SSR153D	63-88-06-121	6/10/2008	2/20/2013	3	35/0	N/Y		Hanford	54	5/3/05	5/3/05	950°C newly calcined	?	4.18	0.83		
SSR155HT	ARF-102-85-295	2/8/2005	2/20/2013	3	39.7/0	Y/Y	1	HANFORD	52	6/11/97	11/3/97	950°C GB stored	1.5	9.63	0.98		4.94

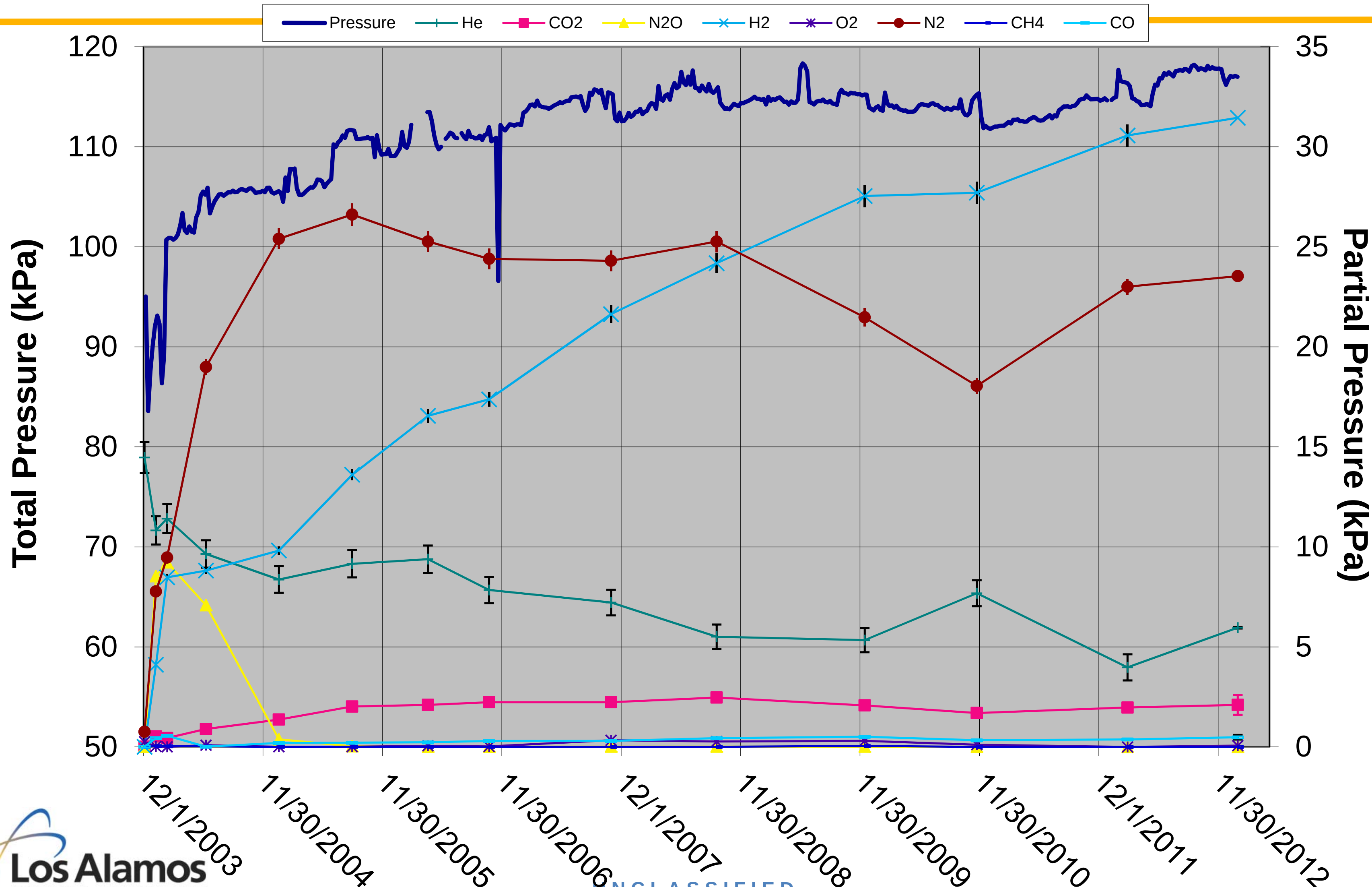
MIS Represented Materials Removed

Reactor	Material	RH (%)	Mass Loss (wt%)	Corrosion
SSR125	MT1490	39	0.15	Spots
SSR 128	07242201A	17	0.62	discoloration
SSR132A	BLO-39-11-14-004	15	0.97	Discoloration
SSR139	520610020	0	0.5	Shiny
SSR150	TS707013	47	0.12	Coating
SSR151A	07032282A	2	0.15	coating
SSR153D	63-88-06-121	0	0.36	Discoloration
SSR155HT	ARF-102-85-295	4	0.02	shiny

Mass loss – heat to 650 ^{o}C for 15 minutes

Corrosion – visual inspection of bucket; buckets will be section as time allows

SSR125 MT-1490



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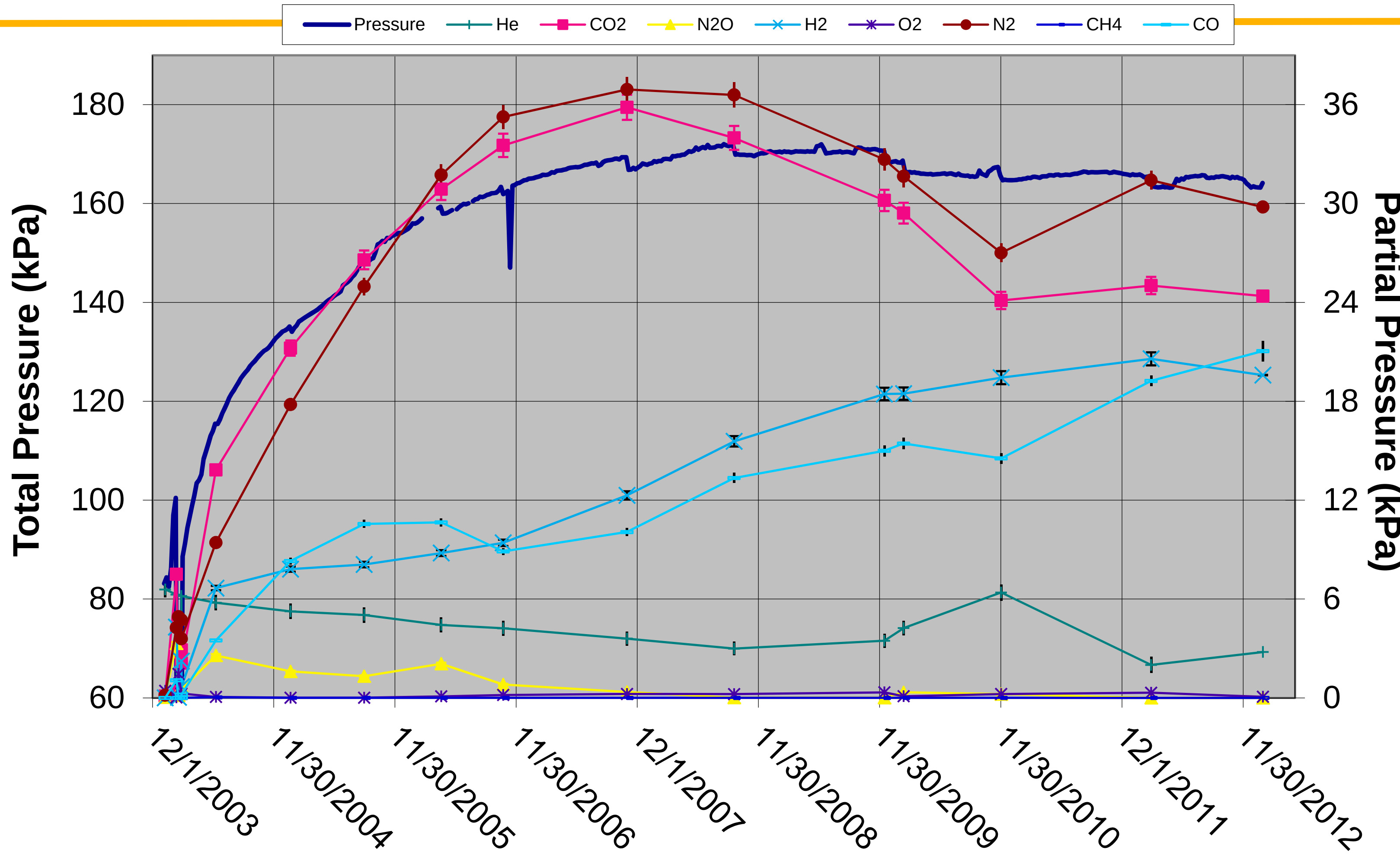
SSR128 7242201



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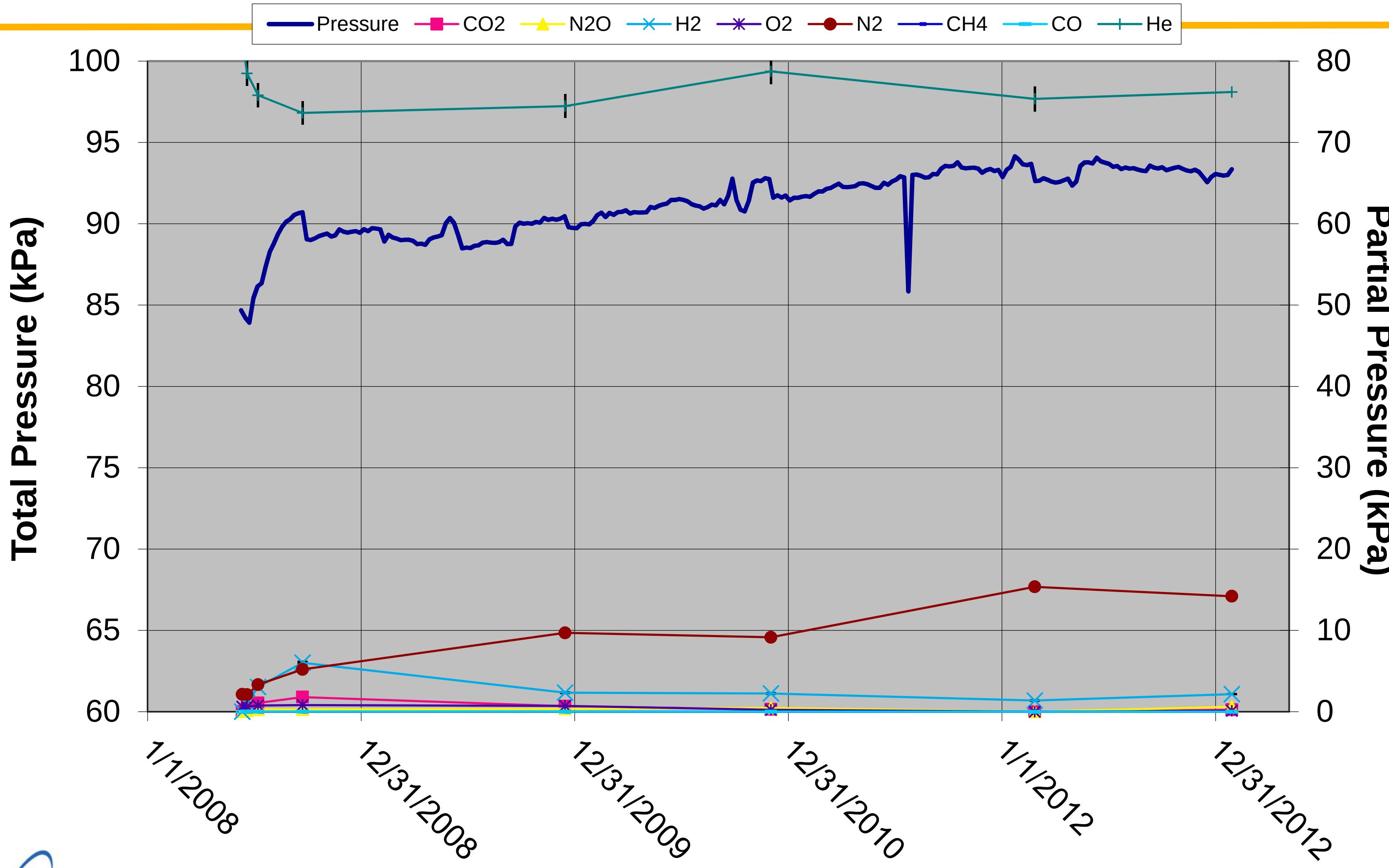
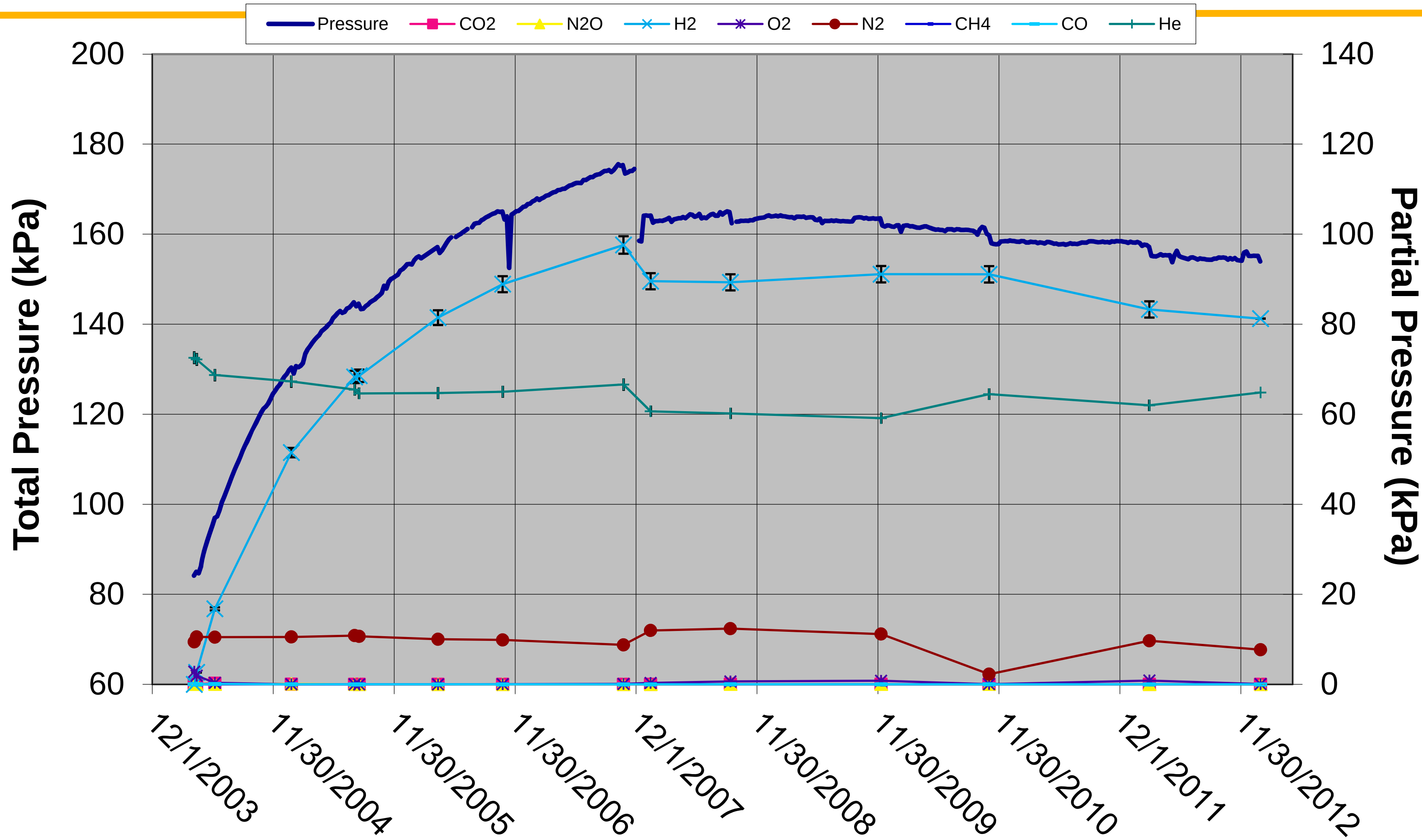
SSR132A BLO39 with 0.52% added water



SSR139 520610020



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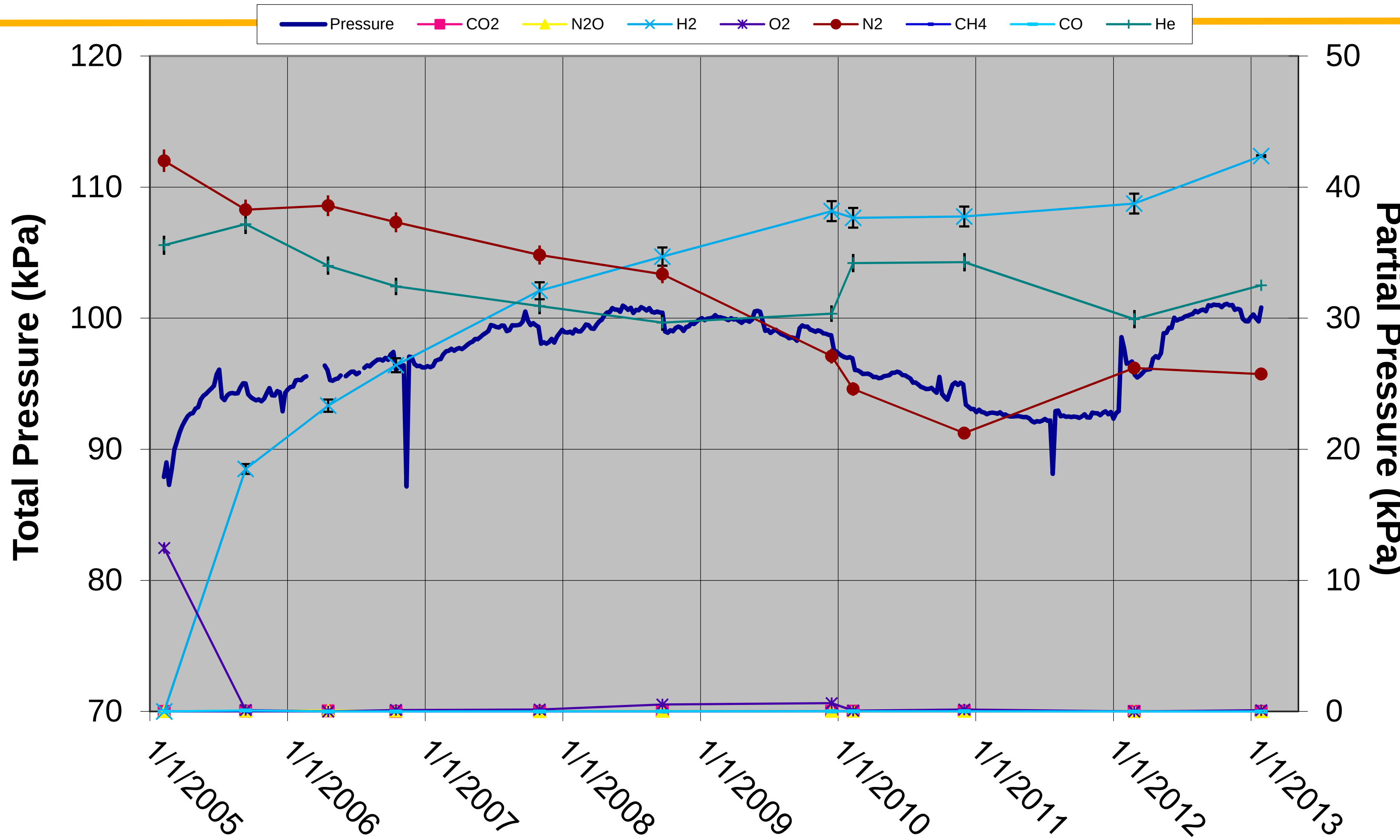
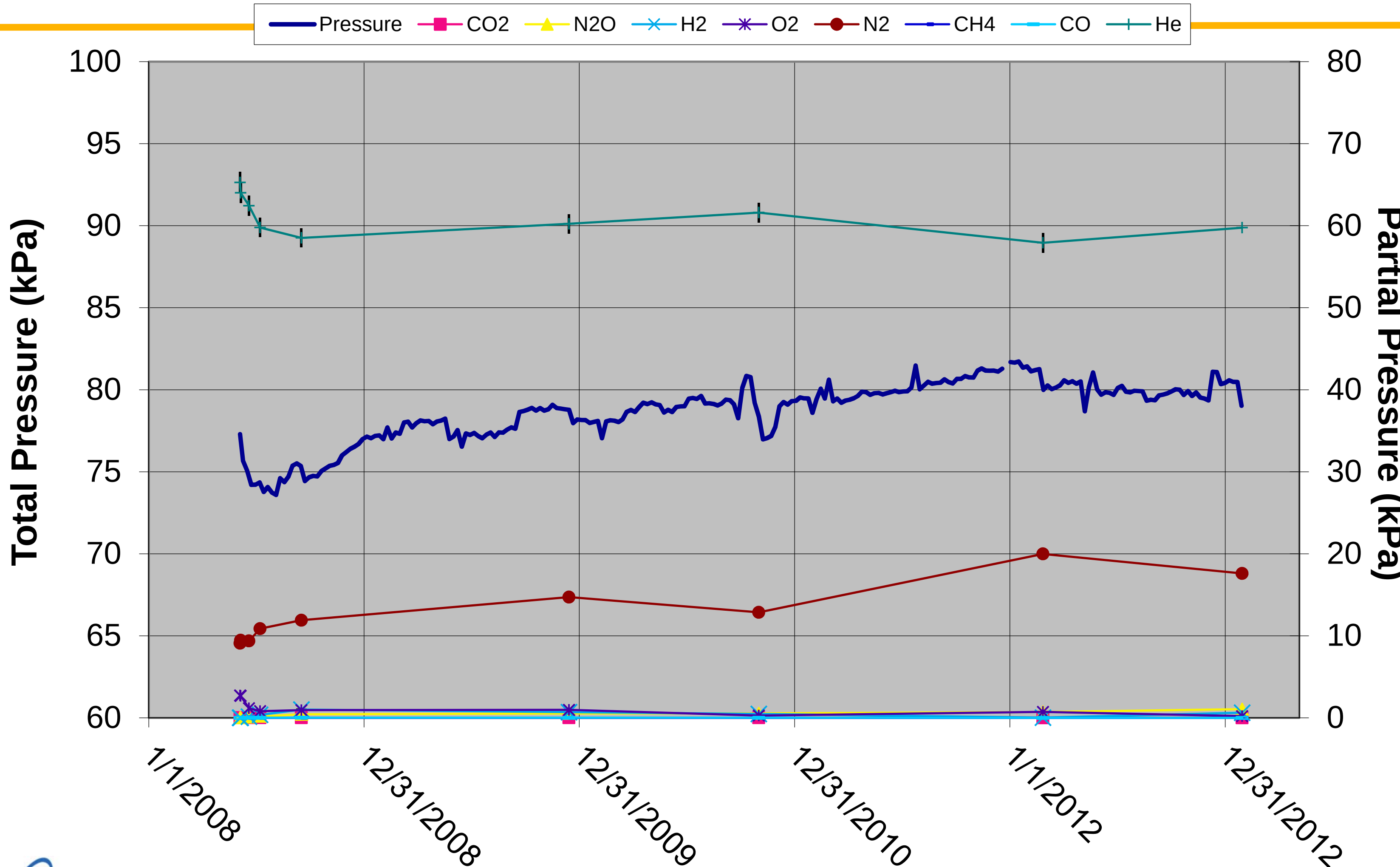
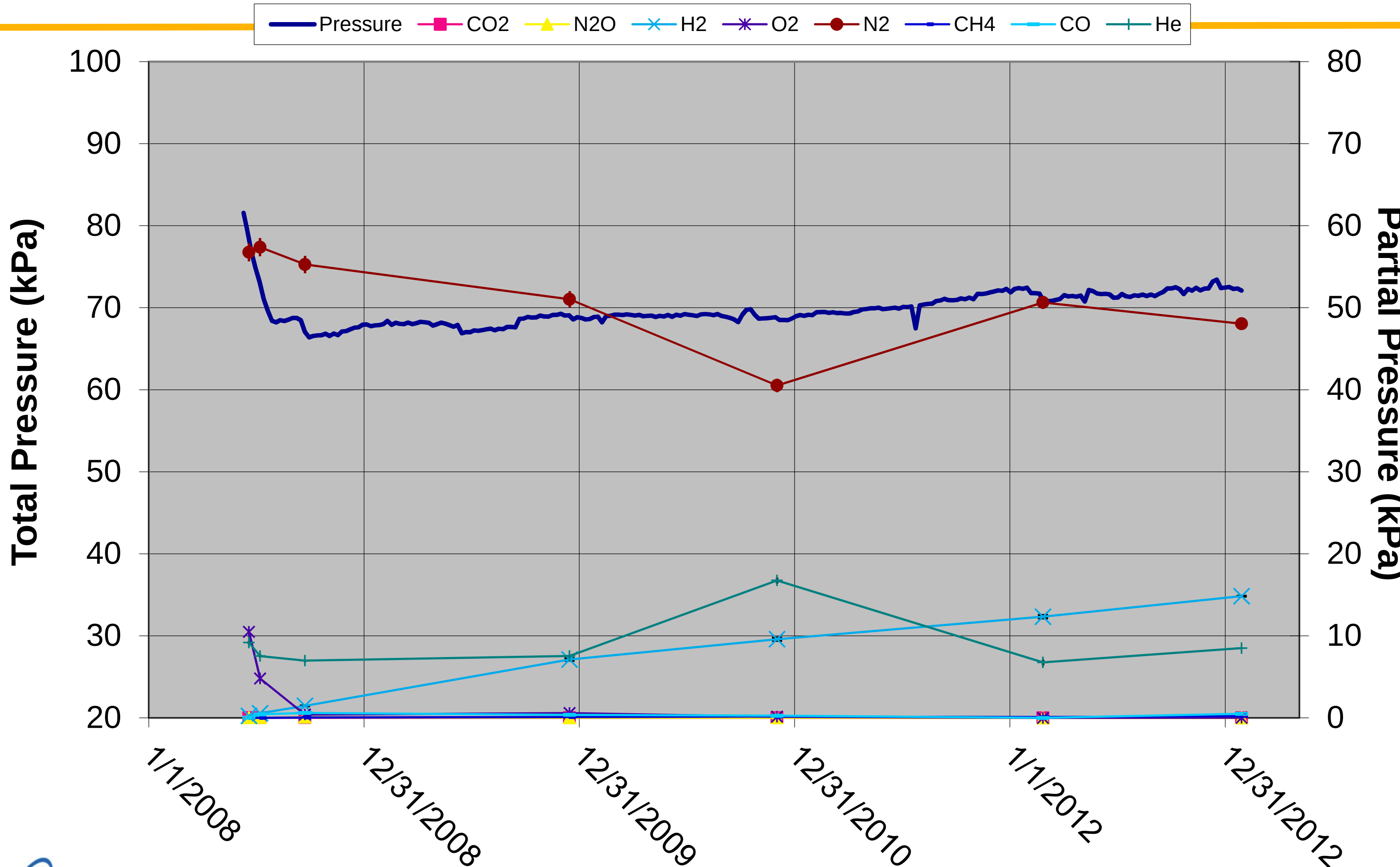
SSR150 TS70713



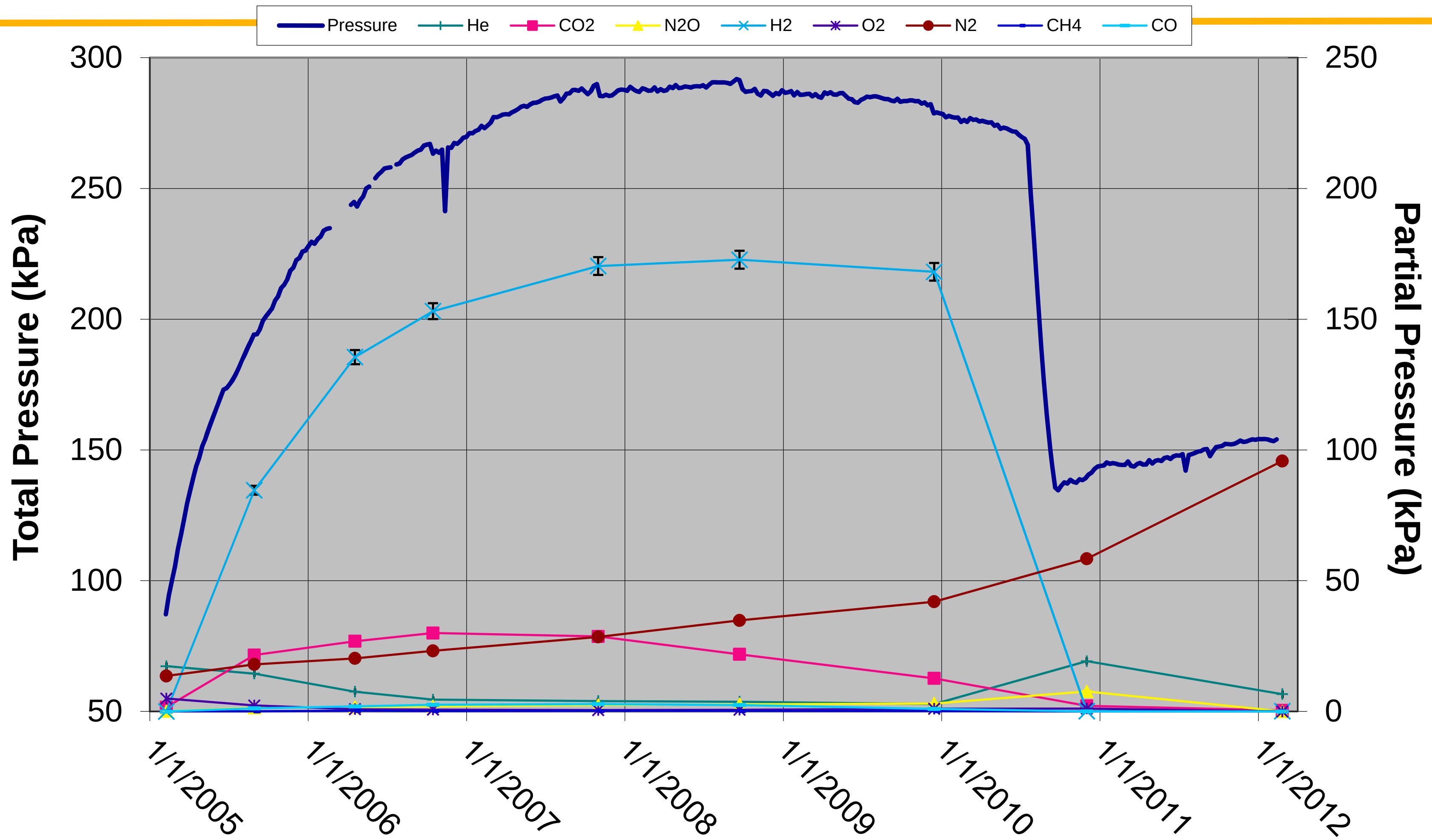
SSR151A 10.01 g 7032282 with



SSR153D 4.81g of 63-88-06-121 with 0.54wt% water



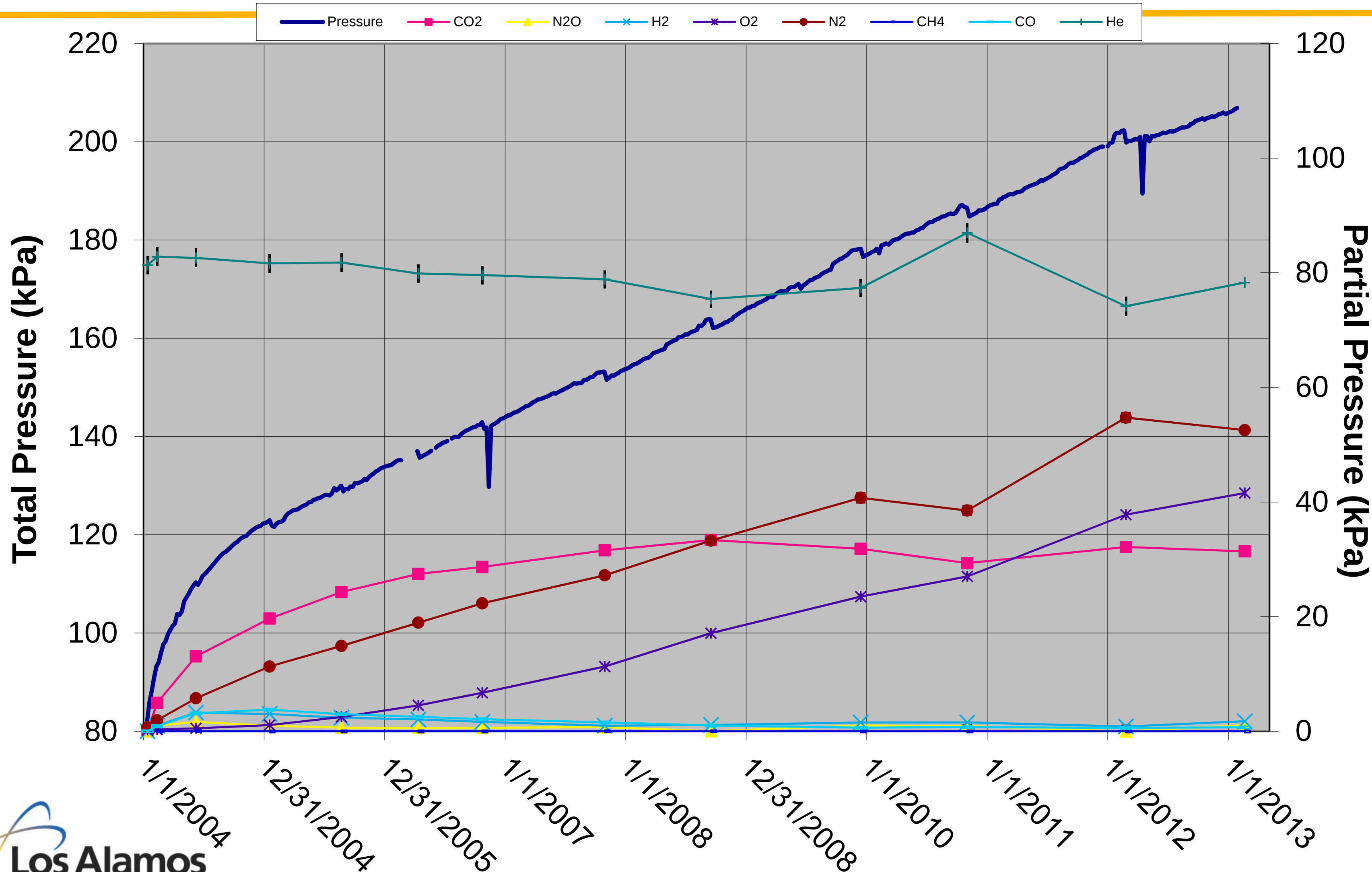
SSR155HT ARF-102-85-295



Materials with bounding behaviors

Reactor	Material	Behaviour
SSR122	7161856 – a high-purity oxide	O_2 generation w/o H_2
SSR130	C06032A – 74% Pu with chloride	Highest pressure – H_2
SSR137	11589A – 77% Pu with chloride	H_2 and O_2 generation
SSR155	ARF-102-85-295 – 28 to 40% Pu with chloride	May overtake SSR130 for highest pressure

SSR122 7161856



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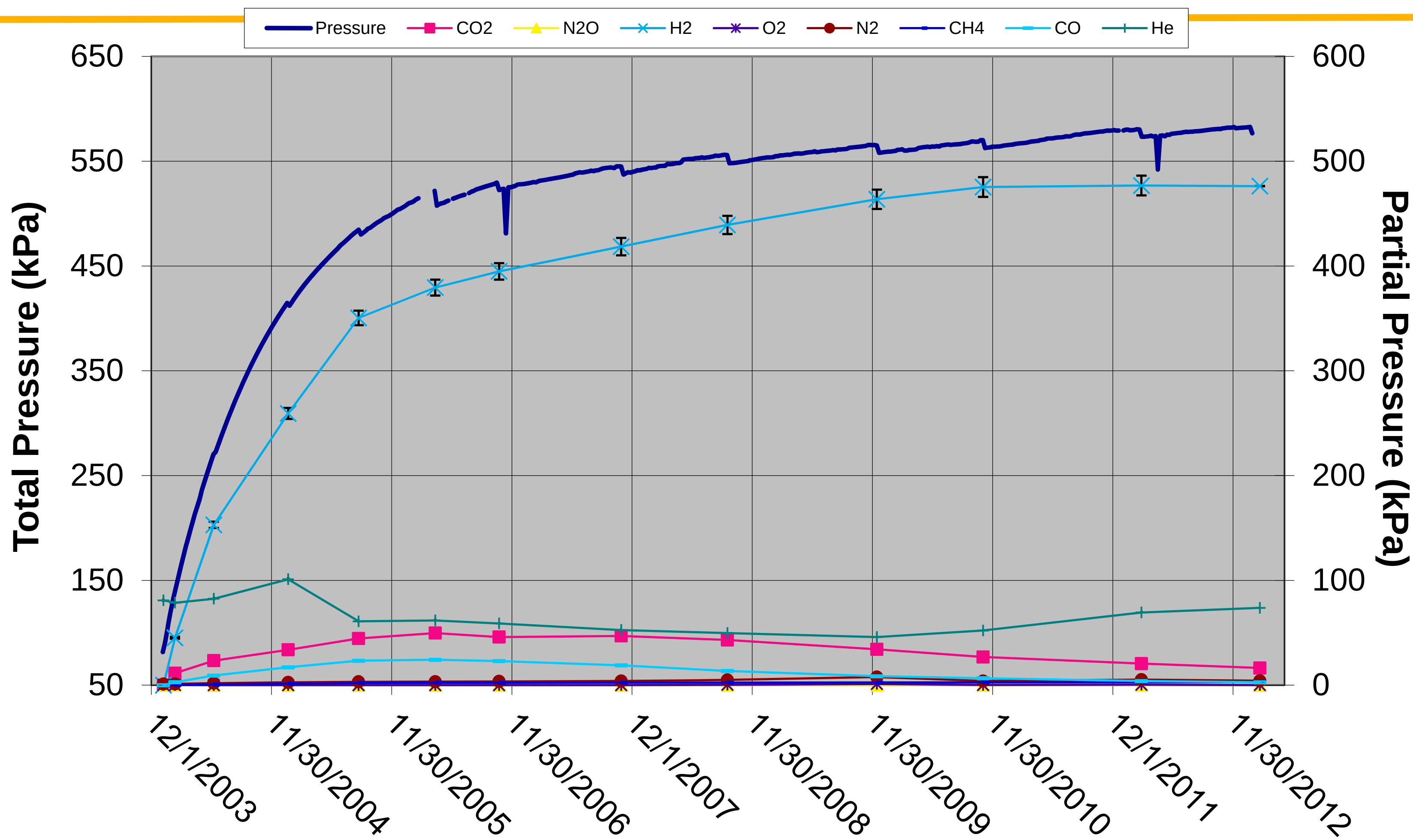
SSR130 C06032A



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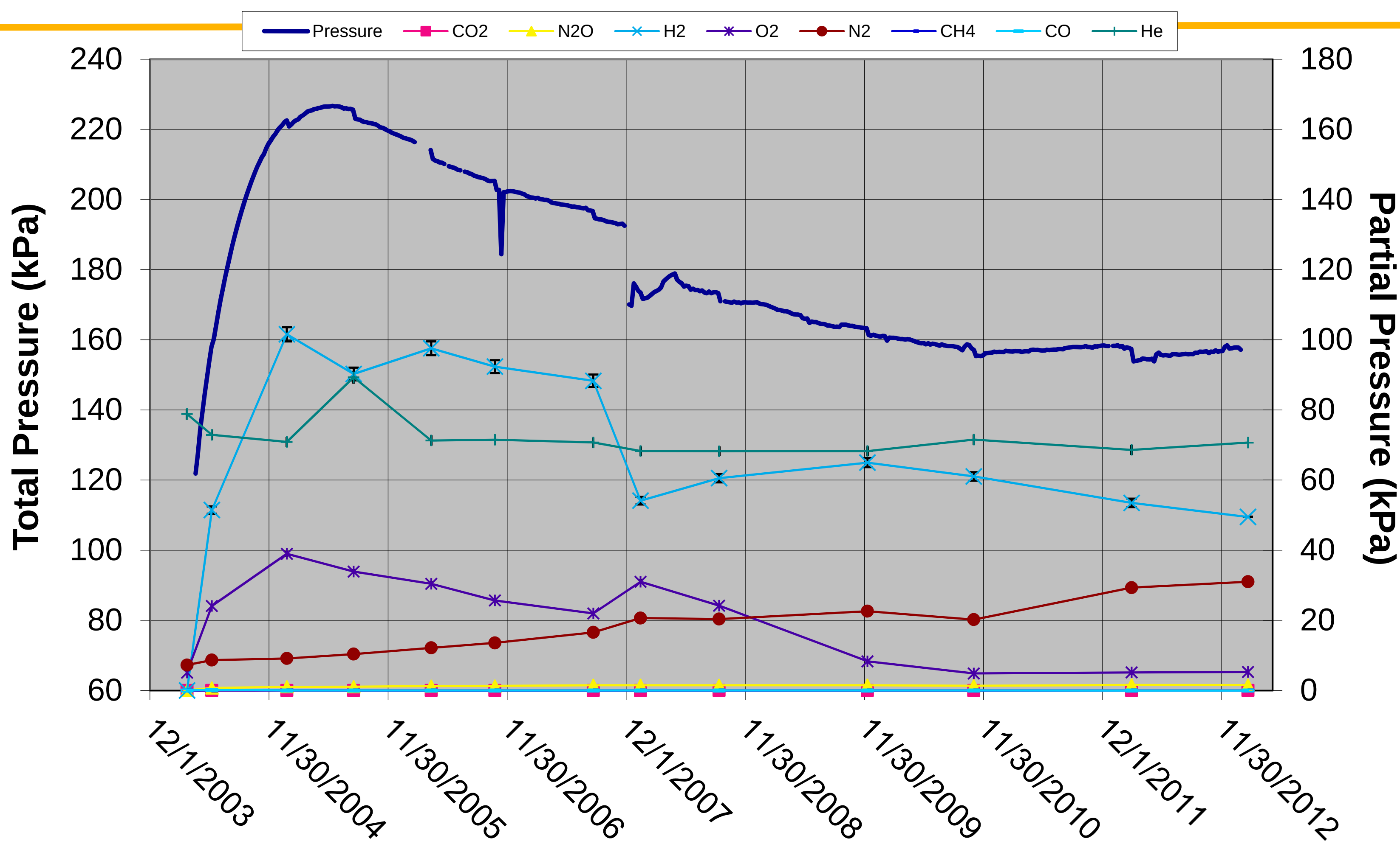
SSR137 11589



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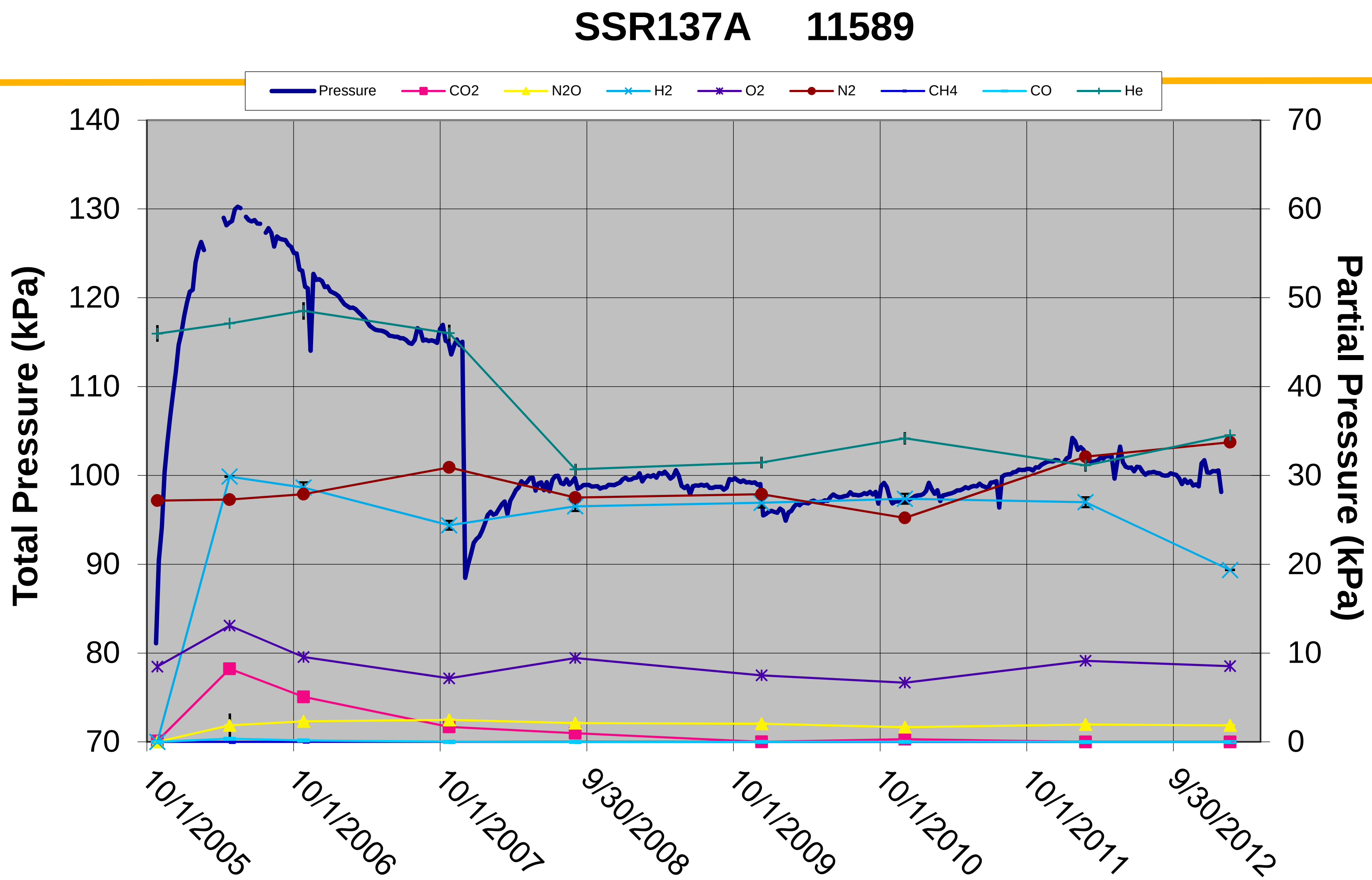

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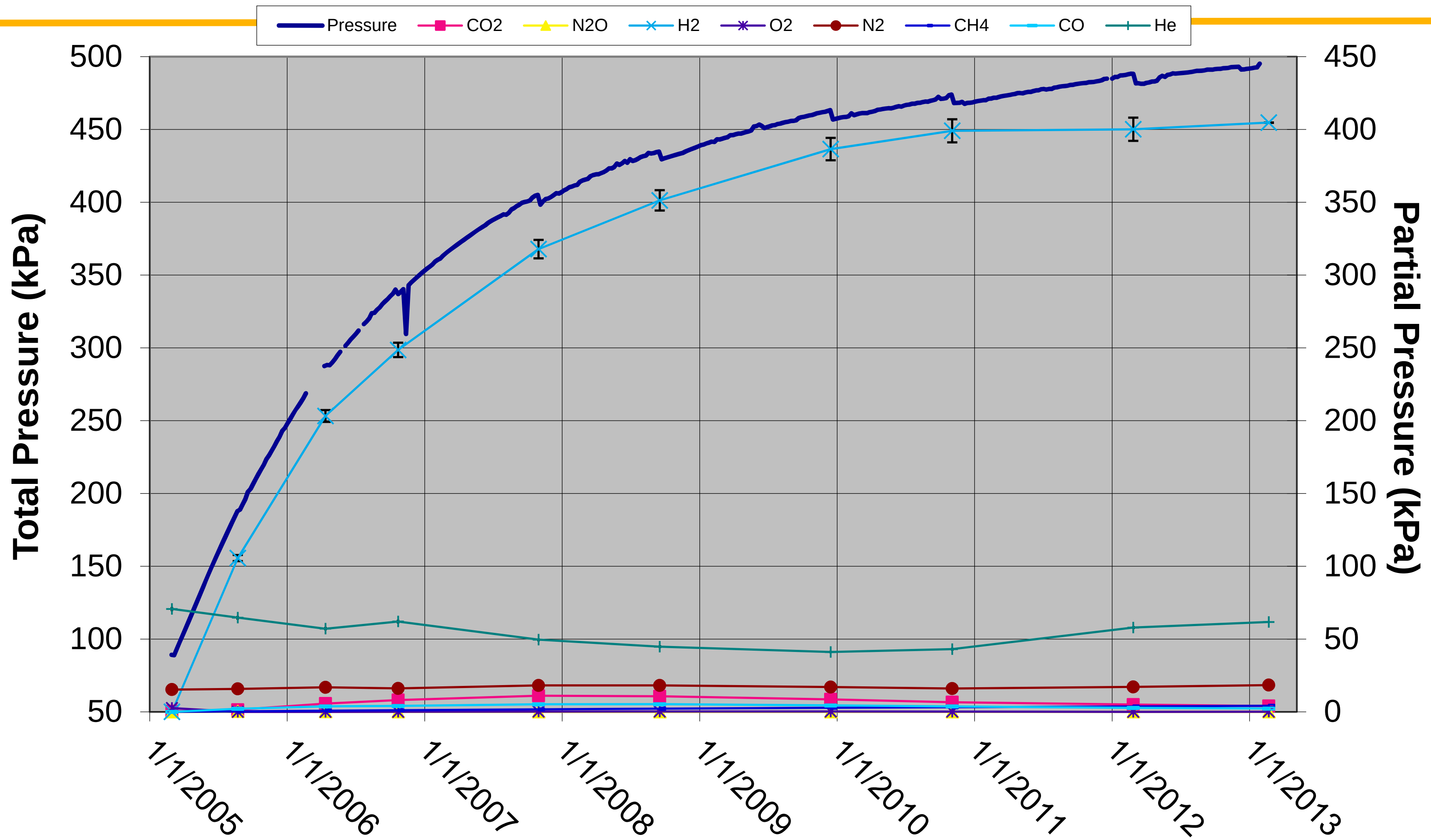
SSR155 ARF-102-85-295



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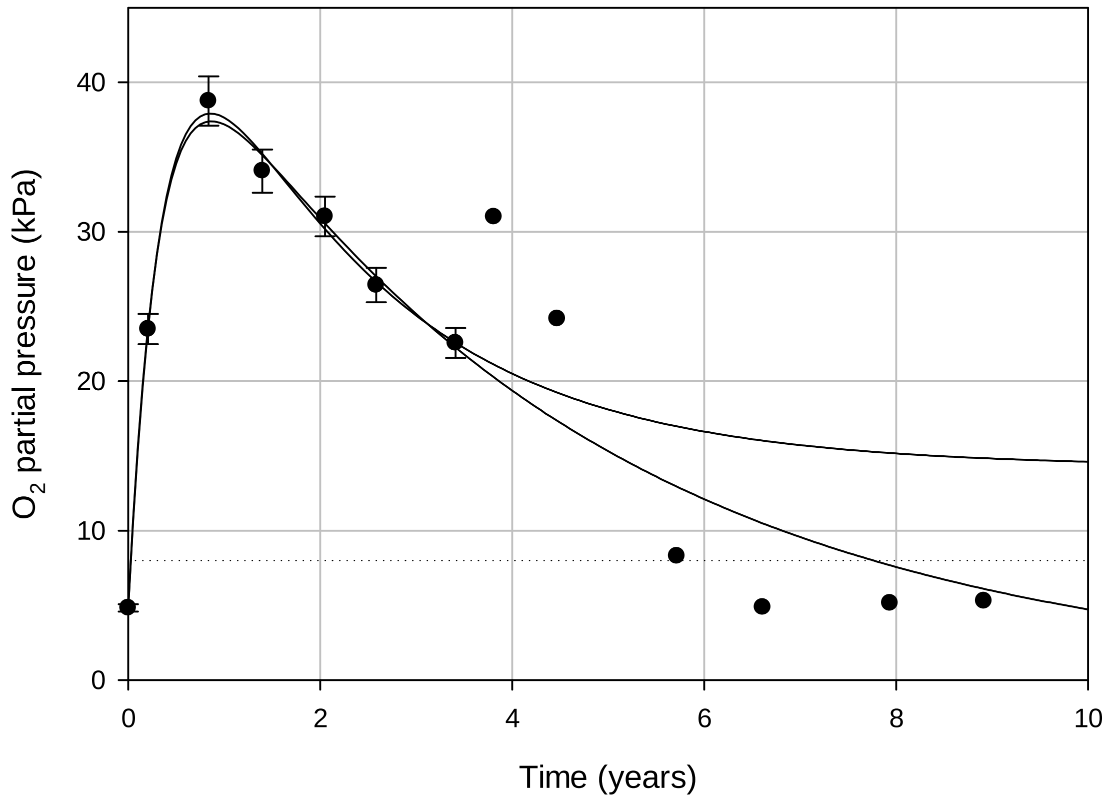
Oxygen partial pressure 11589A

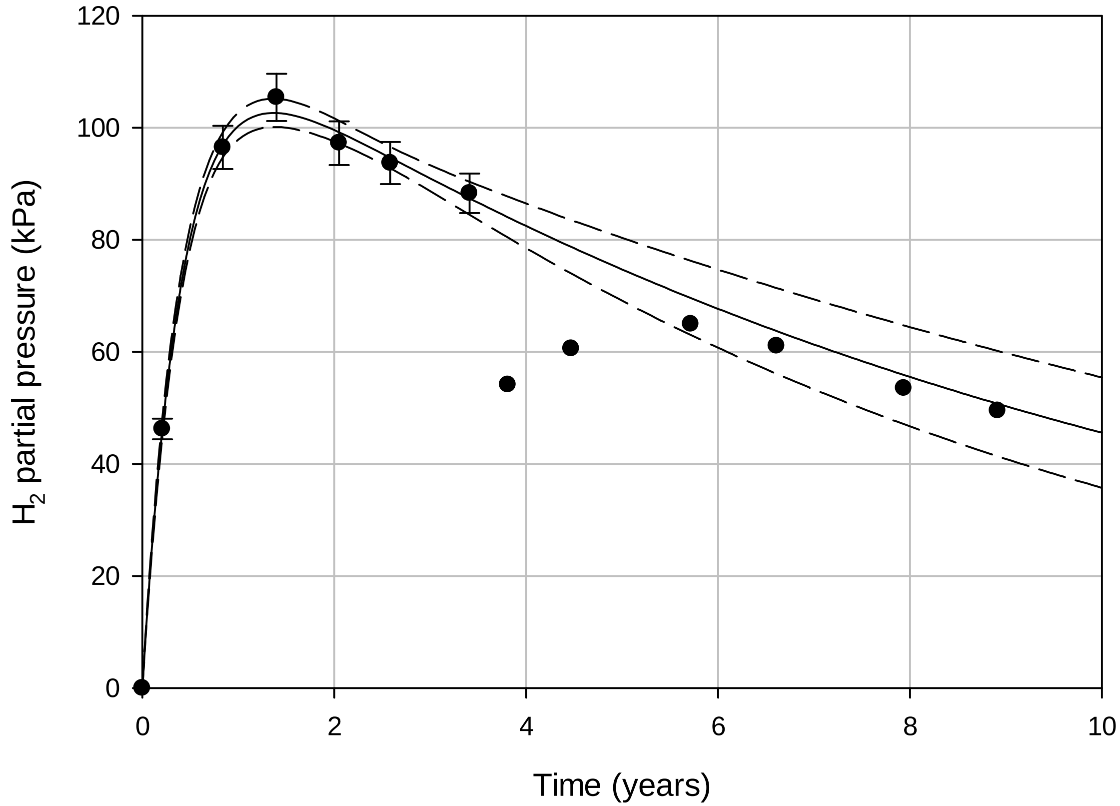
Two reaction models were fit to the data.

In one model the oxygen maintains a steady state value. In the other the oxygen goes to zero.

Could not distinguish with the data at that time. Current data is consistent with the model where the oxygen goes to zero.



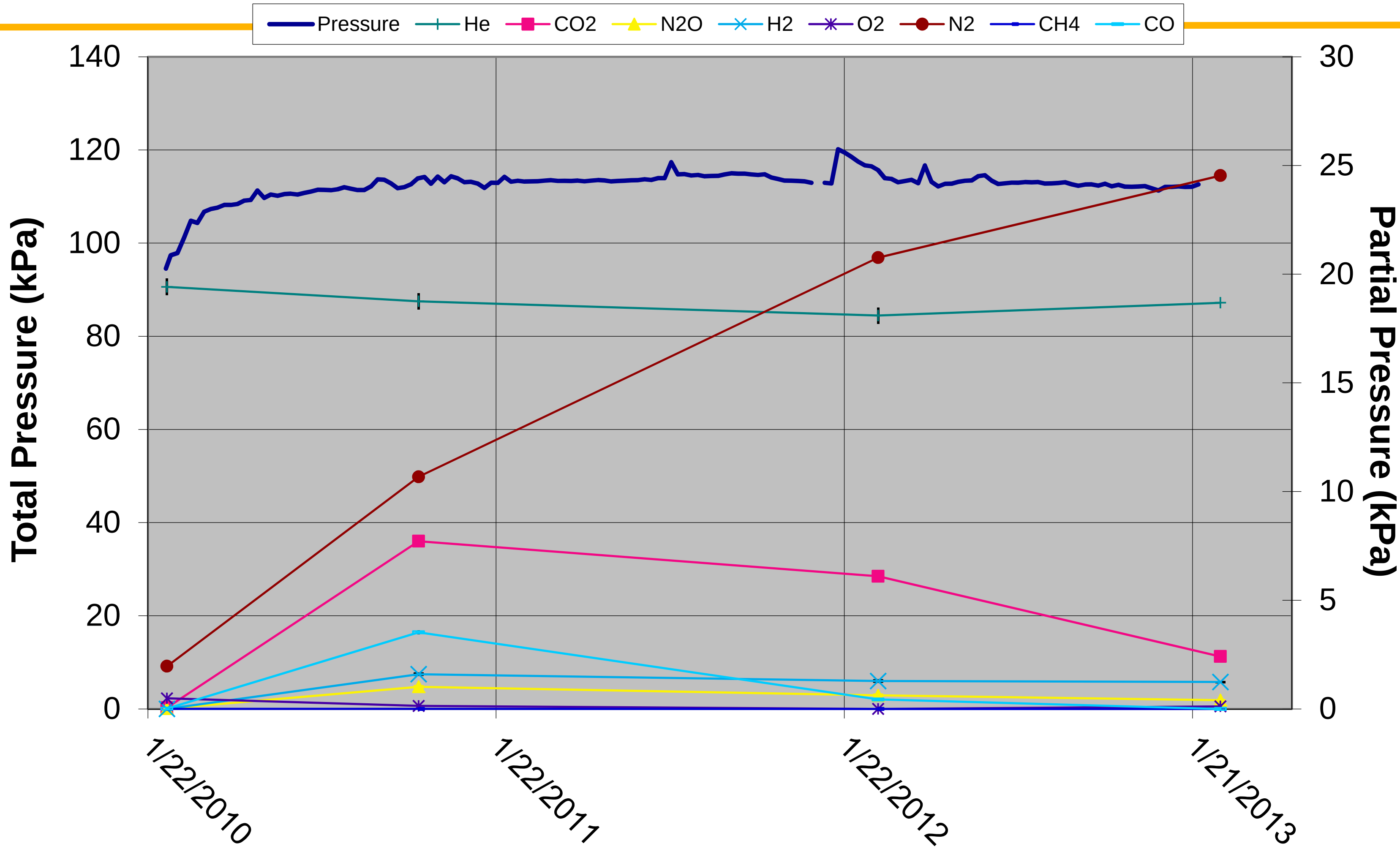
Hydrogen partial pressure of 11589A



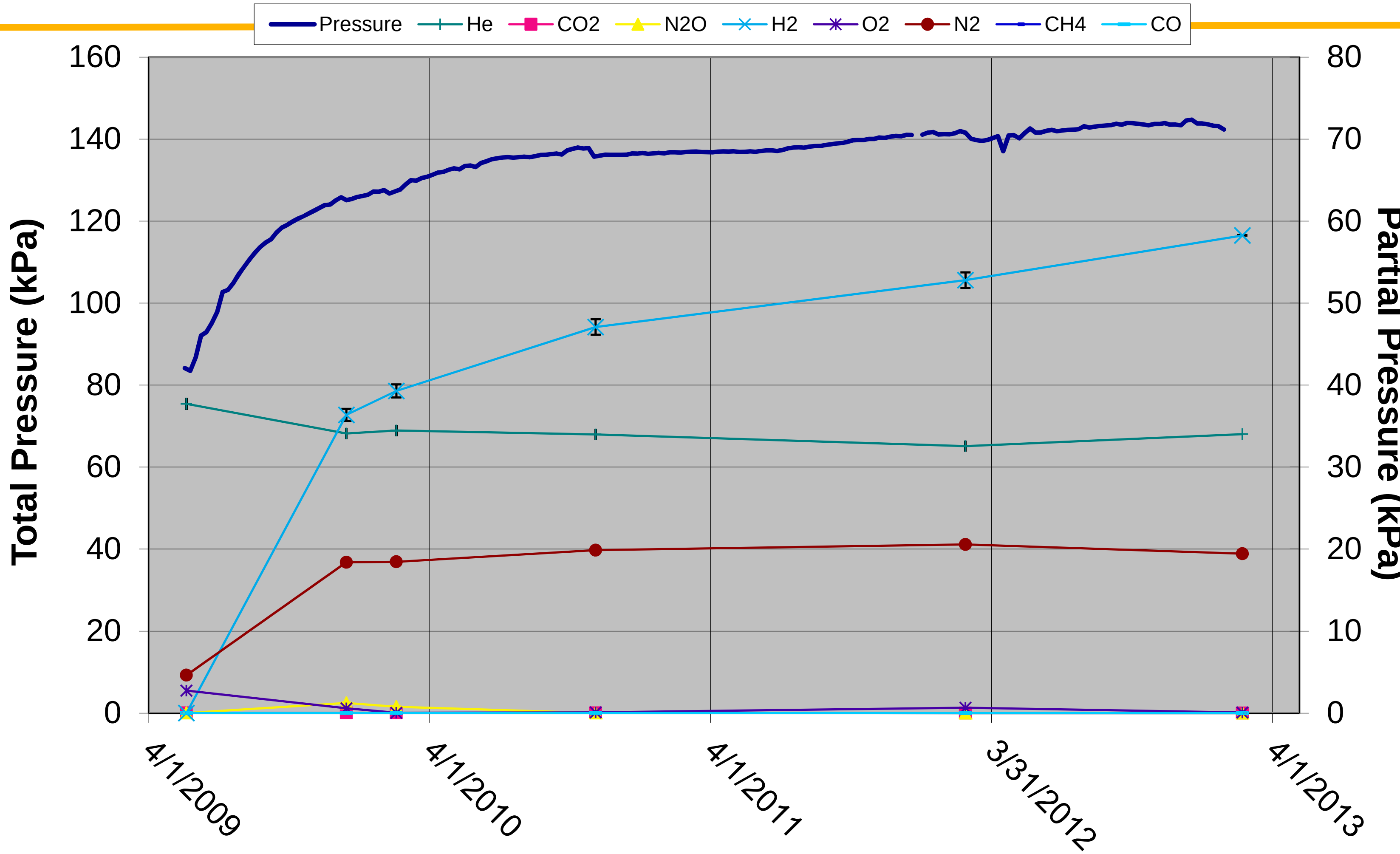
LANL material loaded

Material	SSR	Pu (%)	Cl (%)	Pyc. Den. (g/cm^3)	Bulk (g/cm^3)	SSA (m2/g)	Moisture Added (%)
~~CXLPROD091901~~	~~203~~	~~87.6~~	~~0.03~~	~~11.2~~	~~2.2~~	~~4.5~~	~~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%

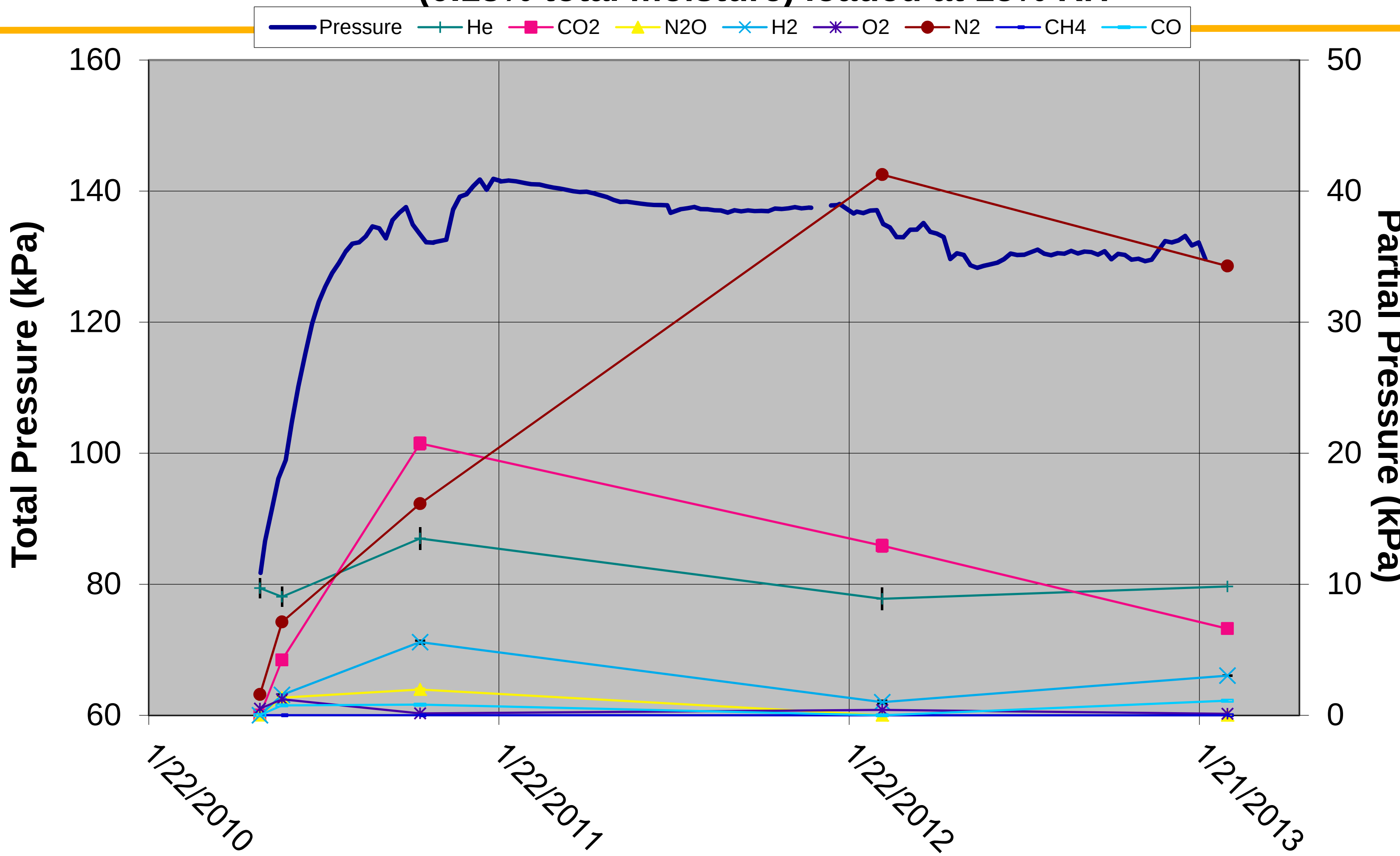
10 g CXLPROD021202C-SUR with 0.48-0.02% moisture



9.94 g CXLOX091802A-SUR-C with ~0.49% moisture



10 g 04272-CC-220-AS ("Thorium sample") with 0.02% added moisture (0.13% total moisture) loaded at 15% RH



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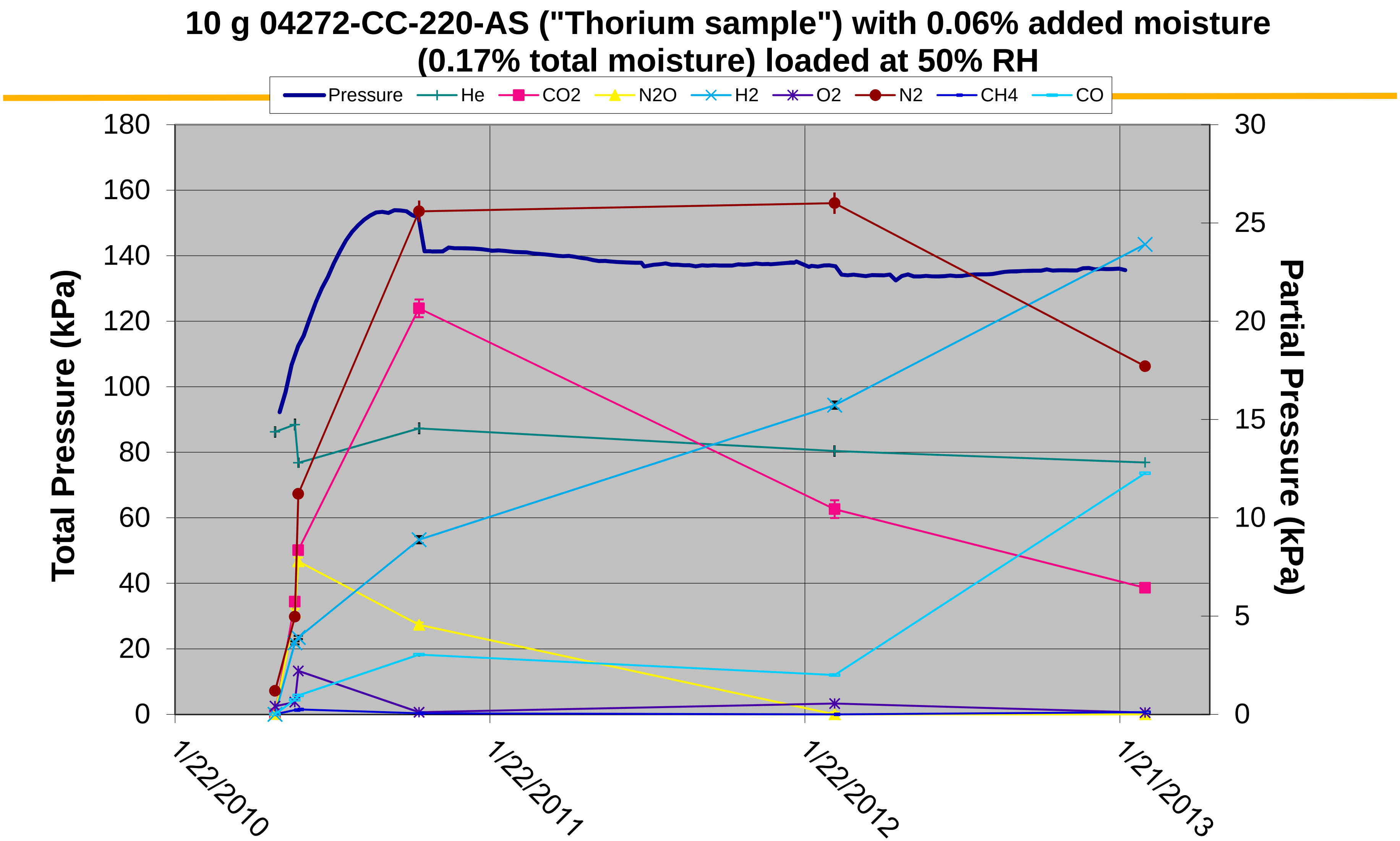
10 g 04272-CC-220-AS ("Thorium sample") with 0.06% added moisture (0.17% total moisture) loaded at 50% RH
Pressure
He
CO2
N2O
H2
O2
N2
CH4
CO
Total Pressure (kPa)
Partial Pressure (kPa)
180
160
140
120
100
80
60
40
20
0
30
25
20
15
10
5
0
1/22/2010
1/22/2011
1/22/2012
1/21/2013

3013 Cross Reference Table

DE Run No.	3013 ID	ISP BIN	Sample Type
2007-1	R600885	Pressure	Random
2	R601722	Pressure	Random
3	R601957	Innocuous	Random
4	R600719	P & C	Random
5	R610735 C06032	P & C	Judgmental
6	R610697 ARF	P & C	Judgmental
7	R601285	P & C	Random
2008-1	R602731	P & C	Random
2	R601318	Pressure	Judgmental
3	H000898(RFETS)	P & C	Random
4	R610327	P & C	Random
5	R610298	P & C	Random
6	R610324	P & C	Random
7	H001992	P & C	Random
8	H003157	P & C	Random
9	R610584	P & C	Random
10	R610578	P & C	Random
11	H001916	P & C	Random
12	H002088	Pressure	Random
13	H003409	P & C	Random
14	H002573 ARF	P & C	Judgmental
15	H002534 ARF	P & C	Judgmental
16	R610679	P & C	Random
17	H002750	P & C	Random
2009-1	H004099 Moist	P & C	Judgmental
2	H004111 ARF	P & C	Judgmental
3	H002554	P & C	Random
4	H001941	P & C	Random
5	R602498 11589	P & C	Judgmental
6	H002509 ARF	P & C	Judgmental
7	H002565 Cl H2O	P & C	Judgmental
8	H002657 Cl H2O	P & C	Judgmental
9	R611398 11589	P & C	Judgmental
10	H002200	P & C	Random
11	H002667	P & C	Random
12	H002715	P & C	Random
13	R610700	P & C	Random
14	R610764	P & C	Random
15	R610573	P & C	Random
16	R610558	P & C	Random
17	R610806	P & C	Random
18	H003119	Pressure	Random
19	H002195	Pressure	Random

DE Run No.	3013 ID	ISP BIN	Sample Type
2010-1	H004251 Moist	P & C	Judgmental
2	H002496 F. Mat	P & C	Judgmental
3	H003710	P & C	Random
4	H003655 Moist GB	P & C	Judgmental
5	H002447	P & C	Random
6	R610627	P & C	Random
7	H003900 F. Mat	P & C	Judgmental
8	H003650 Moist	P & C	Judgmental
9	H002567	P & C	Random
10	H002728	P & C	Random
11	H002786	P & C	Random
12	H003077	P & C	Random
13	H003367	P & C	Random
14	H003704	P & C	Random
15	R610785	P & C	Random
16	R610826	P & C	Random
17	R610853	P & C	Random
18	S001721	P & C	Random
2011-1	H003443 Moist/Cl	P&C	Judgmental
2	S002129 Moist	P&C	Judgmental
3	H002592	P&C	Random
4	H003337	P&C	Random
5	S001105 Ratio	P&C	Judgmental
6	H003343 Ratio	P&C	Judgmental
7	H003371 Ratio	P&C	Judgmental
8	H003526	P&C	Random
9	H003565	P&C	Random
10	R611131	P&C	Random
11	H003625	P&C	Random
12	L000178	P&C	Random
LANL	H003328	P&C	Judgmental
2012-1	H001209 High H20 to 650	P	Judgmental
2	H002574 High H2O w/o salt	P&C	Judgmental
3	H001513 Highest H20 to 650	P	Judgmental
4	H003390 Highest H2O to 350	P&C	Judgmental
5	L000075	P&C	Random
6	H004012	P&C	Random
7	H004048	P&C	Random
8	R610960	P&C	Random
VSD 10	S002250 (FY'14)	P&C	Random

Can Corrosion Categories

0	Nothing or Wipeable coating
0*	Rocky Flat can if corrosion is observed
1	Adherent coating on convenience can
2	Pitting <50 µm on convenience can
3A	Suspected pitting >50 µm on convenience can – pit covered with corrosion product
3B	Confirmed pitting >50 µm on convenience can – generally confirmed with SEM
4	Adherent coating on inner can
5	Pitting <50 µm on inner can
6	Pitting >50 µm on inner can
7	SCC on inner can