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Title: Surveillance and Monitoring Program Review March 25 & 26, 2014

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Surveillance and Monitoring Program Review

March 25 & 26, 2014

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3013 Surveillance and Monitoring Annual Program Review
Savannah River Site, Building 766H Room 2138
March 25, 26 2014

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8:00 AM	0:15	Welcome/ Introductions	B. Hackney
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8:15 AM	0:15	K Area FY13 status and FY14 plans	B. Hackney
8:30 AM	0:45	3013 Oxide, Gas, Pressure Analysis in DE, Flow Sheet Changes for Future DEs	J. Scogin, J. Duffey
9:15 AM	0:20	DE Gas Analysis Between Inner and Outer	J. Duffey
9:35 AM	0:20	**BREAK**	
9:55 AM	0:40	3013 Container Analysis and Categorization from DE	J. Mickalonis
10:35 AM	0:40	Representative Material (LANL Small Scale Status)	K. Veirs
		Corrosion Work	
11:15 AM	0:30	Review of Corrosion Conditions, Pitting, SCC and Ties to 3013 Inventory	K. Veirs
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8:20 AM	0:15	Review Team Comments	T. Venetz
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8:35 AM	0:20	ARIES Update: Status and Path Forward	S. McKee
8:55 AM	0:15	3013 Material Disposition - K Area	A. Gunter
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9:40 AM	0:20	Prompt Gamma Update	J. Narlesky
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10:30 AM	0:15	M441.1-1 and the SAVY 4000	K. Veirs
10:45 AM	0:15	M441.1-1 LLNL Implementation	D. Riley (K. Veirs presentor)
11:00 AM	0:20	M441.1-1 SRS / SRNL Implementation	S. Hensel
11:20 AM	1:00	**LUNCH 766-H Cafeteria**	
12:20 PM	0:20	Gap Material	K. Dunn
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1:00 PM	0:30	Aging Data for 9975 Surveillance	B. Daugherty
1:30 PM	0:30	Current Findings and Path Forward for 9975 Surveillance	B. Hackney
2:00 PM	0:45	**Closeout Action Items**	All
2:45 PM	0:20	**BREAK**	
MIS - WG	2:00	**MIS-Working Group Meeting (Meeting Action Items, SRNL and LANL AOP**	MIS WG

MIS ANNUAL MEETING
MARCH 2014

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Small-Scale Update

D. Kirk Veirs

LANL Team: John Berg, Josh Narlesky, Ed Romero, Leonard Trujillo, Kirk Veirs, Laura Worl

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Summary of 2012 Activity

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.

Summary of 2013

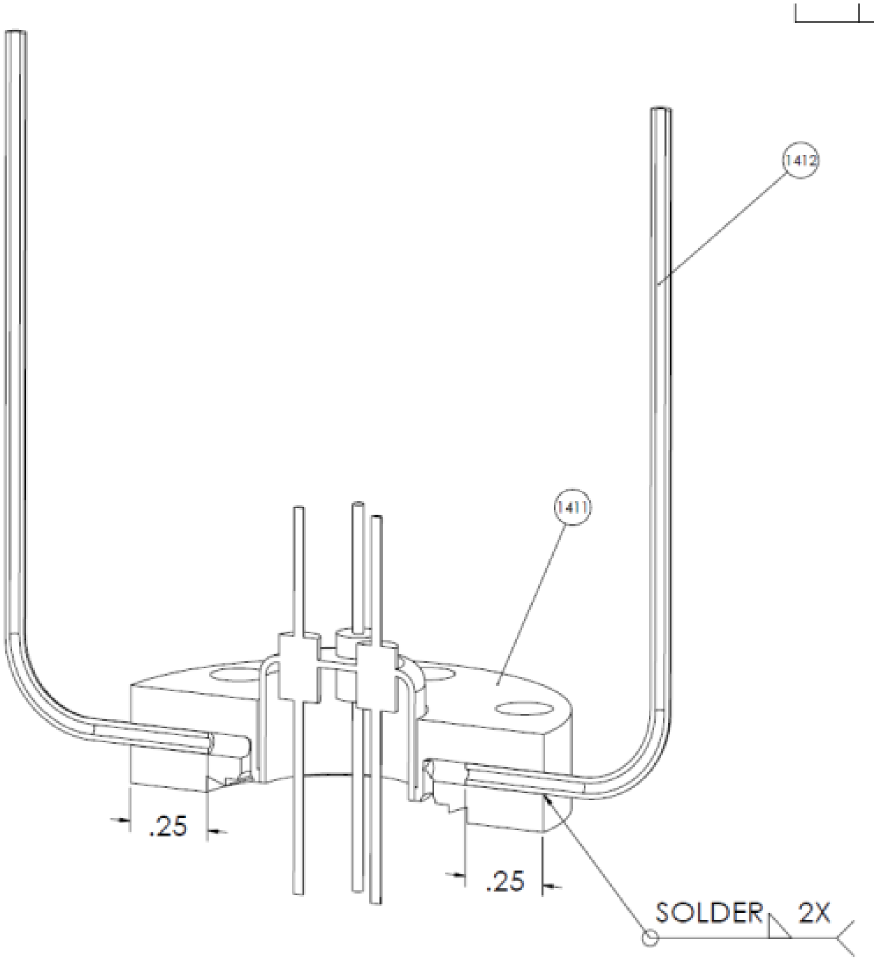
- **Prepared to execute "Test Plan to Evaluate Initial Rates of H_2 and O_2 Generation in Sealed Containers of High-purity, High Surface Area PuO_2 as a Function of Relative Humidity in Packaging Atmospheres".**
- **New containers with RH sensors with 5 ml gas volume. He leak checked and ready to be introduced.**
- **Waiting to receive freshly prepared material when shutdown occurred in June 2013.**
- **Since then modified procedures. They have moved from SME oriented to Conduct of Operations oriented.**
- **All small-scale activities are now authorized, however the aqueous processing is still not operational which we need for the freshly prepared material.**

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.



MIS represented materials with surveillance terminated

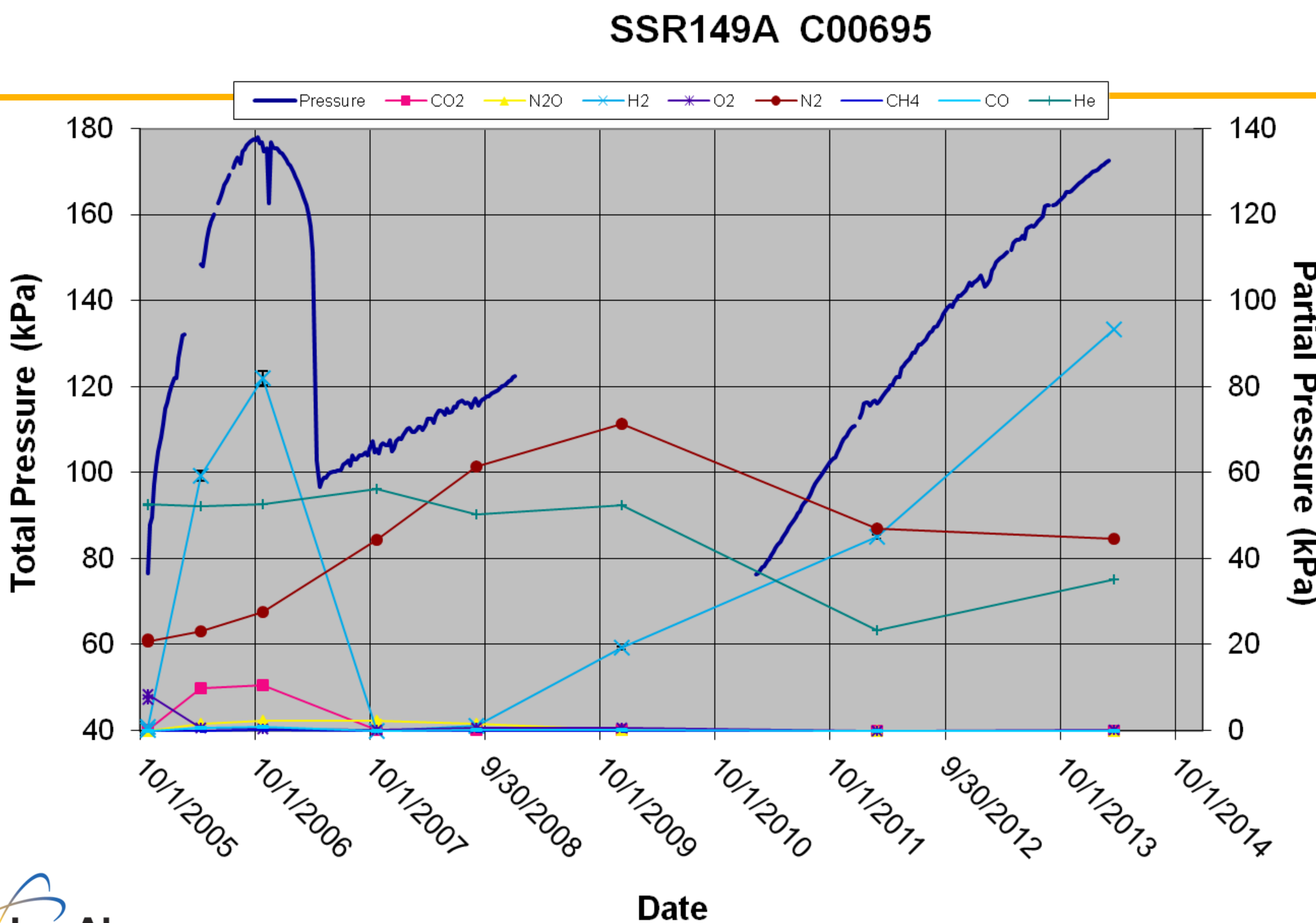
SSR Number	MIS SAMPLE ITEM	Date Started	Date Removed
SSR123	TS707001	12/16/2003	3/2/2010
SSR124	5501579	12/17/2003	3/2/2010
SSR125	MT-1490	1/8/2004	2/20/2013
SSR126	669194	12/10/2003	11/5/2007
SSR128	7242201	1/8/2004	2/20/2013
SSR129A SSR129	5501407 5501407	1/7/2004 10/24/2005	6/27/2007 6/27/2007
SSR131	ARF-102-85-223	1/7/2004	11/5/2007
SSR132	BLO-39-11-14-004	1/8/2004	1/25/2007
SSR132A	BLO-39-11-14-004	6/10/2008	2/20/2013
SSR133	PSU-84-06-05	1/14/2004	11/6/2007
SSR135	SCP711-56	1/15/2004	11/6/2007
SSR139	520610020	4/6/2004	2/20/2013
SSR140	7242165	3/24/2004	11/5/2007
SSR141	7242141 (fur ball)	3/25/2004	5/19/2010

SSR Number	MIS SAMPLE ITEM	Date Started	Date Removed
SSR142	PBO-47-09-012-023	4/7/2004	6/18/2007
SSR143	ARF-102-85-355	4/7/2004	3/2/2010
SSR145	64-85-12-1858	3/25/2004	7/9/2007
SSR147	CAN92	1/26/2005	5/19/2010
SSR148	C00024A	1/26/2005	5/19/2010
SSR149A SSR149	C00695 C00695	1/27/2005 10/25/2005	5/2/2005
SSR150	TS707013	3/13/2007	2/20/2013
SSR151	7032282	1/27/2005	8/17/2006
SSR151A	7032282	6/4/2008	2/20/2013
SSR152	41-85-08-1379B	2/8/2005	11/6/2007
SSR153	63-88-06-121	5/5/2005	4/28/2008
SSR153D	63-88-06-121	39609	2/20/2013
SSR154	ARF-102-85-114-1	2/1/2005	11/6/2007
SSR155HT	ARF-102-85-295	38391	2/20/2013
SSR156	PuF4-1	2/8/2005	5/19/2010
SSR162	MISSTD	8/22/2005	1/25/2007

Pink items had inconclusive data and were repeated.

C00695

- The initial rate pressure increase is one of the highest, but not the highest: C00695 – 492 kPa/yr vs C06032A – 600 kPa/yr.
- Loaded three times and each has leaked.
- No oxygen generated.
- For modifying the 3013 Pressure Equation may want to study this material again.
- Recommendation – remove SSR149A and SSR149B and examine for corrosion.



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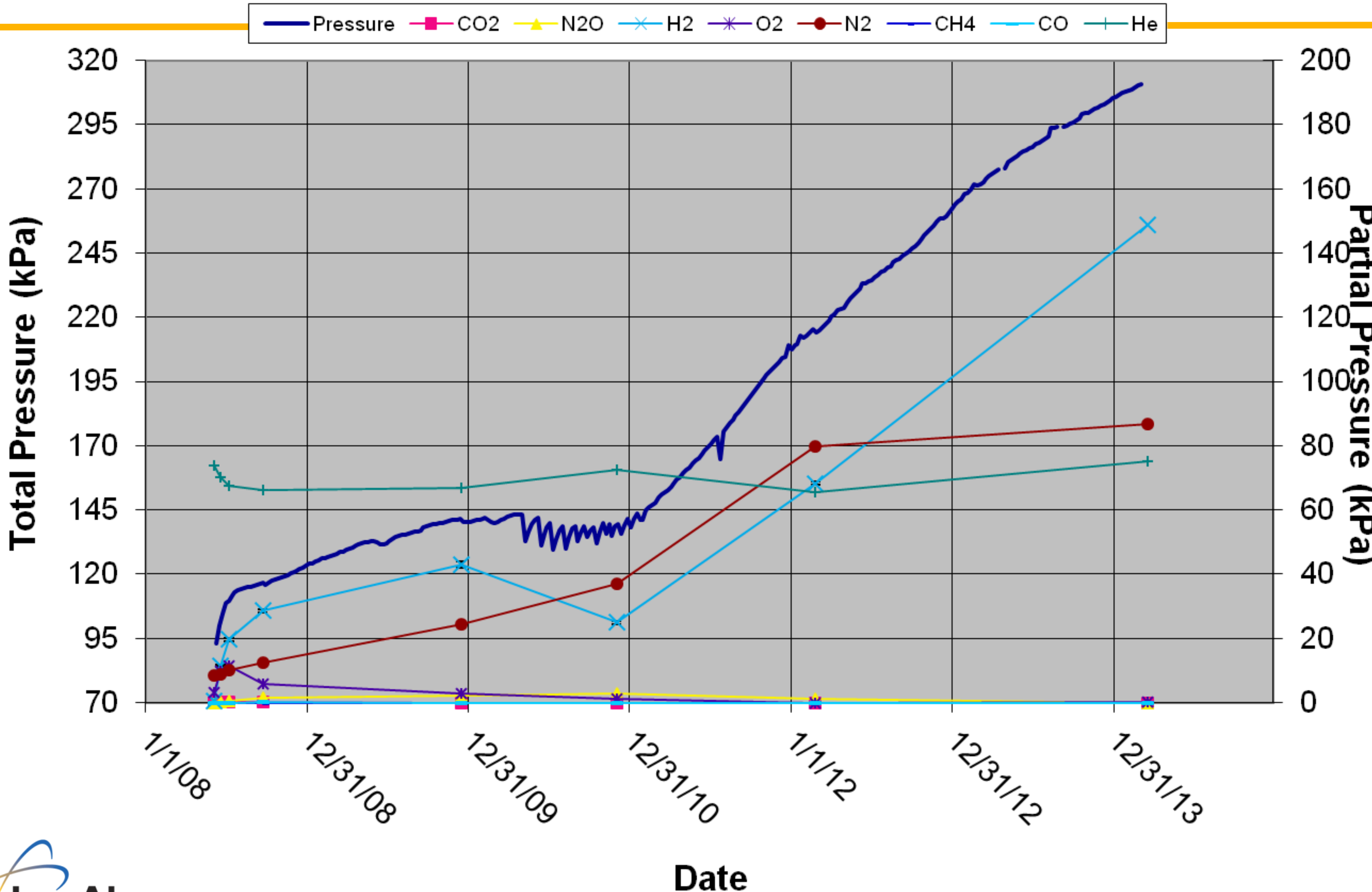
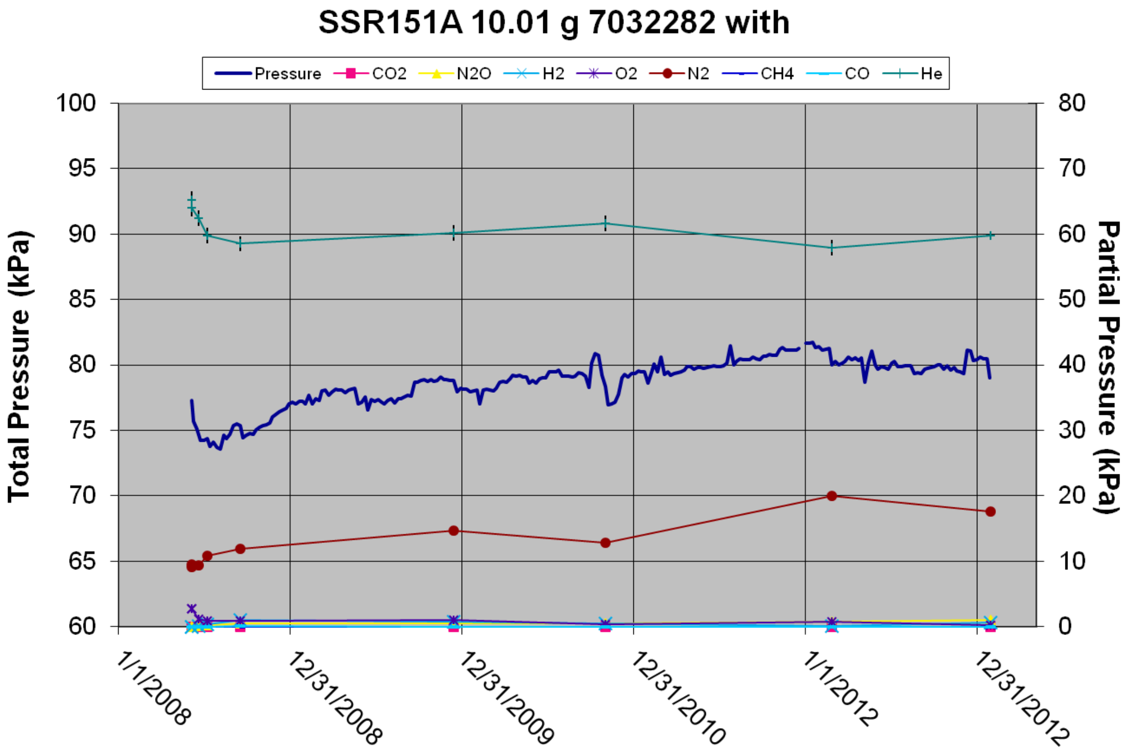
SSR149B 10.0 g C00695(reloaded)



7032282

- **Original container leaked.**
- **Second loading verified no H2 or O2 generation.**



63-88-06-121

- Original loading showed a slow rate of H_2 generation and O_2 depletion before the container leaked.
- Second loading showed the same.
- No further work needed.

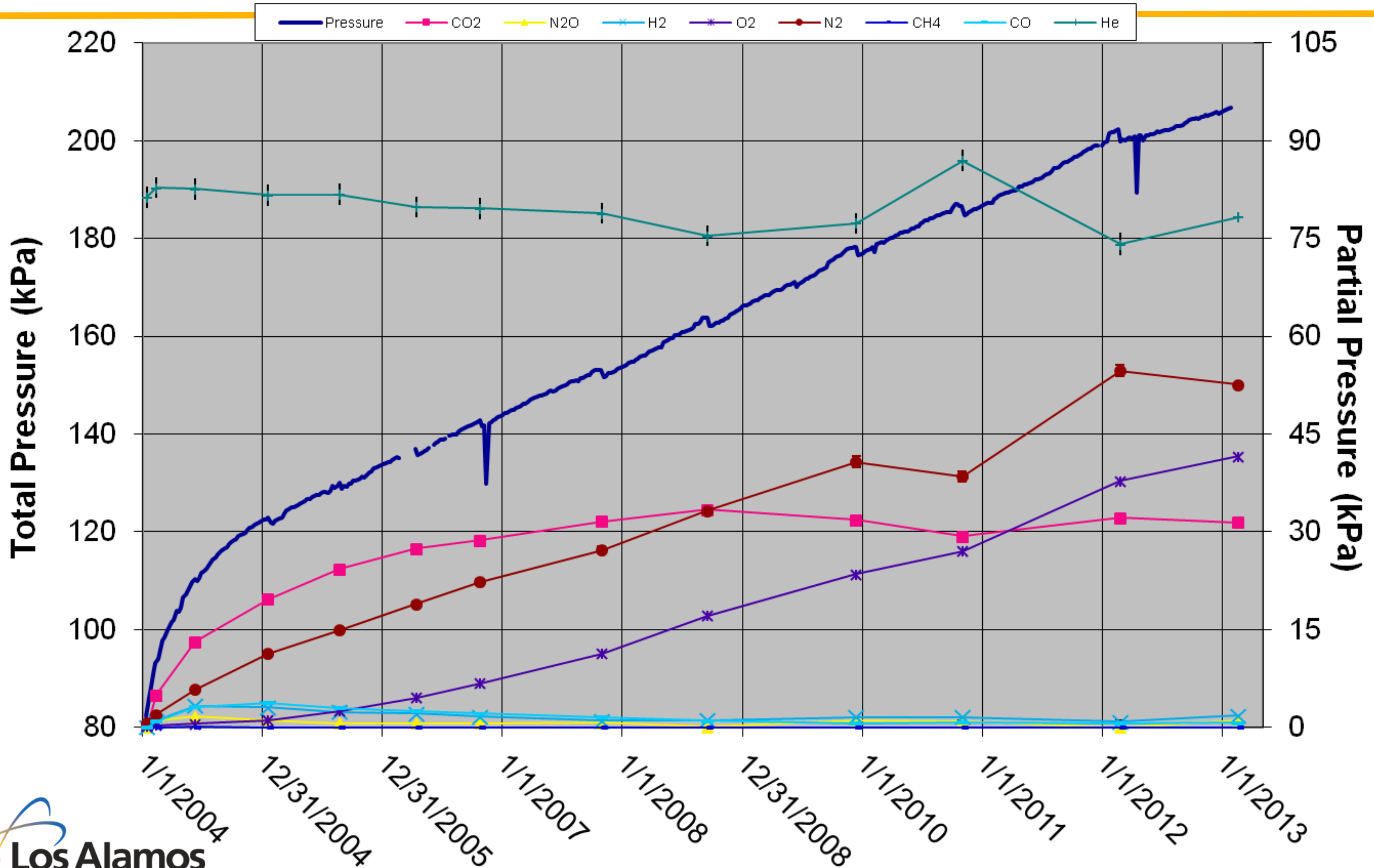
MISSTD-1

- Original loading showed O_2 and H_2 generation with the O_2 generation rate higher than the H_2 generation rate before it leaked.
- Second loading showed the same behavior.
- This material was used in the O_2 and H_2 generation studies conducted a year ago. The O_2 generation rate for low RH was typically higher than the H_2 generation rate in these studies.
- Recommend removing the second loading.

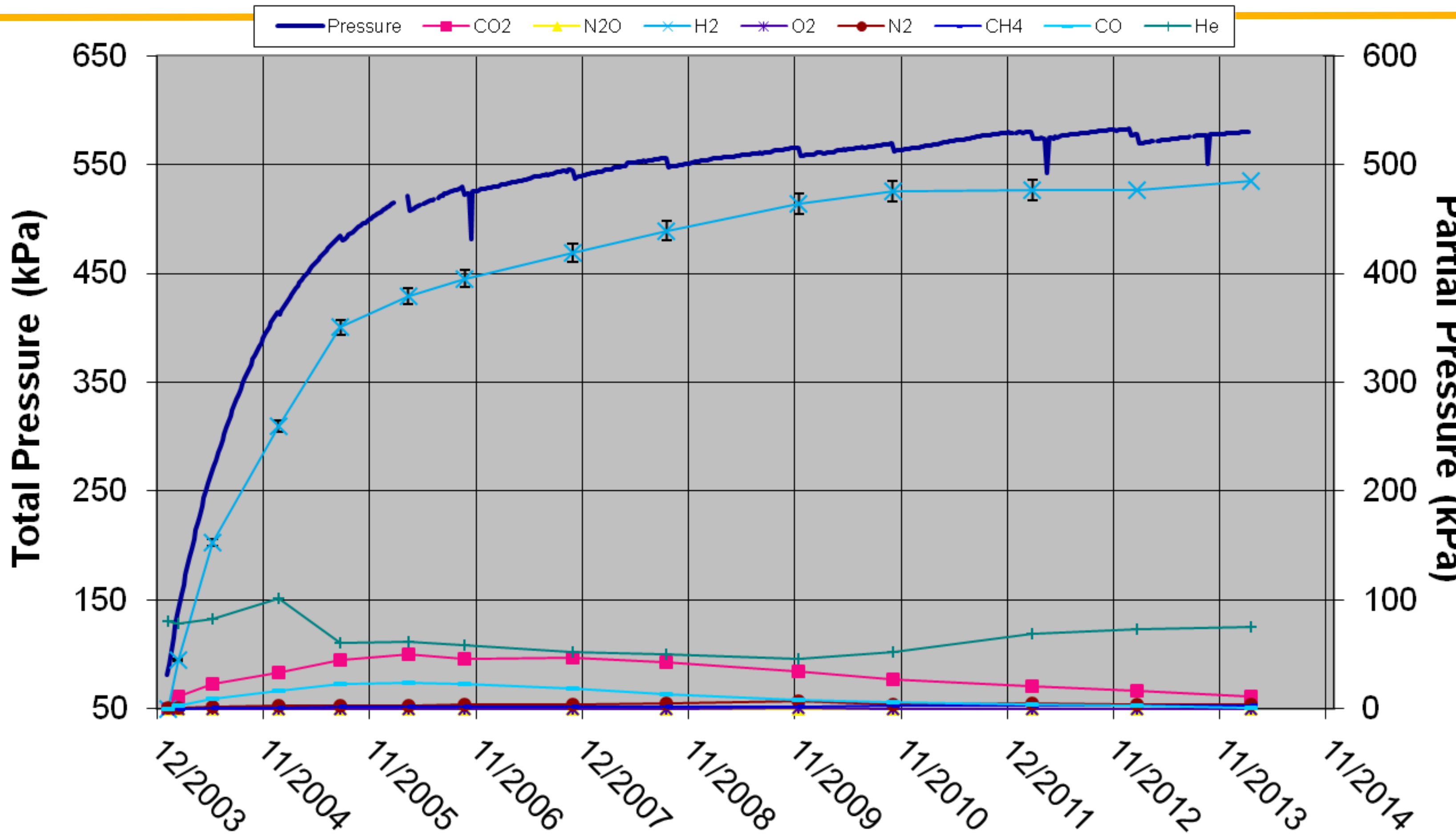
Materials with bounding behaviors

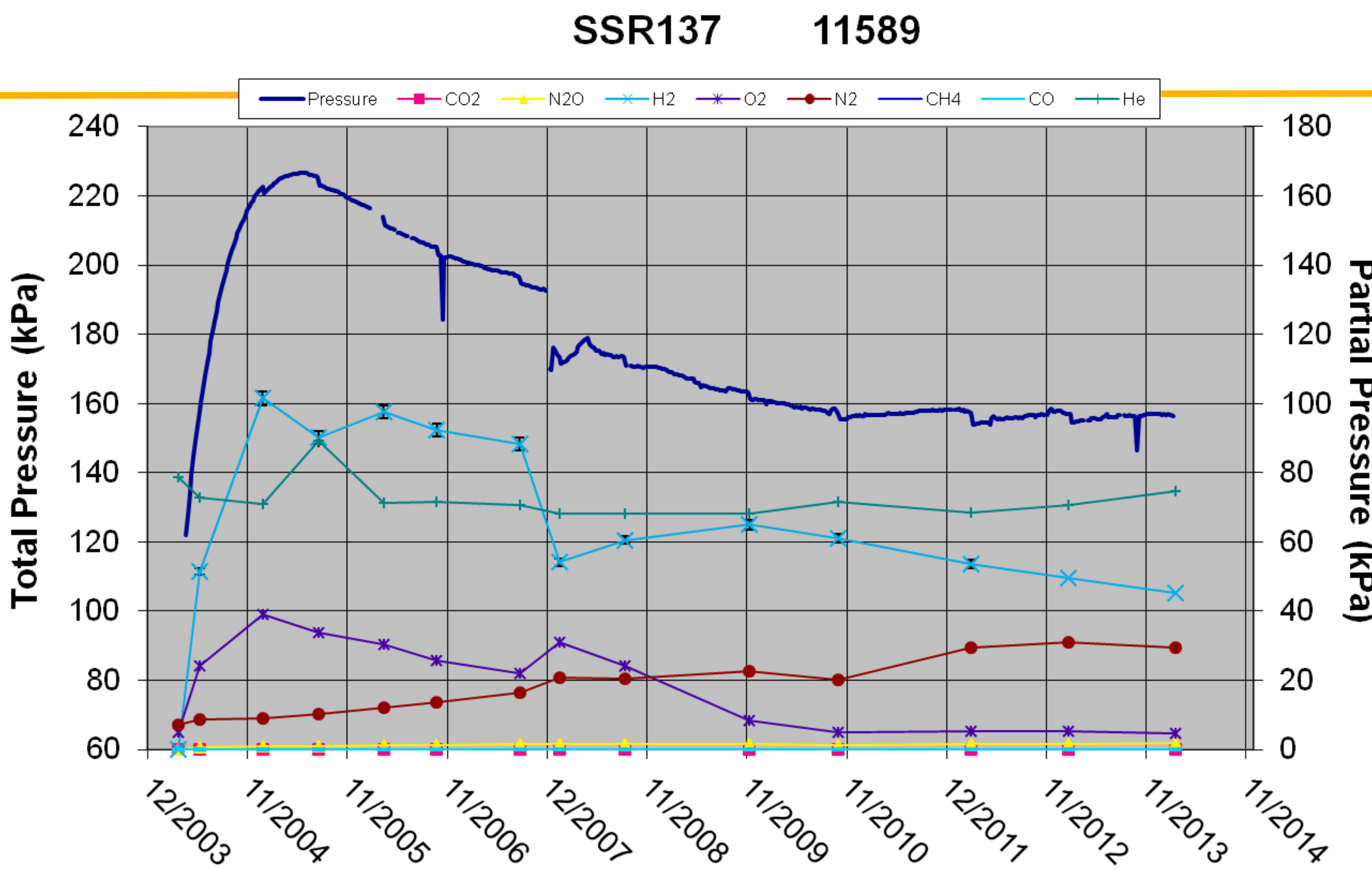
Reactor	Material	Behaviour
SSR122	7161856 – a high-purity oxide	O_2 generation w/o H_2
SSR130	C06032A – 74% Pu with chloride	Highest pressure – H_2
SSR137	11589A – 77% Pu with chloride	H_2 and O_2 generation
SSR155	ARF-102-85-295 – 28 to 40% Pu with chloride	May overtake SSR130 for highest pressure

SSR122 7161856

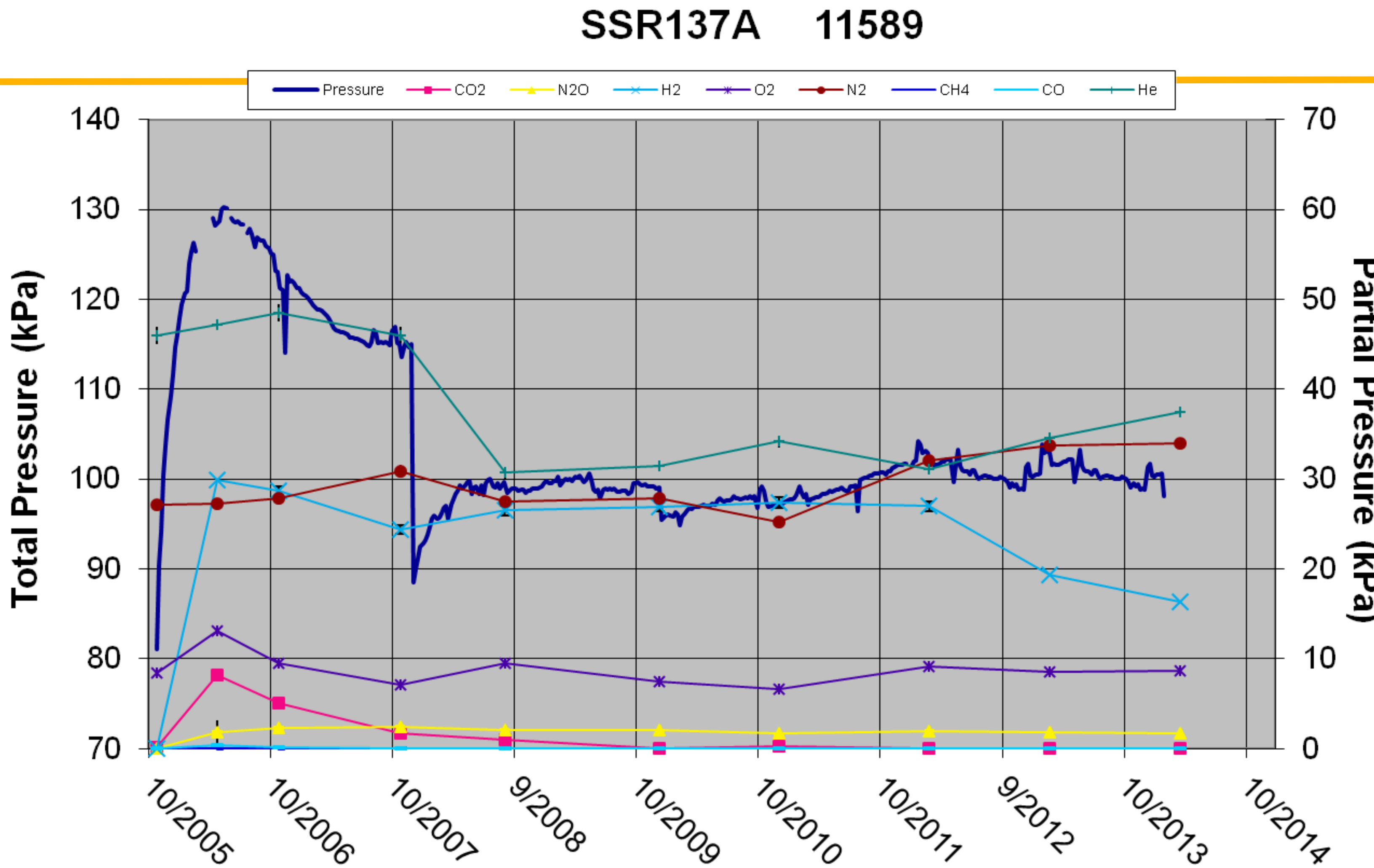


SSR130 C06032A





SSR137 11589
Pressure
CO2
N2O
H2
O2
N2
CH4
CO
He
Total Pressure (kPa)
Partial Pressure (kPa)
240
220
200
180
160
140
120
100
80
60
180
160
140
120
100
80
60
40
20
0
12/2003
11/2004
11/2005
11/2006
12/2007
11/2008
11/2009
11/2010
12/2011
11/2012
11/2013
11/2014



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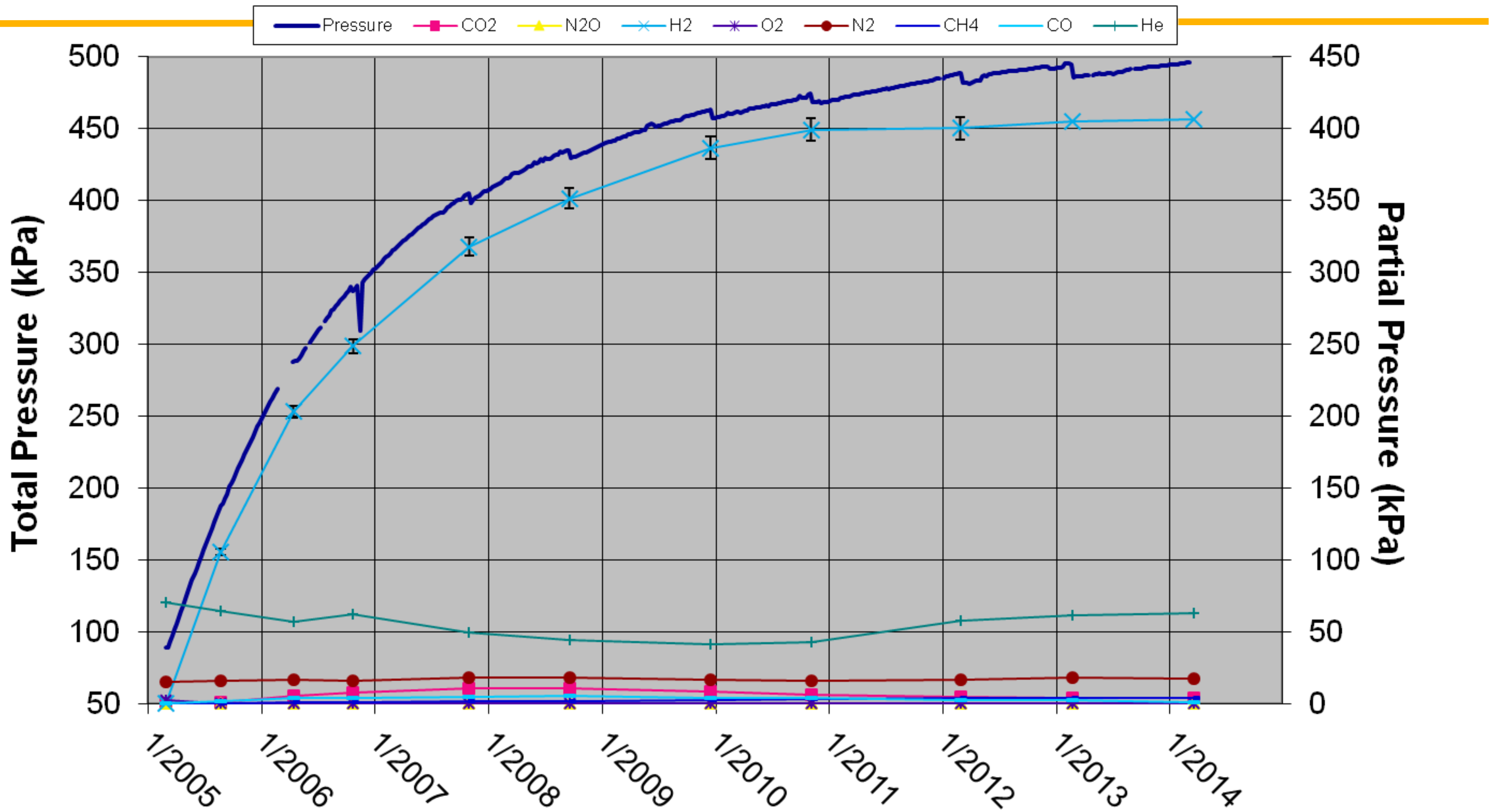
SSR155 ARF-102-85-295

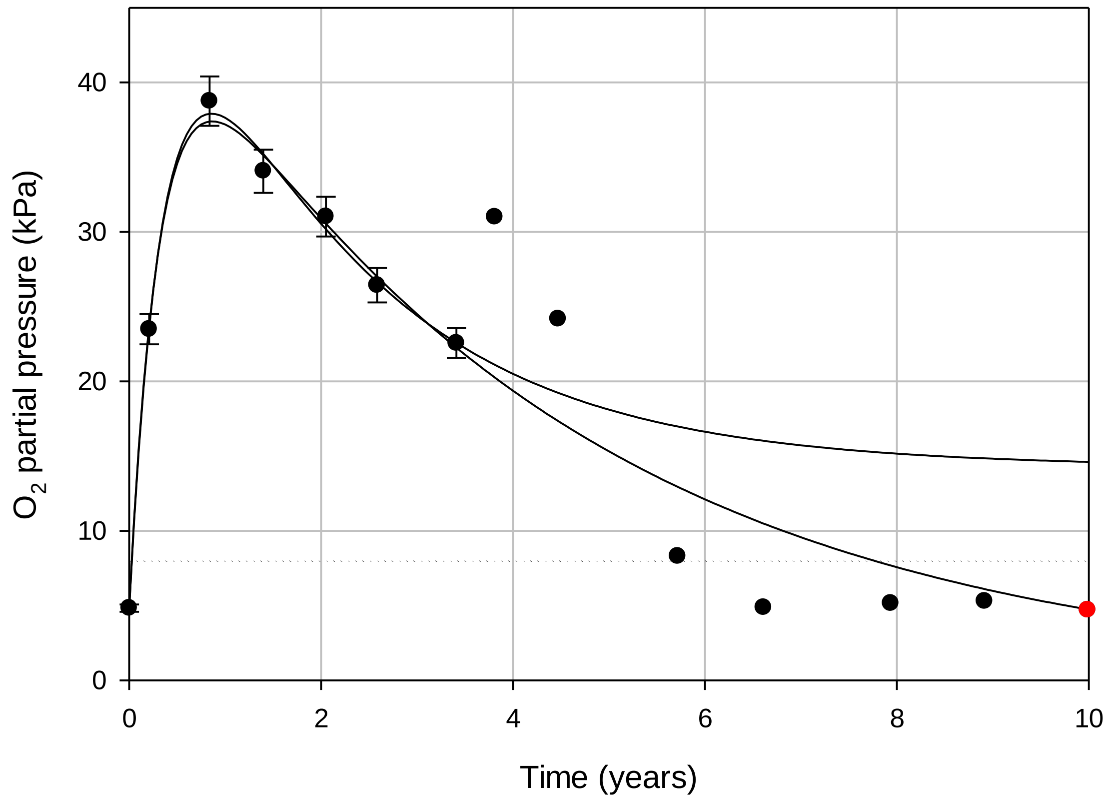


Oxygen partial pressure 11589A

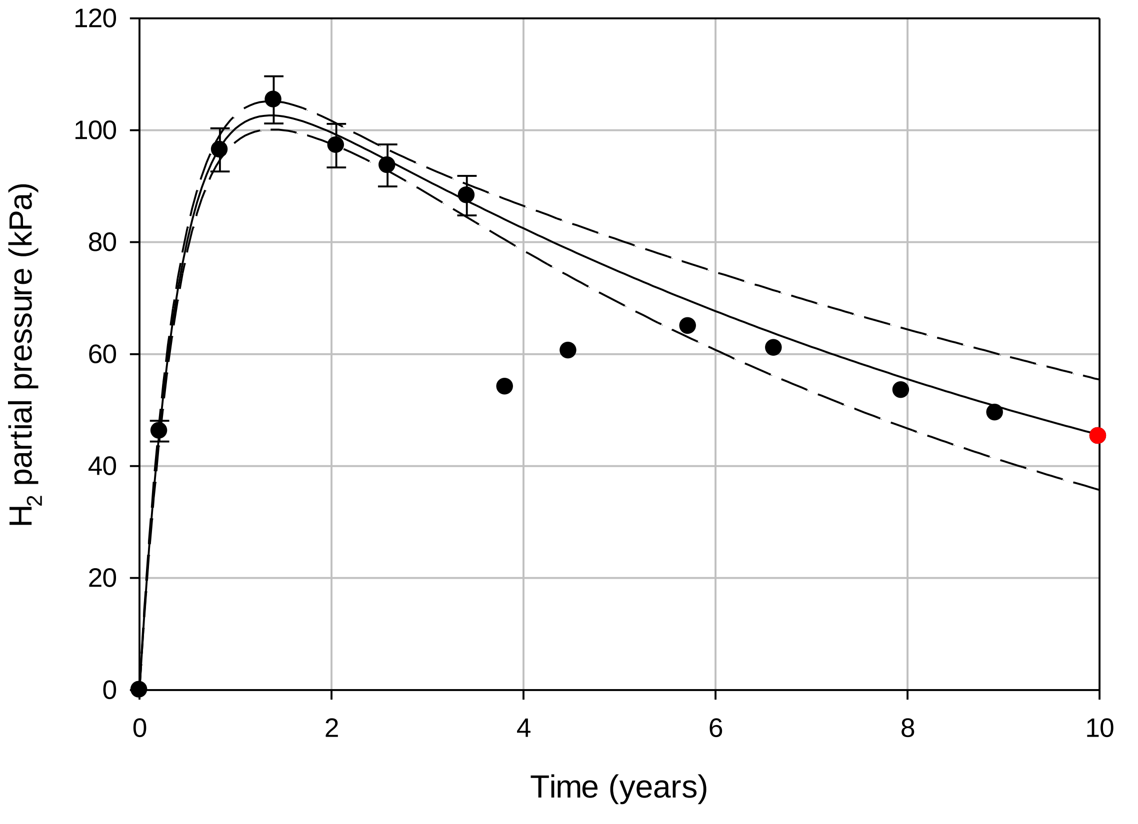
Two reaction models were fit to the data.

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.



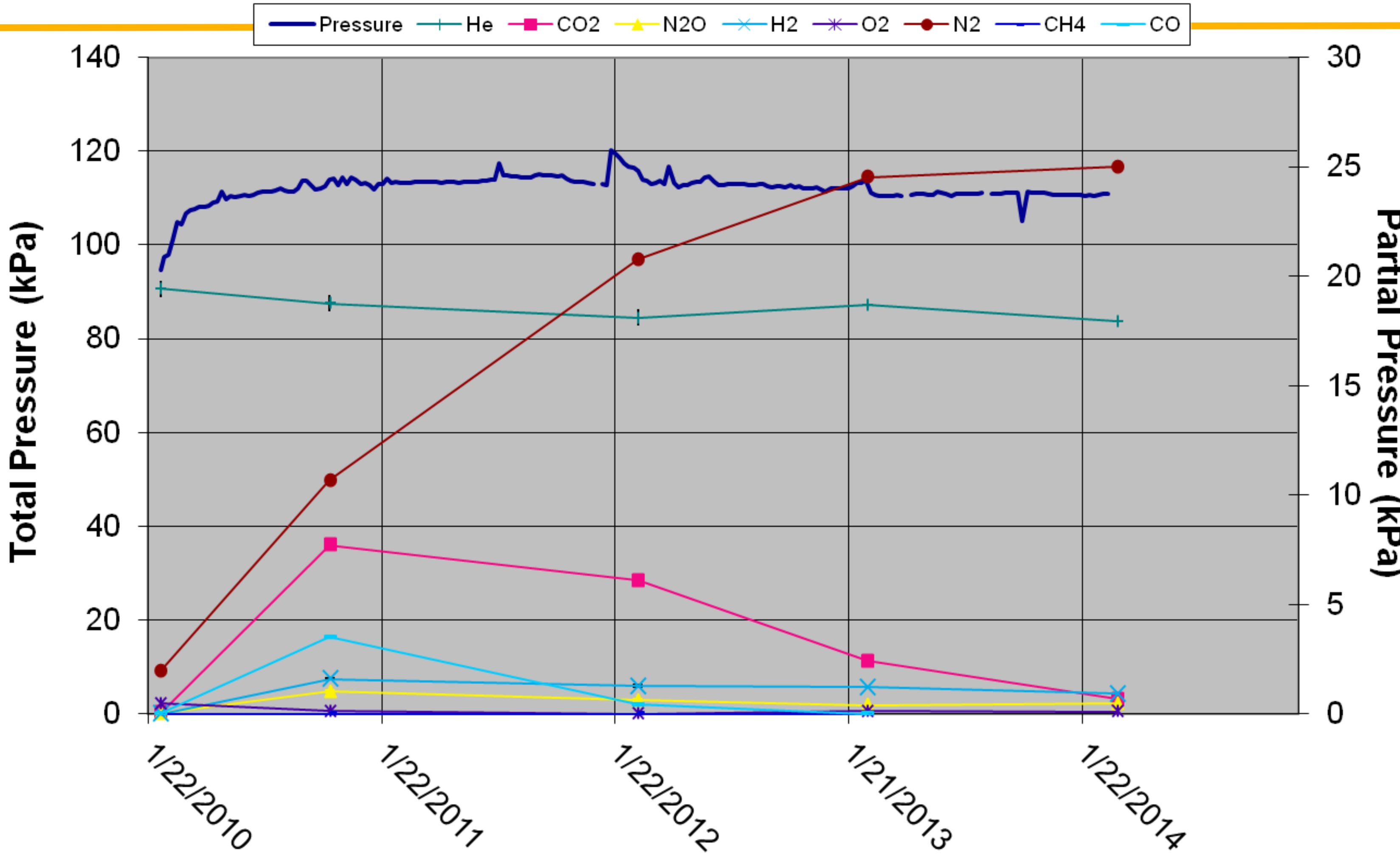
Hydrogen partial pressure of 11589A



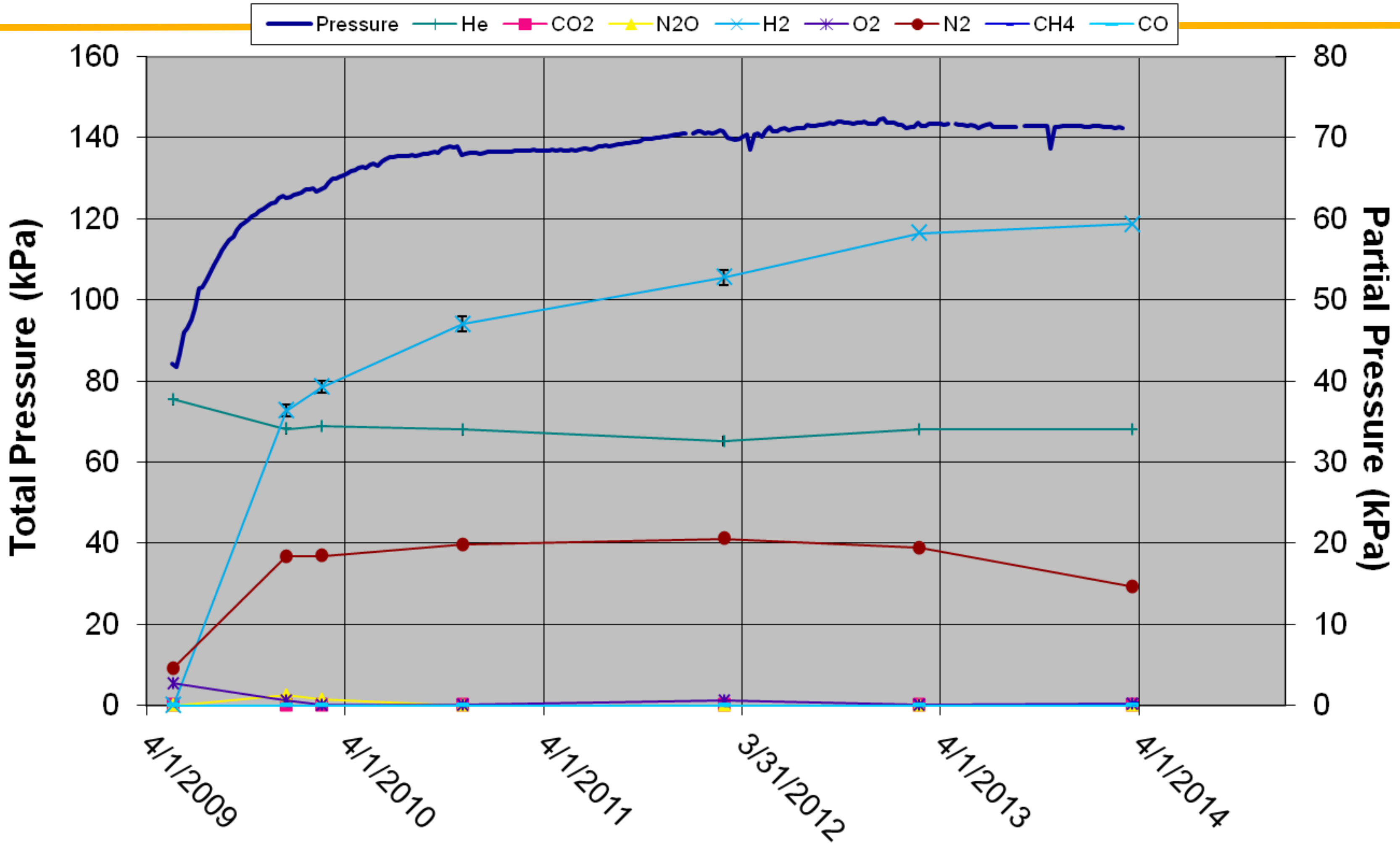
LANL material loaded

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%

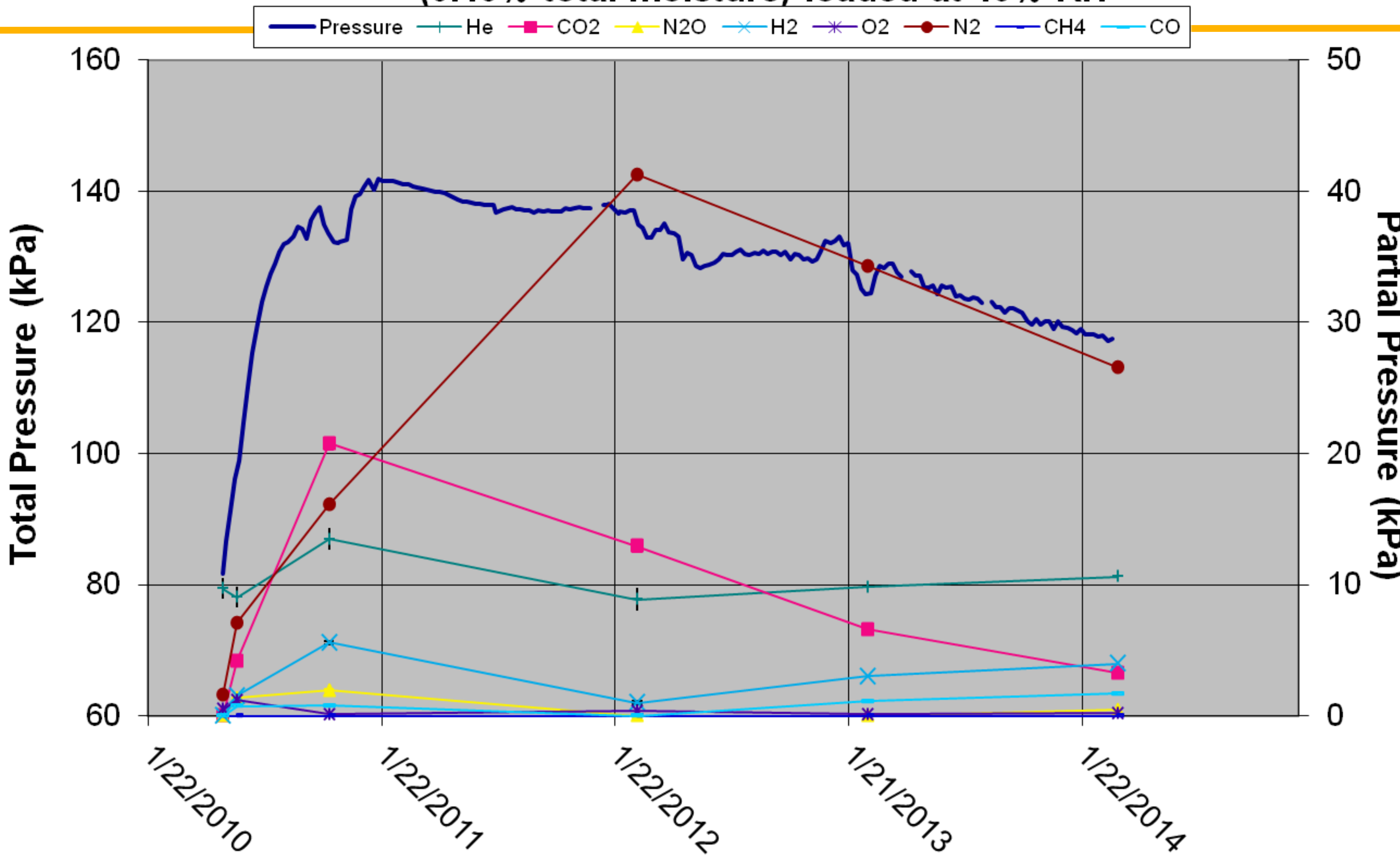
10 g CXLPROD021202C-SUR with 0.46% moisture



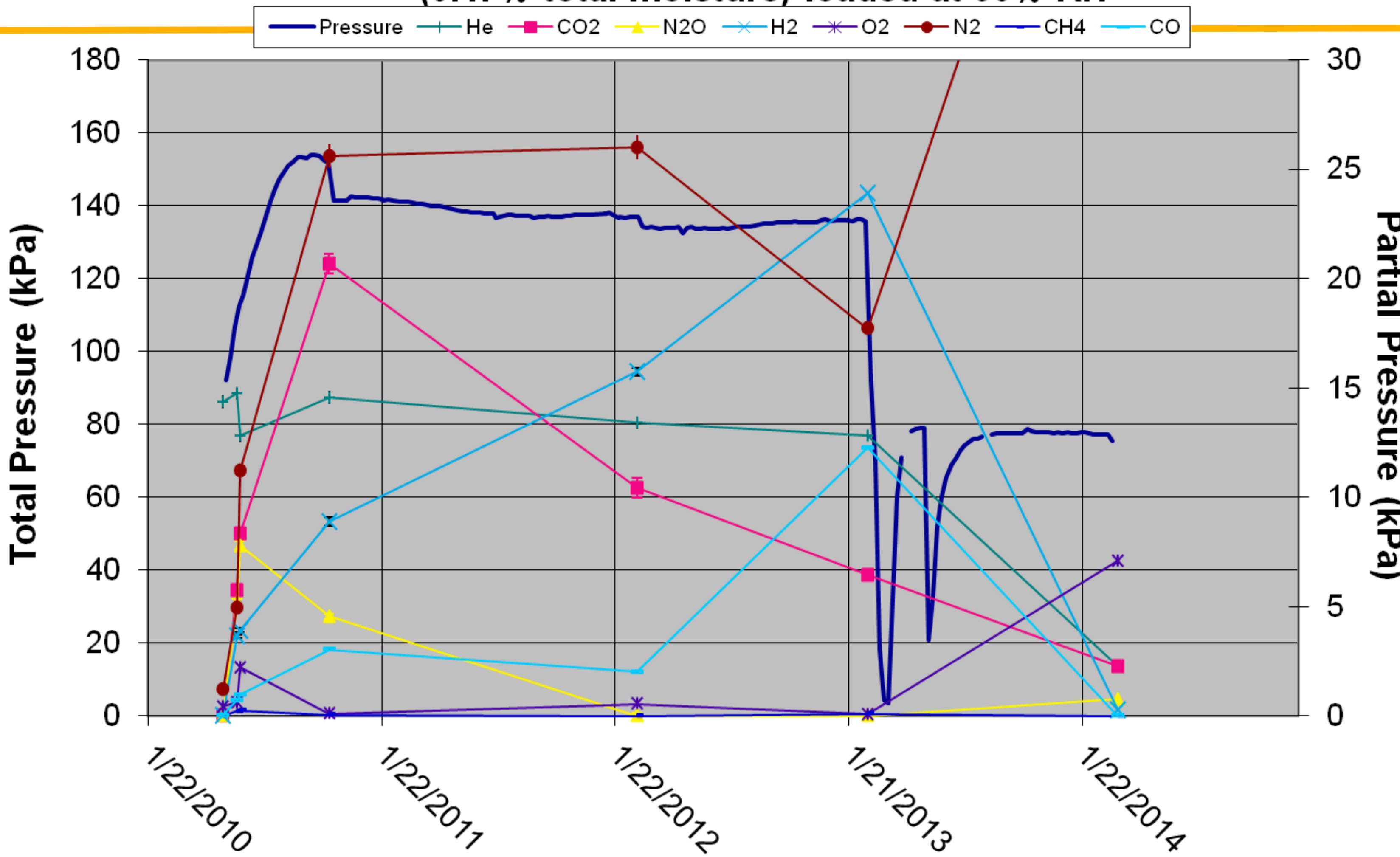
9.94 g CXLOX091802A-SUR-C with ~0.49% moisture



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



10 g 04272-CC-220-AS ("Thorium sample") with 0.06% added moisture (0.17% total moisture) loaded at 50% RH



LANL material recommendations

- CXLPROD091901: reload. Original had a significant H2 gas generation rate.
- CXLPROD021202C: has achieved equilibrium – remove.
- CXLPROD091802A:close to equilibrium – leave another year.
- 04272-CC-220-AS at 15% RH: losing CO_2 and N_2. Leave another year.
- 04272-CC-220-AS at 50% RH: H_2 pressure was still rising when container leaked. Re-load.

H_2 and O_2 generation studies.

- Covered experimental work last annual meeting.
- Have calculated H2 and O2 G-values – these are consistent with Sims et al H2 G-value as a function of monolayer coverage.
- From fit of data, have determined the maximum partial pressures of H2 and O2. The maximum partial pressures are proportional to the initial G-values.
- The amount of H2 andO2 in the gas phase represents less than 3% of the total adsorbed water, therefore at the maximum pressure the rate of formation and the rate of consumption is equal.
- The rate of gas phase radiolytic recombination can be calculated and compared to the rate of consumption.

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

D. Kirk Veirs

LANL Corrosion Team and SRNL Corrosion Team

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What has led to the new Stress Corrosion Cracking Test Plan?

The observations that have led to the new SCC test plan are:

1. Pitting in Hanford containers inner container closure weld region (ICCWR) with chlorine but not sodium, potassium, calcium, magnesium or plutonium in the corrosion products.
2. The presence of a NH_4Cl film in the headspace region of the convenience container.
3. Relative humidity (RH) above 10% during DE.
4. Cracks observed near the ICCWR during boiling $MgCl_2$ solution tests (both hoop and axial) and stresses mapped in the RFETS ICCWR.
5. SCC in teardrop specimens at room temperature.
6. Pitting in teardrop specimens in the headspace of small scale tests near the weld that holds the teardrop closed.

Significance of observations

1. Pitting in Hanford containers inner container closure weld region (ICCWR) with chlorine but not sodium, potassium, calcium, magnesium or plutonium in the corrosion products.

    a. Gas phase transport of chlorine must have occurred. Chlorine is necessary for chloride stress corrosion cracking (SCC) of austinitic stainless steels such as 304.

    b. The ICCWR is the location of a number of important features that increase the possibility of SCC:

        i. High stresses
        ii. Weld sensitization and HAZ
        iii. Weld oxide
        iv. Lower temperatures, therefore higher relative humidity than other regions

    c. The combination of RH, gaseous chloride species, and oxidant were present for a sufficient time to initiate pitting.

Significance of observations

2. The presence of a NH_4Cl film

   a. Indicates that gas phase HCl must have been present at one time.

   b. Verifies the presence of a gas phase chloride species that can transport chlorine to susceptible regions.

   c. Acidifies any liquid that might be present.

3. Relative humidity (RH) above 10% during DE.

   a) The relative humidity is known to decrease with time since container closure therefore the RH at time of closure was higher and could be significantly higher.

   b) Highest RH was 22% which is above the threshold for SCC for $CaCl_2$ salts.

Significance of observations

4. Cracks observed near the ICCWR during boiling $MgCl_2$ solution tests (perpendicular to hoop and axial directions) and stresses mapped in the RFETS ICCWR.

   a. Cracks during boiling $MgCl_2$ tests indicate sufficient stress is present that SCC should be considered as a failure mechanism during service.

   b. The stress mapping of the RFETS inner container is consistent with the cracks in the $MgCl_2$ tests – hoop stresses are highest near the weld; cracks were observed near the weld and appeared to be originating in a region near the weld.

   c. The crack perpendicular to the axial direction ran parallel to the weld around ~60% of the circumference. Pretty close to a worst case condition.

Significance of observations

5. SCC in teardrop specimens at room temperature.
   a. The rule of thumb that SCC does not need to be considered in systems with temperatures less than 70 ^{o}C cannot readily be applied to this system.
   b. Showed that the salts present in MIS materials in concentrations available in MIS materials could cause SCC in 304 stainless steels.
   c. Cracking occurred at about 57% RH which is a RH above what is observed during DE and higher than expected.
6. Pitting in teardrop specimens along the weld that holds the teardrop closed in the headspace of small scale tests.
   a. Shows that any weld region is susceptible to atmospheric corrosion.
   b. Shows that the atmosphere generated by MIS plutonium bearing materials can corrode in weld regions.
   c. Suggests that the weld oxide which hadn't been removed from the teardrop in that region may play a role because the corrosion was most intense at this region.

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?

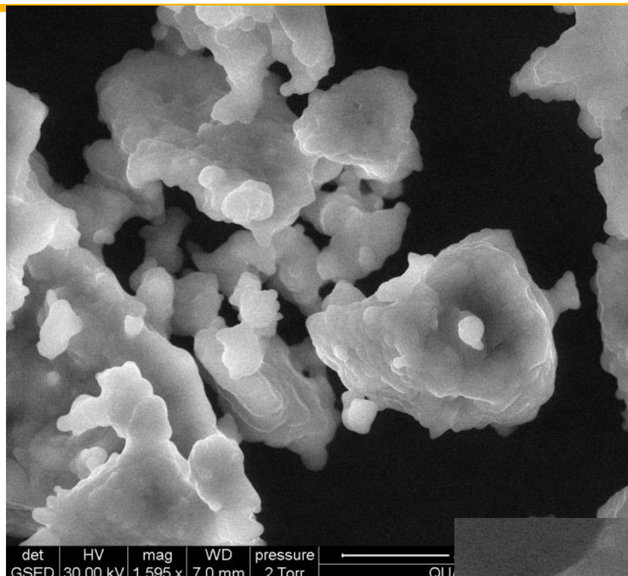
1. Did we misunderstand the literature? No, $CaCl_2$ is more aggressive at lower RHs (Duque)

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.

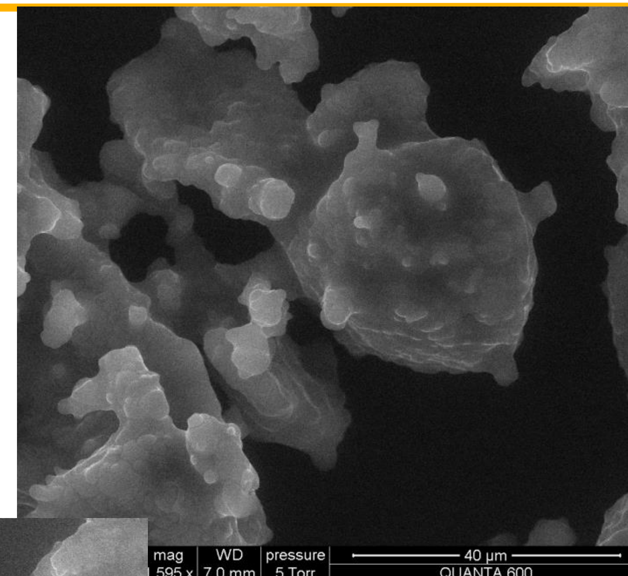
3. Is there a size dependence of the liquid droplets on the ability to cause SCC or pitting? Yes (Berg)

2010 Ca ER salt

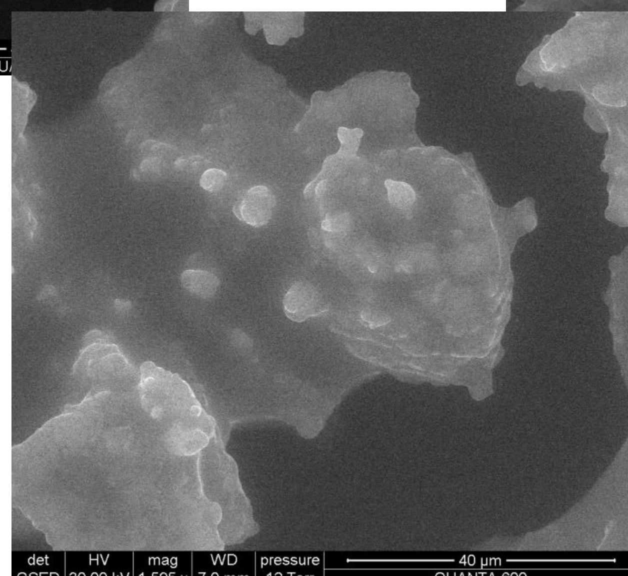
- 9%RH



- 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)

Review of Corrosion Conditions, Pitting, Stress Corrosion Cracking, and Ties to the 3013 Inventory

3013 Surveillance and Monitoring Program Review
March 25, 2014
Savannah River Site

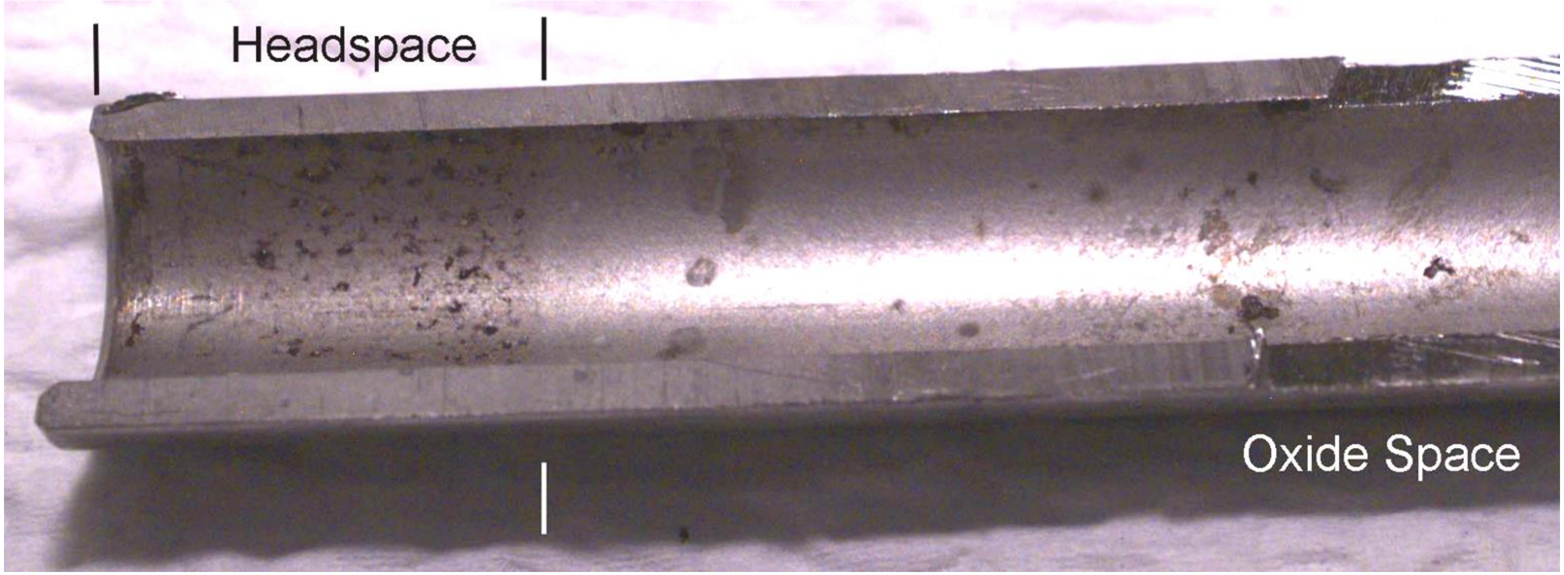
Outline

- Some shelf-life containers and some DE containers have shown pitting corrosion on their interior surfaces.
- Corrosion occurs both in contact with the chloride-containing oxide and in regions in communication with the oxide only through transport of gases. Headspace corrosion is more prevalent.
- Pit growth modeling from observational data project that through-wall pitting is not a likely mode of container failure because the pit growth rate is too slow.
- Stored material has been shown capable of inducing SCC in SS test coupons under when exposed to high humidity and when in direct contact with the coupon. SCC has not been induced in with only gas phase contact.

Outline

- RH needed to induce SCC in contact region is higher than one would predict from the literature on the aggressiveness MgCl2 and CaCl2 solution deposits as a function of RH, and higher than RH found in storage to date.
- SCC failure dramatic enough to expose IC to direct material contact leading to SCC is unlikely.
- Headspace corrosion remains a concern because a through-wall flaw due to SCC could expose the outer container to a corrosive environment.
- Therefore, the current focus of corrosion work in the MIS Program has shifted to quantifying the extent and potential severity of headspace corrosion.

Shelf-life studies – LANL Small-Scale ARF-102-85-223



- Uniform discoloration in the headspace region.
- Many small pits in the headspace region.

Shelf-life studies – LANL Large-Scale PMAXBS

- Lid of Large-Scale container. 316L for 100 days. HAZ show extensive patches of corrosion.
- Walls of container in contact with material are shiny.

- LLNL lid sample in headspace.
- Corrosion seen in crevice (sample opened for illustration).
- Similar sample in contact region shows no corrosion in crevice.

Shelf-life studies – LANL Small-Scale

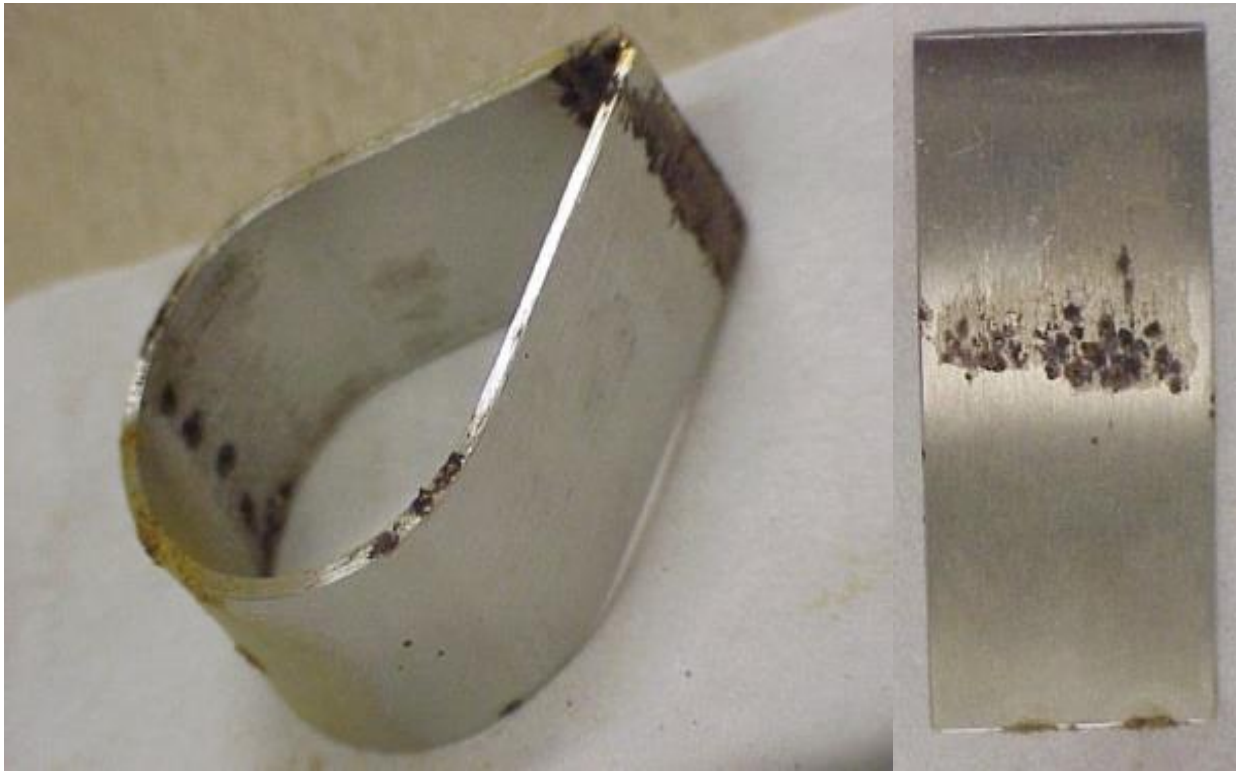
- Body constructed of 316L SS.
- Material in inner bucket – material never directly in contact with body.
- High-purity oxide (PEOF1) with 5wt% $CaCl_2$.
- Body used multiple times – corrosion observed to start with 3.1 waters of hydration.
- Small-Scale Studies: Oxygen Generation and Corrosion, presented by Ed Garcia, Surveillance & Monitoring Annual Meeting, Jan. 2007.

Shelf-Life Studies – SRS corrosion Series 4

- Metal samples 304L SS; material was high-purity oxide with 2% salts, 0.2% $CaCl_2$. Loaded with ~0.5wt% water.

- Teardrop specimen half in material and half in headspace. The weld at the top was in the headspace region. Corrosion observed in the heat-affected zone.

- STATUS REPORT FOR SRNL 3013 CORROSION TESTS, WSRC-STI-2008-0046.



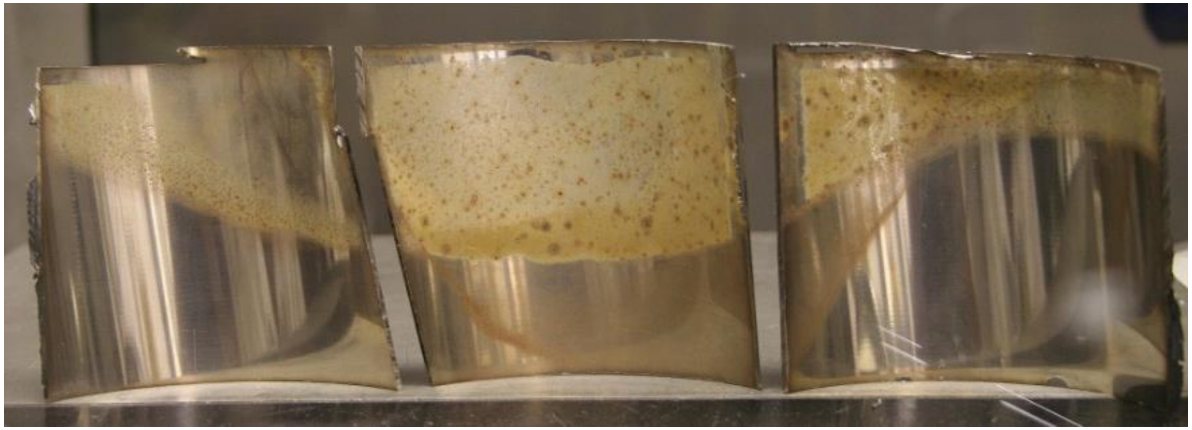
SRS DE of H004111 – Film on convenience container.

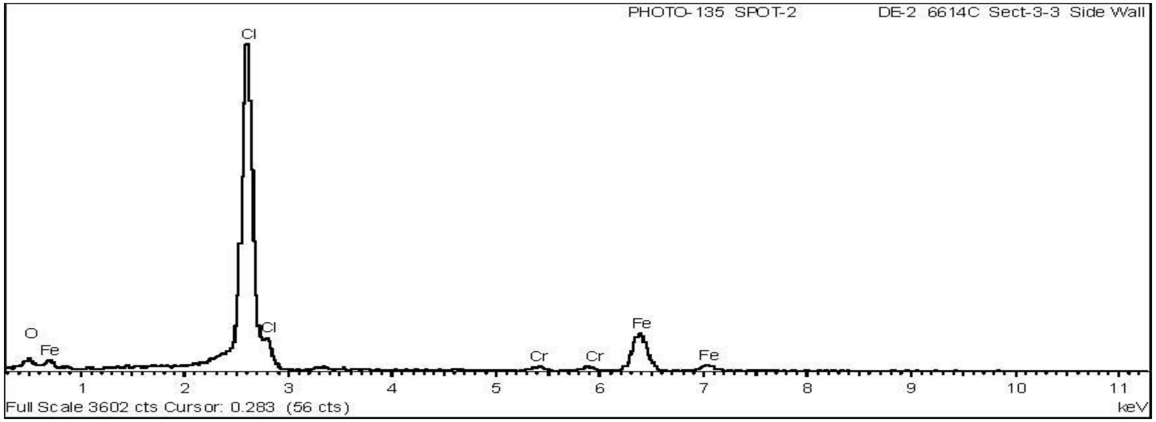
- Film observed on convenience container wall above material.

- Film contained chloride but not Na, K, Ca, and Mg.

- Film could be removed. XRD of film material indicated NH_4Cl.

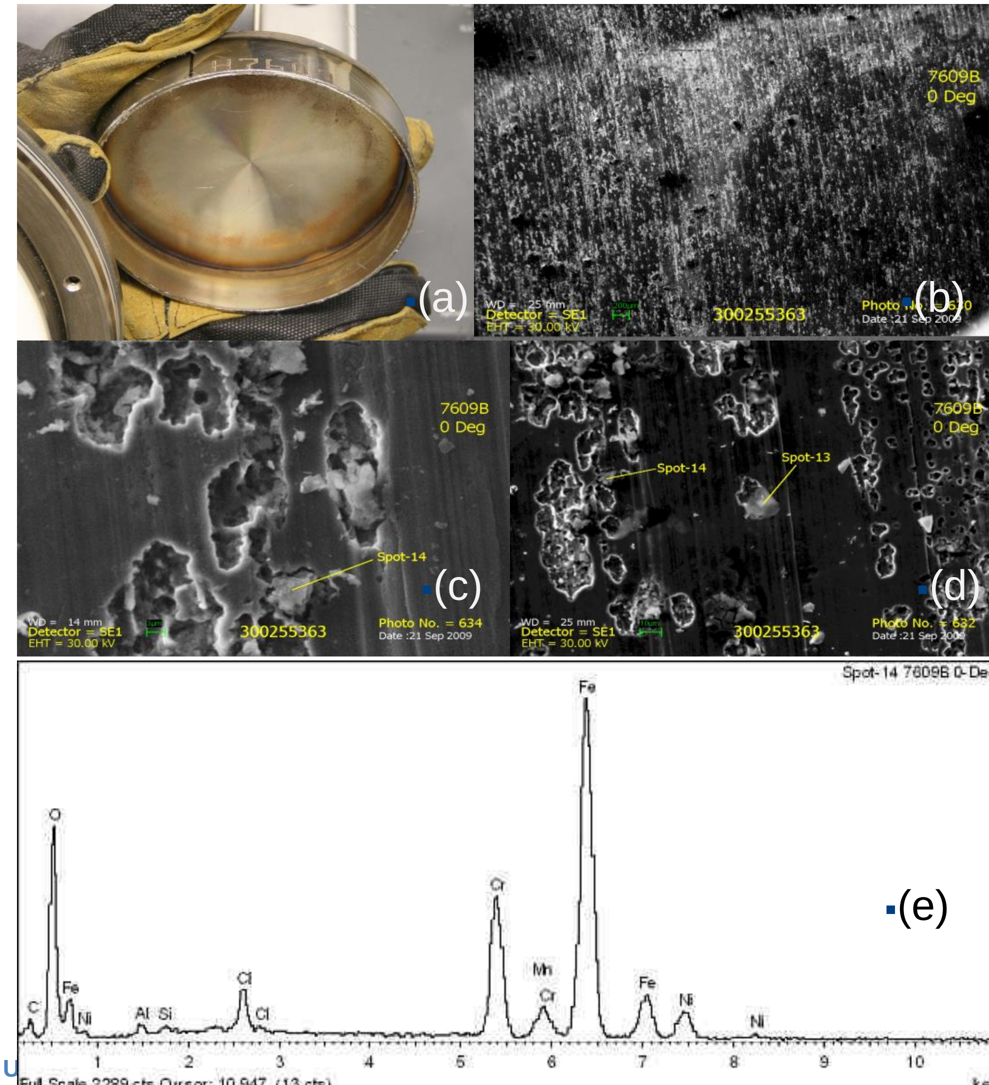
- SS under film was not pitted or corroded.





SRS DE of H004111 – Pitting of inner container lid.

- Pitting corrosion observed on lid but not on walls.
- Corrosion observed in ring pattern reflecting the convenience container lid construction.
- Material in pit contained chlorine and the elemental components of SS, but not Pu, Na, K, Mg, or Ca.



Discussion – Composition of H004111 Material and Gas

Material and gas-phase contents of H004111.

Salt contents		Gas composition	
Cl	5.8%	He	32%
K	3.0%	N_2	48%
Na	1.8%	H_2	20%
Ca	0.05%	O_2	0%
Mg	0.08%		
H_2O	0.26%		
PuO_2	82%		

Summary of Previous Corrosion Observations

- SCC observed after 5.5 and 11 months at RT in 2 welded, stressed 304L SS teardrop (TD) coupons in contact with
  - 98% PuO_2/2% salt with 0.2% $CaCl_2$ (4a)
  - Loaded with ~0.6% H_2O at ~ 75% RH
- SCC not observed in equivalently exposed 316L SS TD coupons

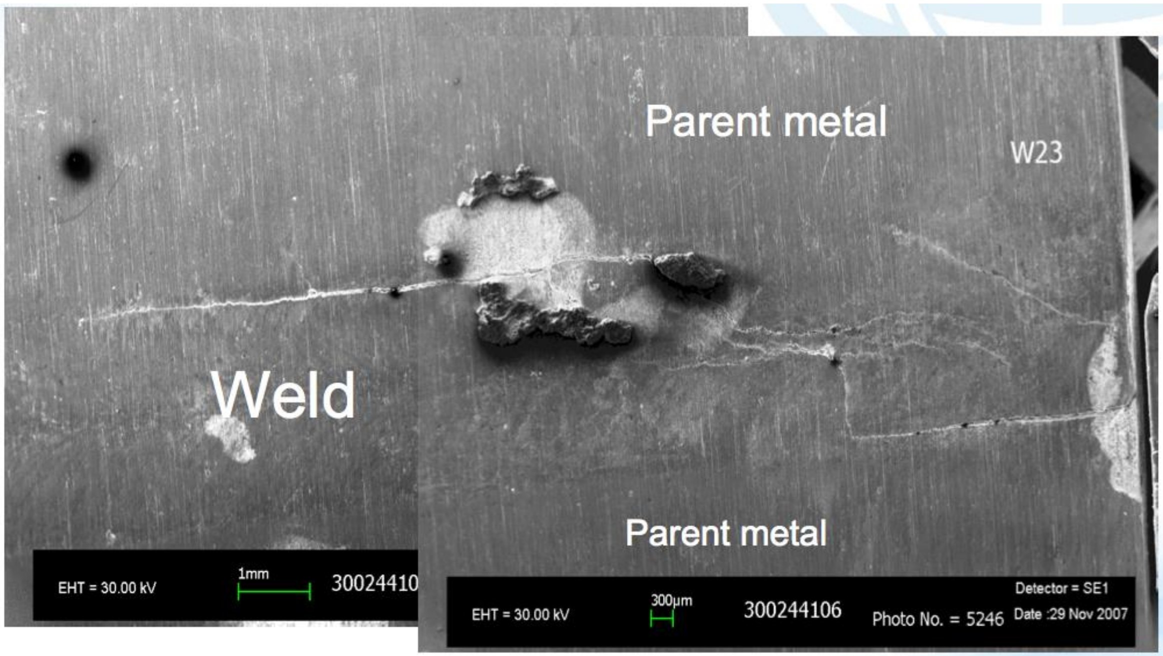
SCC not observed in 304L TD coupons in solid contact with 98% PuO_2/2% salt with 0.9% $CaCl_2$ (4b)

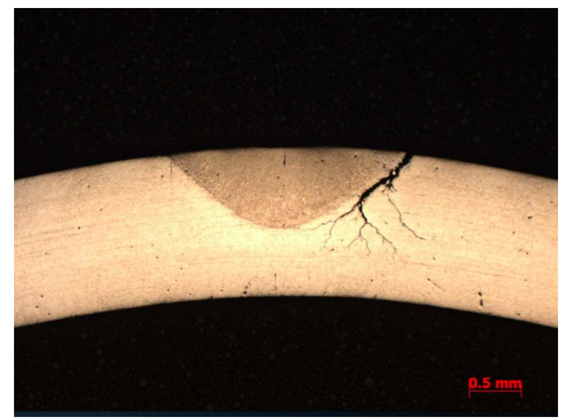
- SCC not observed in any coupons exposed to headspace atmosphere
- Pitting corrosion observed mainly in flat coupons exposed to mixtures with 2% total salt containing $CaCl_2$

Documented in SRNL-STI-2008-00486

▪Pitting and SCC observed in coupons from test container 4a-3.

SRNL observed SCC in teardrop exposed to PuO_2 with added $NaCl/KCl/CaCl_2$ and high RH (75% initially).

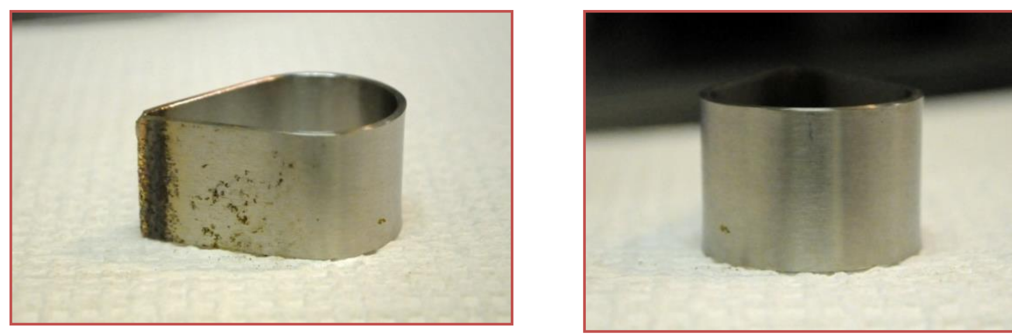




Test Series 1 – 340 Days

- 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

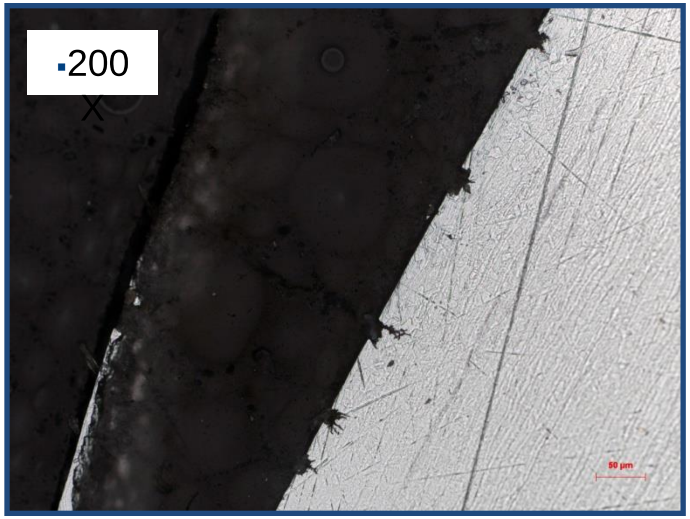
▪Oxide/Salt Exposure



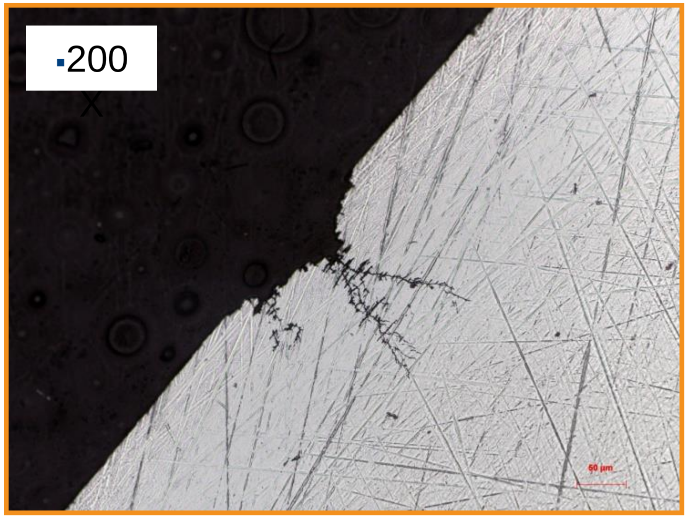
▪Vapor Exposure

Test Series 1 – Cross Sectional Metallography

- 85-Day Exposur
e

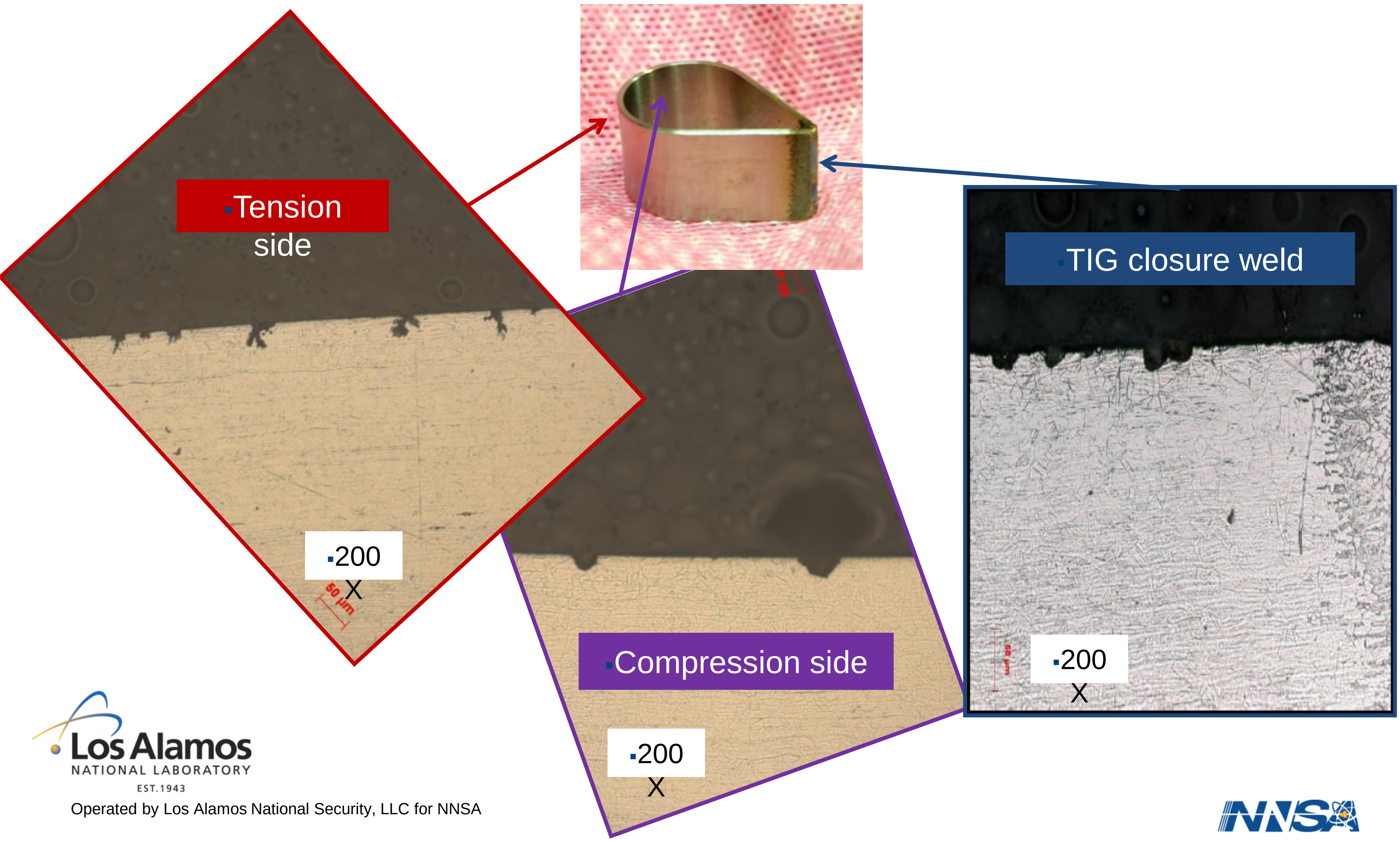


- 175-Day Exposur
e



Test Series 1 – Cross Sectional Metallography

- Teardrop exposed to salt for 85 days at 54%



Overview Presentation

Test Plan for Assessing Potential for Stress Corrosion Cracking in the 3013 Inner Container Closure Weld Region (FY 2014) LA-UR-14-20785 (March 2014)

LANL: *J. M. Berg, D. K. Veirs, E. J. Kelly, J. G. Duque, S. A. Joyce, L. A. Worl, J. E. Narlesky, M. A. Stroud*

SRNL: *J. M. Duffey, J. I. Mickalonis, K. A. Dunn*

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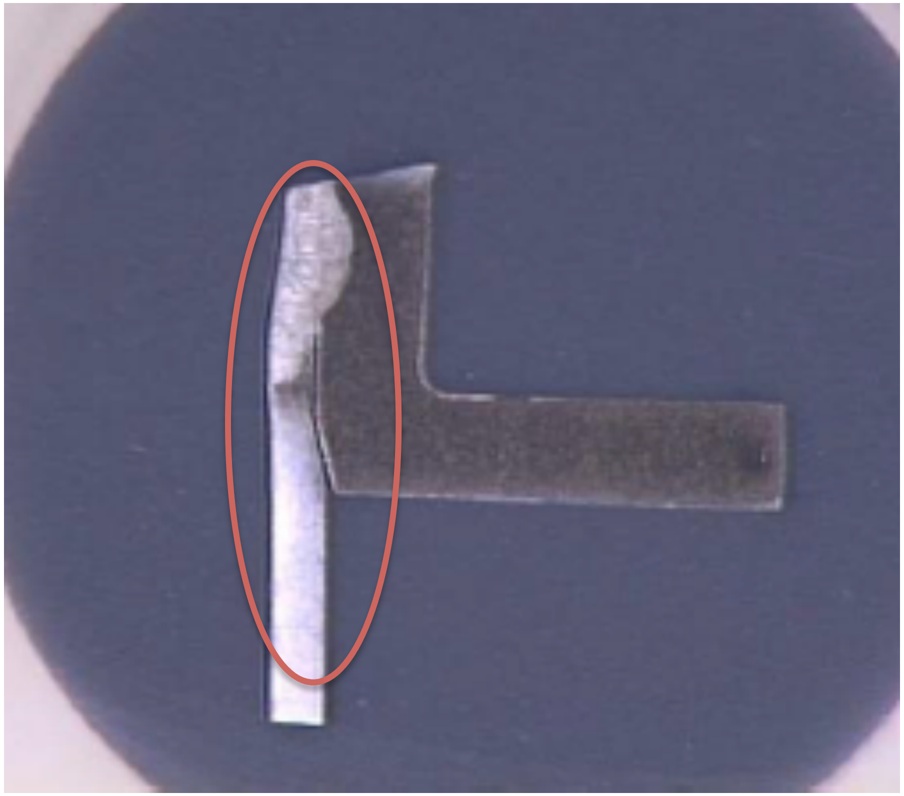
The Issue

- Microscopic examinations of samples from the closure welds of five inner containers in DE, the only ones examined to date, have all shown apparent localized pitting corrosion. *J. Mickalonis and K. Dunn, MIS presentation, Feb. 2013.*
- The container walls adjacent to this weld contain sufficient residual stress to undergo stress corrosion cracking under extreme conditions. *J. Mickalonis, SRNL-STI-2009-00121*
- Unknowns:
  - Extent and variability of the current corroded condition in the container inventory.
  - Likelihood a through-wall flaw exists now in the inventory.
    - Due to pitting alone.
    - Due to stress corrosion cracking.
  - Likelihood a through wall flaw will develop in the future.
    - Is corrosion ongoing or only early in the storage period?

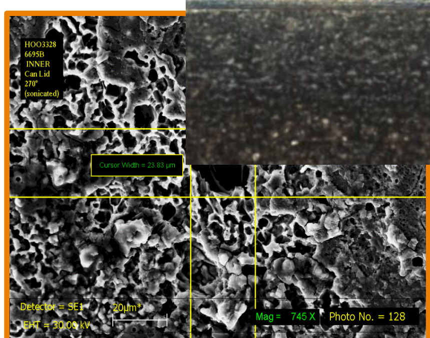
Inner Container Closure Weld Region (ICCWR)

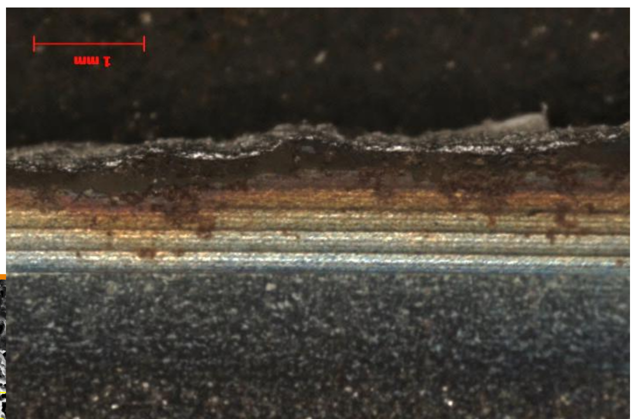


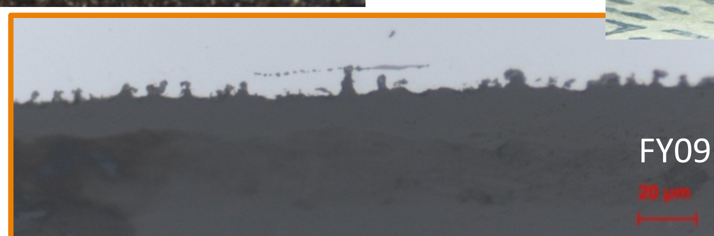
Cross sectional image of a sample of the closure weld from a container produced at Hanford and destructively evaluated at SRS/SRNL.
(Image taken from Nelson et al., SRNL-STI-2010-00064, JNMM 2010.)

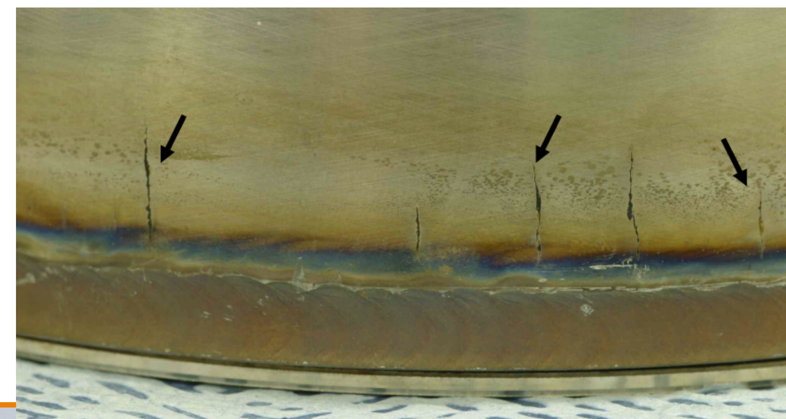
Reasons for to focus on closure weld region

- SRNL observed pitting corrosion in all of the limited DE samples examined thus far.
- SRNL tests induced localized SCC in that area under extreme conditions.
- IC breach could expose outer container to similar corrosive conditions, though to a lesser degree.









Path to Address Concern

- Use DE activities to show:
  - Current extent of pitting corrosion is limited.
  - Low likelihood of through-wall cracks thus far.
- Identify factors needed to get SCC in ICCWR and characterize them in the current inventory.
- Show that one or more of these factors are either below a crucial limit or drop below that limit with time.

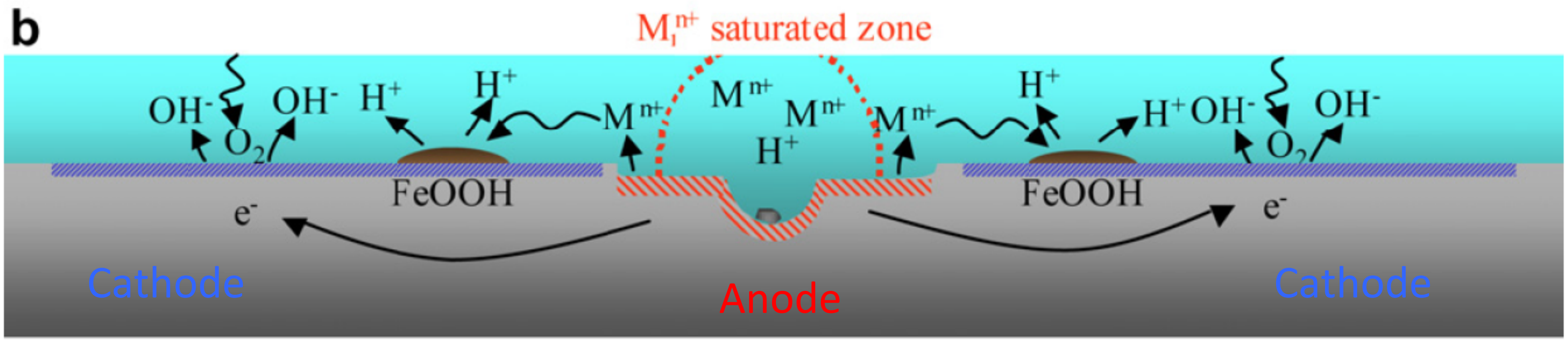
Factors to consider

- Weld effects.
  - Weld oxide could provide a higher corrosion risk in the closure weld region.
  - Chromium depletion in the heat effected zone provides a zone for pitting.
- Stress effects.
  - Welding creates a high localized stressed region for stress corrosion cracking SCC) to occur.
  - Identify locations where residual stress is sufficient to allow SCC and potential inner can breach.
- Temperature of weld region and difference from temperature of stored material.
- Surface deposit chemistry due to gas condensation or reaction.
  - Surface density and chemical form of chloride in the ICCWR and consequences for aqueous layer formation and droplet sizes.
- Gas composition and changes with time.
  - Relative humidity in cooler zone (ICCWR) support persistent aqueous droplets.
  - Oxygen, reported in documents as an oxidant for corrosion and corrosion growth.
  - HCl or Cl_2 as transport of chlorine to surface. Cl_2 could also act as oxidant.

Major Plan Components

- Evaluate the extent of ICCWR corrosion in storage (DE).
- Determine crucial reactants and container surface properties needed for corrosion there.
  - DE samples and literature review.
- Run corrosion tests that vary the crucial conditions over realistic ranges to determine which might limit likelihood of SCC.
- Reproduce known corrosion of ICCWR and test whether it progresses to SCC under plausible storage conditions.

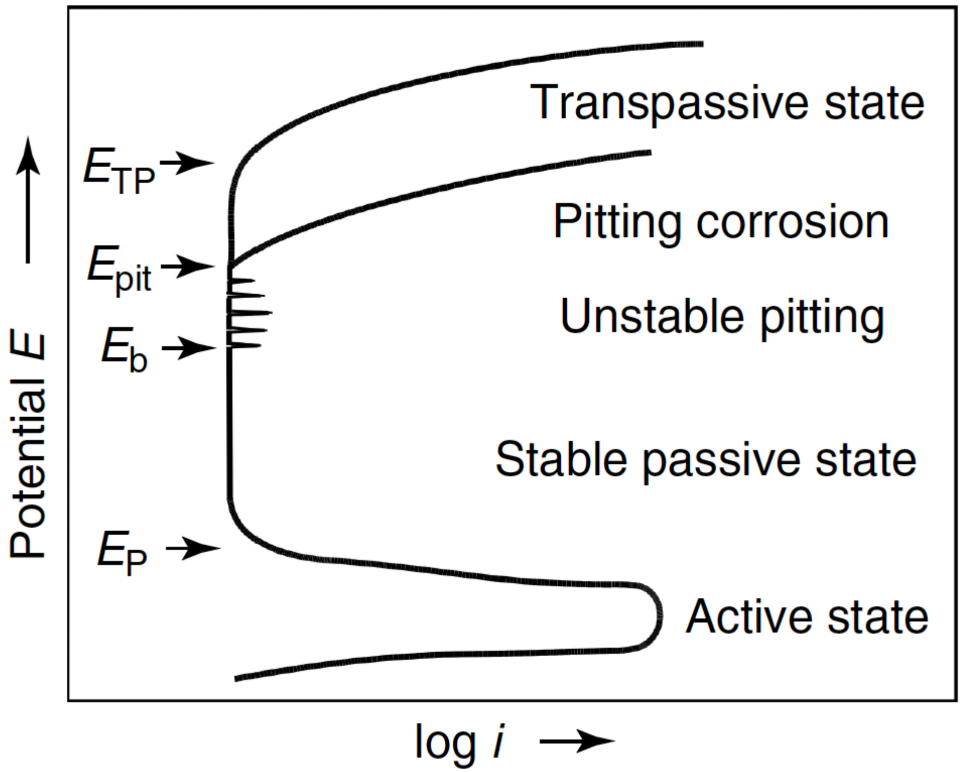
Pitting corrosion under a thin electrolyte layer or droplet



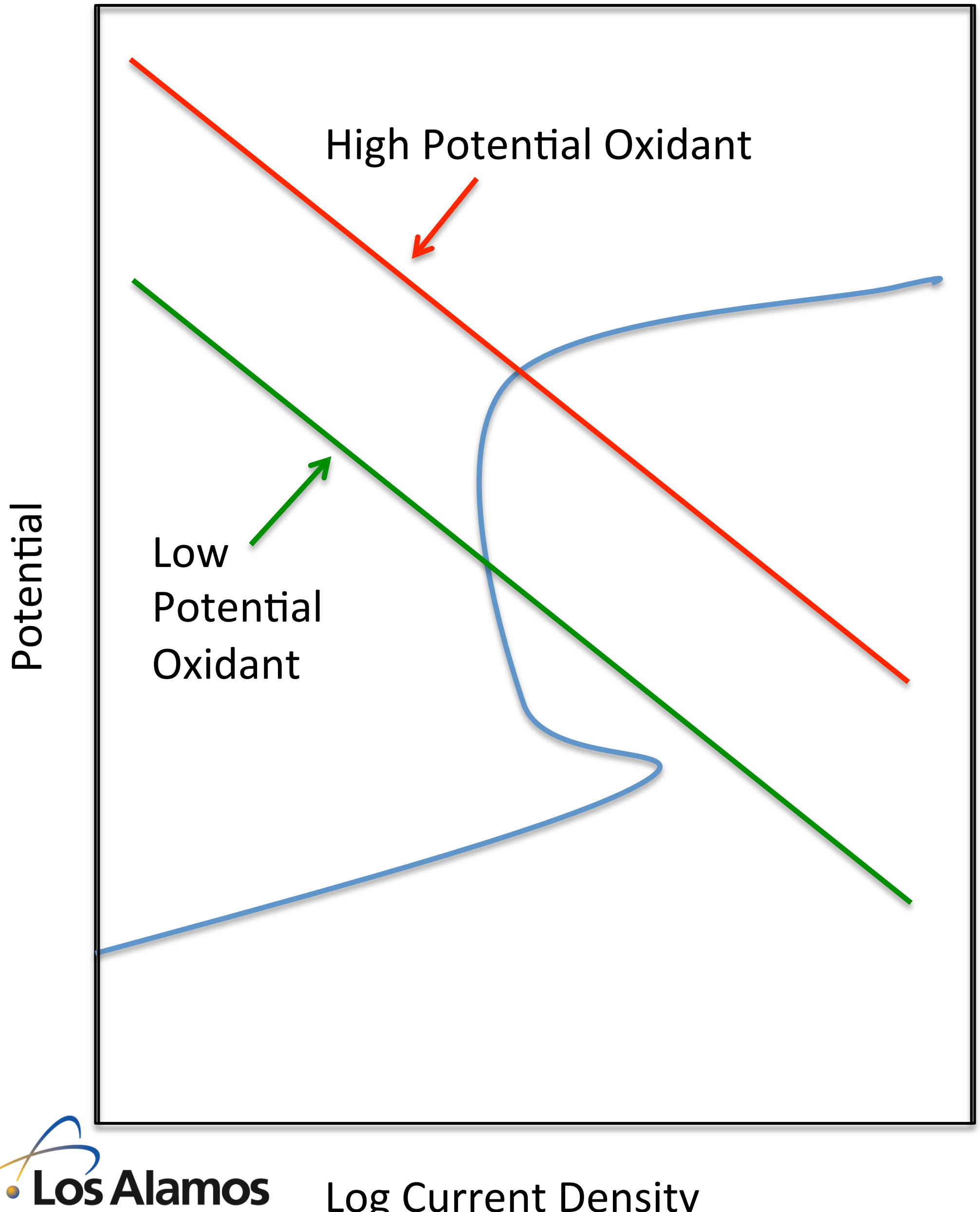
Y. Tsutsumi et al. / Corrosion Science 49 (2007) 1394–1407

- Anodic regions where metal is oxidized and removed
- Cathodic regions where an oxidant is reduced.
- In atmospheric corrosion, the oxidant is usually oxygen but may be another gas or solution component (Cl_2, HOCl).
- Oxidant must be continuously replenished for the reaction to continue.

Importance of electrochemical potential at corroding site

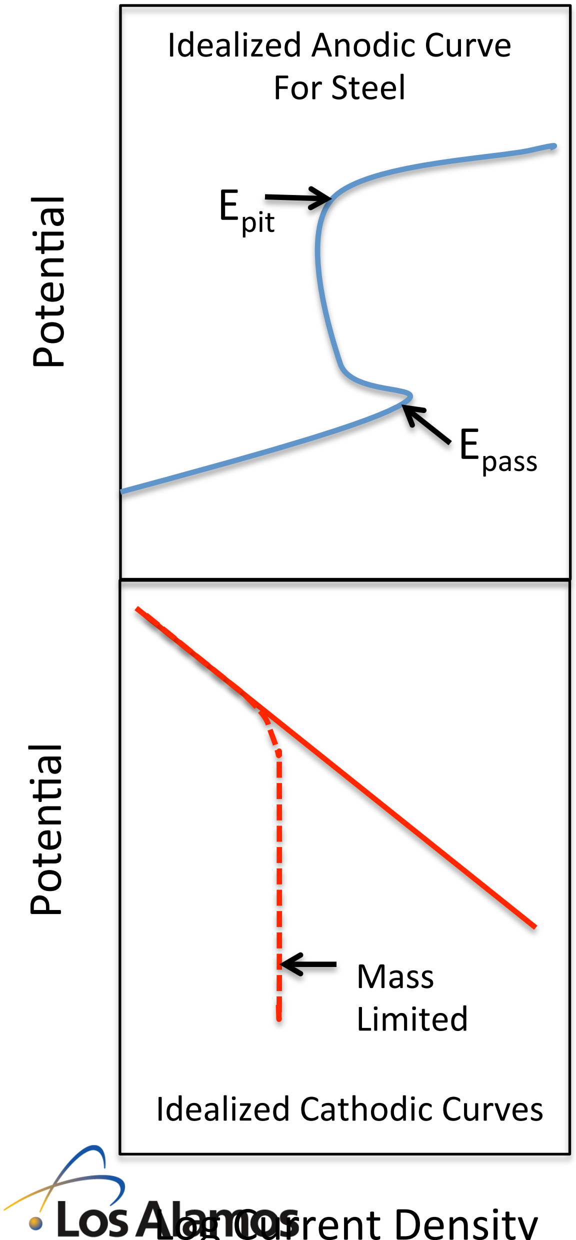


- Potential must be positive enough to break down passive layer and sustain that breakdown.
- Pitting is also possible at lower potential but is interrupted by re-formation of passive layer.



The point where the anode and cathode curves intersect determines the corrosion potential.

For 304 Stainless, E_{pit} in chloride solutions is generally between 0 and 0.4 V. Only high potential oxidants such as O_2(E_0 =1.23V) or Cl_2(E_0 =1.36V) have sufficient potential to induce pitting.

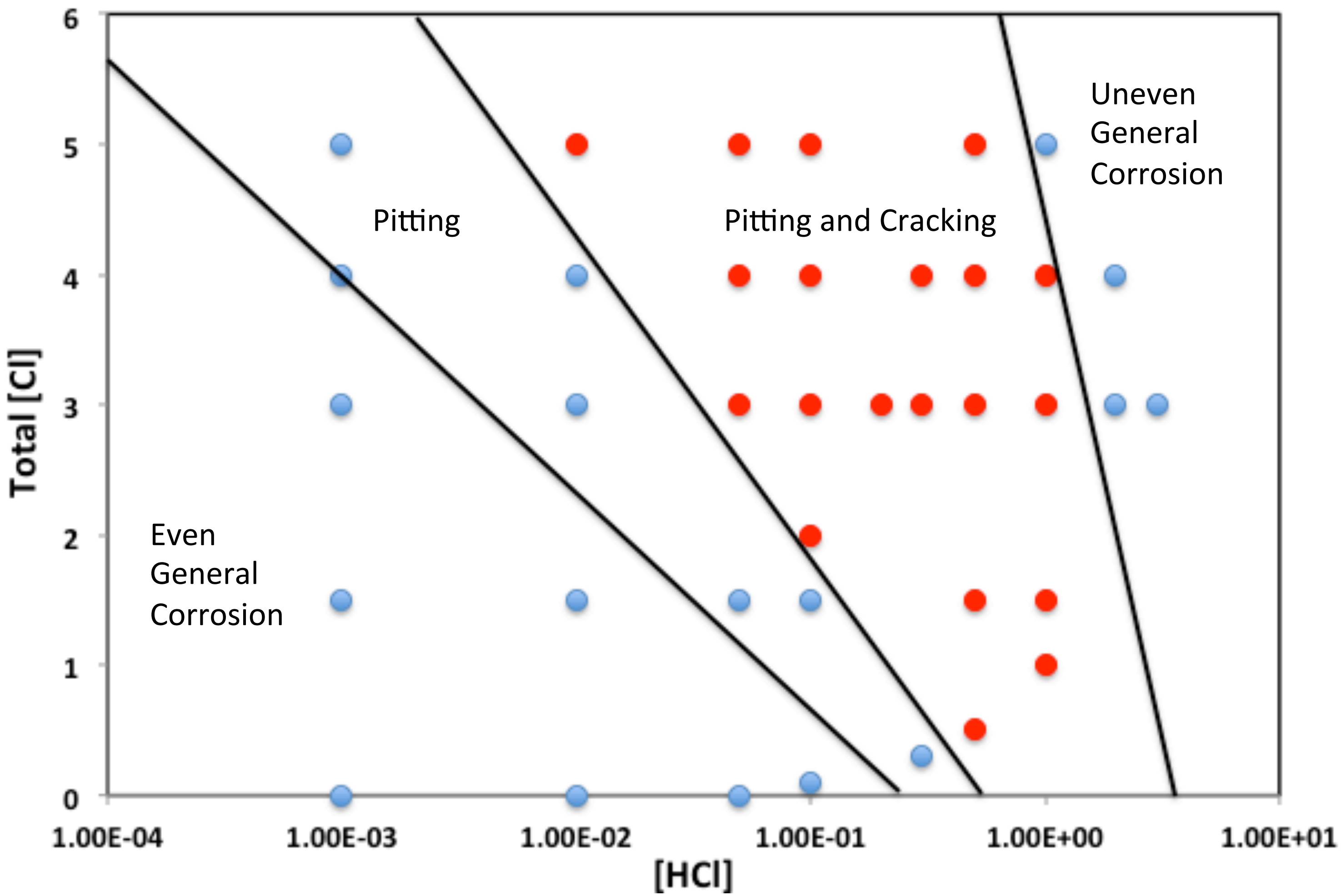


E_{pit} is the potential above which pitting can occur.
Increasing [Cl^-] decreases E_{pit}.
Weld oxides can lower E_{pit} with respect to base metal.

E_{pass} is the passivation potential. The metal is passsivated above this potential by an electrochemical produced oxide.
Decreasing the pH tends to increase E_{pass}.

Cathodic curves can be mass-transport limited at low oxidant concentrations. As the concentration decreases the limiting current decreases.

Significance of Cl on the surface



Influence of droplet size and thickness

J. Jiang et al. / Electrochimica Acta 54 (2009) 3623–3629

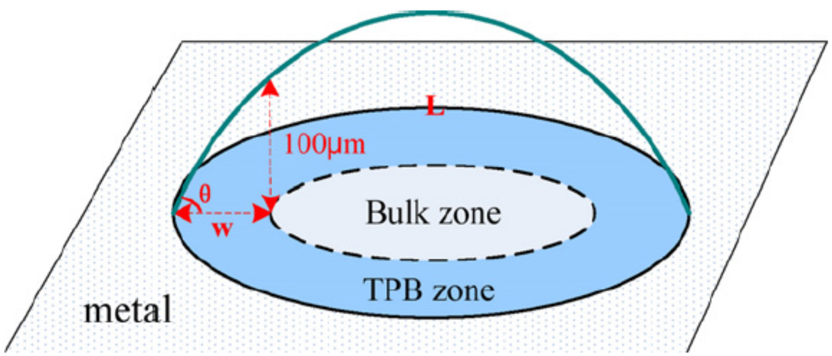


Fig. 3. The geometry of an electrolyte droplet attached on a planar metal surface.

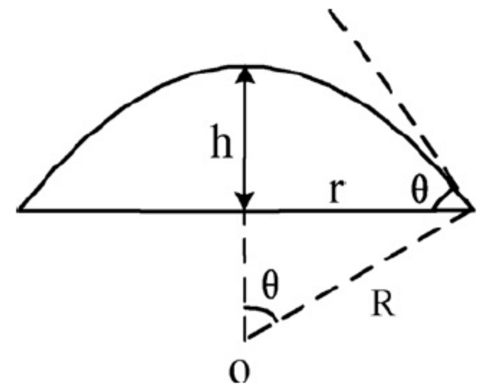


Fig. 5. The geometry of droplet.

J. Jiang et al. / Electrochimica Acta 54 (2009) 1426–1435

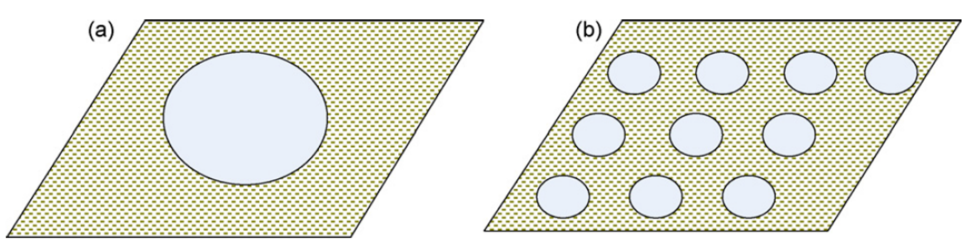


Fig. 21. Geometry of the droplet on a metal surface.

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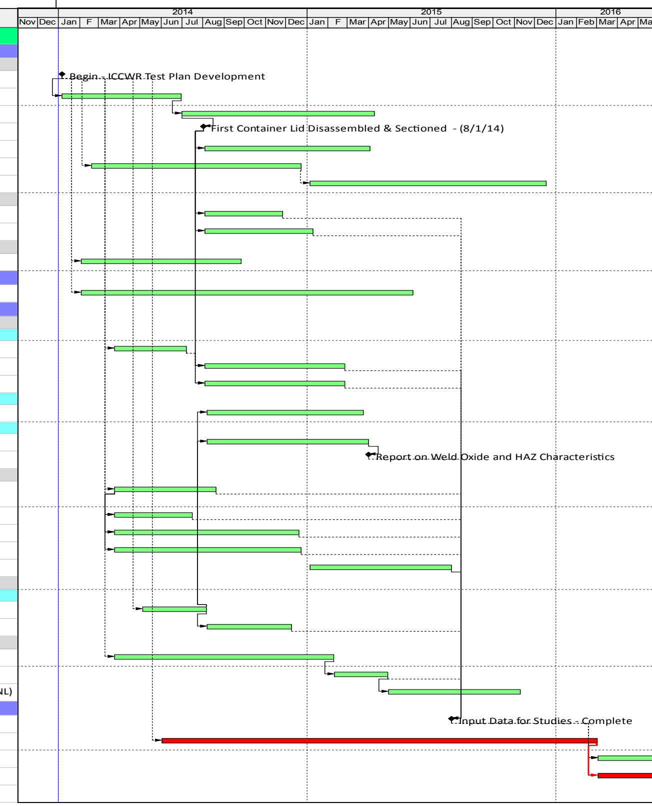
Major Plan Components

- Evaluate the extent of ICCWR corrosion in storage (DE).
- Determine crucial reactants and container surface properties needed for corrosion there.
  - DE samples and literature review.
- Run corrosion tests that vary the crucial conditions over realistic ranges to determine which might limit likelihood of SCC.
- Reproduce known corrosion of ICCWR and test whether it progresses to SCC under plausible storage conditions.

Initial Conceptual Schedule

SCC-2014-TP | Data Date: 01-Jan-14 | Run Date: 13-Mar-14 12:29

Activity ID	Activity Name	Original Duration	Start	Finish	Roles
SCC-2014-TP	**SCC 2014 Test Plan - Initial Conceptual Schedule**	1780.0d	06-Jan-14	04-Dec-20	
SCC-2014-TP.3.1	***DE Examination of ICCWR***	485.0d	06-Jan-14	18-Dec-15	
SCC-2014-TP.3.1.1	**Disassemble and Section IC Lids from FY-14 DE Containers**	485.0d	06-Jan-14	18-Dec-15	
TP10100	Begin - ICCWR Test Plan Development	0.0d	06-Jan-14*		
TP10200	Develop and Test New Lid Disassembly Method	123.0d	06-Jan-14	30-Jun-14	MICKALONIS JOHN (SRNL)
TP10300	Disassemble and Section IC Lids from FY-14 DE Containers	188.0d	01-Jul-14*	09-Apr-15	MICKALONIS JOHN (SRNL)
TP10400	First Container Lid Disassembled & Sectioned - (8/1/14)	0.0d		01-Aug-14	
TP10500	Low Magnification Examination of Full Circumference of ICCW Surface Area of All FY-14 DE Containers	161.0d	04-Aug-14	03-Apr-15	MICKALONIS JOHN (SRNL)
TP10600	Setup Confocal Microscope	214.0d	18-Feb-14*	23-Dec-14	MICKALONIS JOHN (SRNL)
TP10700	Confocal Microscope Examination of ICCWR from DE Containers	241.0d	05-Jan-15*	18-Dec-15	MICKALONIS JOHN (SRNL)
SCC-2014-TP.3.1.2	**Measure Surface Cl Contamination of Sections from the IC**	103.0d	04-Aug-14	09-Jan-15	
TP10800	by Leaching and Ion Chromatography	80.0d	04-Aug-14	26-Nov-14	DUFFY JOHN (SRNL)
TP10900	by SEM / EDS	103.0d	04-Aug-14	09-Jan-15	MICKALONIS JOHN (SRNL)
SCC-2014-TP.3.1.3	**Develop ICCWR Sampling Plan**	166.0d	03-Feb-14	26-Sep-14	
TP11000	Develop ICCWR Sampling Plan	166.0d	03-Feb-14*	26-Sep-14	KELLY ELIZABETH J
SCC-2014-TP.3.2	***IC Breach Detection Methods***	332.0d	03-Feb-14	05-Jun-15	
TP11100	Evaluate Use of Gas Analysis of Inner and Outer Containers to Indicate Leakage Prior to DE	332.0d	03-Feb-14*	05-Jun-15	DUFFY JOHN (SRNL)
SCC-2014-TP.3.3	***Characterize Corrosion Environment***	410.0d	24-Mar-14	09-Nov-15	
SCC-2014-TP.3.3.1	**ICCWR Surface Characterization**	252.0d	24-Mar-14	01-Apr-15	
SCC-2014-TP.3.3.1.1	***Characterize the Weld Oxide of Selected DE Containers***	227.0d	24-Mar-14	25-Feb-15	
TP11200	Develop Protocol	74.0d	24-Mar-14*	07-Jul-14	DUQUE JUAN, MICKALONIS JOHN (SRNL)
TP11300	Perform Examinations NR Samples	134.0d	04-Aug-14	25-Feb-15	DUQUE JUAN
TP11400	Perform Examinations of Samples from DE	134.0d	04-Aug-14	25-Feb-15	MICKALONIS JOHN (SRNL)
SCC-2014-TP.3.3.1.2	***Assess the Degree of Sensitization for Samples Taken from IC Closure Welds During DE***	150.0d	07-Aug-14	24-Mar-15	
TP11500	Assess the Degree of Sensitization for Samples Taken from IC Closure Welds During DE	150.0d	07-Aug-14	24-Mar-15	MICKALONIS JOHN (SRNL)
SCC-2014-TP.3.3.1.3	***Potentiostatic Test in Chloride Bearing Solutions with Samples Taken from NR Hanford Con***	156.0d	07-Aug-14	01-Apr-15	
TP11600	Potentiostatic Test in Chloride Bearing Solutions with Samples Taken from NR Hanford Containers	156.0d	07-Aug-14	01-Apr-15	MICKALONIS JOHN (SRNL)
TP11700	Report on Weld Oxide and HAZ Characteristics	0.0d		01-Apr-15	
SCC-2014-TP.3.3.2	**Roles of Gaseous Components in IC Corrosion**	341.0d	24-Mar-14	31-Jul-15	
TP11800	Compile & Issue a Written Summary of the Levels of O2 and H2O Detected Initially & as a Function of Time	106.0d	24-Mar-14*	20-Aug-14	DUFFY JOHN (SRNL), NARLESKY JOSHUA E, VEIRS DOUGLAS K
TP11900	Design & Conduct Experiment to Detect the Rate & Form of Chlorine Transport from Impure PuO2 to the ICCWR Surface	81.0d	24-Mar-14*	16-Jul-14	NARLESKY JOSHUA E
TP12000	Document Literature Survey on Role of Gasses	188.0d	24-Mar-14*	19-Dec-14	JOYCE STEPHEN A, BERG JOHN M
TP12910	Perform NR Small Scale Experiments to Test Gas Effects on Corrosion	191.0d	24-Mar-14*	23-Dec-14	DUQUE JUAN
TP12920	Deposit Chlorine on Test Weld Samples & Determine Chemical Form	146.0d	05-Jan-15*	31-Jul-15	JOYCE STEPHEN A
SCC-2014-TP.3.3.3	**Determine Residual Stress in ICCWR**	150.0d	05-May-14	09-Dec-14	
SCC-2014-TP.3.3.3.1	***Measure Residual Stress in Samples of ICCWR of a Hanford Container Non-Rad (NR)***	150.0d	05-May-14	09-Dec-14	
TP12100	Measure Residual Stress in Samples of ICCWR of a Hanford Container Non-Rad (NR)	66.0d	05-May-14*	06-Aug-14	STROUD MARY A
TP12200	Vendor Performs Analysis and Issues Report on Results	84.0d	07-Aug-14	09-Dec-14	STROUD MARY A
SCC-2014-TP.3.3.4	**Wall Temperature and Condensation**	406.0d	24-Mar-14	09-Nov-15	
TP12300	Develop a Model for Temperature Gradients using Thermal Conductivity from Oxide to ICCWR	216.0d	24-Mar-14*	09-Feb-15	HENSEL STEVE (SRNL)
TP12400	Estimate RH of Gas in Contact with ICCWR	56.0d	10-Feb-15	29-Apr-15	BERG JOHN M
TP12500	Develop Conceptual Designs for Tests of Condensation	134.0d	30-Apr-15	09-Nov-15	JOYCE STEPHEN A, MICKALONIS JOHN (SRNL)
SCC-2014-TP.5	***Shelf Life Studies***	1678.0d	02-Jun-14	04-Dec-20	
TP12550	Input Data for Studies - Complete	0.0d		31-Jul-15	
TP12600	Develop and Run Prototype Tests of Corrosion Test Specimens and Test Apparatus	428.0d	02-Jun-14*	02-Mar-16	VEIRS DOUGLAS K, DUFFY JOHN (SRNL)
TP12700	Use Specimens to Developed Above in Small-Scale Studies with PuO2/Salt Material at Bounding Conditions (Short Term	454.0d	03-Mar-16	05-Jan-18	NARLESKY JOSHUA E
TP12800	Use Specimens Developed Above in Small-Scale Studies with PuO2/Salt Material at Bounding Conditions (Long Term)	1183.0d	03-Mar-16	04-Dec-20	DUFFY JOHN (SRNL)
TP12900	ICCWR Test Plan Development Project - Complete	0.0d		04-Dec-20	



Actual Work — Critical Remaining Work — Remaining Work — ◆ Milestone

Appendix C: SCC 2014 Test Plan - Initial Conceptual Schedule

Primavera Systems, Inc.

Los Alamos NATIONAL LABORATORY EST. 1943

NNSA

Initial Conceptual Schedule

SCC-2014-TP

Activity ID	Activity Name	Original Duration	Start	Fi
SCC-2014-TP	**SCC 2014 Test Plan - Initial Conceptual Schedule**	1780.0d	06-Jan-14	04
SCC-2014-TP.3.1	***DE Examination of ICCWR***	485.0d	06-Jan-14	1
SCC-2014-TP.3.1.1	**Disassemble and Section IC Lids from FY-14 DE Containers**	485.0d	06-Jan-14	1
TP10100	Begin - ICCWR Test Plan Development	0.0d	06-Jan-14*	
TP10200	Develop and Test New Lid Disassembly Method	123.0d	06-Jan-14	3
TP10300	Disassemble and Section IC Lids from FY-14 DE Containers	188.0d	01-Jul-14*	0
TP10400	First Container Lid Disassembled & Sectioned - (8/1/14)	0.0d		0
TP10500	Low Magnification Examination of Full Circumference of ICCW Surface Area of All FY-14 DE Containers	161.0d	04-Aug-14	0
TP10600	Setup Confocal Microscope	214.0d	18-Feb-14*	2
TP10700	Confocal Microscope Examination of ICCWR from DE Containers	241.0d	05-Jan-15*	1
SCC-2014-TP.3.1.2	**Measure Surface Cl Contamination of Sections from the IC**	103.0d	04-Aug-14	0
TP10800	by Leaching and Ion Chromatography	80.0d	04-Aug-14	2
TP10900	by SEM / EDS	103.0d	04-Aug-14	0
SCC-2014-TP.3.1.3	**Develop ICCWR Sampling Plan**	166.0d	03-Feb-14	2
TP11000	Develop ICCWR Sampling Plan	166.0d	03-Feb-14*	2
SCC-2014-TP.3.2	***IC Breach Detection Methods***	332.0d	03-Feb-14	0
TP11100	Evaluate Use of Gas Analysis of Inner and Outer Containers to Indicate Leakage Prior to DE	332.0d	03-Feb-14*	0
SCC-2014-TP.3.3	***Characterize Corrosion Environment***	410.0d	24-Mar-14	0

Initial Conceptual Schedule

SCC-2014-TP.3.3 Characterize Corrosion Environment	
SCC-2014-TP.3.3.1 ICCWR Surface Characterization	
SCC-2014-TP.3.3.1.1 Characterize the Weld Oxide of Selected DE Containers	
TP11200	Develop Protocol
TP11300	Perform Examinations NR Samples
TP11400	Perform Examinations of Samples from DE
SCC-2014-TP.3.3.1.2 Assess the Degree of Sensitization for Samples Taken from IC Closure Welds During DE	
TP11500	Assess the Degree of Sensitization for Samples Taken from IC Closure Welds During DE
SCC-2014-TP.3.3.1.3 Potentiostatic Test in Chloride Bearing Solutions with Samples Taken from NR Hanford Co	
TP11600	Potentiostatic Test in Chloride Bearing Solutions with Samples Taken from NR Hanford Containers
TP11700	Report on Weld Oxide and HAZ Characteristics
SCC-2014-TP.3.3.2 Roles of Gaseous Components in IC Corrosion	
TP11800	Compile & Issue a Written Summary of the Levels of O2 and H2O Detected Initially & as a Function of Time
TP11900	Design & Conduct Experiment to Detect the Rate & Form of Chlorine Transport from Impure PuO2 to the ICCWR Surf
TP12000	Document Literature Survey on Role of Gasses
TP12910	Perform NR Small Scale Experiments to Test Gas Effects on Corrosion
TP12920	Deposit Chlorine on Test Weld Samples & Determine Chemical Form
SCC-2014-TP.3.3.3 Determine Residual Stress in ICCWR	
SCC-2014-TP.3.3.3.1 Measure Residual Stress in Samples of ICCWR of a Hanford Container Non-Rad (NR)	
TP12100	Measure Residual Stress in Samples of ICCWR of a Hanford Container Non-Rad (NR)
TP12200	Vendor Performs Analysis and Issues Report on Results
SCC-2014-TP.3.3.4 Wall Temperature and Condensation	
TP12300	Develop a Model for Temperature Gradients using Thermal Conductivity from Oxide to ICCWR
TP12400	Estimate RH of Gas in Contact with ICCWR
TP12500	Develop Conceptual Designs for Tests of Condensation

Initial Conceptual Schedule

SCC-2014-TP.3.3.3 Determine Residual Stress in ICCWR	
SCC-2014-TP.3.3.3.1 Measure Residual Stress in Samples of ICCWR of a Hanford Cc	
TP12100	Measure Residual Stress in Samples of ICCWR of a Hanford Container Non-Rad (NR)
TP12200	Vendor Performs Analysis and Issues Report on Results
SCC-2014-TP.3.3.4 Wall Temperature and Condensation	
TP12300	Develop a Model for Temperature Gradients using Thermal Conductivity from Oxide t
TP12400	Estimate RH of Gas in Contact with ICCWR
TP12500	Develop Conceptual Designs for Tests of Condensation
SCC-2014-TP.5 Shelf Life Studies	
TP12550	Input Data for Studies - Complete
TP12600	Develop and Run Prototype Tests of Corrosion Test Specimens and Test Apparatus
TP12700	Use Specimens to Developed Above in Small-Scale Studies with PuO2/Salt Material
TP12800	Use Specimens Developed Above in Small-Scale Studies with PuO2/Salt Material at E
TP12900	ICCWR Test Plan Development Project - Complete

Slides for talk on specific tasks (end of the day on Tuesday)

Outline of Tasks in Test Plan

- *DE Surveillance of Inner Container Surfaces in Closure Weld Region*
- *Additional DE Surveillance to Determine if the IC Has Been Breached*
- *Establish Crucial Characteristics of ICCWR and its Environment for Shelf Life Studies*
  - Investigation of welding alteration of container surface.
  - The roles of gaseous components in IC corrosion.
  - Determination of residual stress in IC closure weld samples.
  - Surface temperature of IC Closure Weld Region and its Effect on Liquid Phase.
- *Design and conduct small-scale corrosion experiments*
  - Sample and test vessel to duplicate crucial characteristics

Establish Crucial Characteristics of ICCWR and its Environment for Shelf Life Studies

- Characteristics to replicate in designing tests:
  - Welding alteration of container surface.
  - Residual stress in IC closure weld samples
  - Surface temperature of IC closure weld region
  - Chloride deposit form and surface density
- Characteristics to vary that may limit corrosion or restrict it to certain storage times or containers.
  - Presence and time-varying concentrations of an oxidizing gas.
  - Relative humidity to support aqueous layer.
  - Excursions in surface temperature of IC closure weld region with transport or changing storage location.

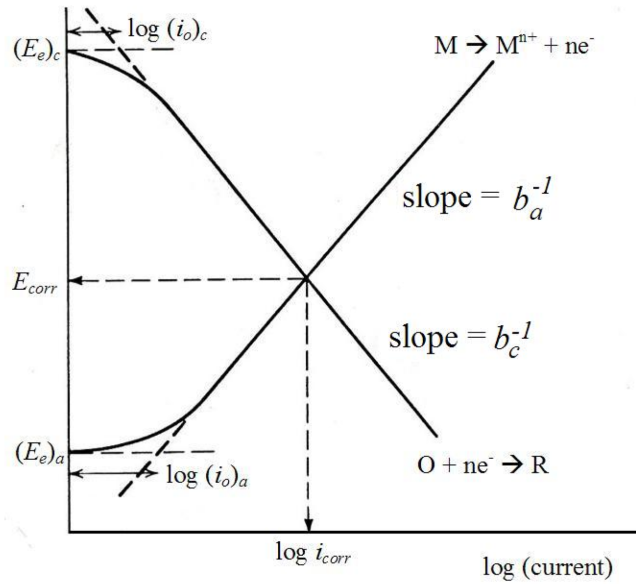
Design and conduct small-scale corrosion experiments

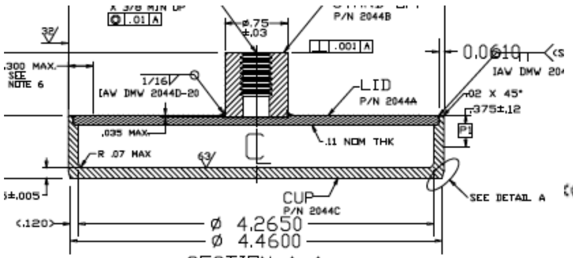
- Characteristics to replicate in sample:
  - Welding alteration of container surface.
  - Residual stress in IC closure weld samples
  - Chloride deposit form and surface density
- Design features of test vessel.
  - Ability to vary atmosphere.
  - Ability to control relative humidity.
  - Ability to control temperature.
  - Visual or other near real-time sample inspection capability.

Extra slides follow this

Factors promoting, localizing and possibly limiting corrosion at ICCWR

- Deposits and debris from oxidation of the container surface during the welding process.
- Sensitization to corrosion in the heat-affected zone (HAZ) from welding.
- Residual stresses from welding.
- Exposure to water vapor during storage.
- Potential for local condensation of water vapor due to possible cooler surface temperature.
- Cl-containing deposits on surface presumed to originate from deposition of a volatile, chloride-containing radiolysis product of chloride-containing impurities in the PuO_2.
- Exposure to gases that may act as oxidants in corrosion reactions (O_2 and possibly Cl_2 or HOCl).
- Constrained geometry between the lid and the container wall in the ICCWR.


log $(i_o)_c$
$(E_e)_c$
M → M^{n+} + ne^-
slope = b_a^{-1}
E_{corr}
slope = b_c^{-1}
$(E_e)_a$
log $(i_o)_a$
O + ne^- → R
log i_{corr}
log (current)



P/N 2044B
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1/16
IAW DMW 2044D-20
LID
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.02 X 45°
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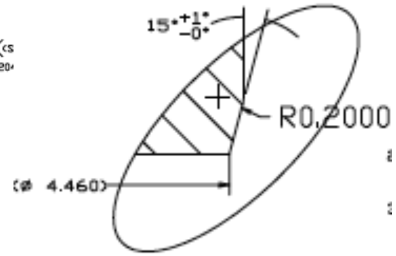

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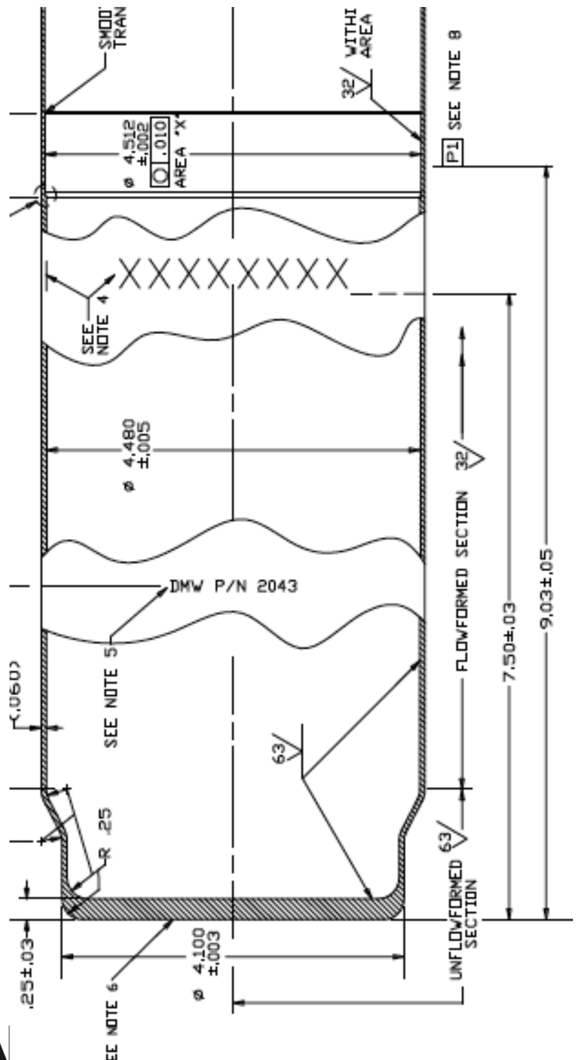
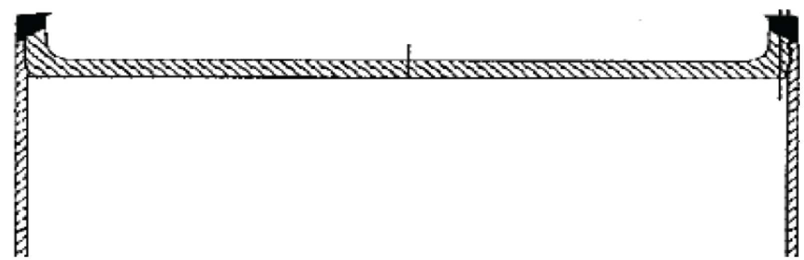
DETAIL A



SEE NOTE 8
ø 4.512 ±.002
AREA 'X'
XXXXXXXX
SEE NOTE 4
ø 4.480 ±.005
FLOWFORMED SECTION
DMW P/N 2043
SEE NOTE 5
7.50±.03
9.03±.05
R .25
UNFLOWFORMED SECTION
ø 4.100 ±.003
.25±.03
SEE NOTE 6



S. Joyce discussion points for Thurs.

Deposition and Characterization of Chlorine on Steel

- Issues: a) Chloride ions in solution known to facilitate localized corrosion of steels and b) chloride salt formation could lead to deliquescence at low RH.
- Need to characterize the amount and type of deposition.
  - Increasing [Cl^-] in solution by 1 order of magnitude lowers the pitting potential by ~150 mV.
  - Chemical form of chloride deposits would assist in determining the minimum RH required for the formation of an electrolytic solution required for corrosion.
- Expose steel coupons with characteristic weld oxide to either HCl or Cl_2 at several RHs and measure surface Cl using SEM/EDS and/or XPS (both give elemental amounts, XPS also gives chemical state information).
  - Ideally requires the results of the task to identify the chlorine-containing species to proceed.
  - Required for water condensation studies.

Water Condensation (I)

- Issue: The availability of water may be a limiting condition as the formation of a liquid-like film is necessary for localized corrosion. RH typically observed to decrease with time, suggesting corrosion could stop when RH drops. The minimum RH necessary for condensation is unknown.
- Influenced by the chemical and physical structure of the surface.
  - Chemical: Deliquescent salts
  - Physical: High porosity weld oxides which may support capillary condensation at lower RH than flat surfaces.

Water Condensation (II): Methods

- Gravimetric: Measure weight gain of steel sample (with weld oxide and chloride deposits) in a microbalance as a function of RH. Similar to previous experiments with salts.
- Electrochemical/Conductivity: Measure the corrosion current (or conductance) of steel electrodes (treated to form weld-like oxides and with chloride deposits) as function of RH. Similar to studies by Yang and Pabalan (MRS, 757 (2003)).
- Surface Area Measurements: Measure characteristic weld oxide surface areas using modified BET techniques. Does not directly measure water condensation, but gives indication of whether weld oxide has sufficient porosity to support condensation. Uses Kr or Xe instead of the conventional N_2 as sorbing gas. (Suzuki, Catalysis Surveys from Japan, 3, 109 (1999)).

Detecting Rate and Form of Chlorine Transport (I)

- Issues: a) Chloride ion known to promote localized corrosion of steel and b) Cl_2 is a potent oxidant and could support corrosion in the absence of O_2.
- Requirements:
  - Distinguishes between HCl and Cl_2.
  - Does not perturb gas generation (*e.g.* not consume or produce significant other species such as water vapor).
  - Operates at the relevant conditions.
  - Minimal interference issues (*i.e.* false positive / false negative).
- Integrating methods: Cl-containing species are captured by reaction or sorption on a substrate. (Daniel Rios reaction scheme)
  - Detection possible even at very low generation rates.
  - Potentially colorimetric (like Dräger tubes)

Detecting Rate and Form of Chlorine Transport (II)

- "Real-time" methods of detecting of Cl-containing species in the gas phase
- Optical spectroscopy
  - Potentially high specificity
  - Detection limits may be too high
- Solid state electrochemical methods such as used in commercial chlorine and HCl gas sensors
  - Sensitivities to 1 ppm (is this enough?)
  - Interferents can be significant

Status of Large-Scale Corrosion Containers

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

March 25, 2014

UNCLASSIFIED

Outline

- Overview
- Packaging Conditions (review)
- Storage Conditions (update)
- *In situ* Corrosion Observations
- DE of High Ca Container
- DE prioritization

- **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}?

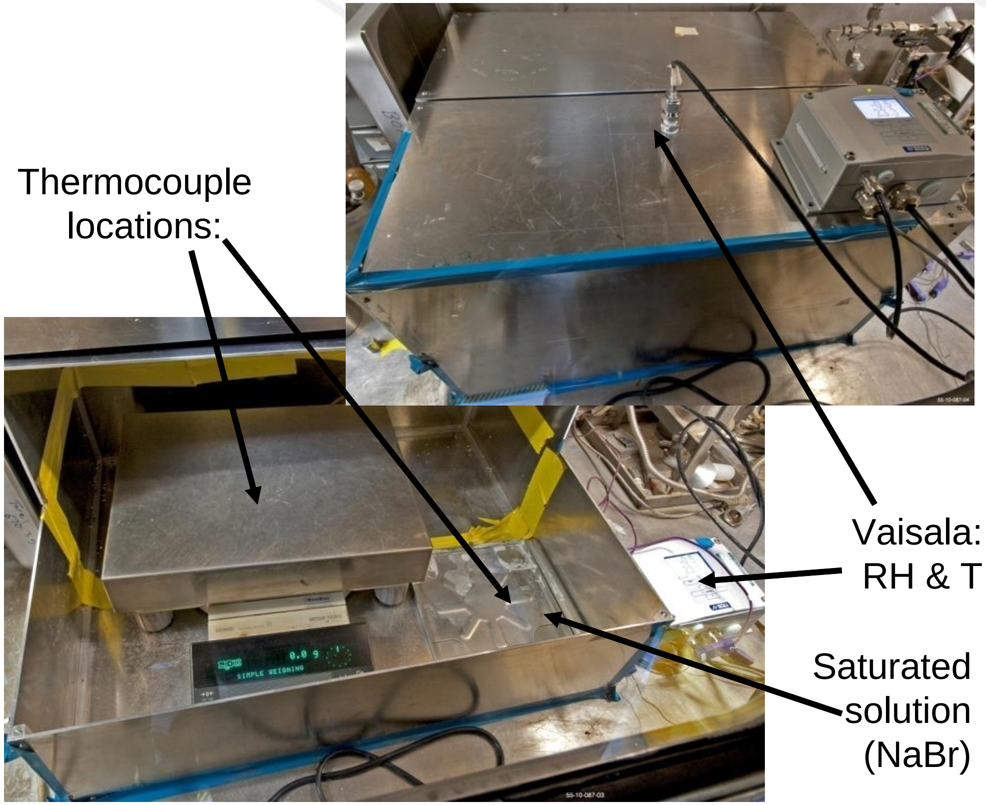
Overview

Material	Material Description	Comments
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)	Loaded: 8/2009
Base material	Scrap oxide from electrorefining process: ~14% Na/K Cl calcined in moist air (Does not have alkaline earth chloride)	Loaded: 9/2009 Completed DE: 9/2012
Low Ca	Base material + 0.34 wt% $KCaCl_3$ (0.28 wt% added moisture at 53% RH)	Loaded: 11/2009 Observed *in situ:* 5/2013
Low Mg	Base material + 0.34 wt% $KMgCl_3$ (0.28 wt% added moisture at 52% RH)	Loaded: 3/2010 Observed *in situ:* 4/2013
High Ca	Base material + 3.4 wt% $KCaCl_3$ (0.39 wt% added moisture at 30% RH)	Loaded: 8/2010 Completed DE: 3/2013
High Mg	Base material + 3.4 wt% $KMgCl_3$ (0.55 wt% added moisture at 8% RH)	Loaded: 9/2010 Observed *in situ:* 4/2013

Packaging Conditions (review)

- 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.

Storage Conditions (current)

Material	Age (mo.)	Storage RH_{max}	HS RH (%)	H_2 Trend	O_2 Gen. / times vented	O_2 Trend	DCB Trend	Corrosion: Supported / Observed
PMAXBS	56	49	0, —	↑	N / 0	0, —	Stable	No(1) / No observation
Base	36	37	0	—	N / 0	0, —	No data	No(1) / None in DE
Low Ca	52	49	15-17, ↓	↑	Y / 2*	↓	Yes†	Yes(2) / Obs. *in situ*
Low Mg	49	41	18-22, —	↑	Y / 1*	↑	Stable	No(1) / Obs. *in situ*
High Ca	31	18	15-18	↓	Y / 2	0, —	Yes	**Yes(2) / Obs. in DE**
High Mg	42	2	0, —	↑	Y / **7***	↓	No data	Never / None *in situ*

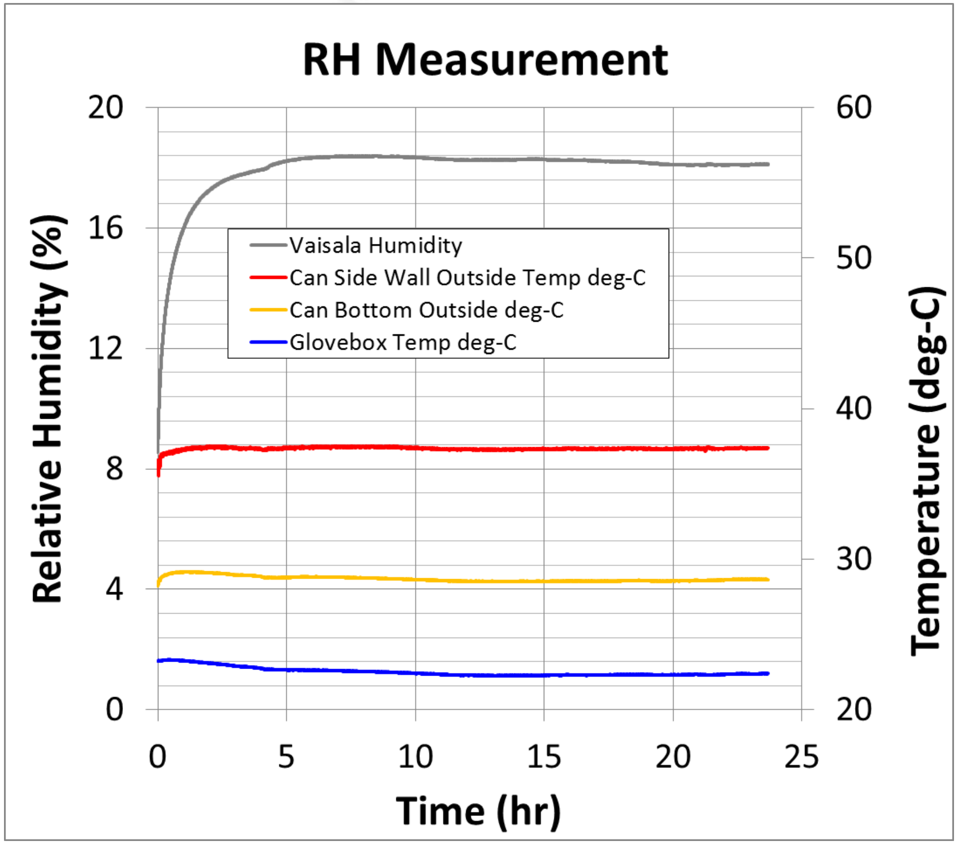
* Container opened for RH measurement, sensor replacement, and *in situ* corrosion observation
† Limited Data
(1) Corrosion supported at an earlier time in storage.
(2) Corrosion supported throughout storage until present time or time of DE

In Situ Observations

- Surfaces visible: upper half of container wall, burst disk, 3 tear drops, top of DCB, lid section, top of crevice specimen
- **Low Ca container & Low Mg container**
  - Corrosion observed at material-air interface
  - Walls dusty; did not appear to have corrosion
  - Burst disk clean/shiny
- **High Mg container**
  - Exposed portion of specimen was shiny
  - Container walls dusty, but did not appear corroded.

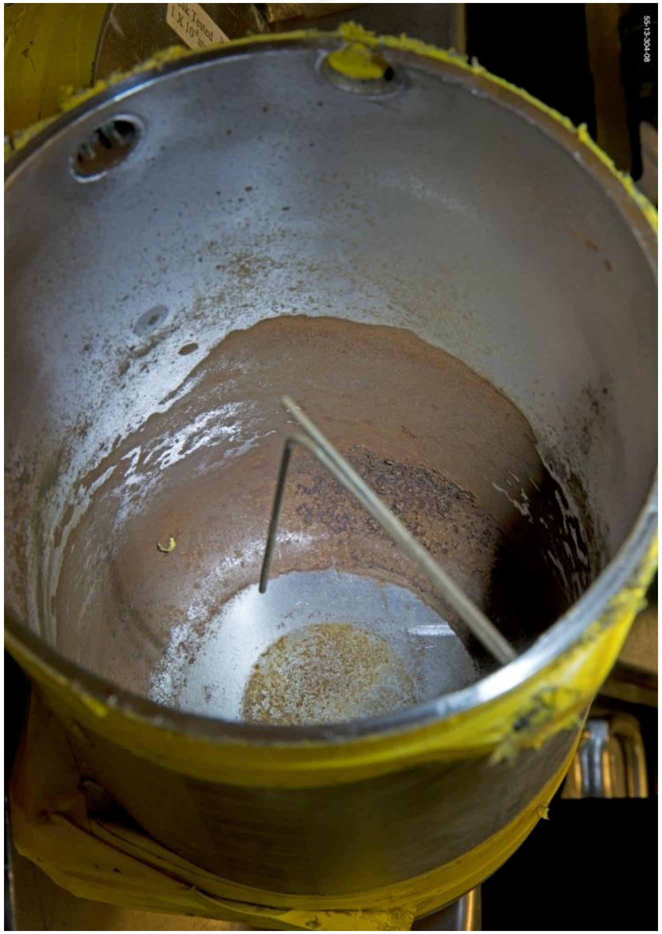
DE of High Ca Container

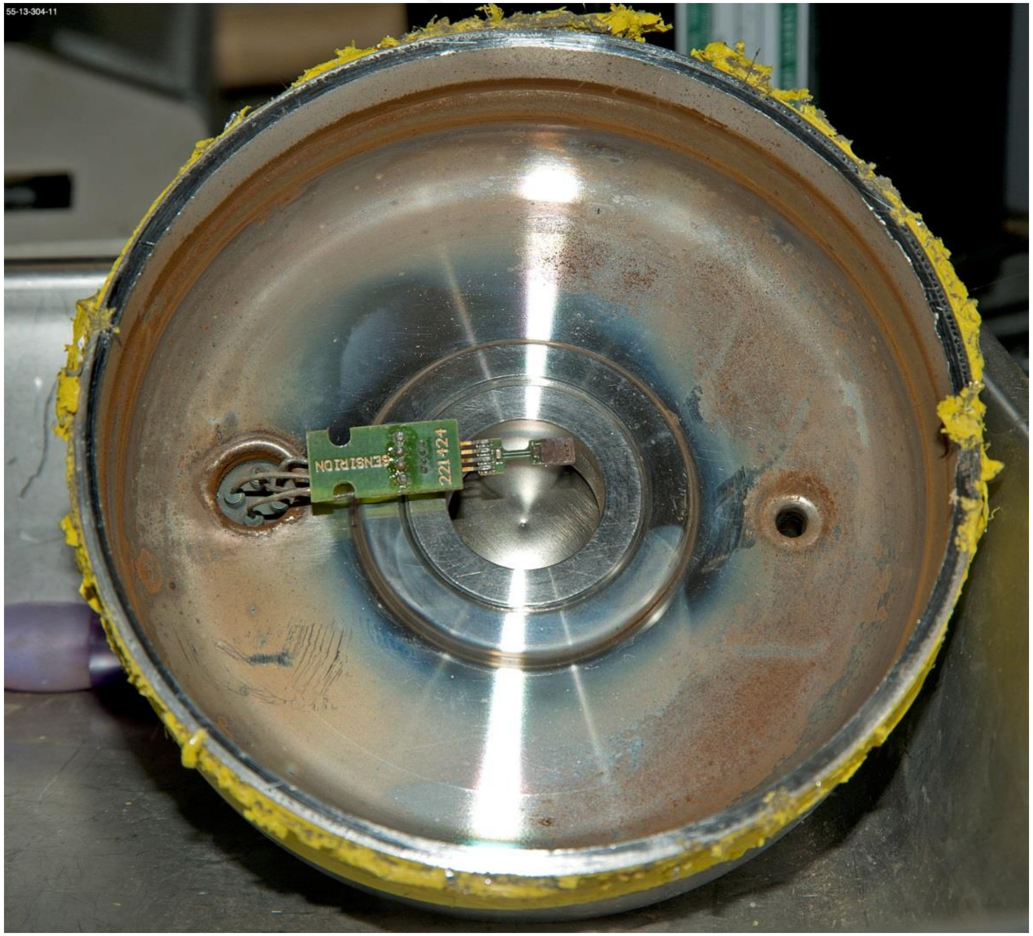
- RH measurement
  - Sensirion (insulated): 15.0% @ 41ºC
  - Vaisala (bare): 18.1% @ 24ºC
- Moisture Measurements
  - **Original:** (addition of moisture): 0.39 wt%
  - **DE:**
    - TGA: pending
    - 200°C moisture loss sample: 0.29 wt%
    - 200°C moisture loss (full batch heating): 0.17 wt%



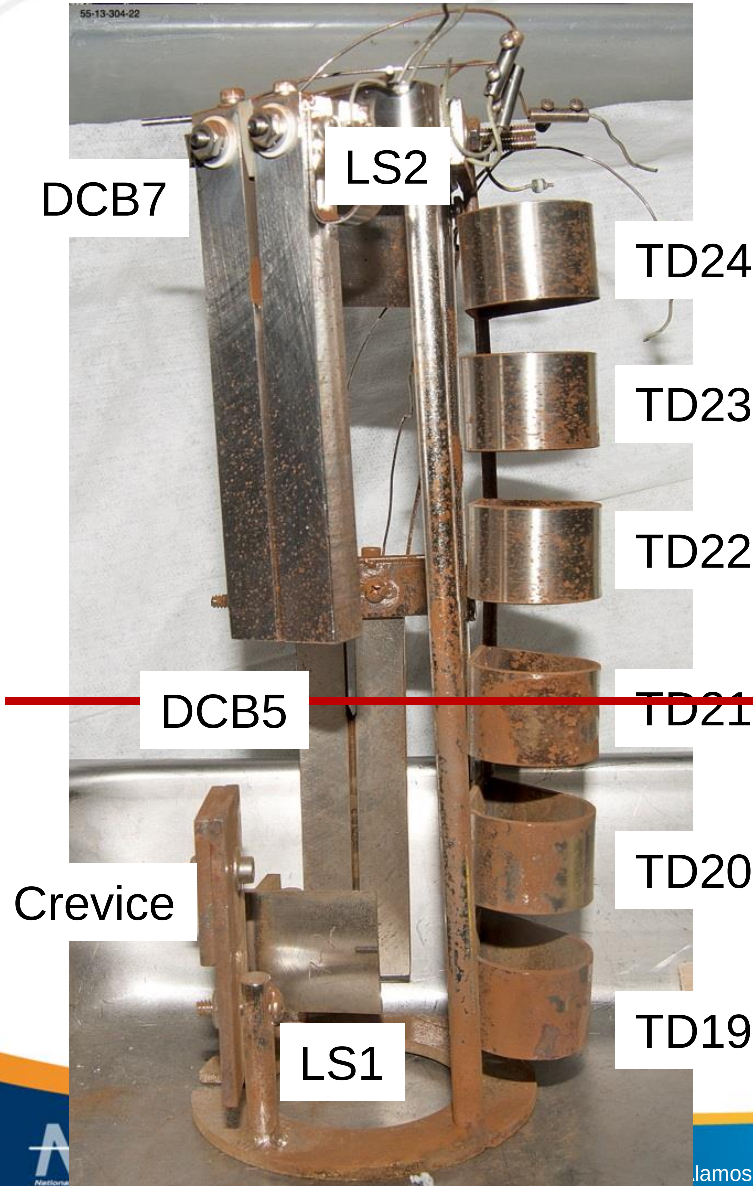
CL: 41.9ºC SW: 37.4ºC

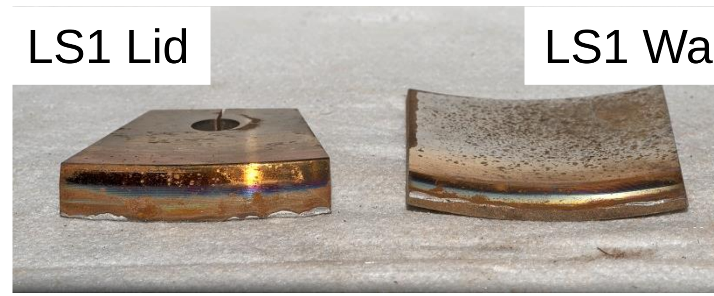
DE of High Ca Container





DE of High Ca Container

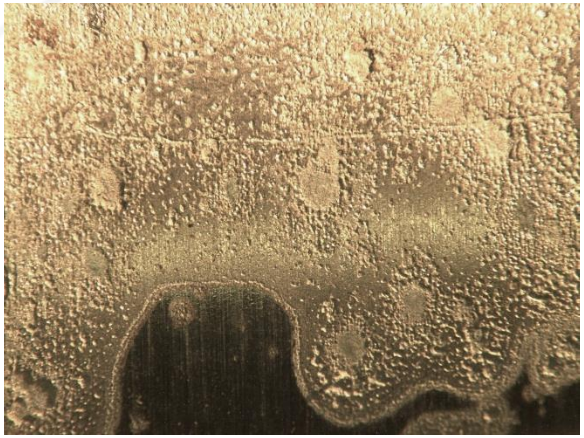


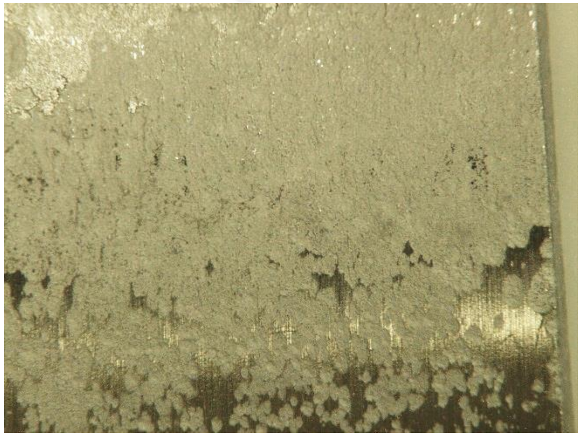


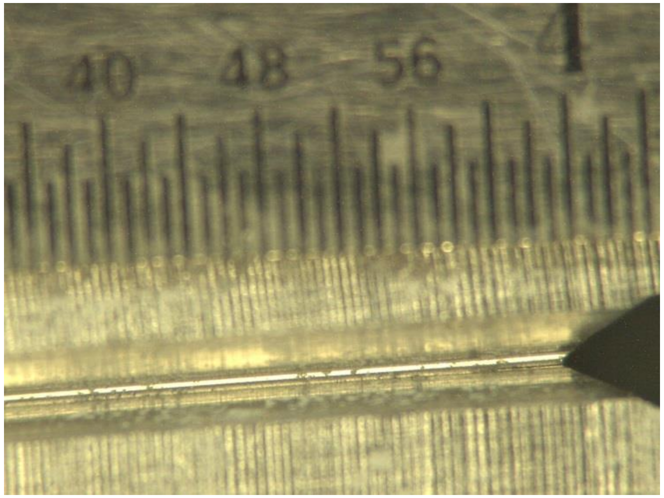
TD21

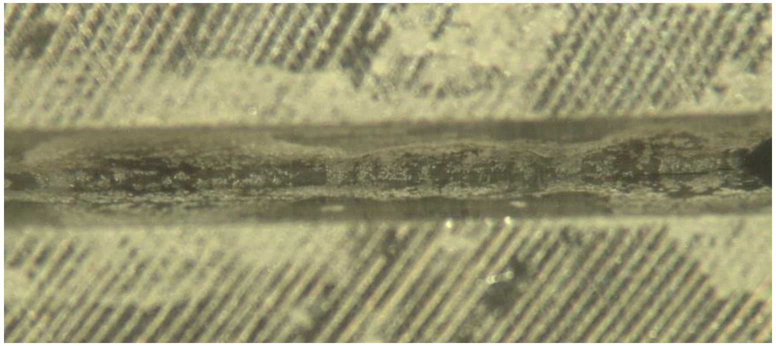
DE of High Ca Container

TD21
Pitting



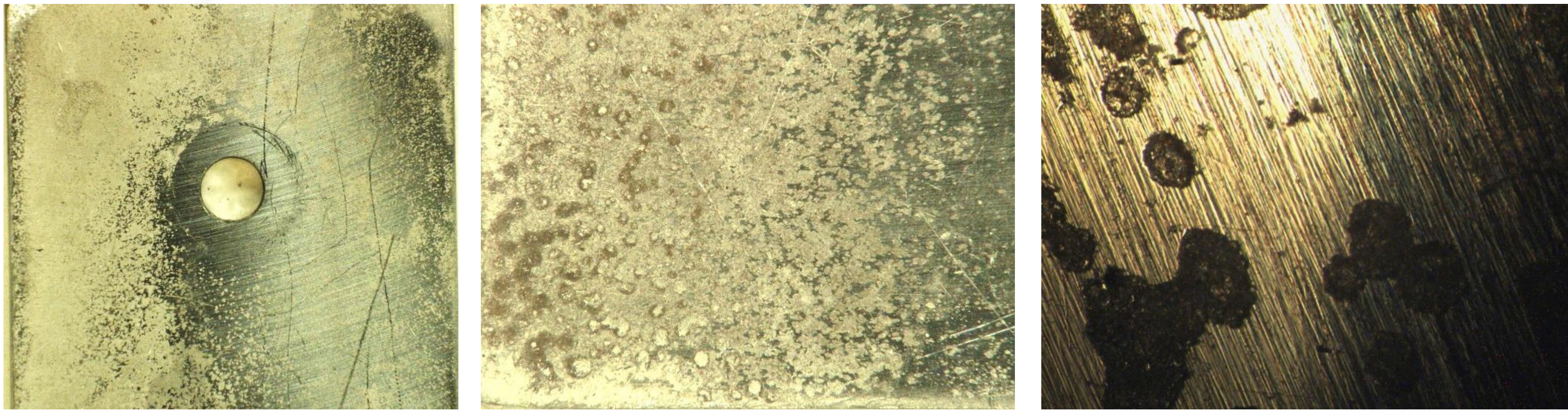


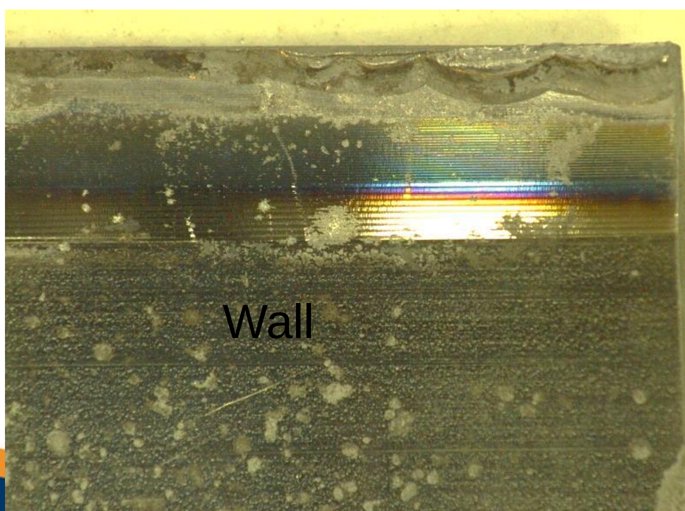


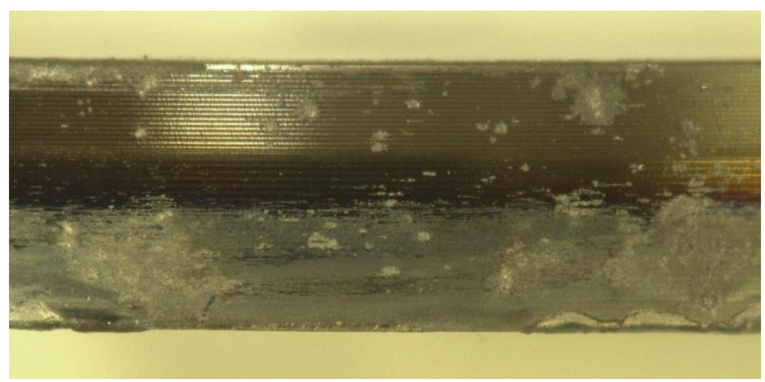


DE of High Ca Container

Pitting on outside of crevice specimen







Lid

Lid section specimen

Discussion of Future Plans

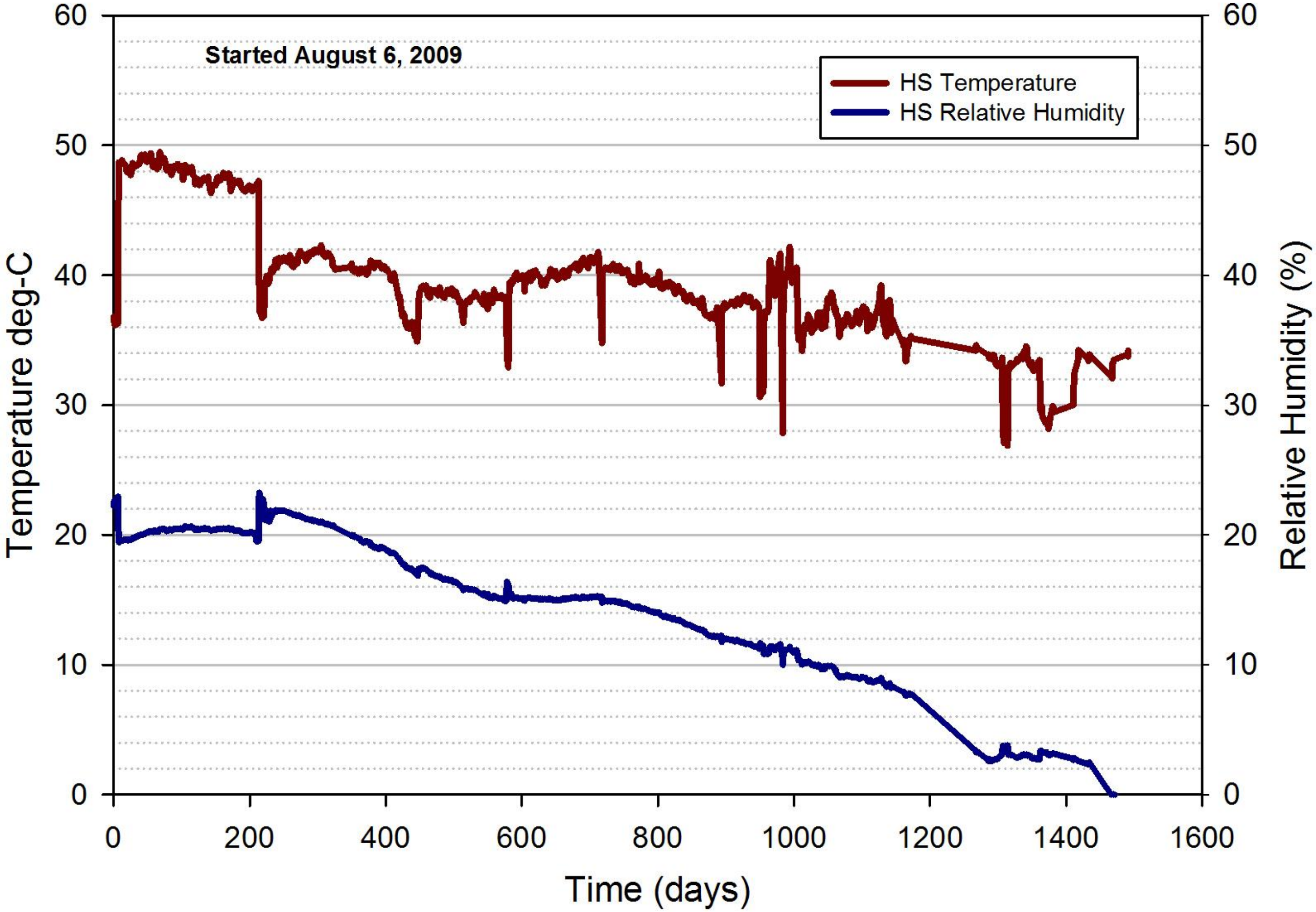
- Resume DE of High Ca Container
  - Measurement of residual stress on DCBs
  - Decontaminate TDs and perform measurement of pit dimensions with confocal microscope
  - Dye penetrant testing
  - Archive corrosion specimens
  - TGA measurement of final moisture
- Resume container DE
  - PMAXBS (0% RH)
  - High Mg: (no corrosion)
- Continued surveillance
  - Low Ca—Supports corrosion, so continue to monitor DCB data
  - Low Mg—Last RH measurement ~20% RH, but below DRH. However, this material may support production of HCl

Additional Slides

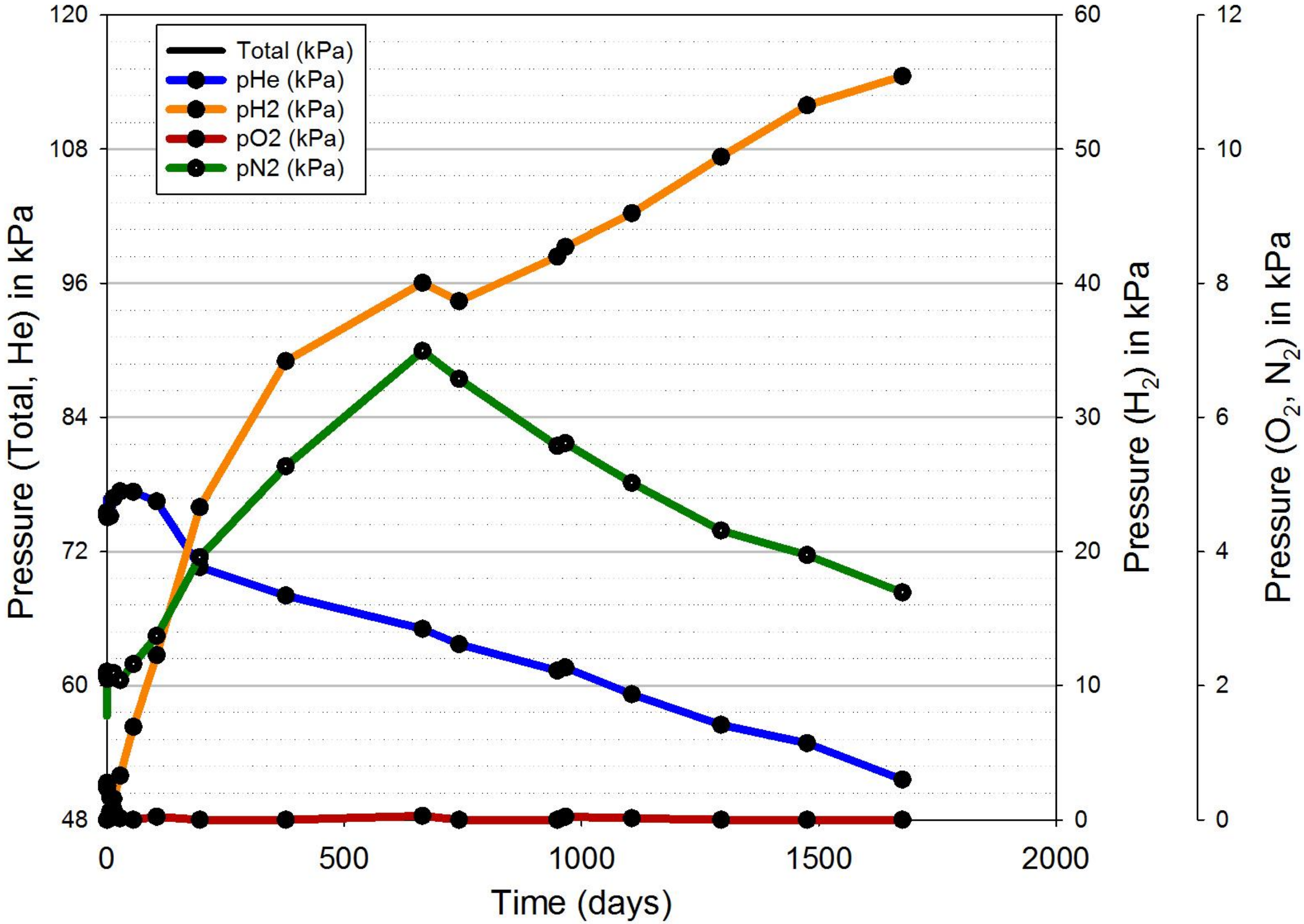
PMAXBS

- Loaded August 2009
- Moisture 0.09 wt%

PMAXBS (0.09 wt% H_2O)



PMAXBS (0.09 wt% H_2O)



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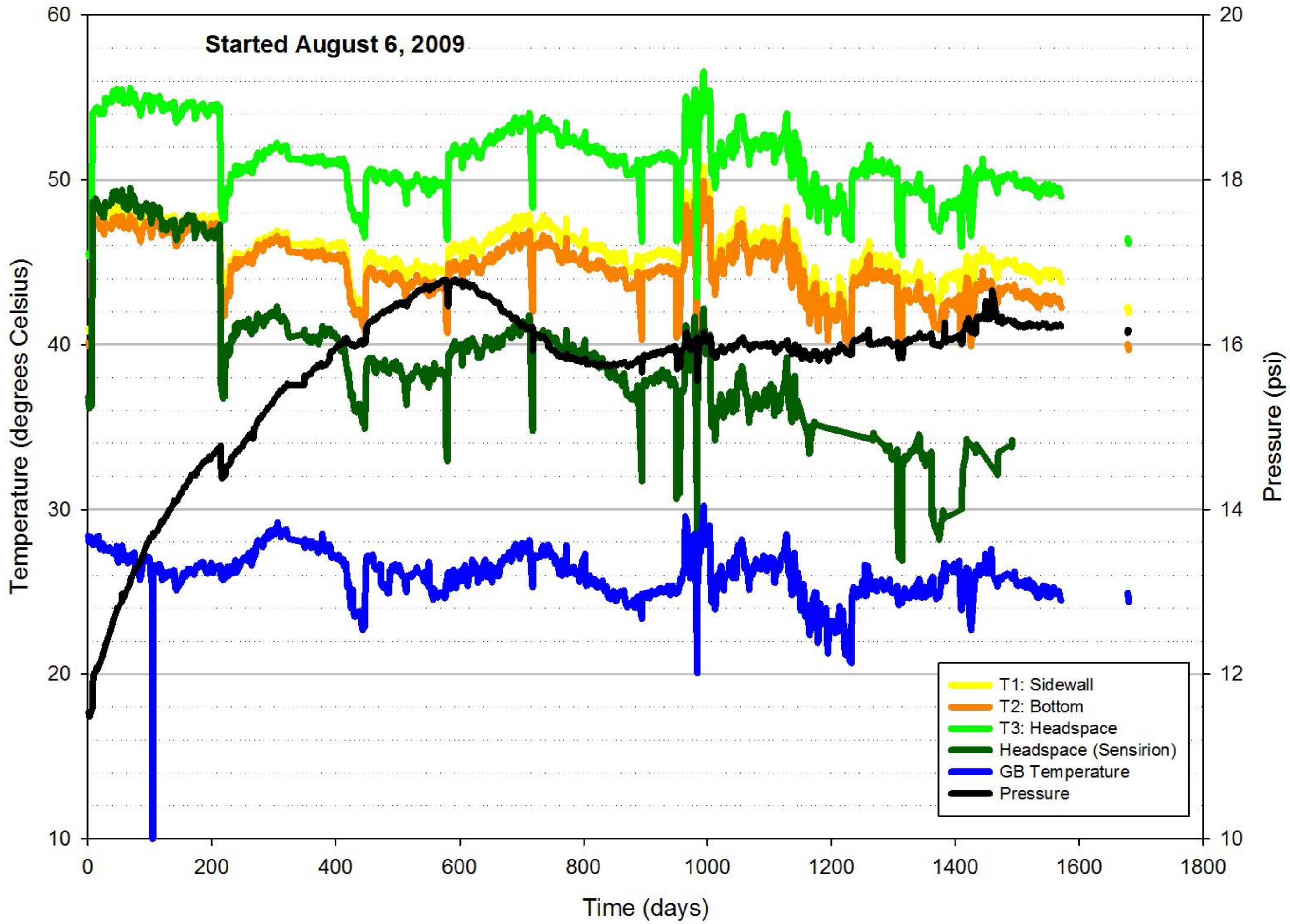
PMAXBS (0.09 wt% H_2O)



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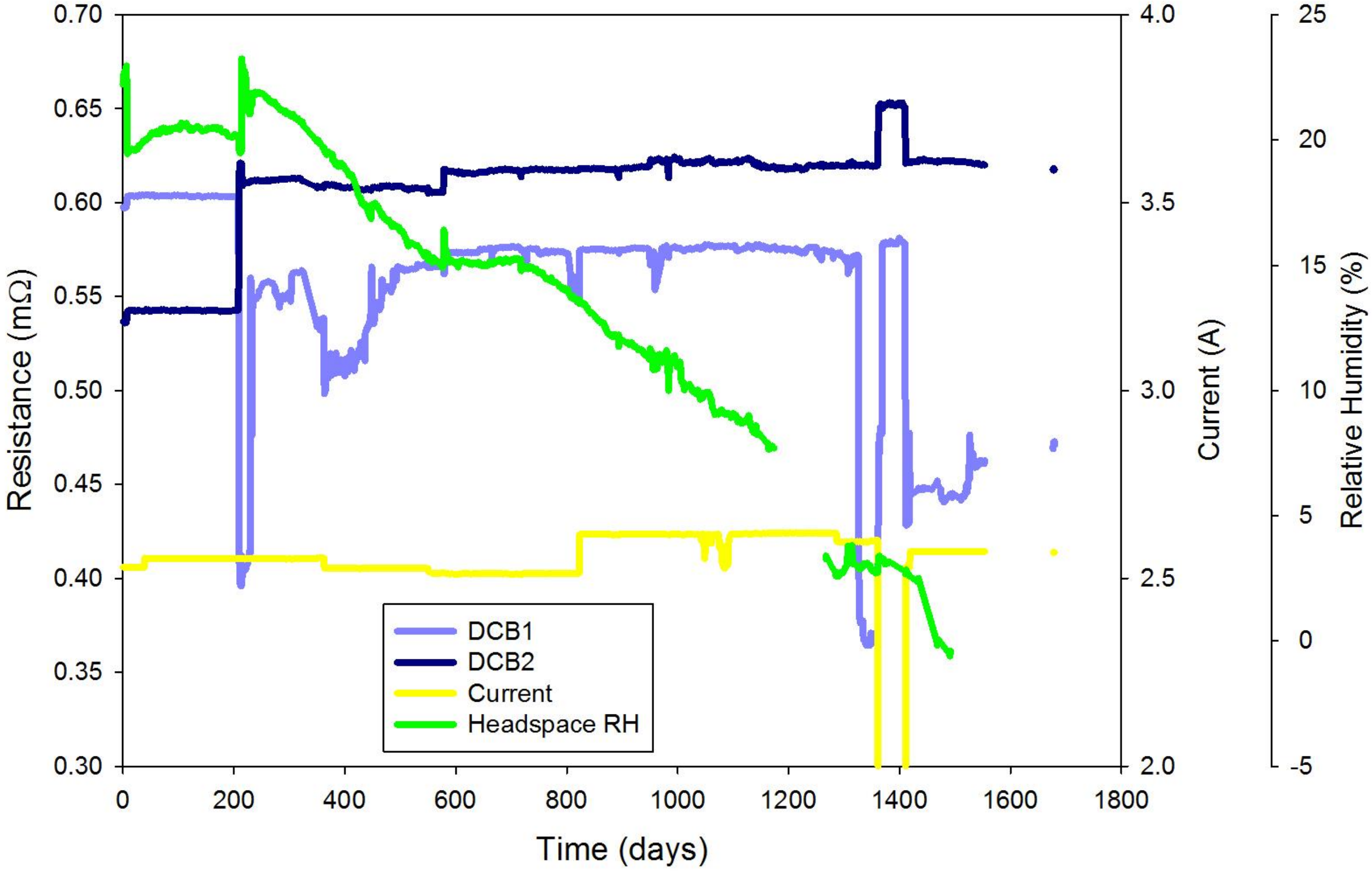
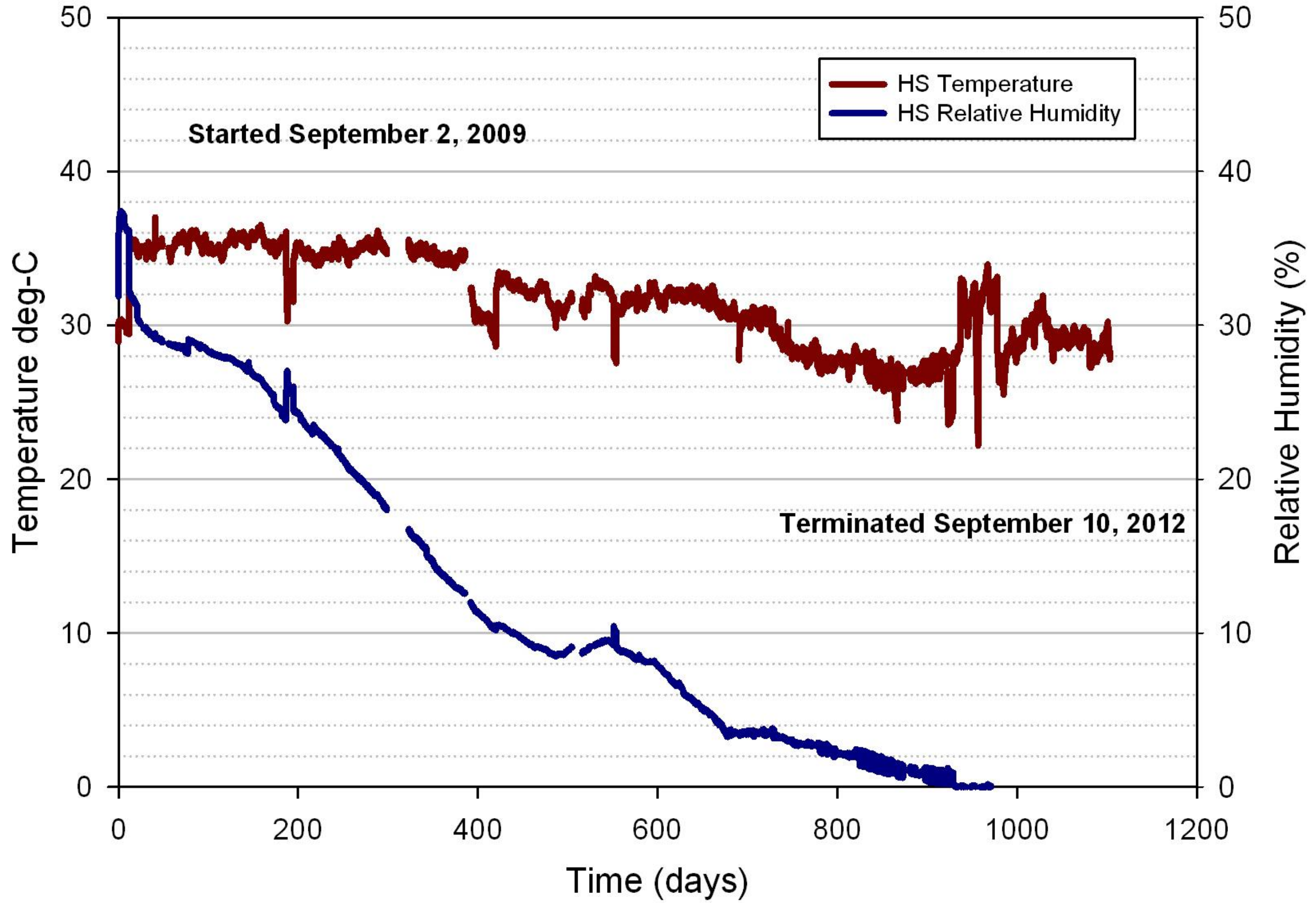
PMAXBS (0.09 wt% H_2O)



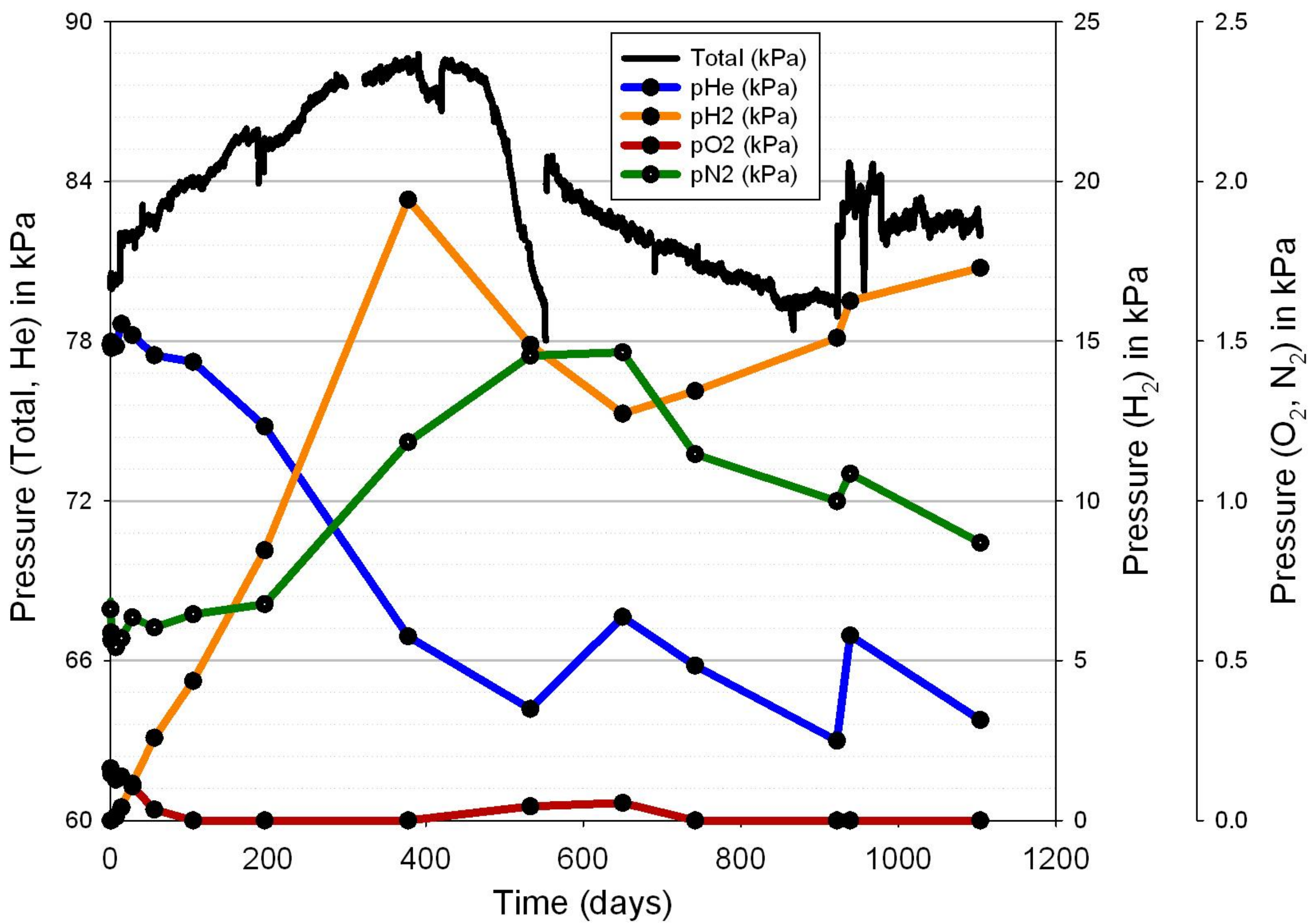
Base Material

- Loaded September 2009
- Moisture 0.05 wt%
- Unloaded September 2012

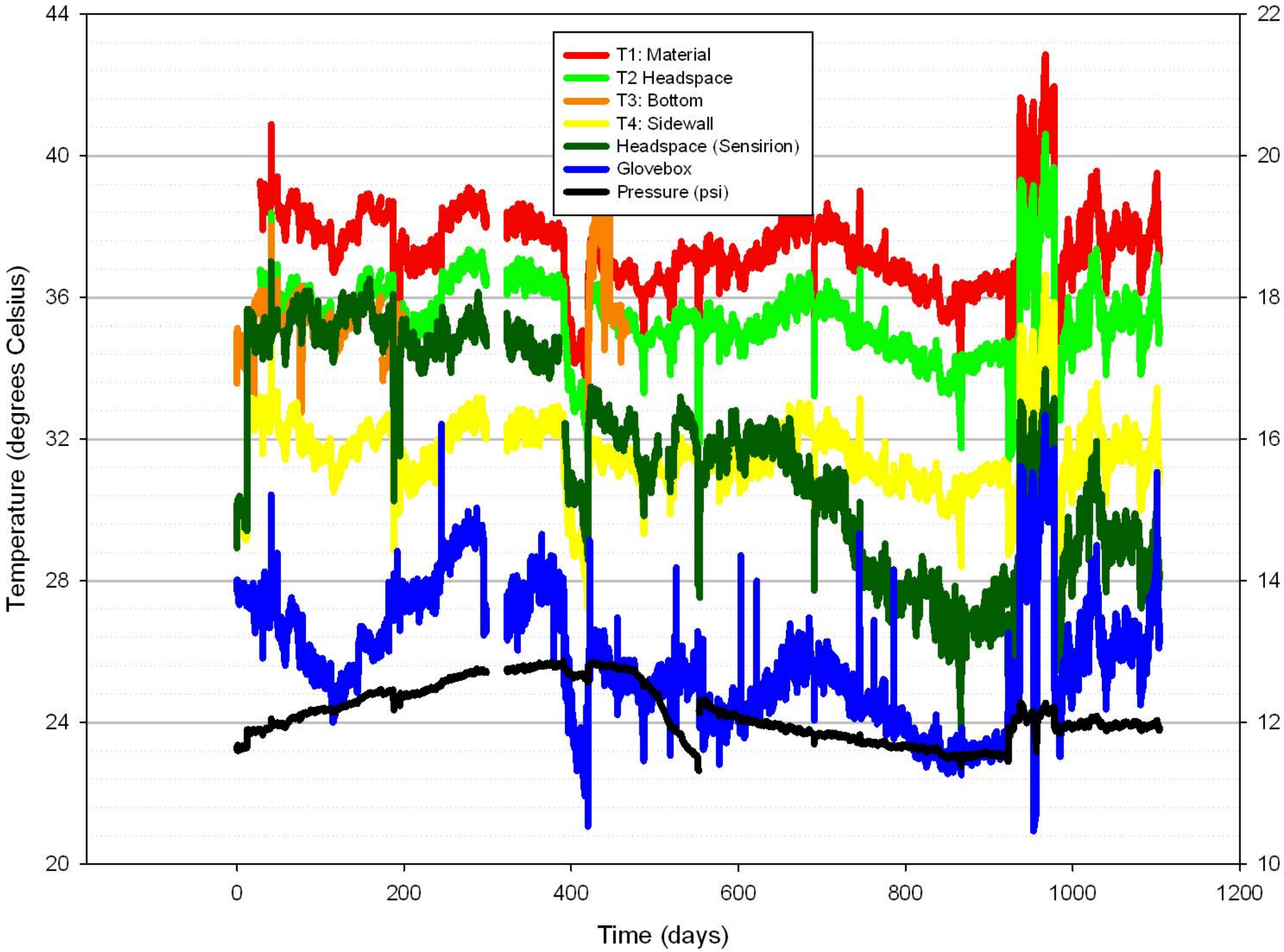
Base Material (0.05 wt% H_2O)



Base Material (0.05 wt% H_2O)



Base Material (0.05 wt% H_2O)



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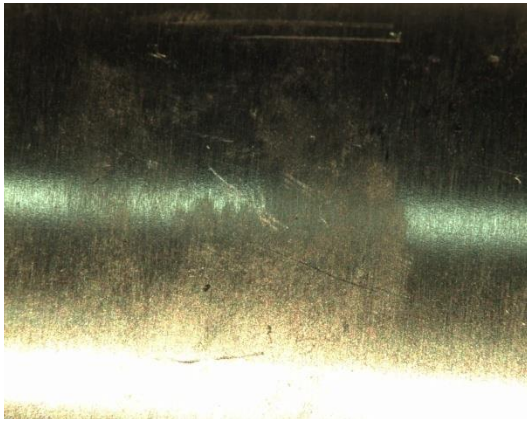
Base Material DE

- <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 DE

Headspace

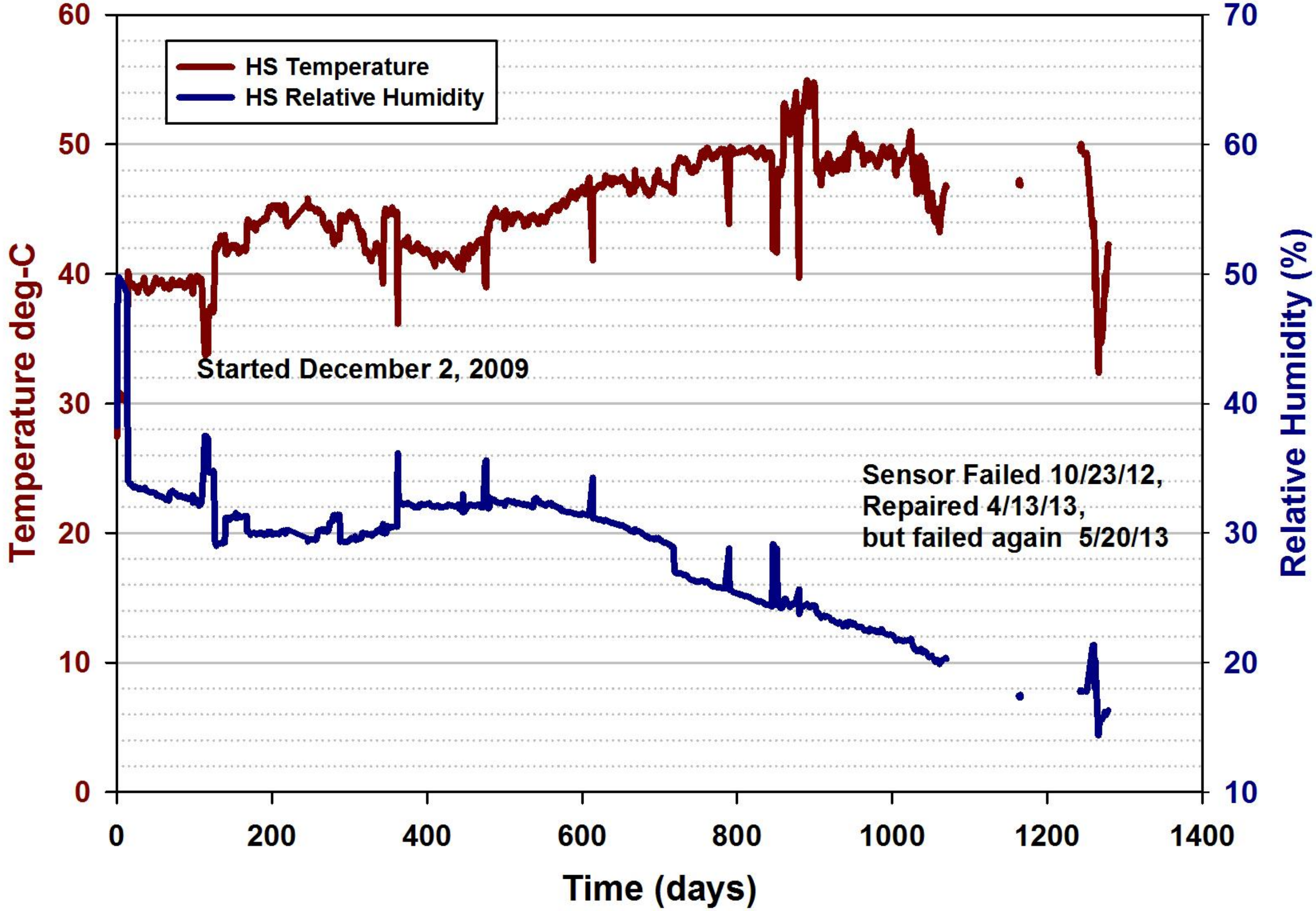

Material


Low Ca

- Loaded November 2009
- 0.33 wt% $KCaCl_3$ added to Base Material
- Moisture: 0.28 wt% (~7 waters of hydration on calcium chloride)

Low Ca (0.28 wt% H_2O)



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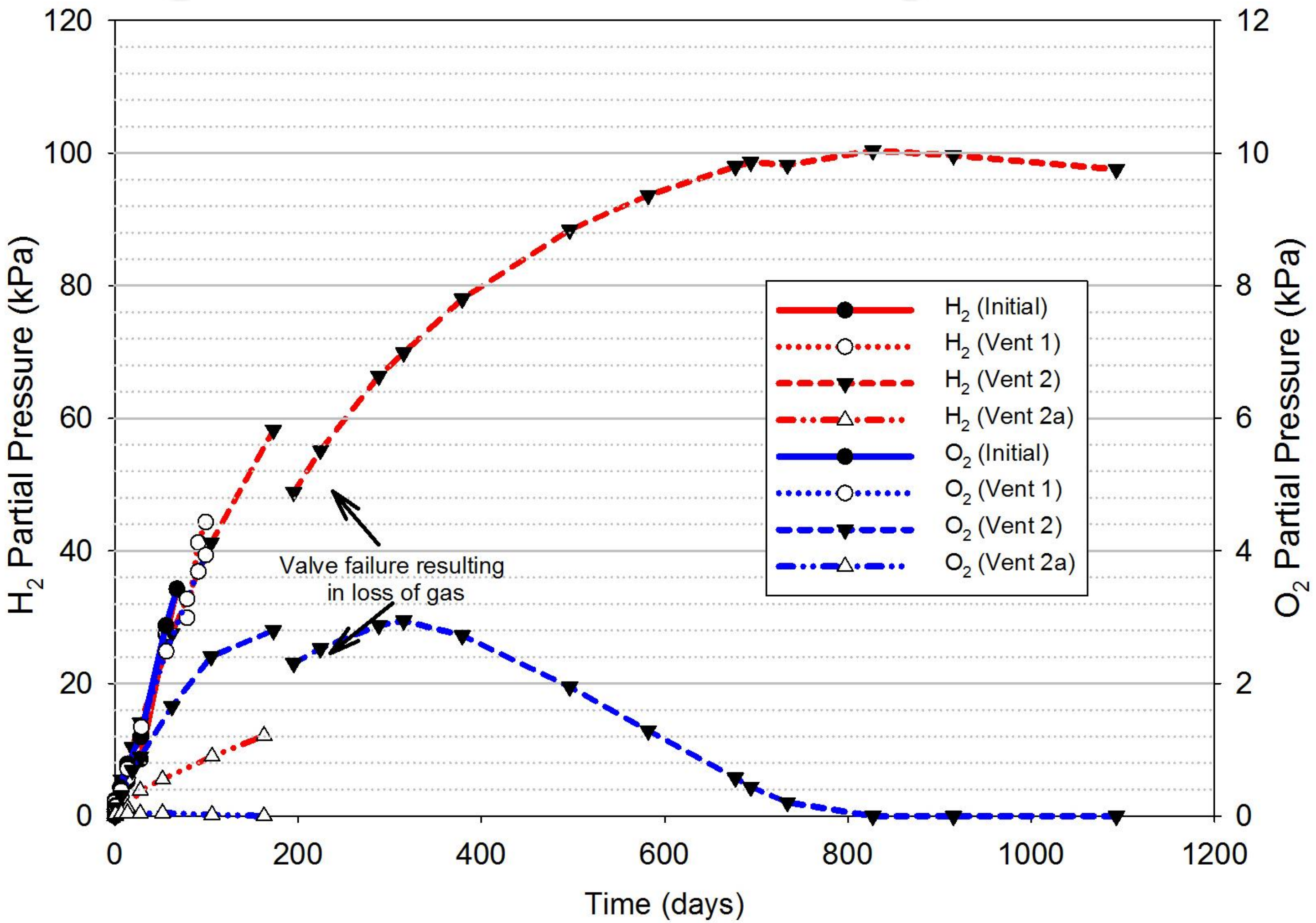
Low Ca (0.28 wt% H_2O)



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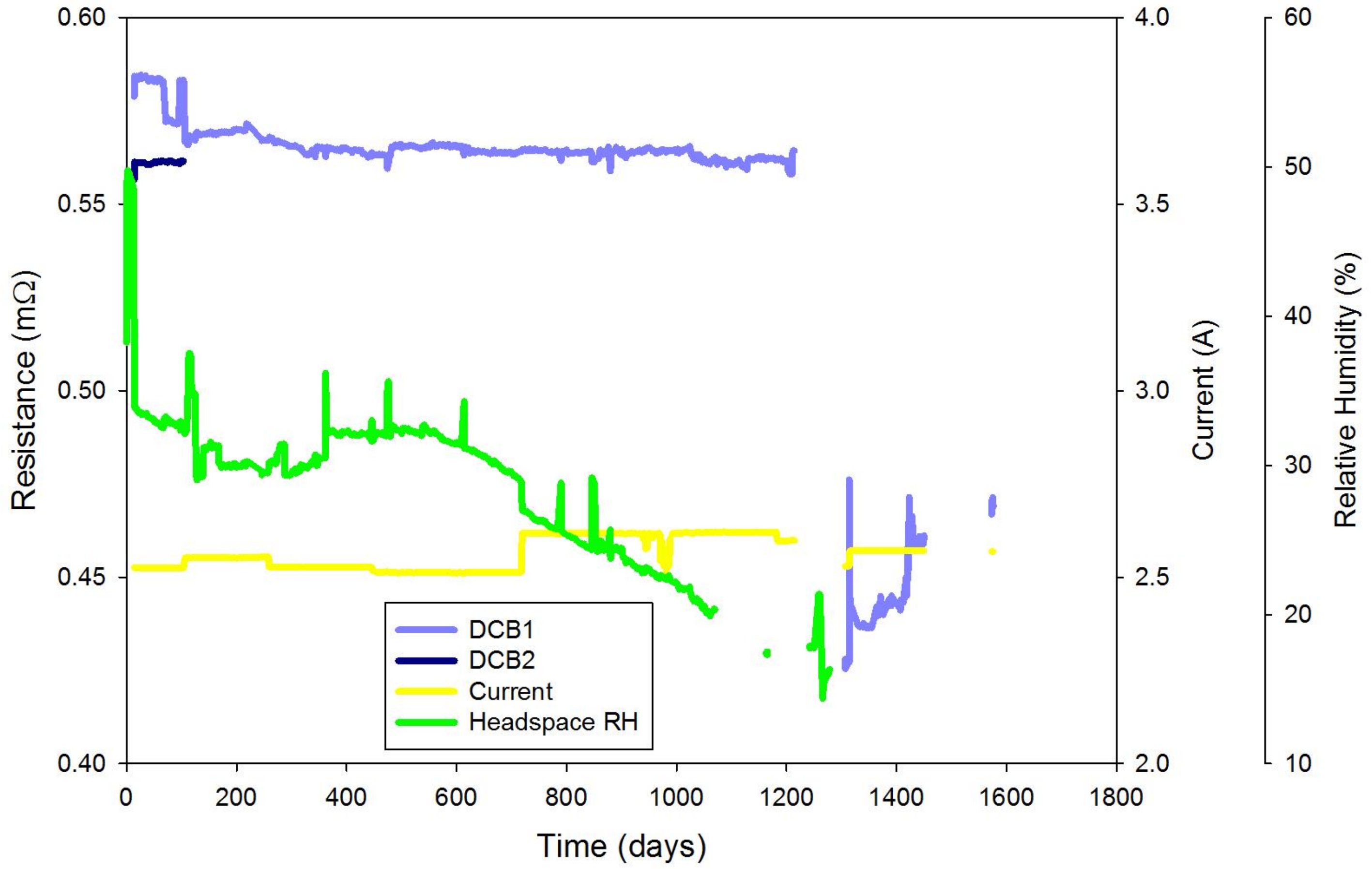
Low Ca (0.28 wt% H_2O)



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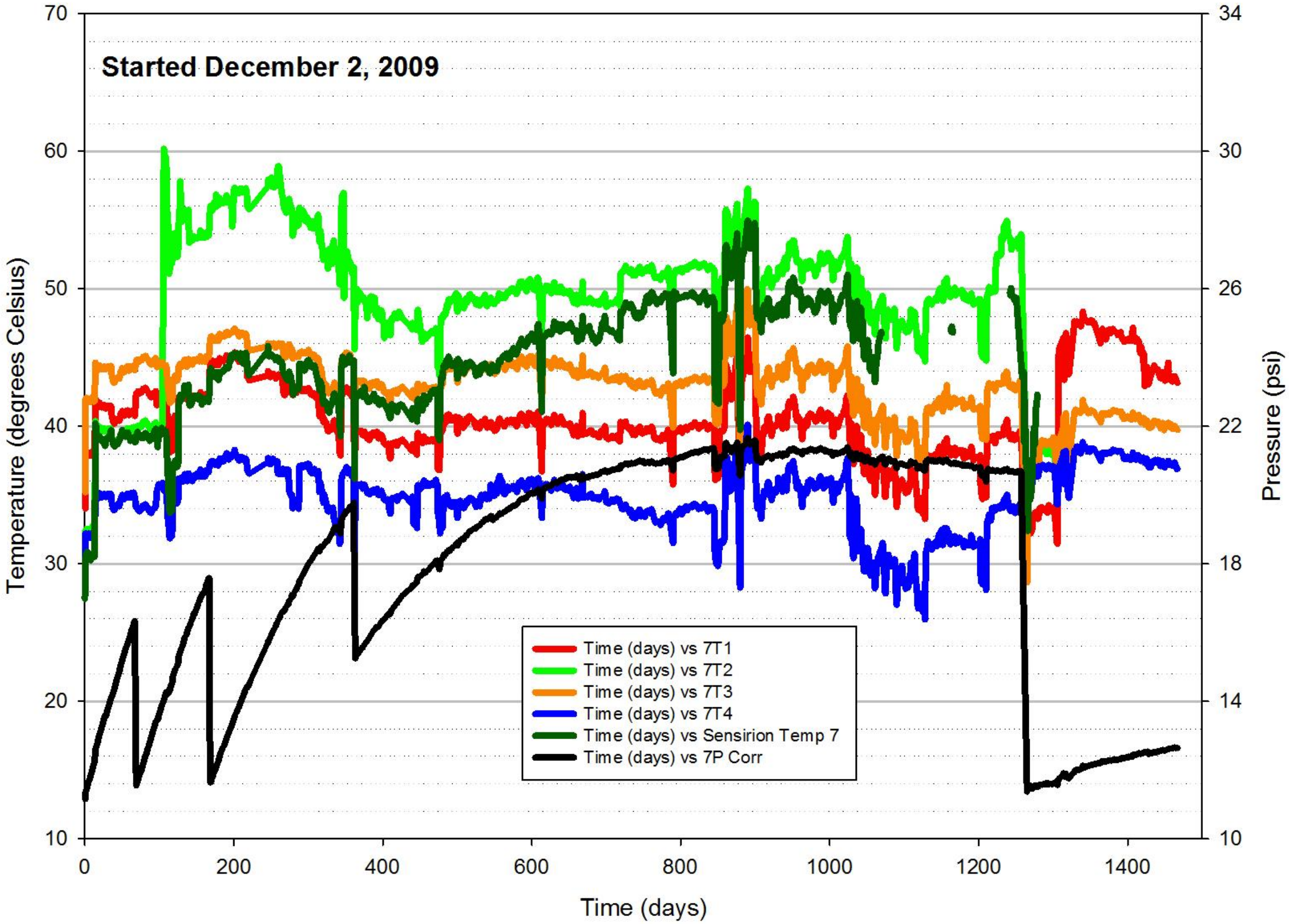
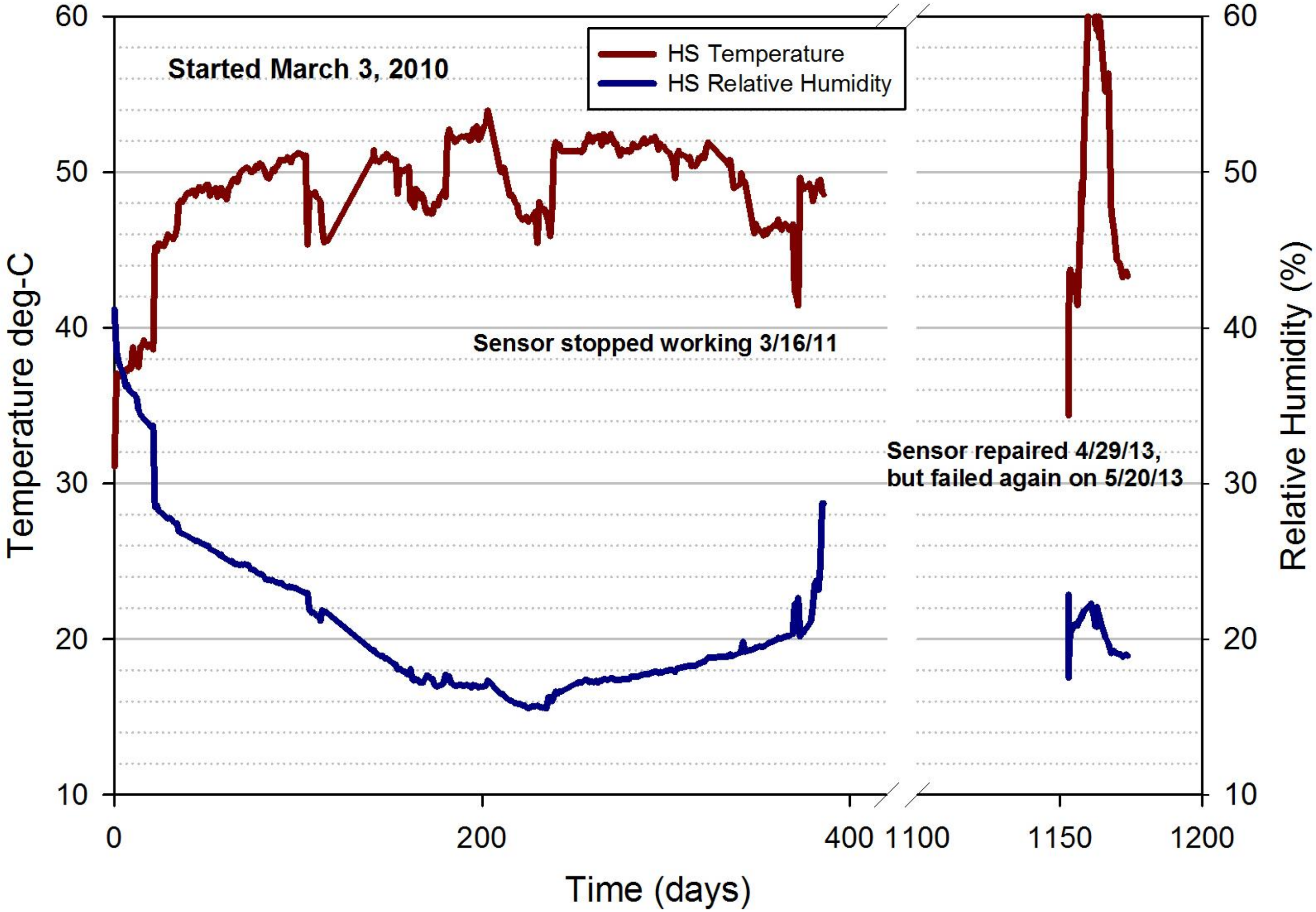
Low Ca (0.28 wt% H_2O)



Low Mg

- Loaded November 2009
- 0.33 wt% $KMgCl_3$ added to Base Material
- Moisture: 0.28 wt% (~7 waters of hydration on magnesium chloride)

Low Mg (0.28 wt% H_2O)



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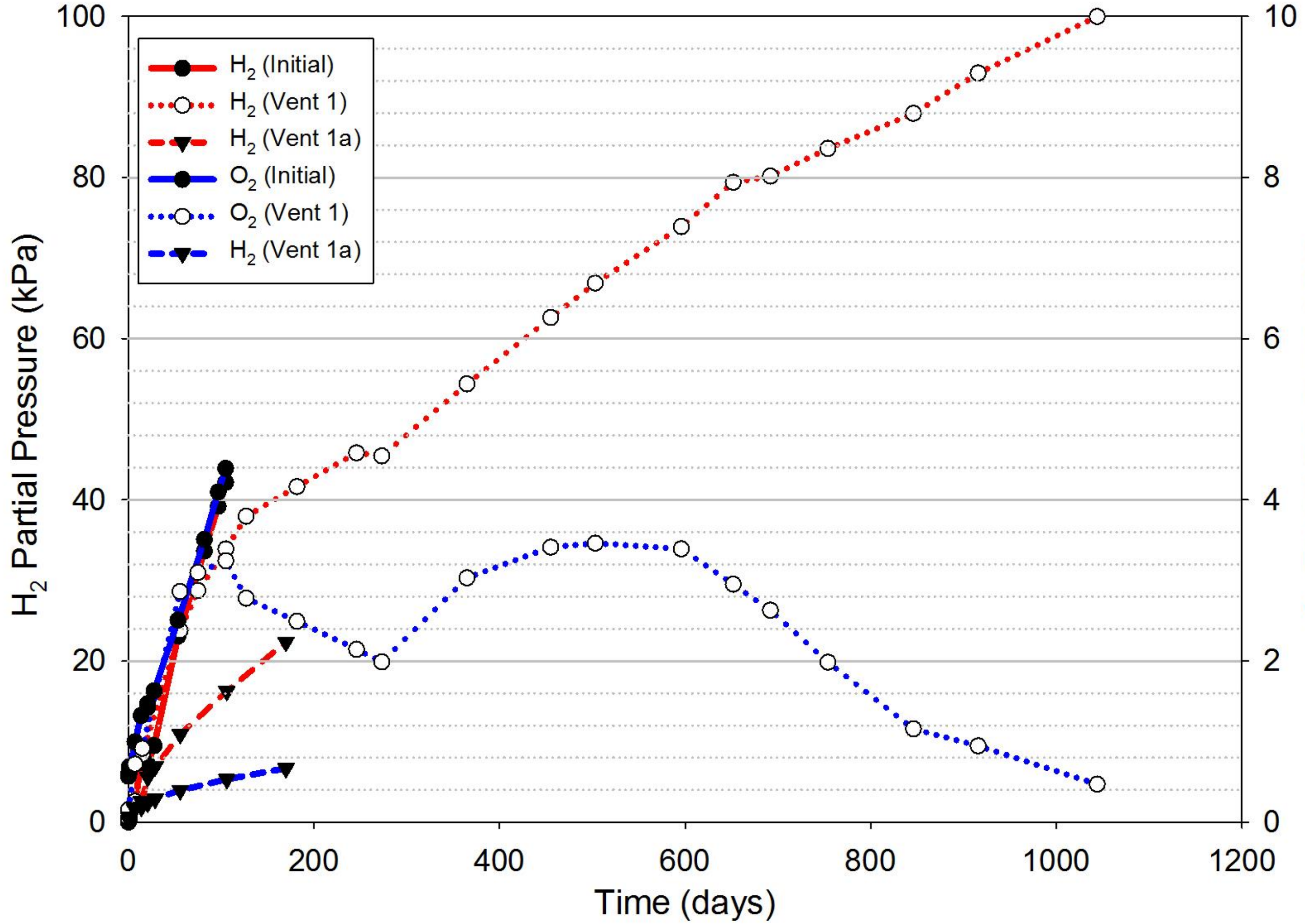
Low Mg (0.28 wt% H_2O)



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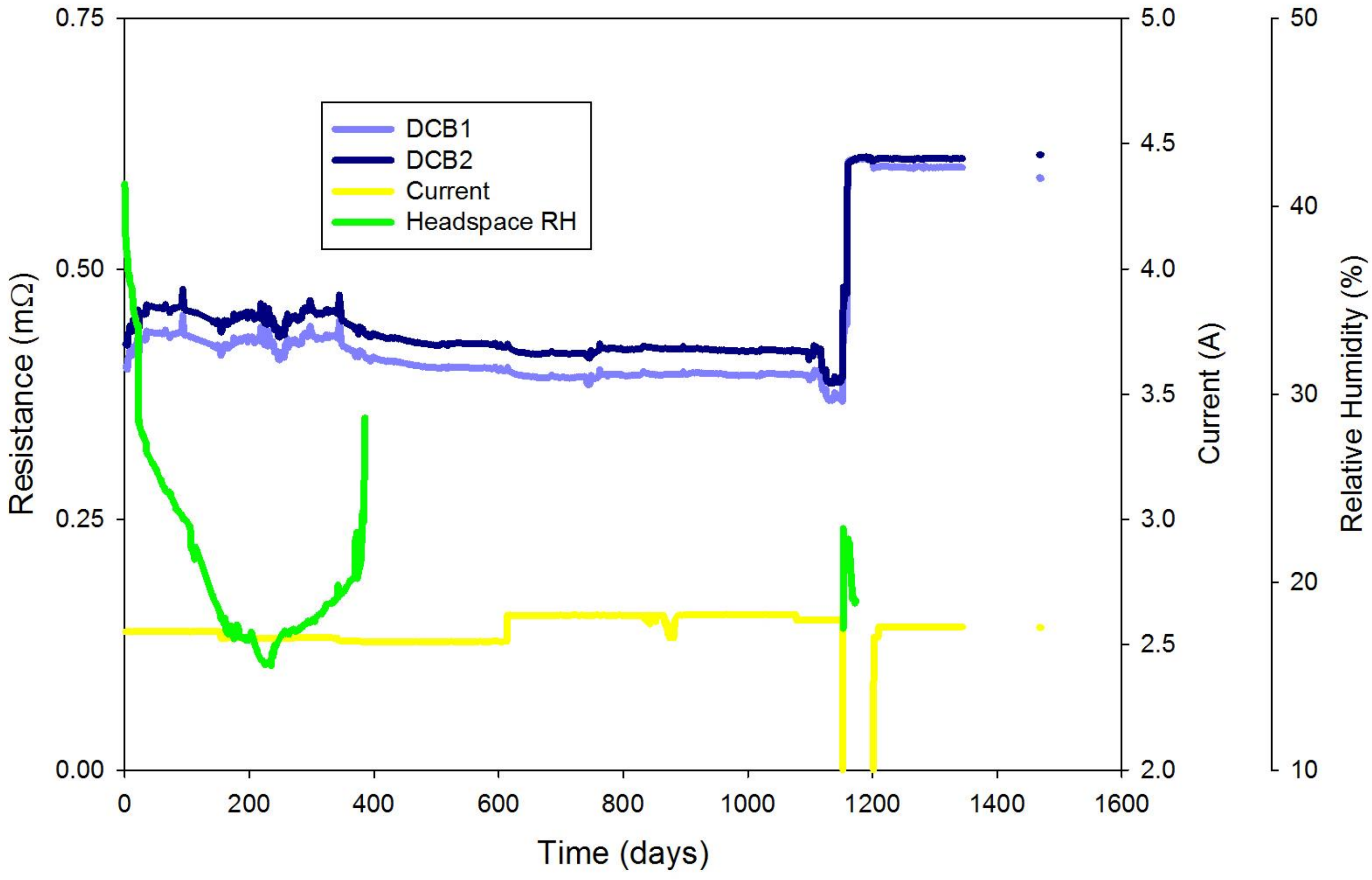
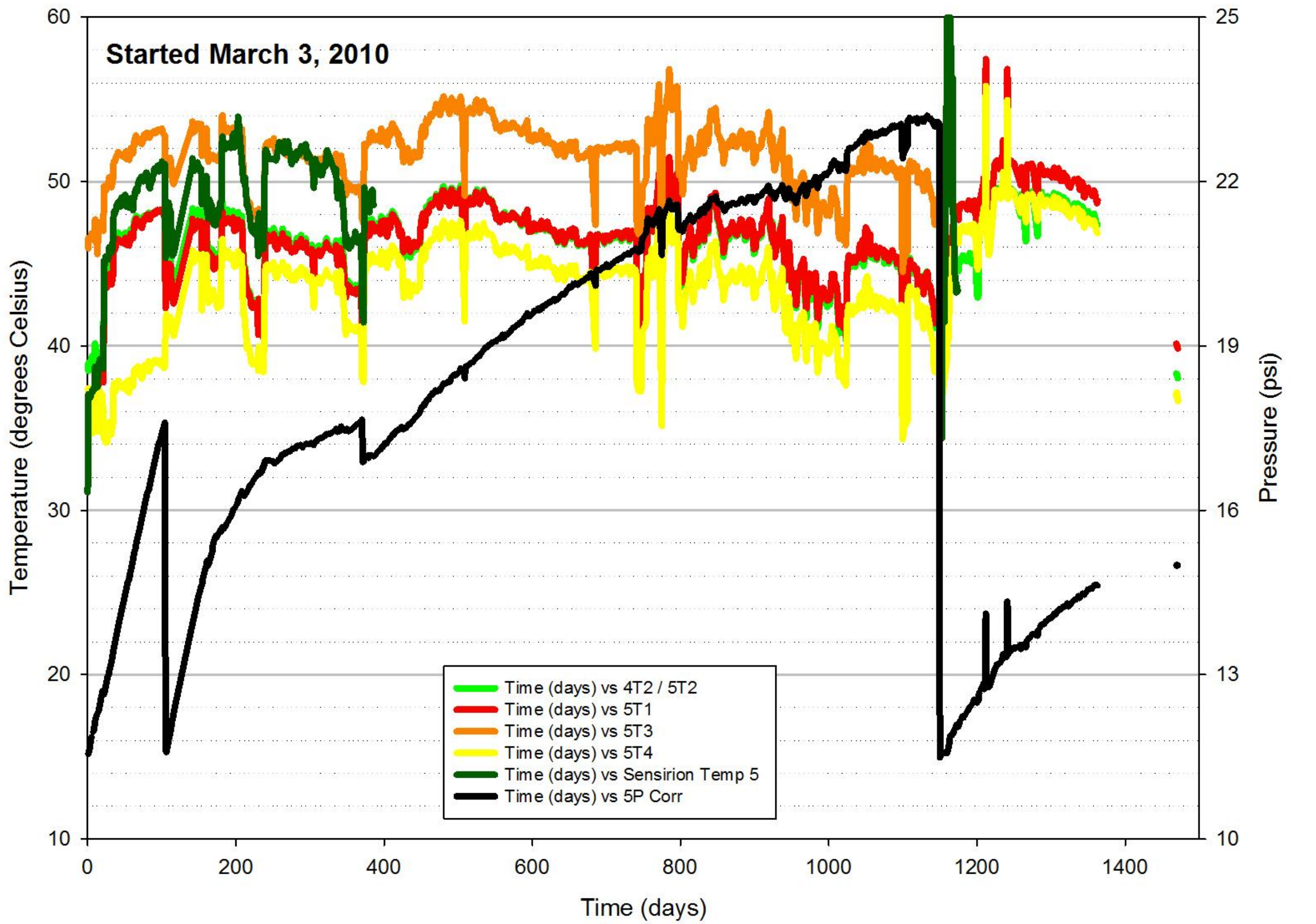
Low Mg (0.28 wt% H_2O)



Low Mg (0.28 wt% H_2O)



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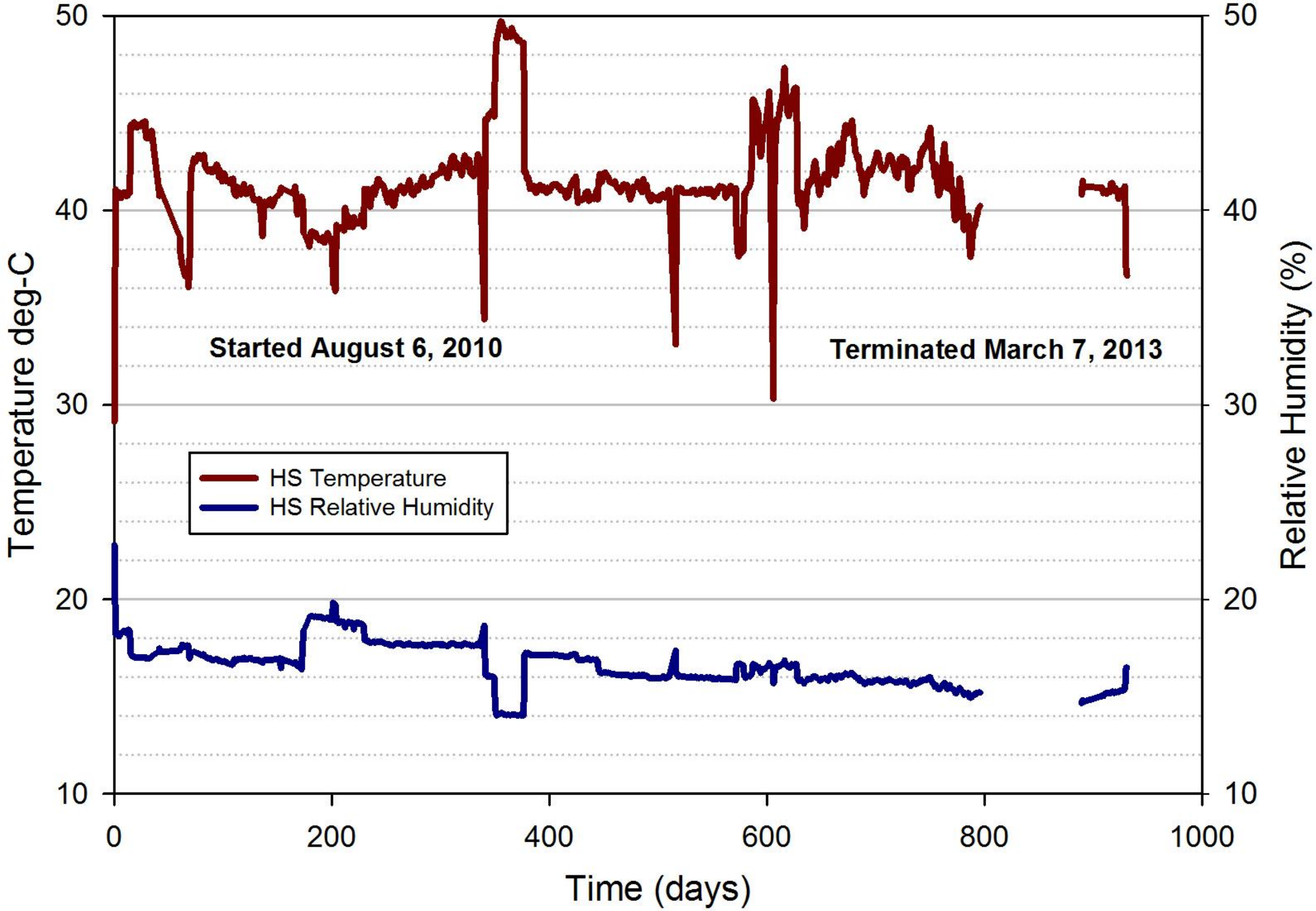
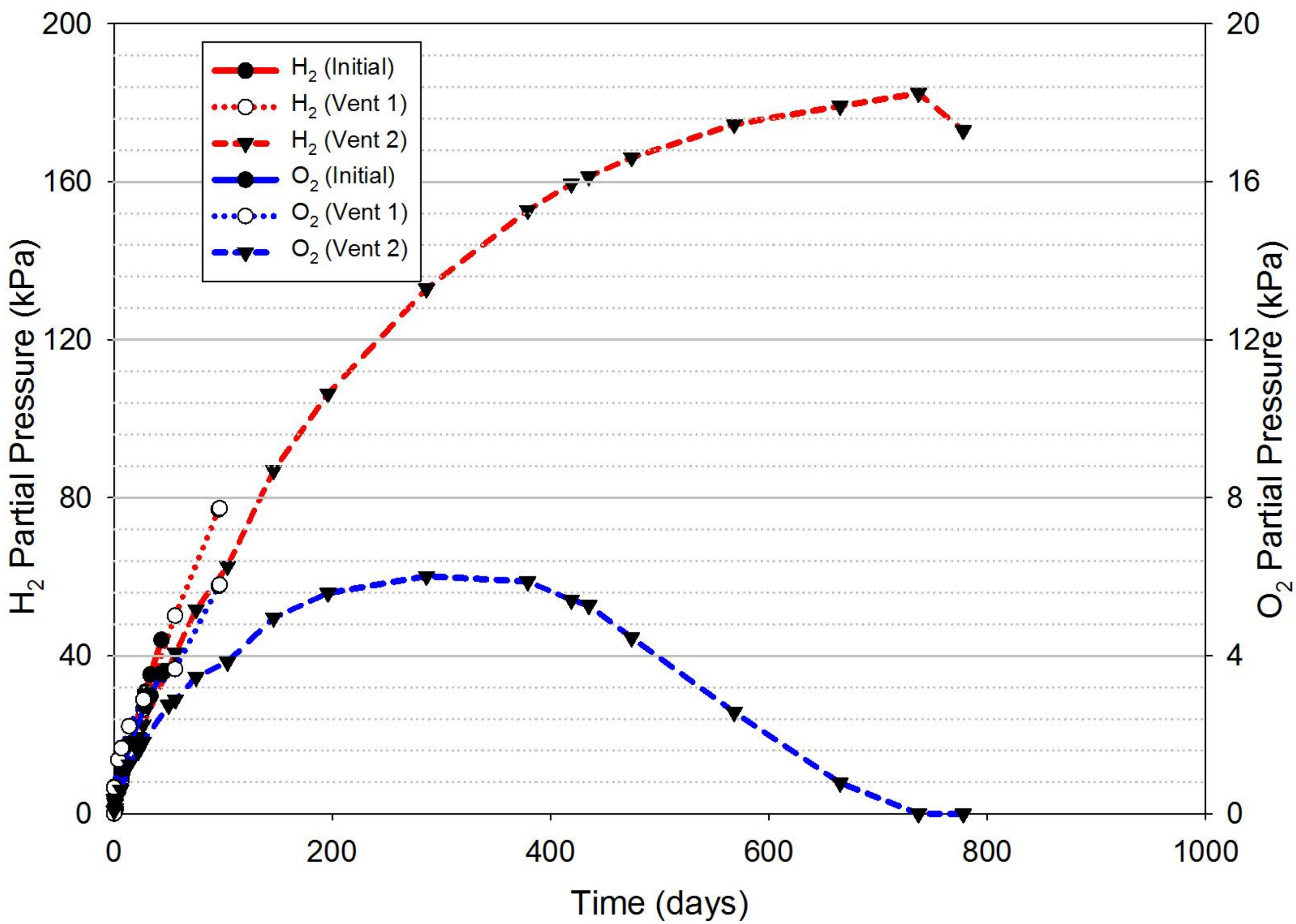
High Ca

- Loaded August 2010
- 3.4 wt% $KCaCl_3$ added to Base Material
- Moisture: 0.39 wt% (~1 water of hydration on calcium chloride)

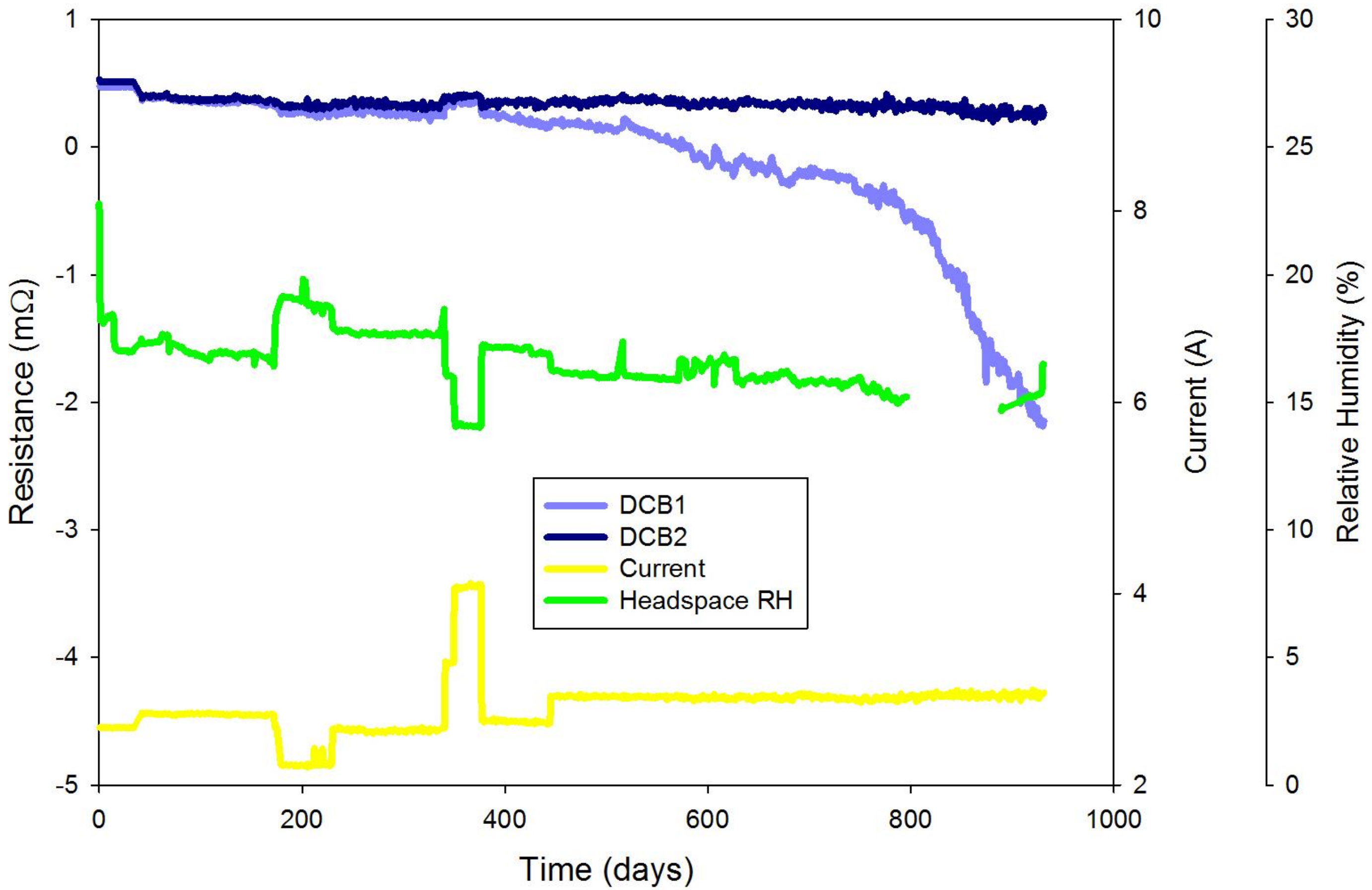
High Ca (0.39 wt% H_2O)



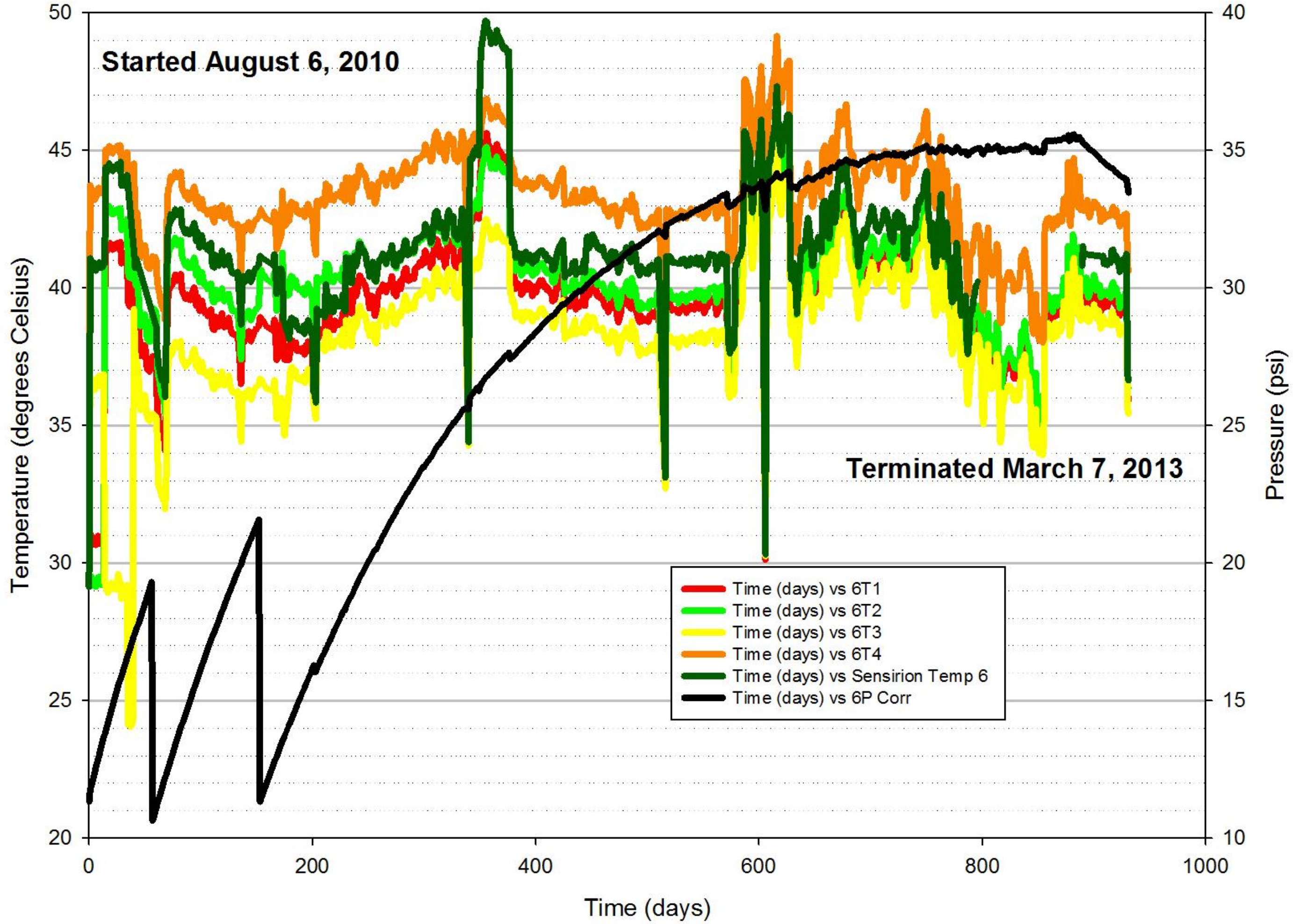
High Ca (0.39 wt% H_2O)



High Ca (0.39 wt% H_2O)



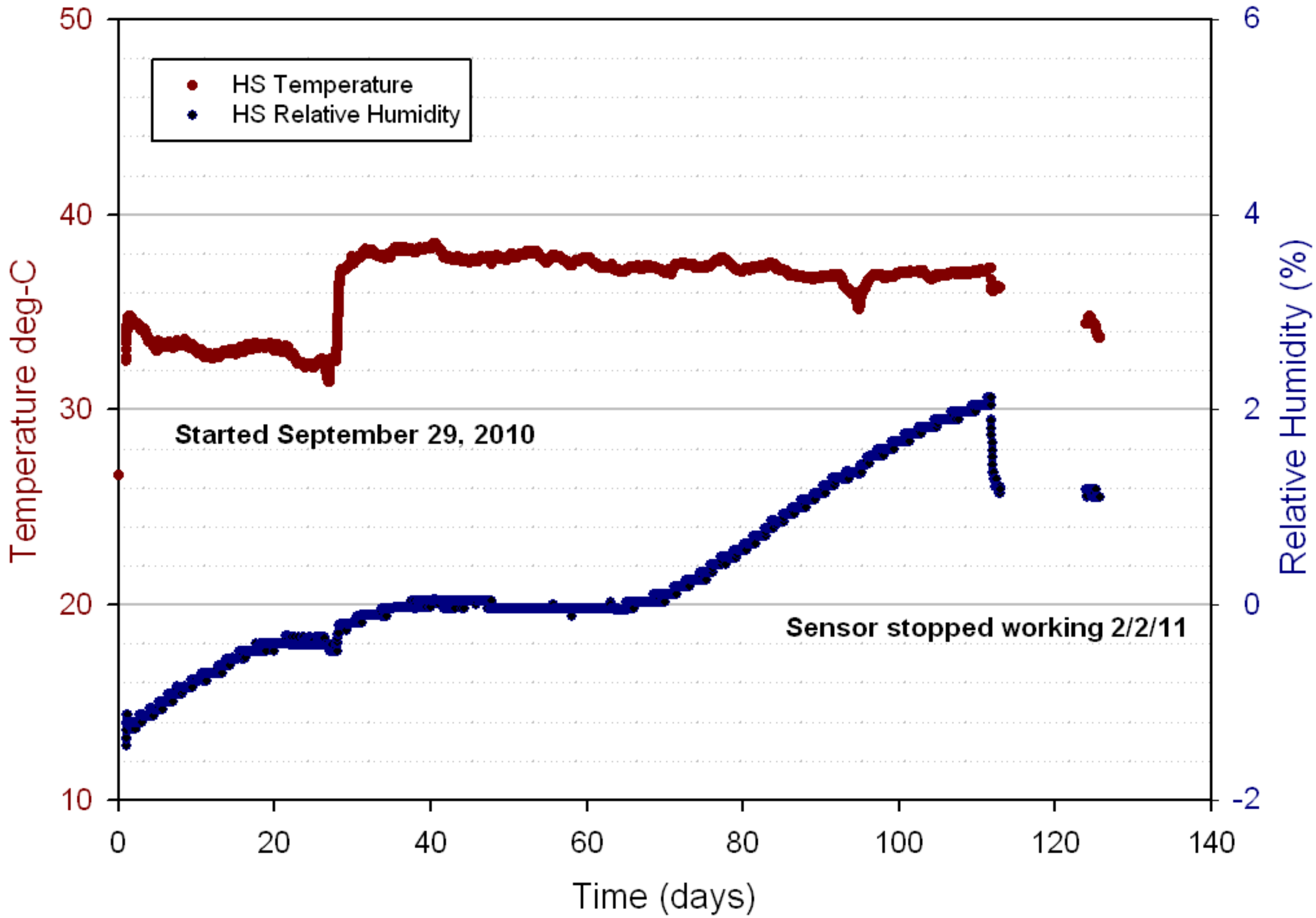
High Ca (0.39 wt% H_2O)



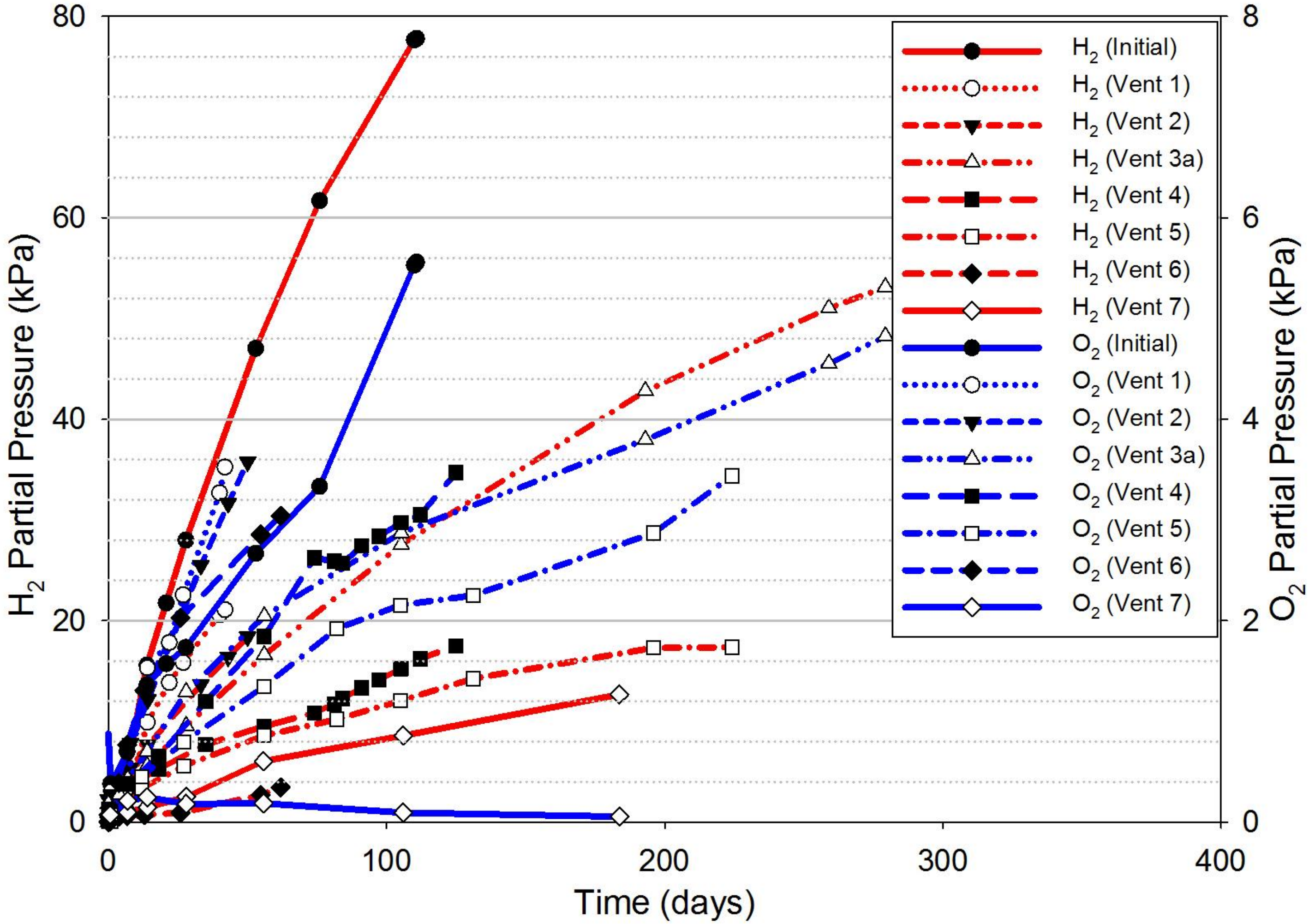
High Mg

- Loaded September 2010
- 3.0 wt% $KMgCl_3$ added to Base Material
- Moisture: 0.55 wt% (~1.6 water of hydration on magnesium chloride)

High Mg (0.55 wt% H_2O)



High Mg (0.55 wt% H_2O)



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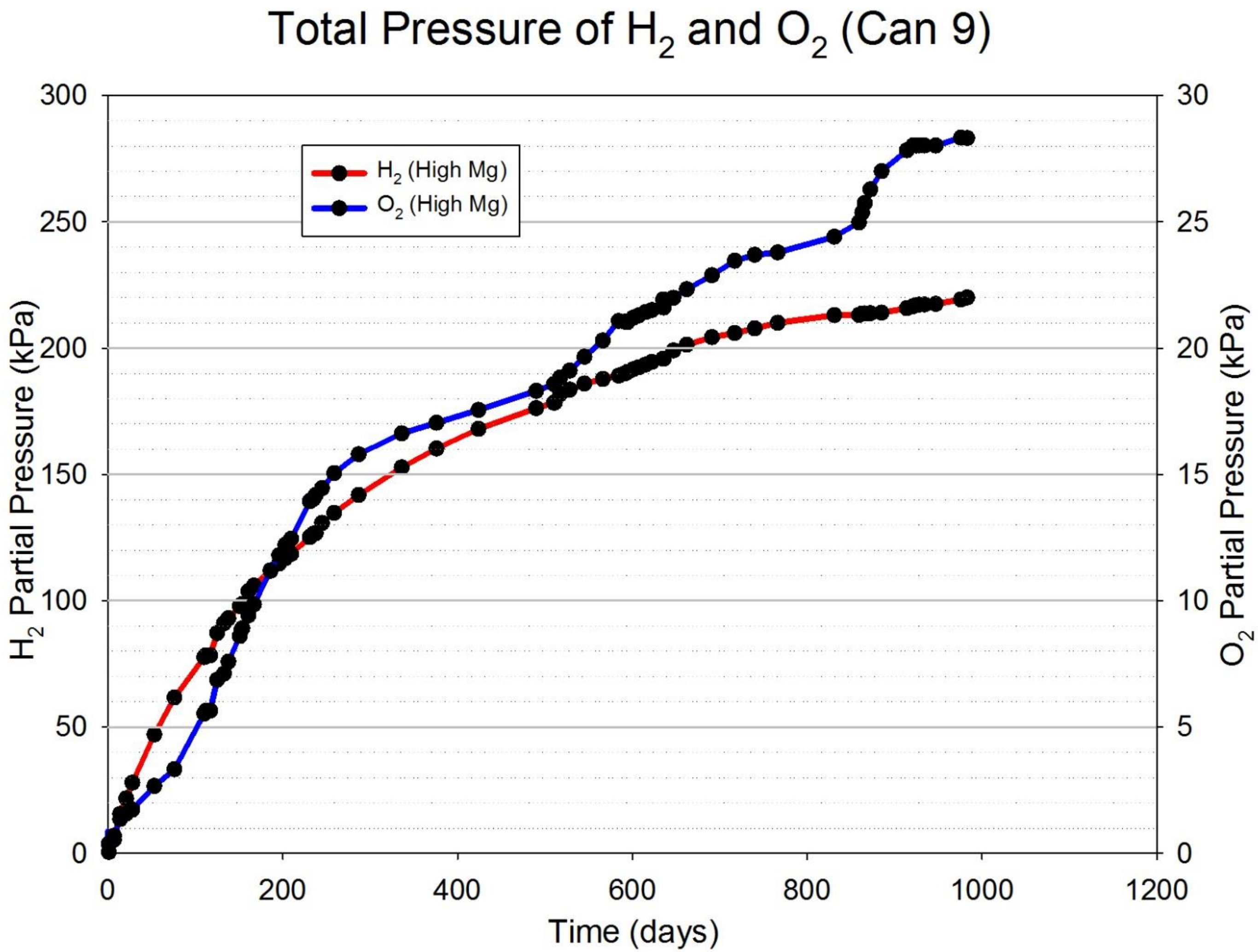
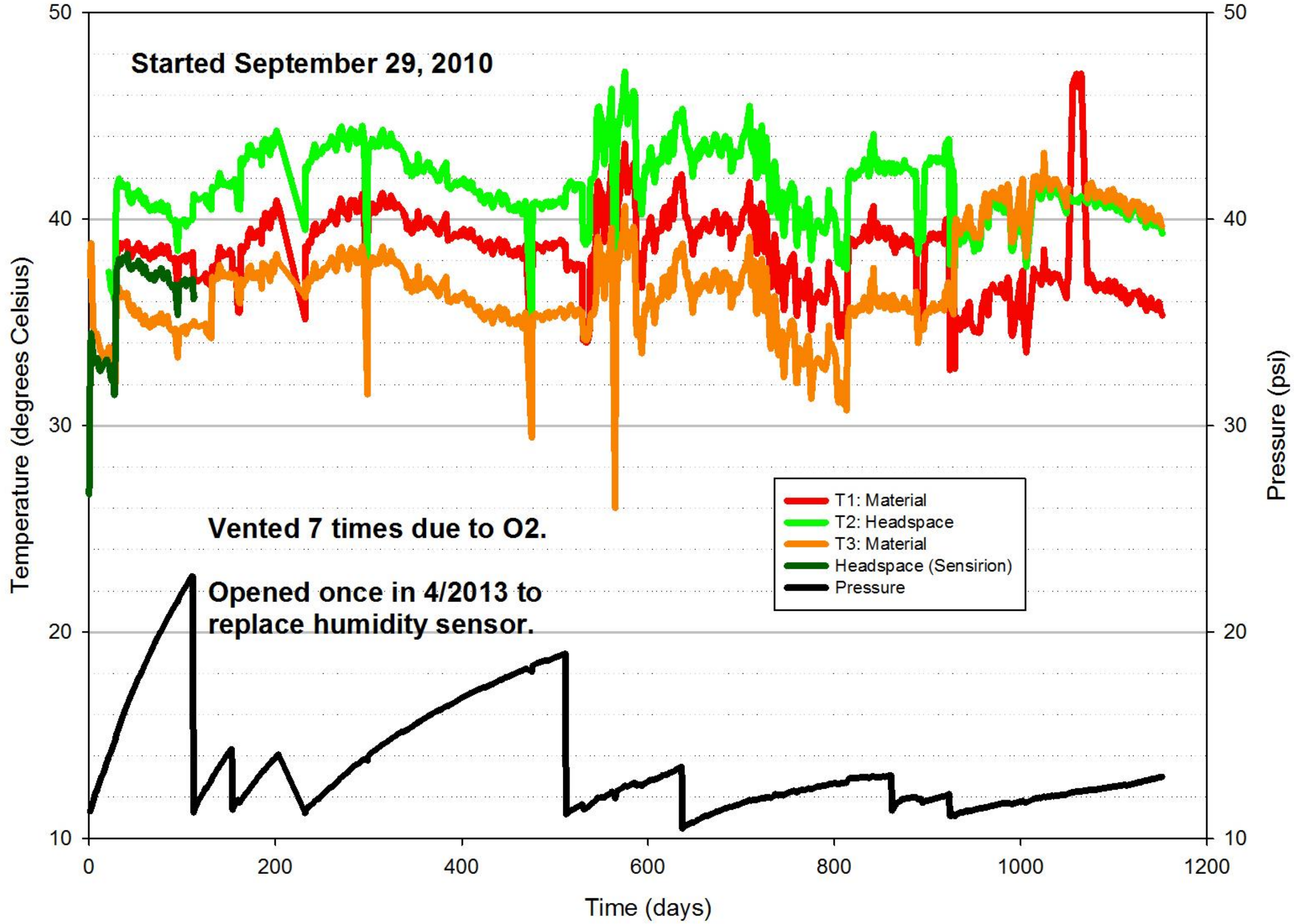
High Mg (0.55 wt% H_2O)



High Mg (0.55 wt% H_2O)



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Additional Slides for Large Scale: Salt Behavior and Phase Diagrams

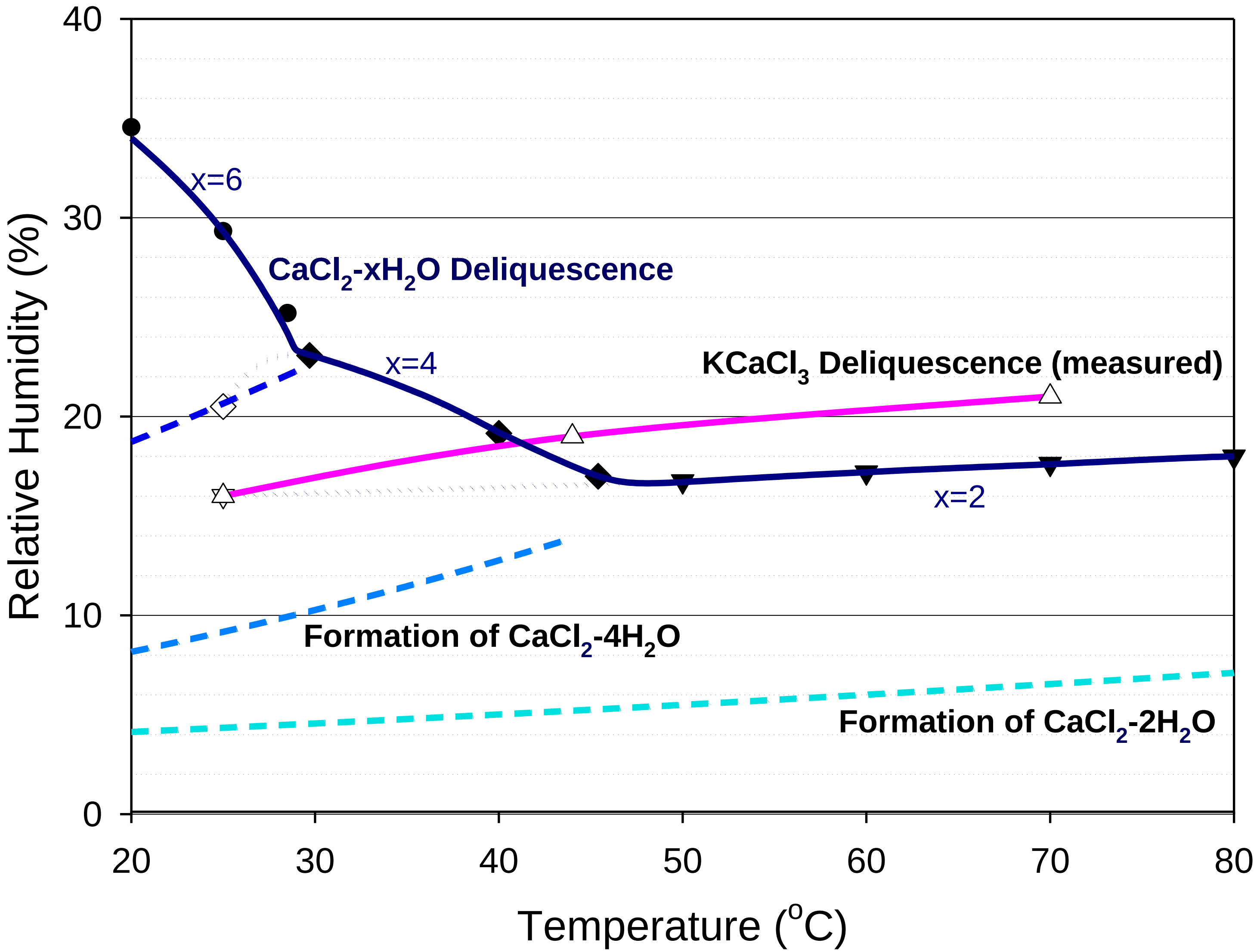
Joshua Narlesky

Los Alamos National Laboratory

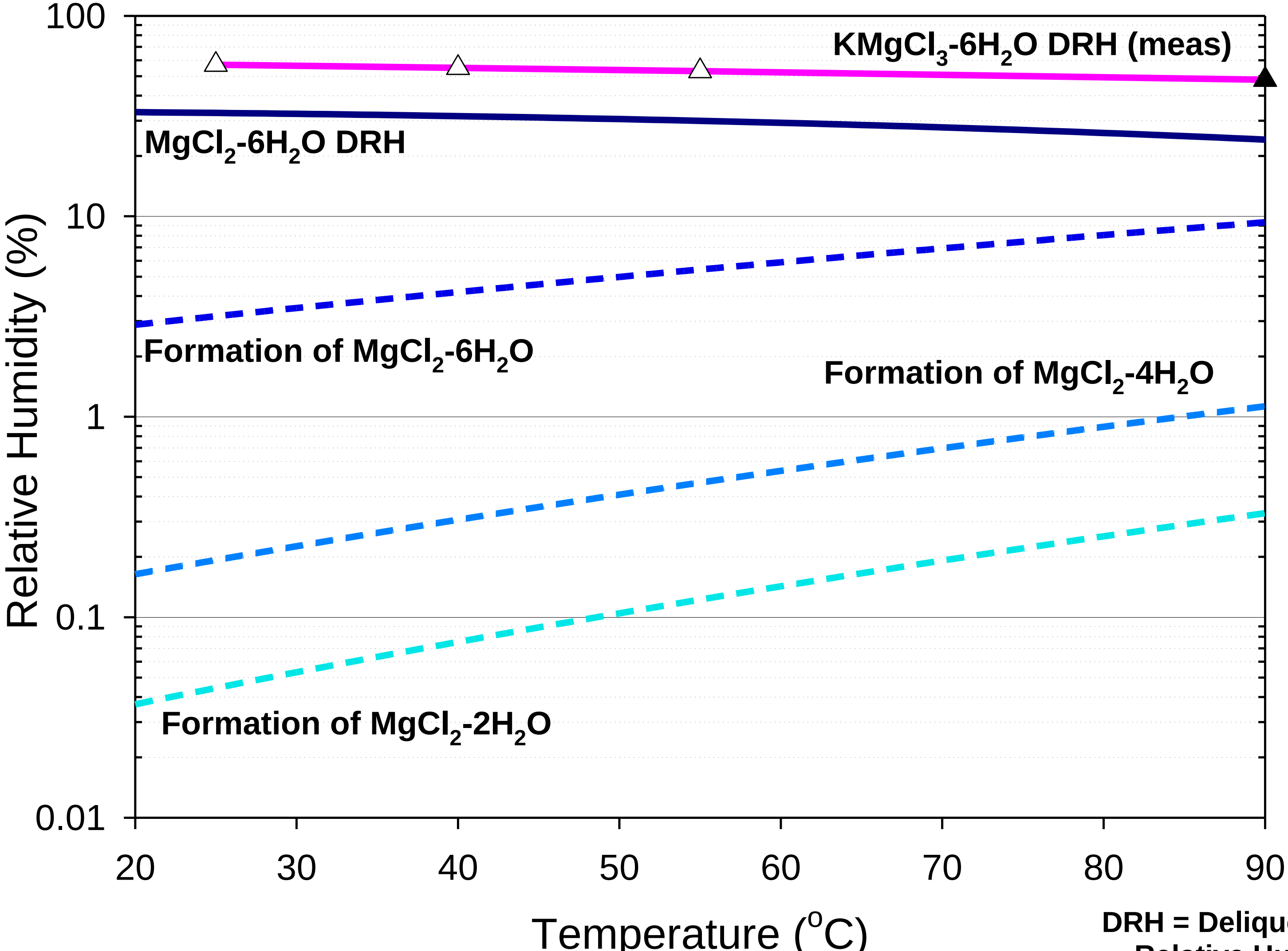
Relative Humidity for Deliquescence and Hydrate Formation

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

Hydration behavior of calcium chloride salts

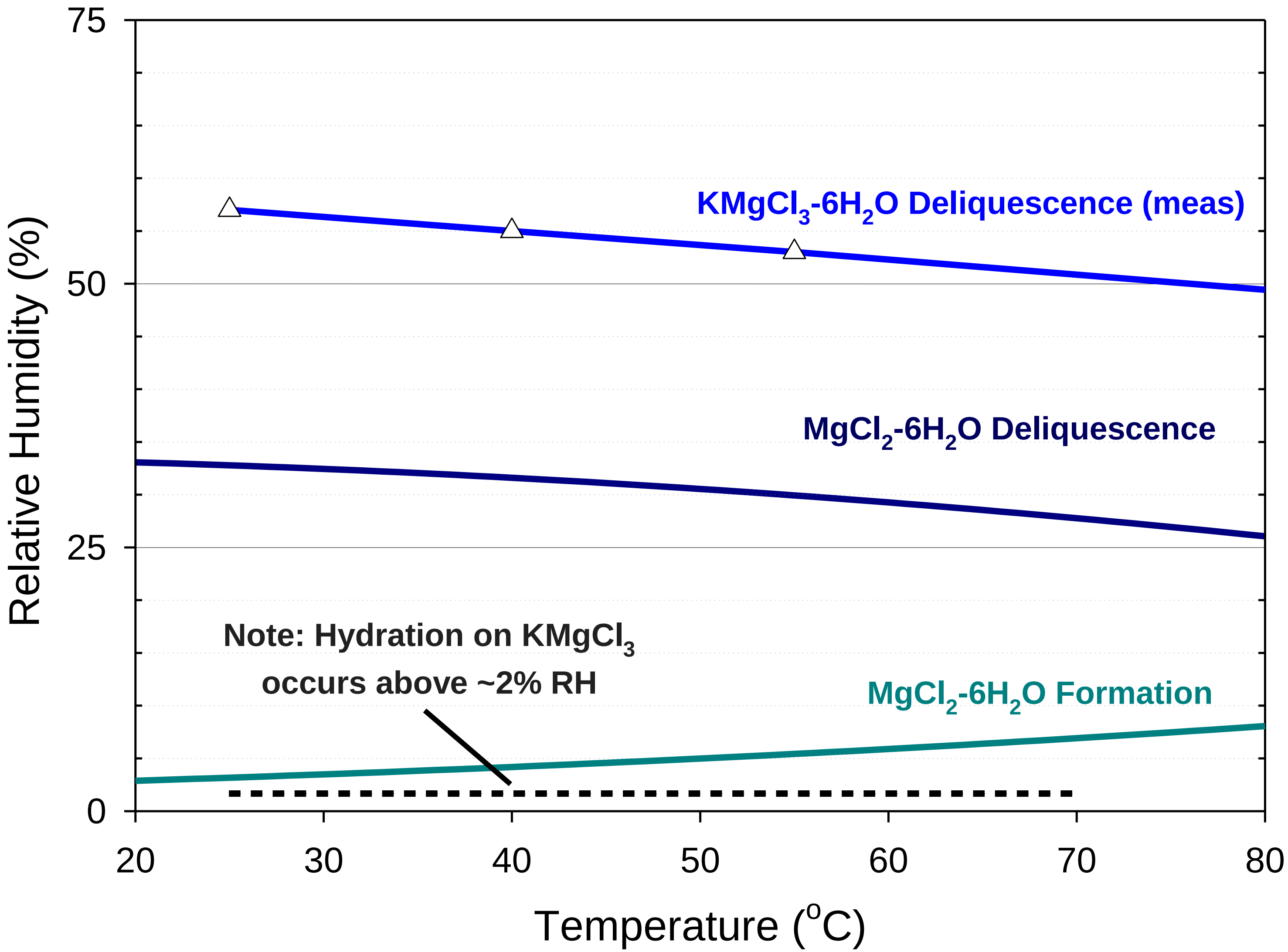


Hydration behavior of magnesium chloride salts

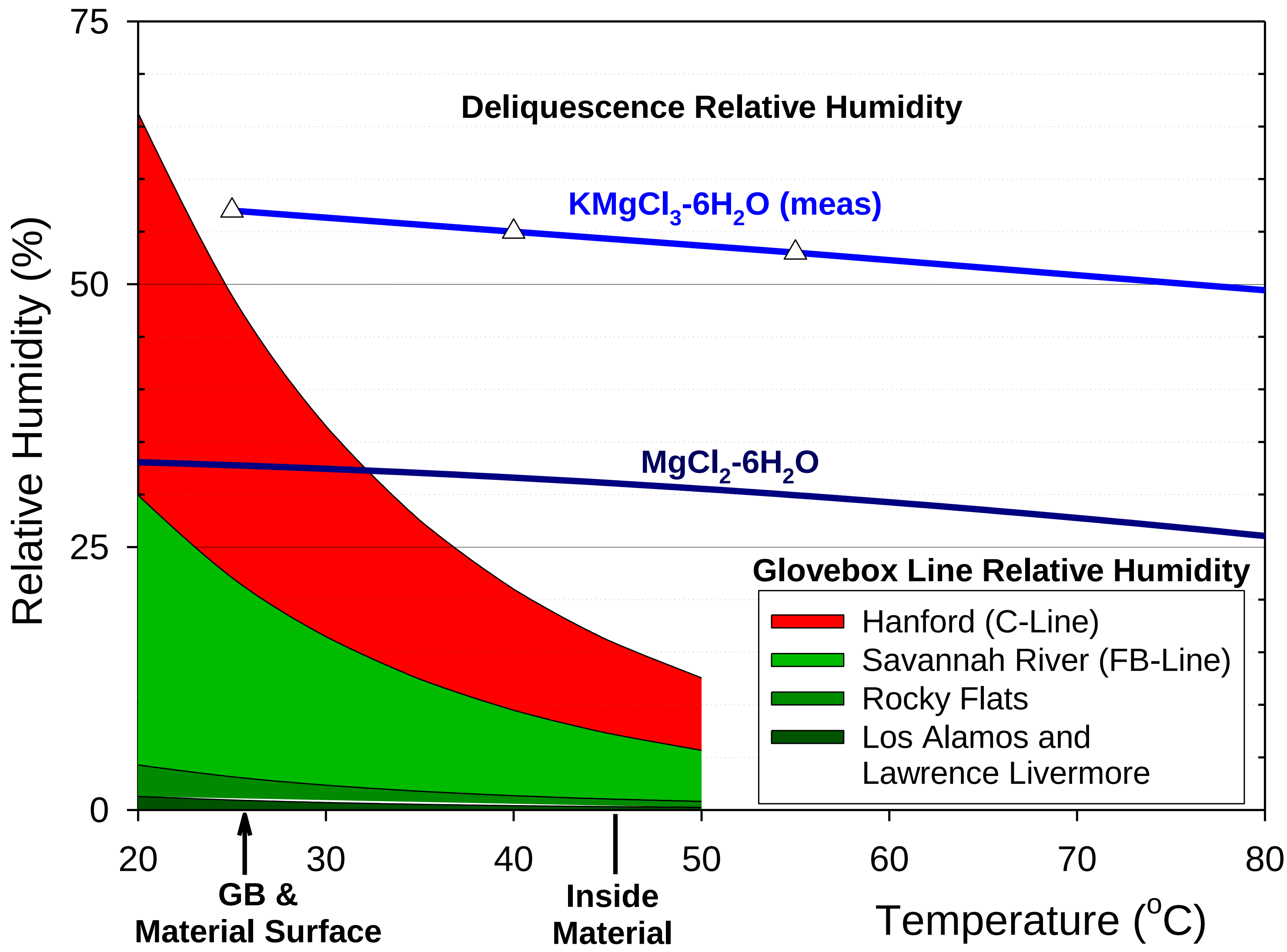


DRH = Deliquescence Relative Humidity

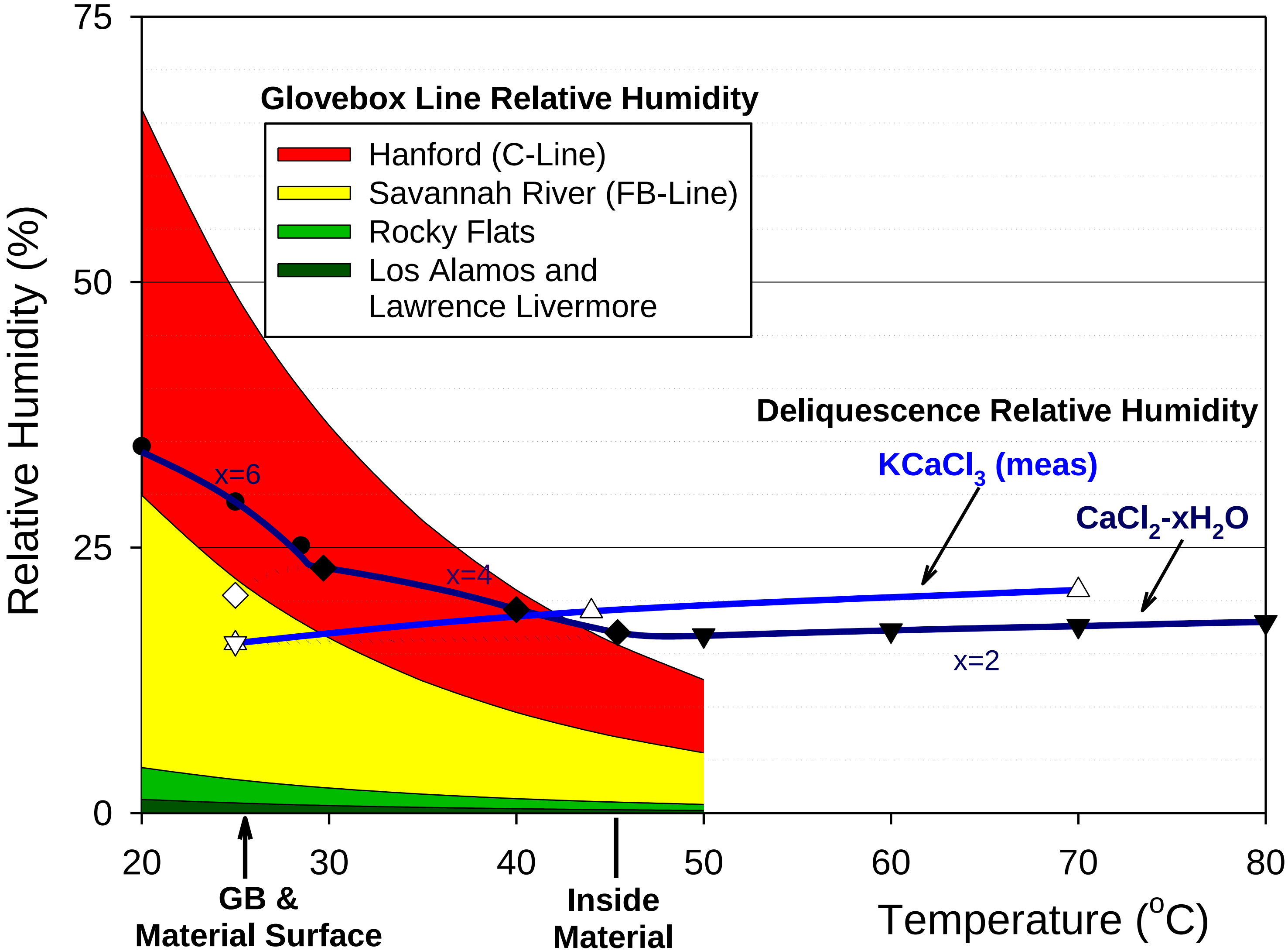
Hydration behavior of magnesium chloride salts



Magnesium Chloride Salt Behavior During Packaging



Calcium Chloride Salt Behavior During Packaging



Status on LANL Studies with Respect to RH, Temp, and Droplet Size

J. G. Duque, D. K. Veirs, J. M. Berg, E. J. Kelly, S. A. Joyce, L. A. Worl, J. E. Narlesky, M. A. Stroud, M. A. Hill

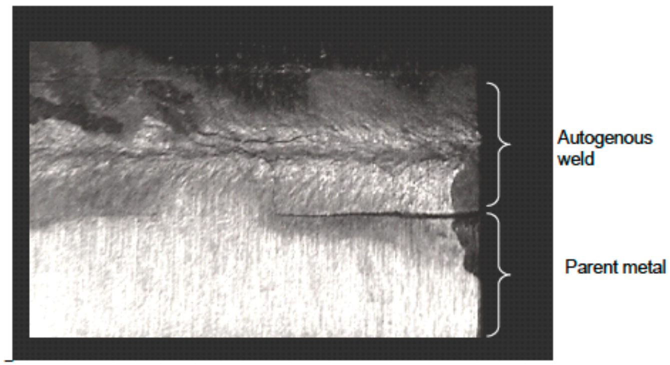
Objective:
Understand conditions at which corrosion(pits and SCC) are promoted: temperature, RH and droplet size.
The ultimate goal is to understand/determine the boundary condition at which corrosion is observed and test these against current inventory.

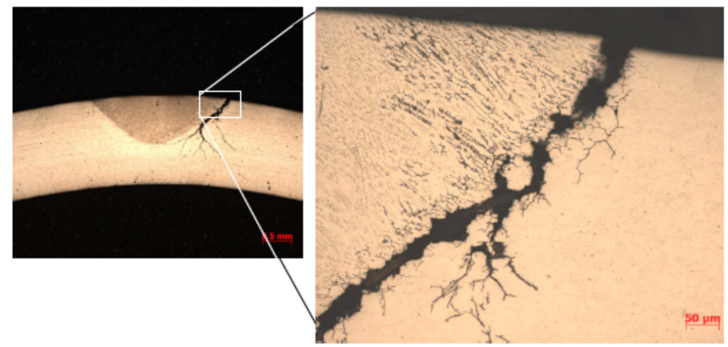
Cold experiments on SS teardrop samples

Previous Shelf Life Corrosion Studies

SRNL observations suggest that high RH and room temperature conditions are needed to support SCC in hot samples.

However, literature data suggests that SCC may occur at much lower RH (as low as the deliquescence point of the salt).





Zapp, SRNL

- Corrosion and SCC in teardrop samples in Pu salts
- Cracking in the heat-affected zone of the autogenous weld
- Corrosion and cracking preferentially for SS 304
- Cracking was transgranular in nature characteristic of chloride-induced SCC
- Cracking was observed in the area in contact with the salt

Tests are planned to define conditions applicable to 3013 storage environments. These results will provide a more detailed matrix of the threshold RH needed for SCC as a function of salt composition and RH

Ties to Program

Microscope examination

    Develop tools to obtain quantitative information for DE

Examine some condition that can promote SSC

    Impact on droplet size

        Limiting size before we cant see pits/cracks

    Temperature

    RH

    Are these factors needed for SSC, what are the limits

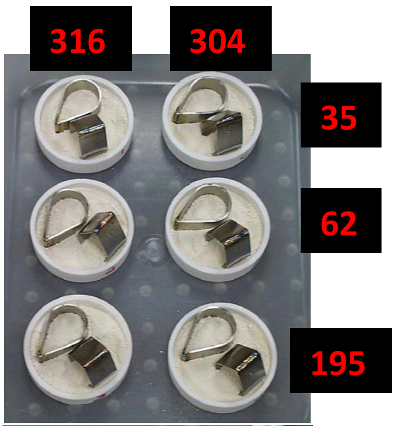
Cl deposition

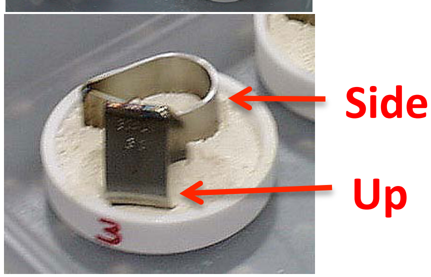
Review of Last Year's Presentation

Expose teardrop specimens to known concentrations of salts and humidity as a function of time

Examine the samples for corrosion evidence
Remove corrosion product and examine pitting/cracking

Salts consisted of mixture of cerium oxide (CeO_2), $CaCl_2$, NaCl, and KCl



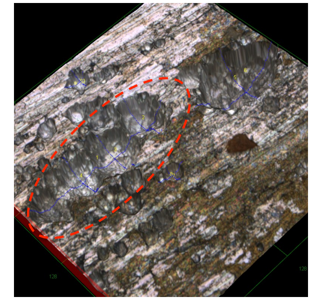


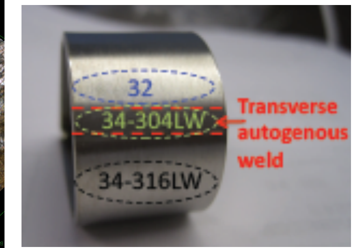
- Relative humidity 57.5%
- Two different types of SS: 316 and 304
- Two different orientations: side, up
- Exposed for 35, 62, and 195 days
- Constant Temperature 30 °C

After specified time, teardrops are examined using an infinite focus optical technique

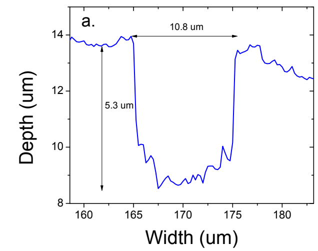
Obtain information on pitting/cracking size

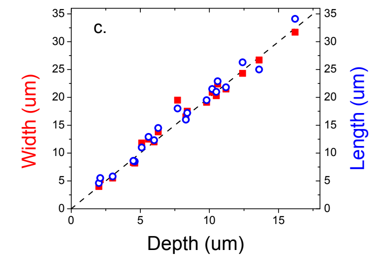
Conclusions:





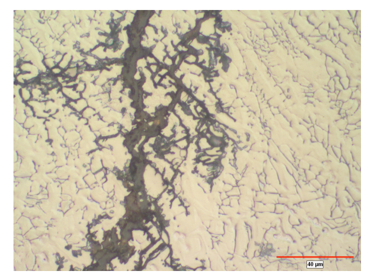
- Observed corrosion pitting and cracking preferentially at or near the heat-affected zone of the transverse autogenous weld

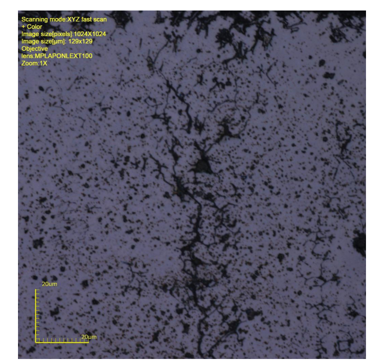




- SS 304 more susceptible to corrosion pitting and cracking, also observed in samples in contact with PuO_2
- Corrosion pits exhibit a hemispherical shape
- Coalescence of pits are more significant with increasing time

- Stress cracking was observed
- Cracking was observed as result of chloride: characterized by the multi-branched pattern





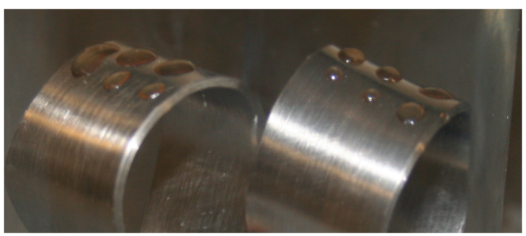
- No corrosion was observe at RH 21.8% but pitting and cracking was observed at RH% 57.5%

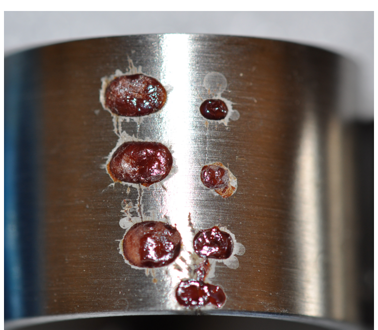
Shelf Life Studies: Small Scale Tests

Sample Geometry and Experimental Conditions

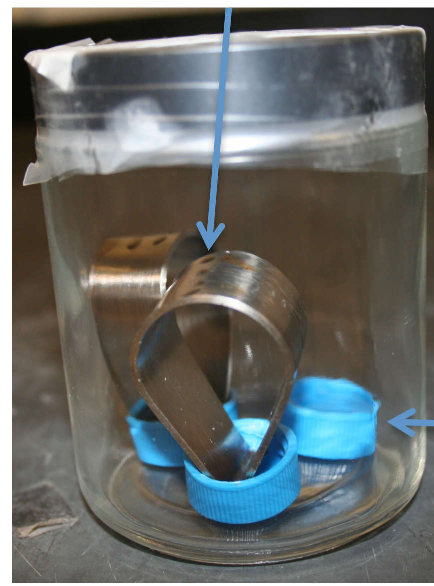
Experimental Parameters:

- Saturated solutions of CaCl2
- Droplets of 0.5, 1, 5, and 10 uL at the surface of teardrops, near the heat-affected zone of the transverse autogenous weld
- Teardrops were placed inside a vial
- RH was held constant using saturated salts
- Vials were placed inside oven at 30 or 50 C
- Samples were left inside oven for 55 days





CaCl2 drops



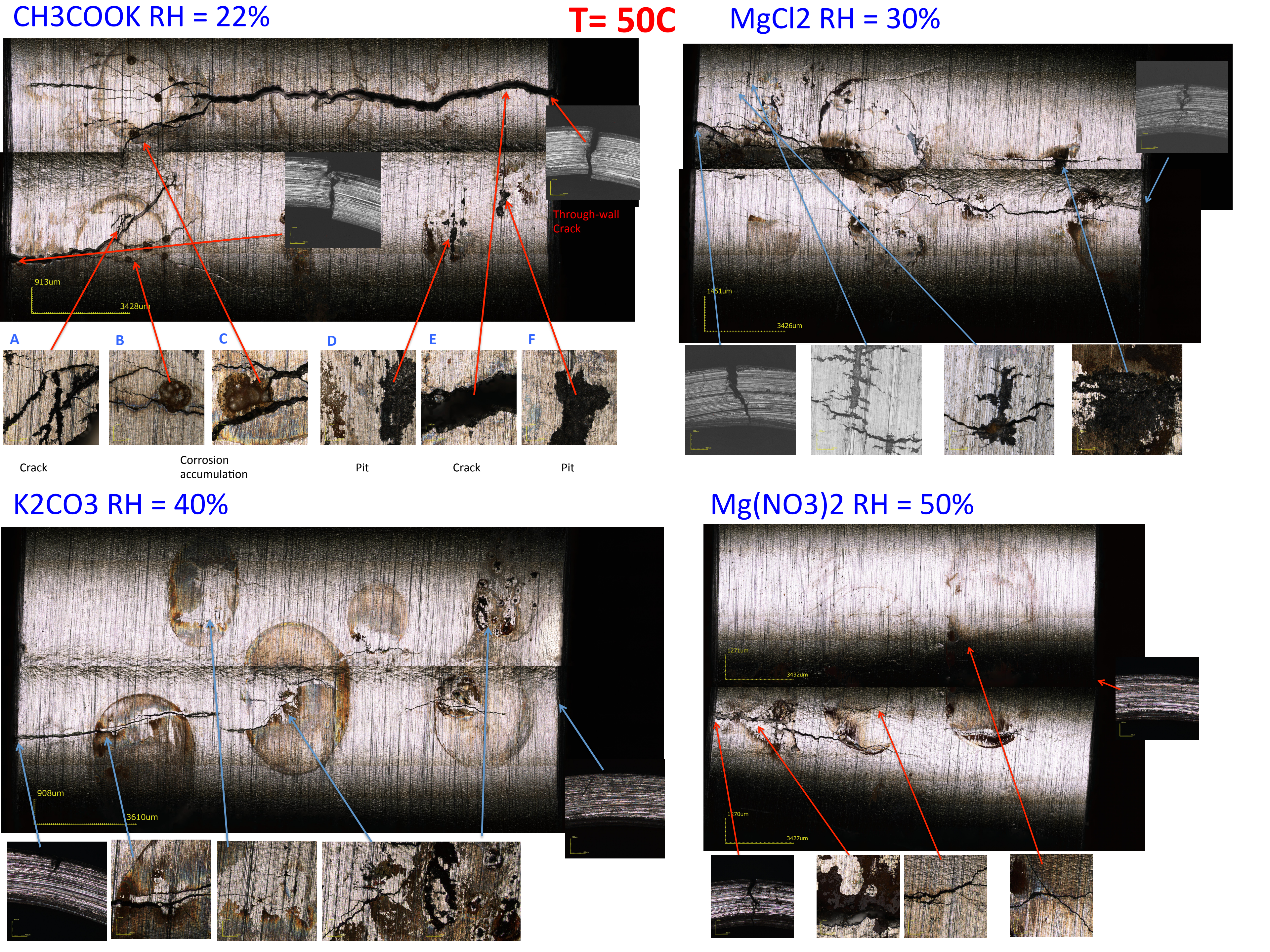
Saturated salt

RH measured inside the glass vials using a sensirion

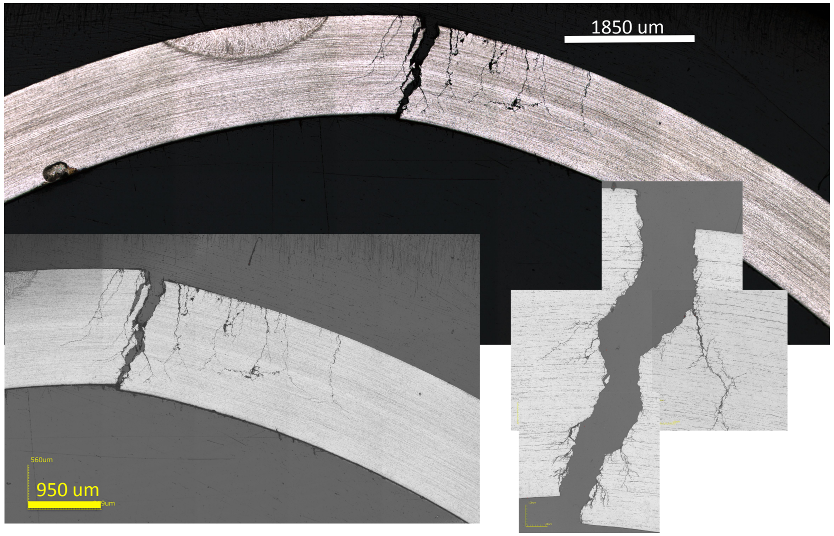
Temperature and RH

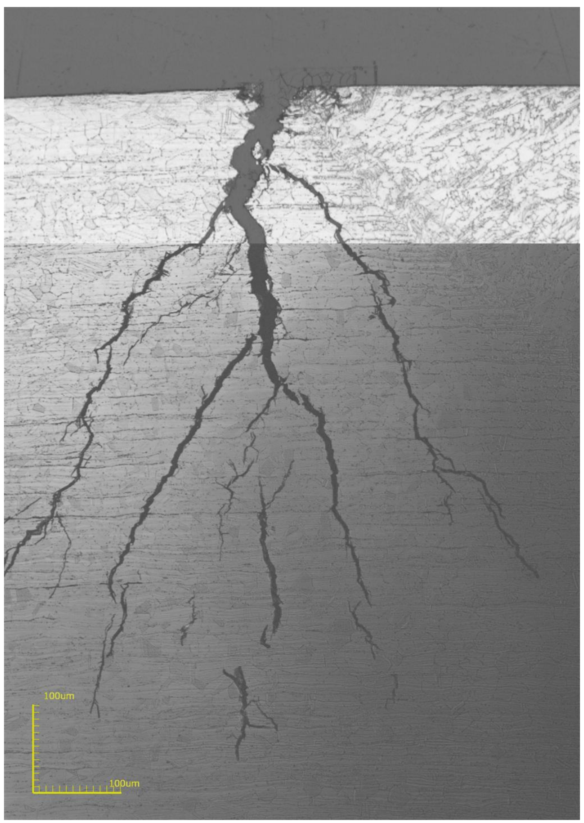
Temp= 30 and 50 C
RH= 20 - 47%

	Expected RH%	Observed RH%
CH_3COOK	21.62	20.05
$MgCl_2$	31.10	26.48
K_2CO_3	43.17	37.82
$Mg(NO_3)_2$	46.93	48.37

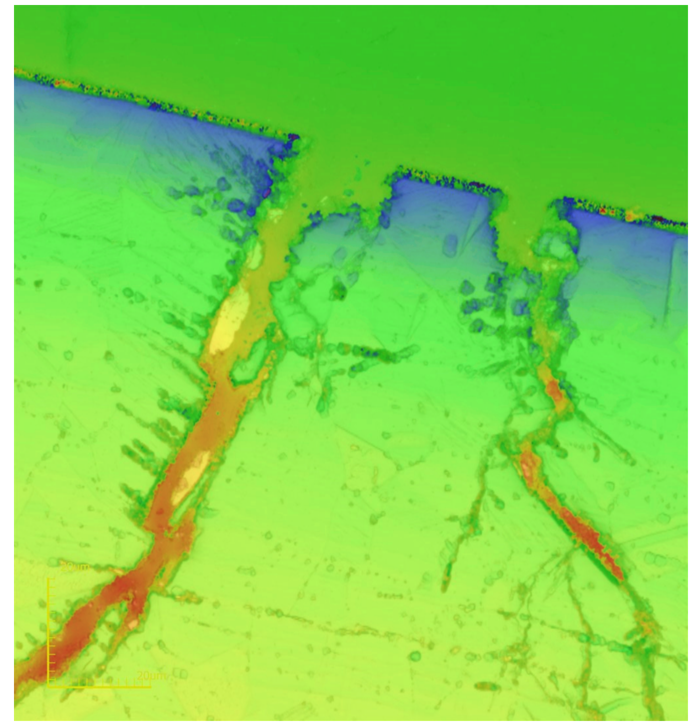


CH3COOK RH = 22%
T= 50C
MgCl2 RH = 30%
Through-wall Crack
913um
3428um
A
B
C
D
E
F
Crack
Corrosion accumulation
Pit
Crack
Pit
1451um
3426um
K2CO3 RH = 40%
908um
3610um
Mg(NO3)2 RH = 50%
1271um
3432um
1270um
3427um



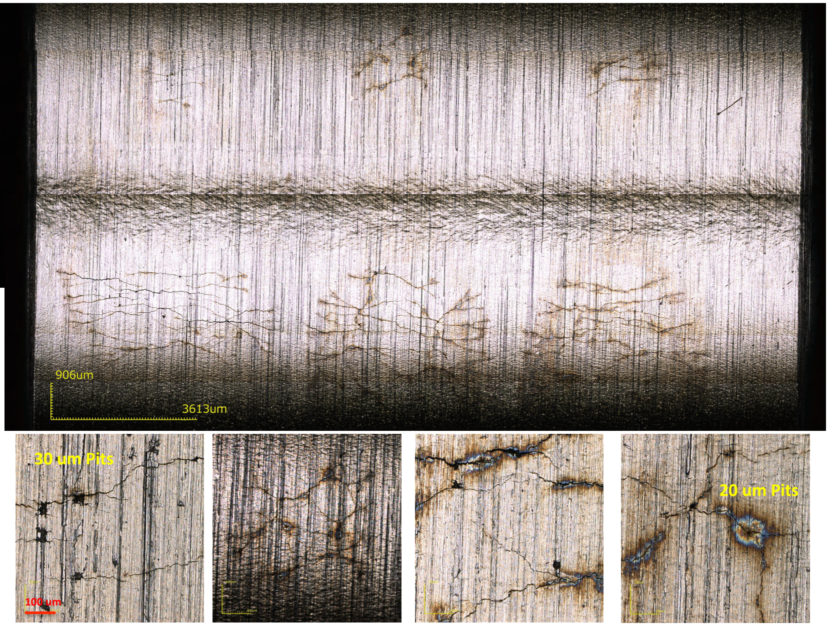


Cross-Section

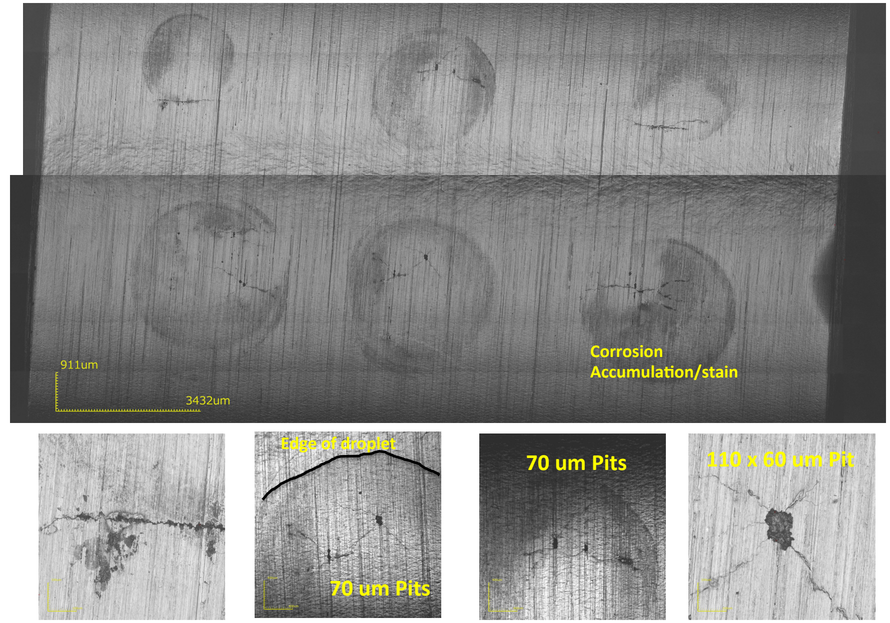


T= 30C

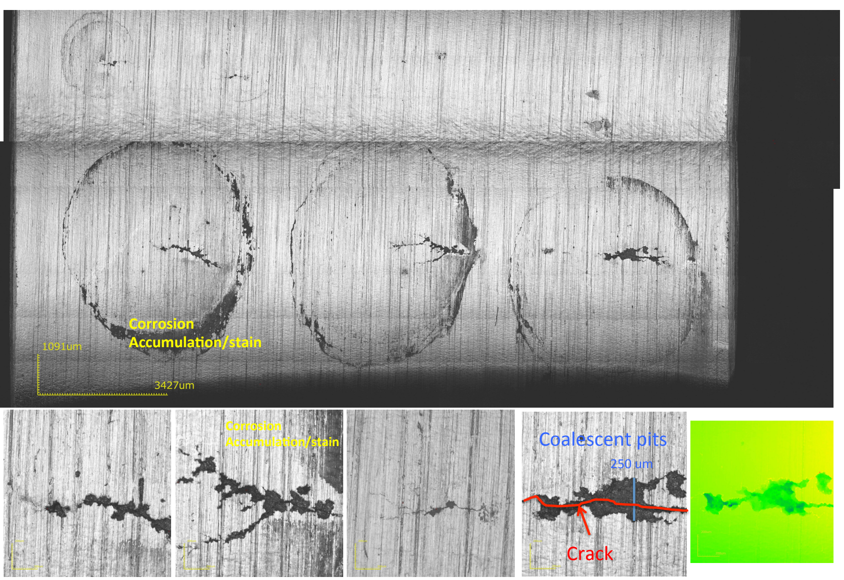
CH3COOK RH = 22%



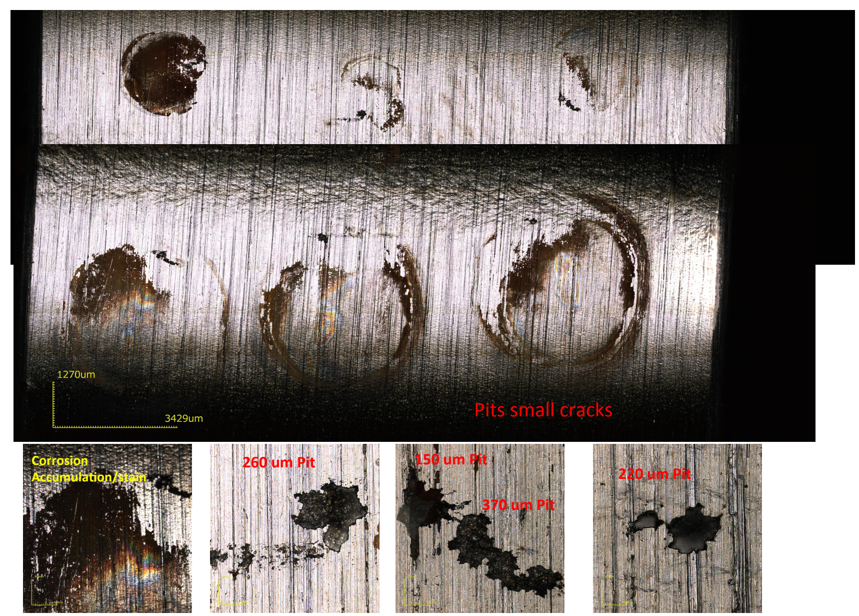
MgCl2 RH = 30%



K2CO3 RH = 40%



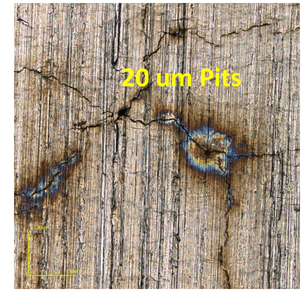
Mg(NO3)2 RH = 50%



Observations:

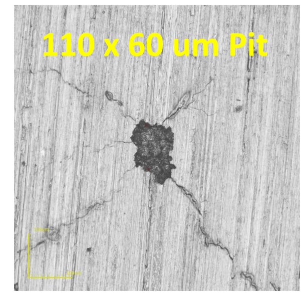
22%

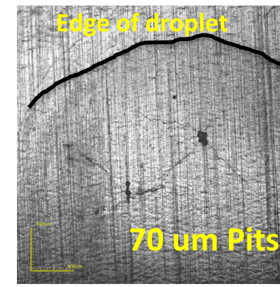
- Significant number of cracks
- Very small pits with ~ 20-30 μm in diameter
- Cracks stopped at the droplet interface
- Cracks are interconnected
- Small amount of corrosion accumulation/stain



30%

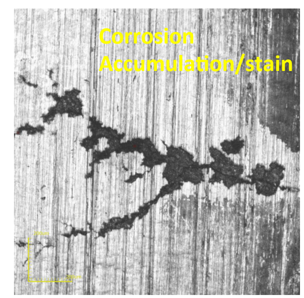
- Degree of cracking decrease in relation to 22%
- The number and size of pits increased
- Pits size in the 70-100 μm
- Pits are the origin of cracks
- Increased amount of corrosion accumulation/stain

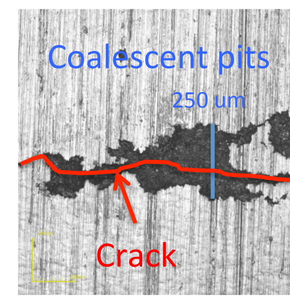




40%

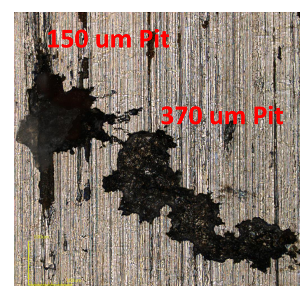
- Number of cracks decreased
- Cracks are observe within coalescing pits
- Elongated pitting in the 100's of μm
- Small amount of corrosion accumulation/stain

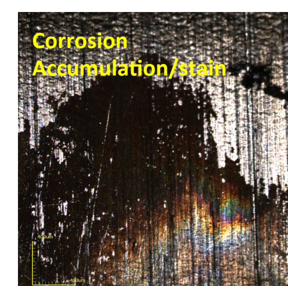




50%

- Surface corrosion is predominate
- Pits in the 100's of μm
- Very low number of cracks
- Mostly corrosion accumulation/stain





Overall Observations

		50°C			30°C		
	RH			Notes			Notes
CH_3COOK	22	A ◆■○	B ◆■○	Both samples exhibit TW SCC at both sides of teardrops, with small number of pits and large cracks	A ■○	B ■○	Lots of small cracks, cracks extend to the perimeter of the droplet. Very small pits
$MgCl_2$	30	A ■○	B ◆■○	Only one sample exhibit TW SCC, however the cracks are in both sides of the specimen, small number of pits	A ■○	B ■○	Small number of cracks with pits
K_2CO_3	40	A ■○	B ◆■○	TW SCC was only observed on sample 26 but only at one side of the specimen, increased number of pits and corrosion product. Cracking appears to be less severed	A ■○	B ■○	Pits are elongated and shallow, very small amount of cracks
$Mg(NO_3)_2$	50	A ■○	B ◆■○	TW SCC was only observed on sample 28 but only at one side of the specimen, increased number of pits and corrosion accumulation while the cracking is less severed	A ■○	B ■○	Lots of surface corrosion, small number of pits and cracks. Pits are elongated and shallow

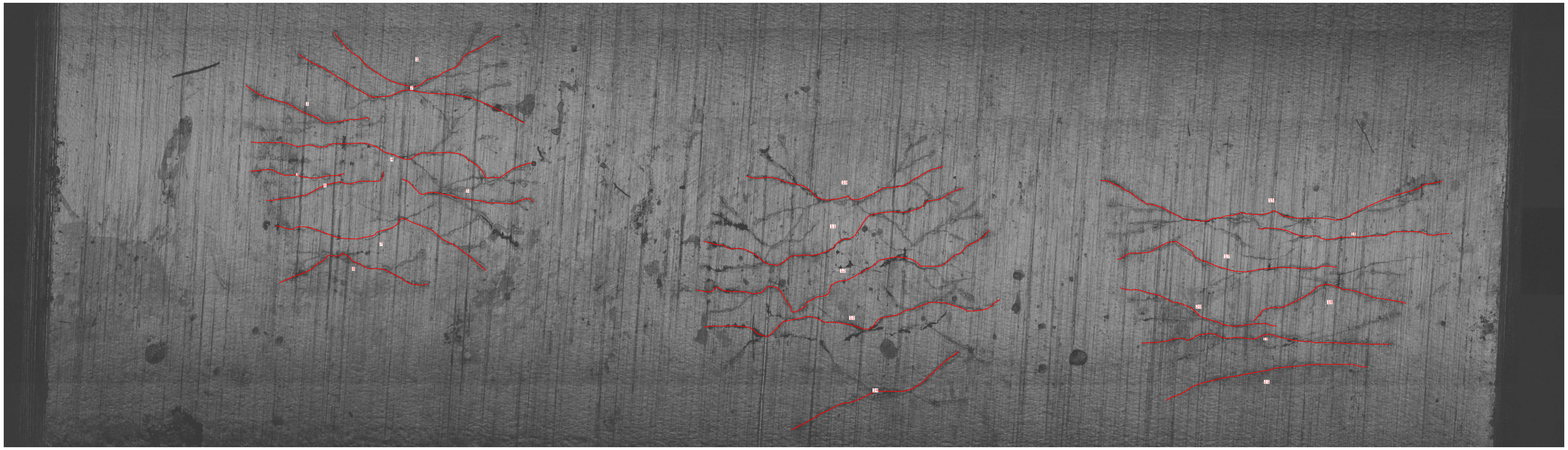
TW SCC = Through wall stress corrosion cracks

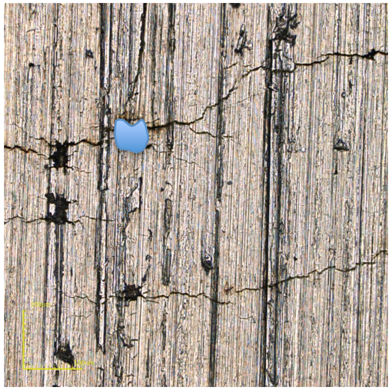
○ Pits
■ Cracks
◆ Through wall crack

Statistics on Crack Length at Different Relative Humilities

The objective is to quantify the cracks and pits as a function of RH.

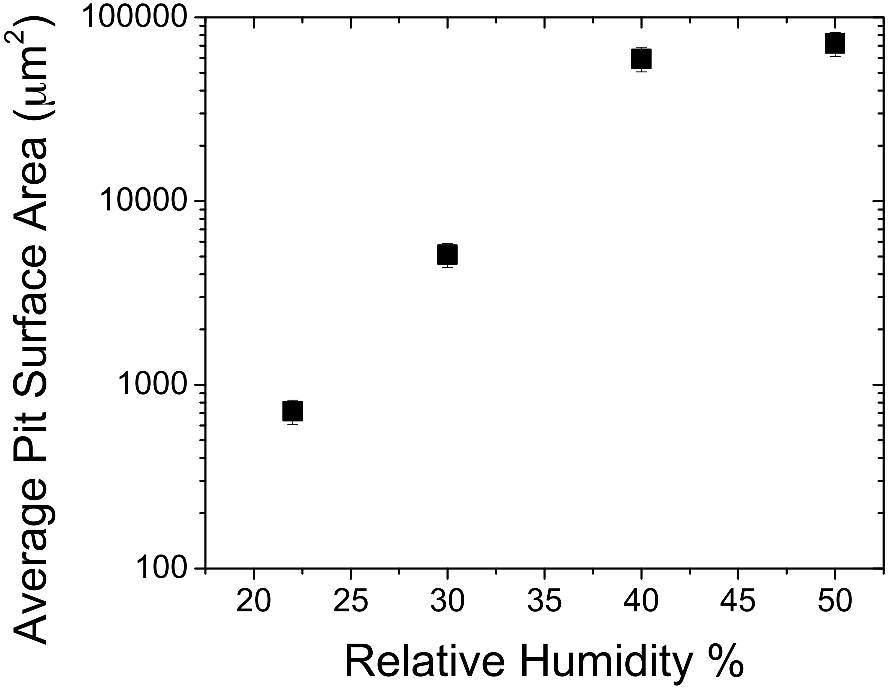
The lengths of the cracks and pit areas were obtained using Image software

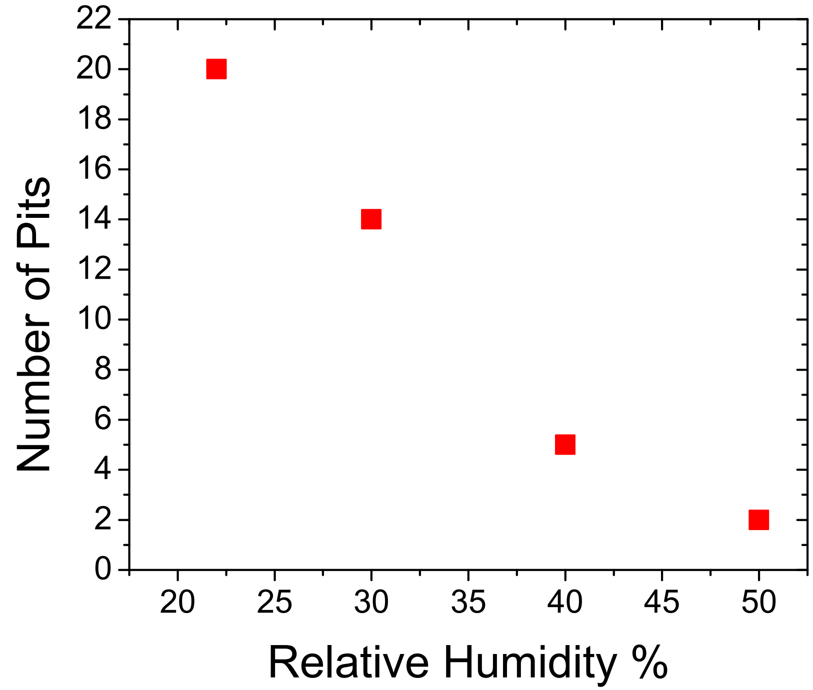




Pit surface area

Pits Surface Area at 30C

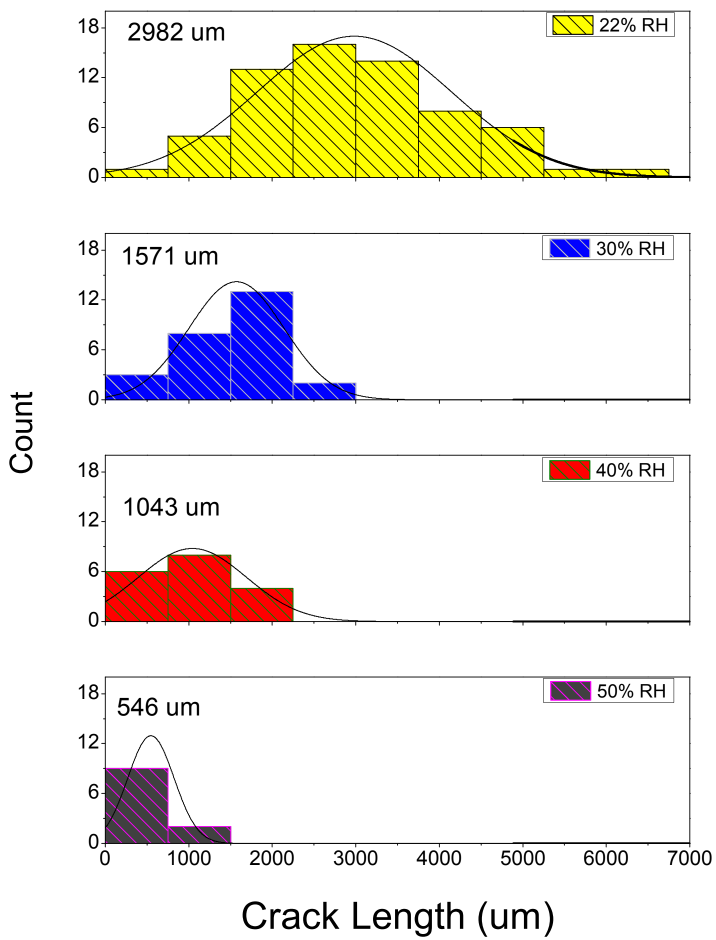


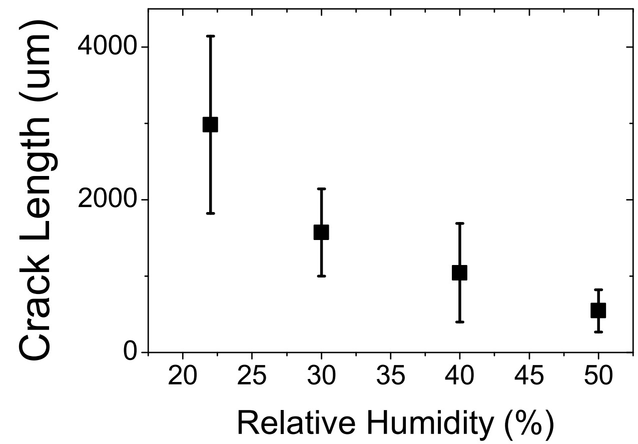


Surface area of the pits increase with increasing Rh, however the number of pits decrease with increasing RH

Cracks

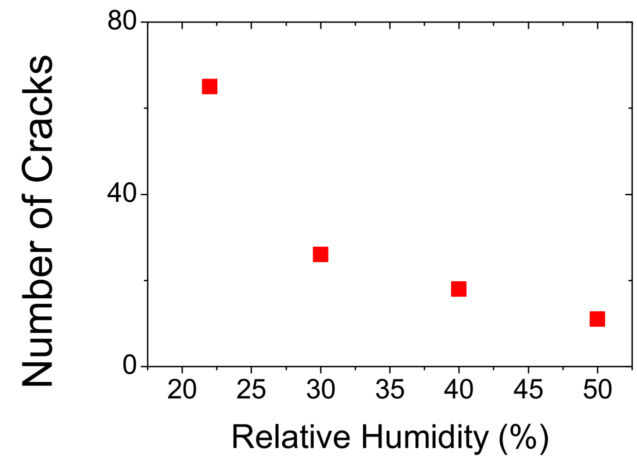
Temperature at 30 C and 90 Days Exposure





Error is the standard deviation

Decreasing crack length with increasing RH



Decreasing number of cracks with increasing RH

Figure 1 shows a significant changes in crack length distribution as a function of RH with longer and higher number of cracks at 22% RH. Histograms fitted with a normal distribution.

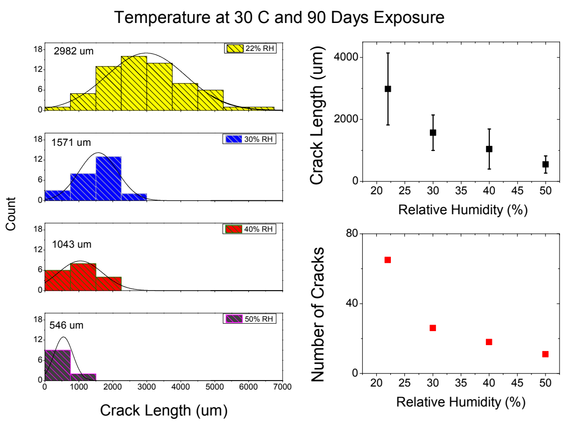
Overall Results

Most aggressive SCC close to the deliquescence od CaCl2 (22% RH) and 50C

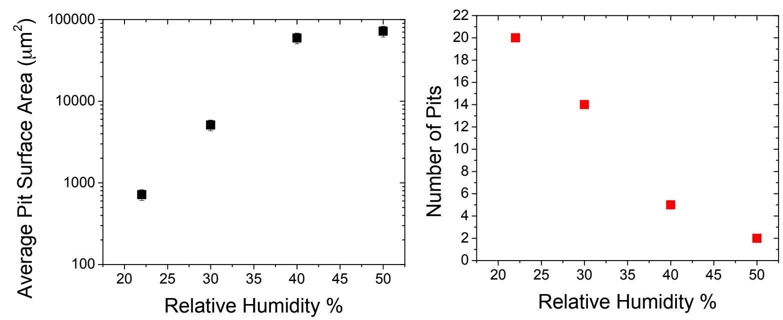
Unable to determine origin of crack

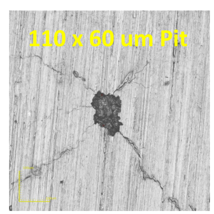
At 30 C the number and length/surface area of cracks/Pits decreases with increasing RH

Cracks



Pits





Lots of cracks originating from pits

Only through-wall cracks at 50C

Worse case scenario however not typical of 3013 storage containers as droplets size are unlikely

Droplet size

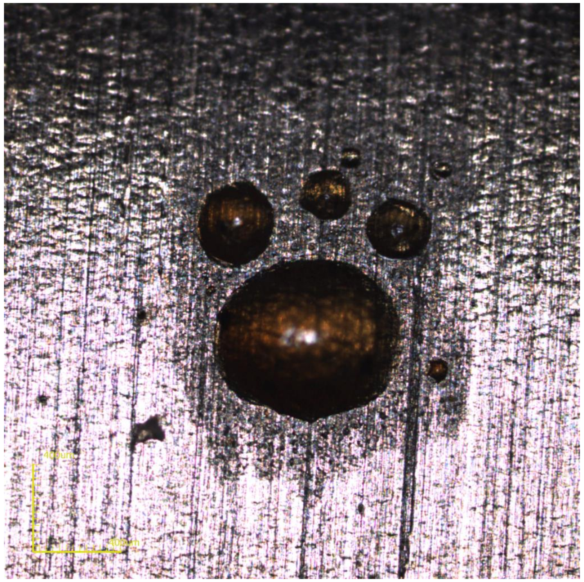
At 50 C and 20% RH

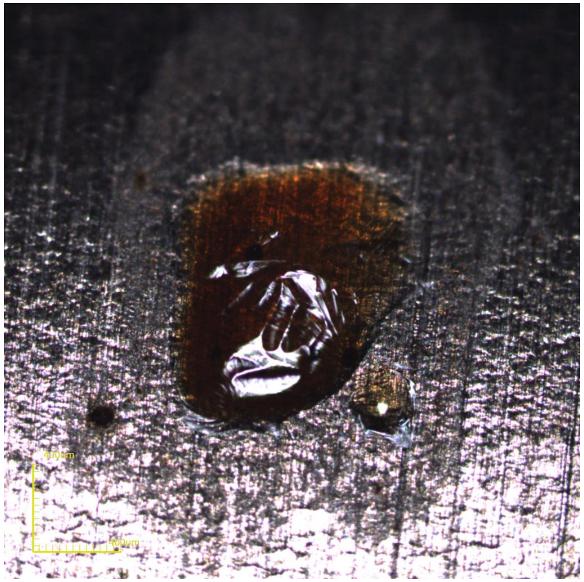
CaCl

Droplets obtained using a pL printer

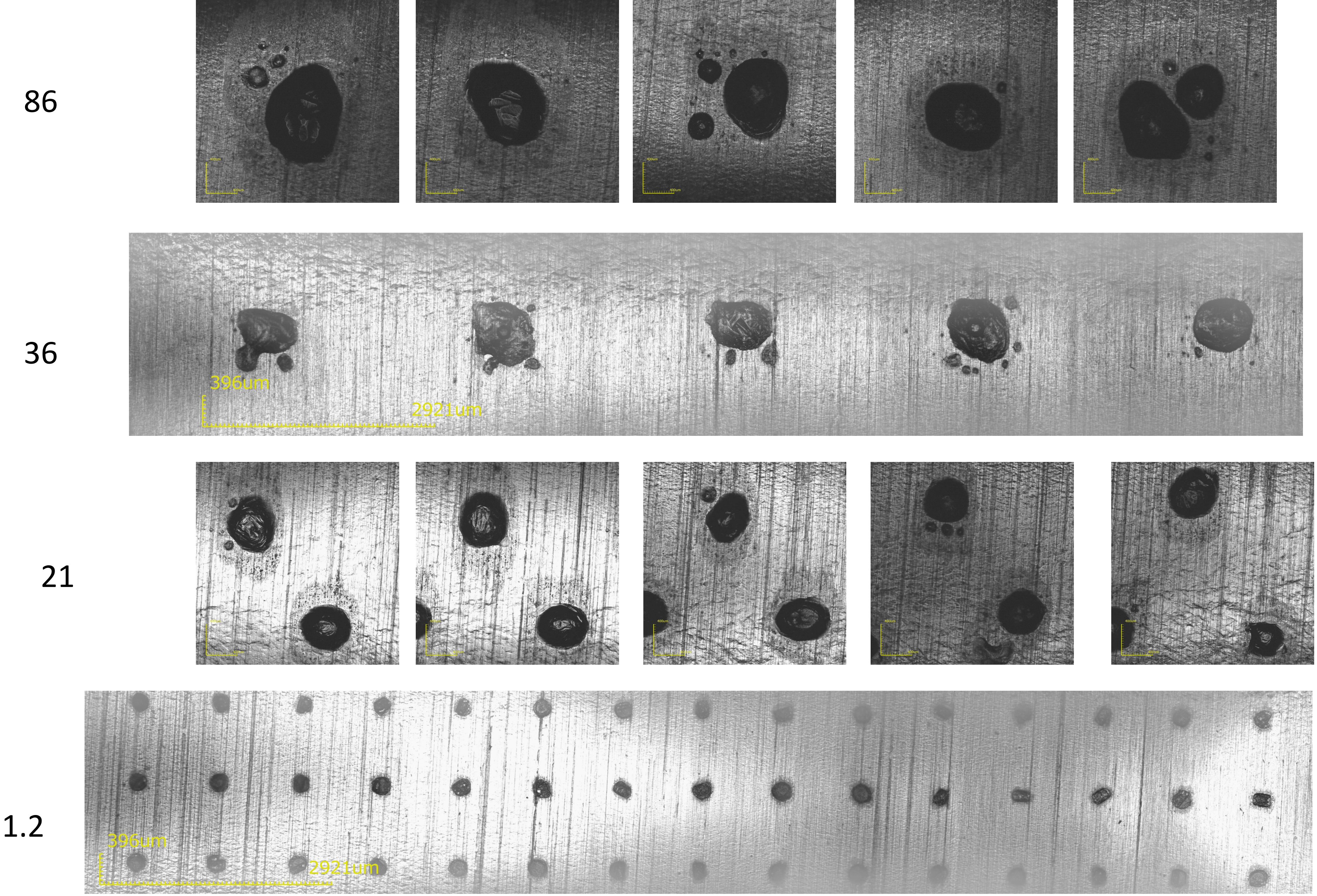
Droplet size in nL

0.001
0.01
0.1
0.3
1.2
21.6
38.8
86.6

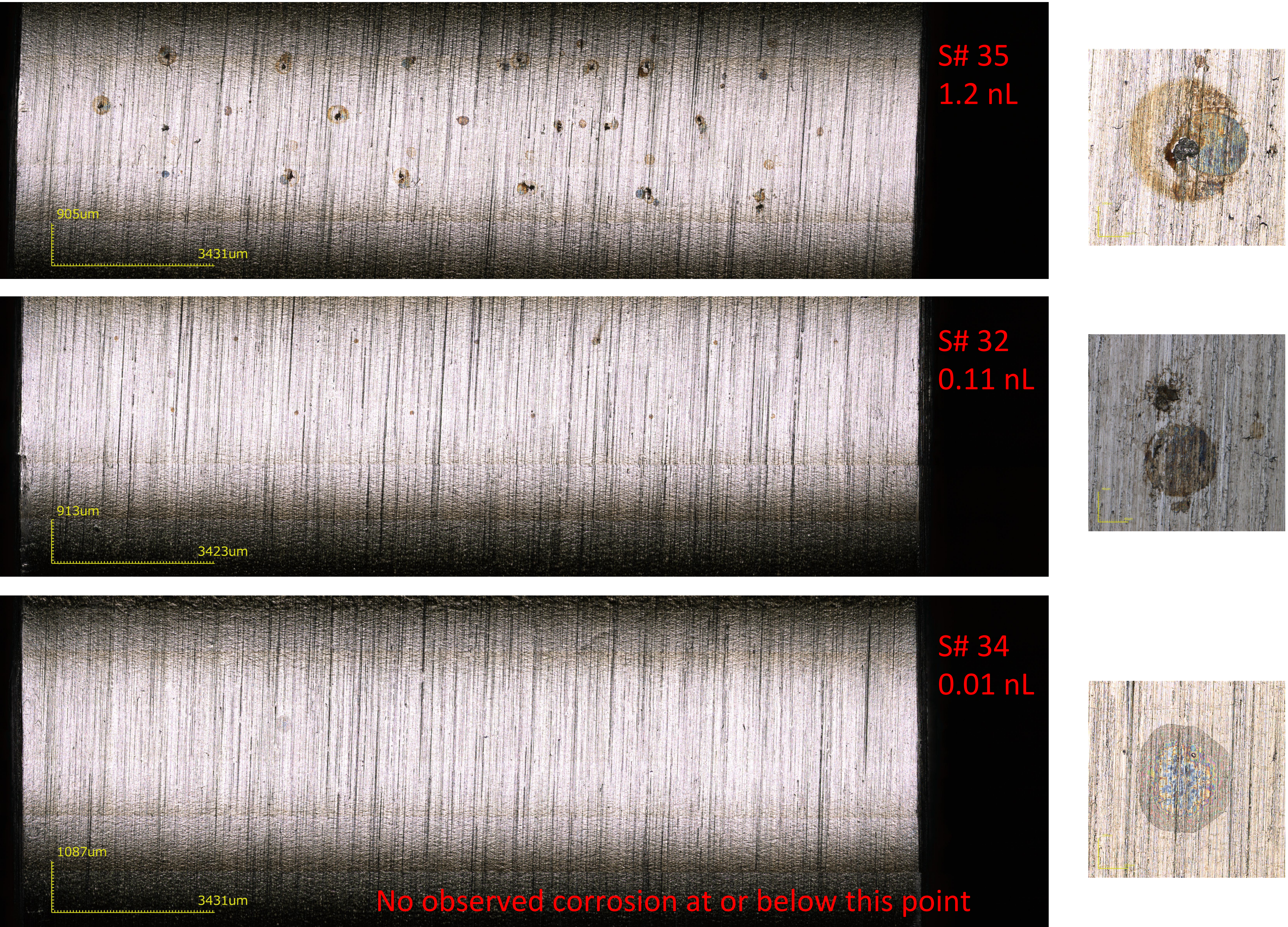




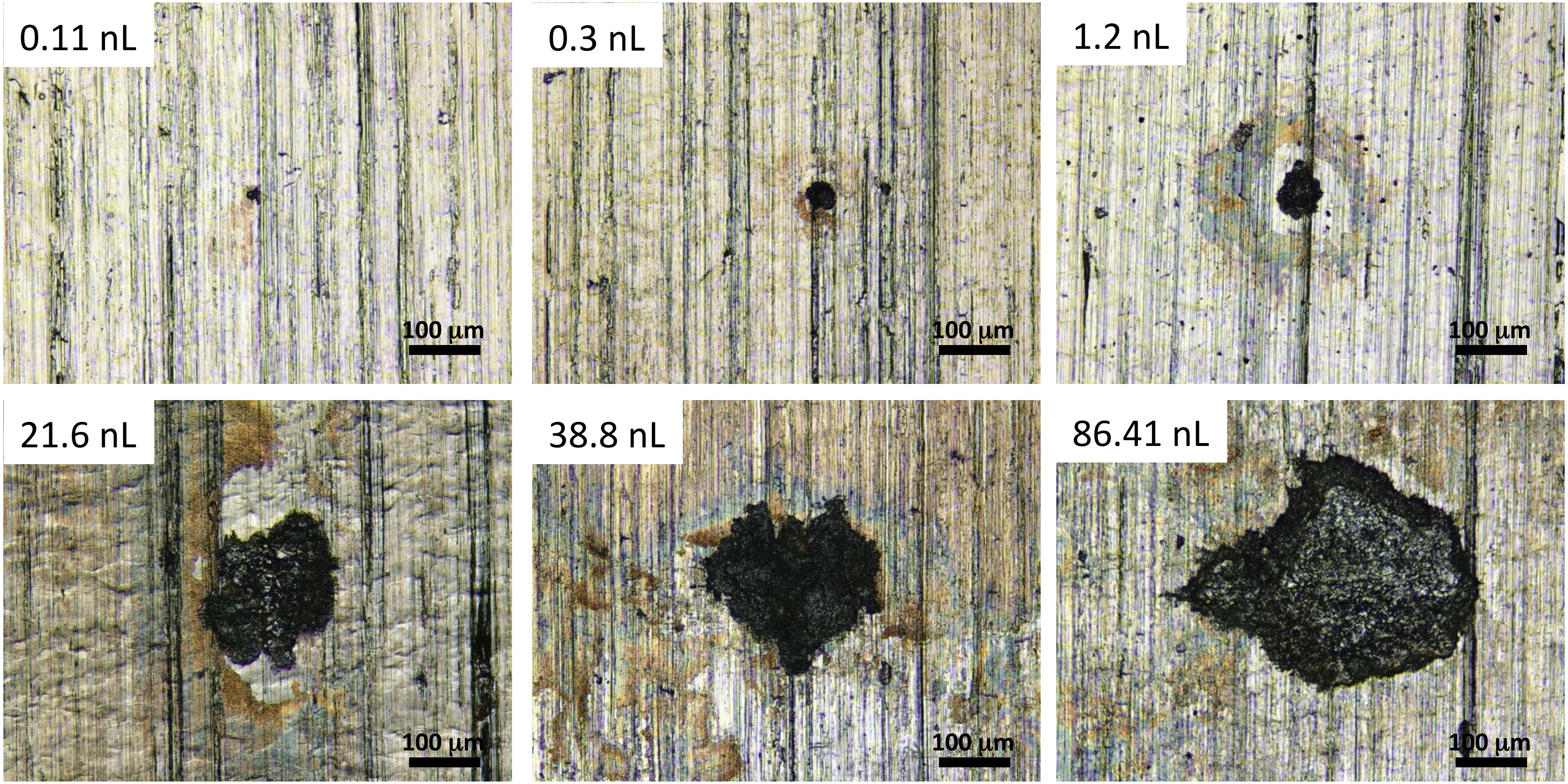
Number of droplets were determinate to be the volume of the big droplets were we saw pits and cracks



More uniform droplets as droplet size decreased


905um
3431um
S# 35
1.2 nL
913um
3423um
S# 32
0.11 nL
1087um
3431um
S# 34
0.01 nL
No observed corrosion at or below this point

Corrosion Pit Cut Off



Pit-size appear to increase with increasing droplet size

At 86, 38, and 21nL we observed >90% pits in each droplet

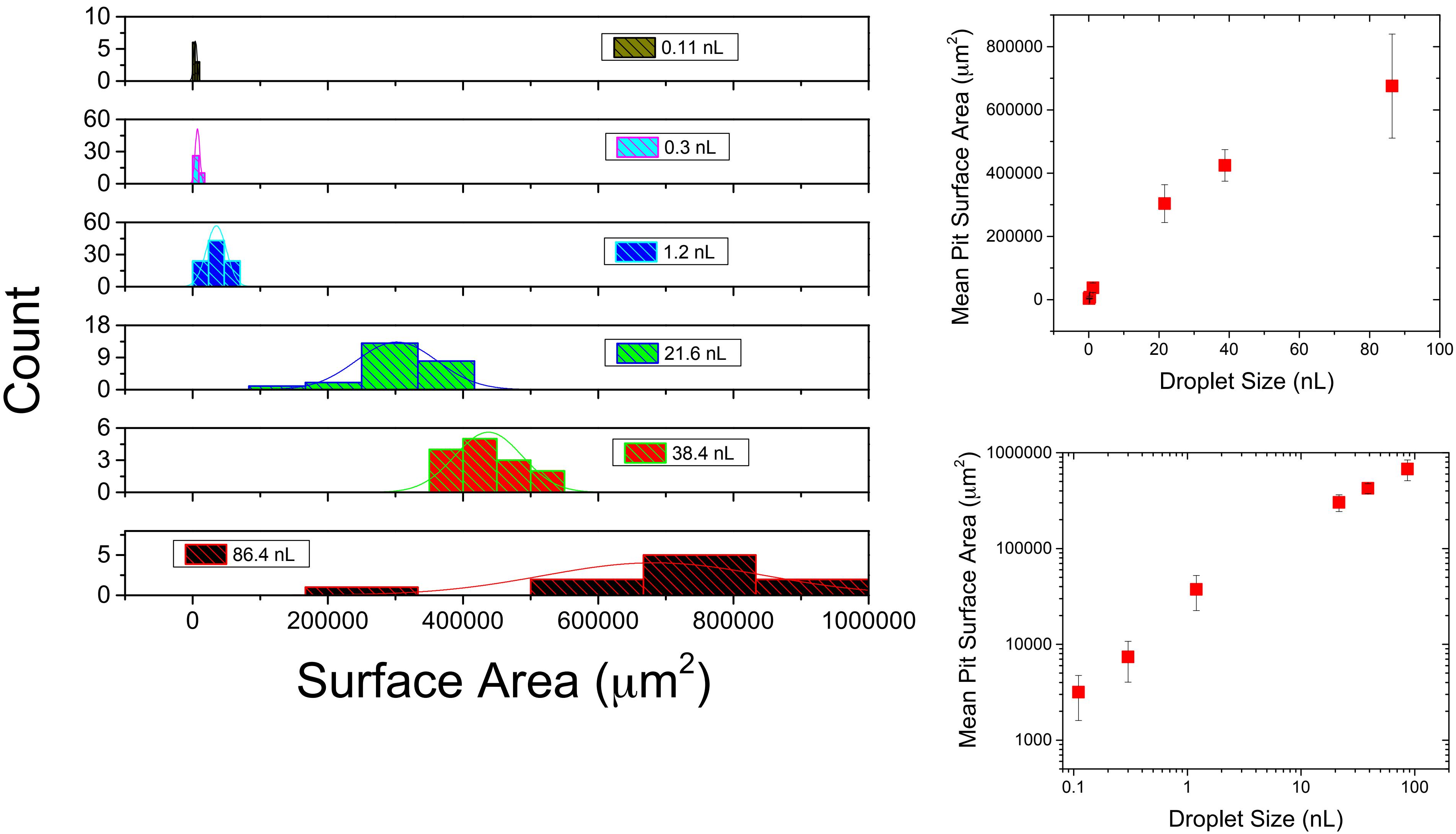
At 1.2nL ~50%

At 0.3nL ~30%

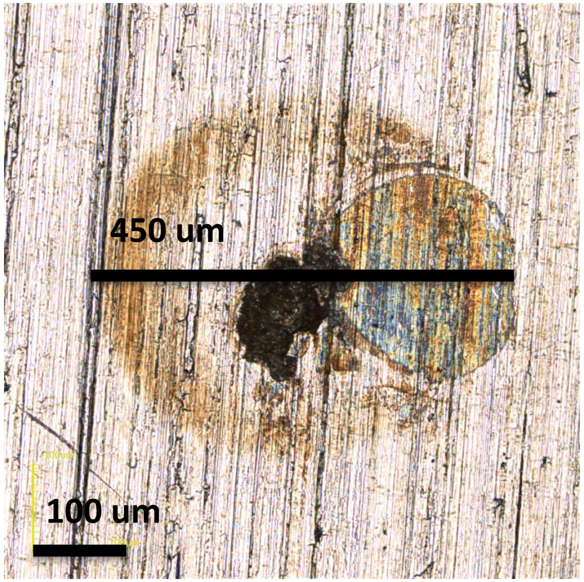
At 0.11nL <10%

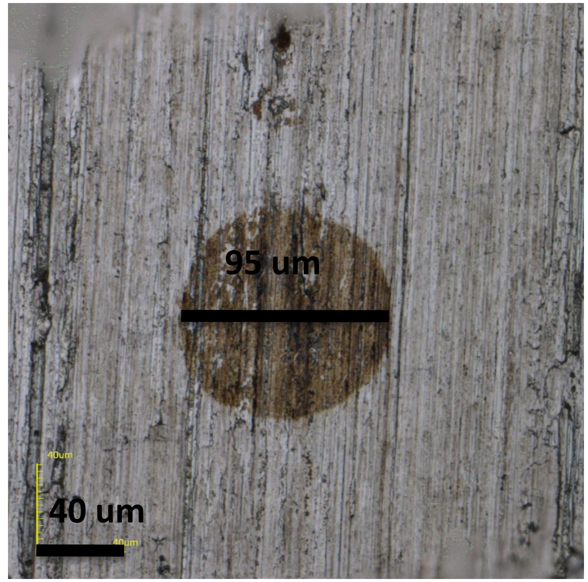
No pits observed below 0.11 nL

Corrosion Pit Surface Area Vs Droplet Size

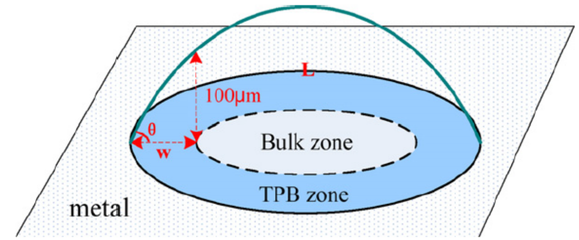


Types of Pits



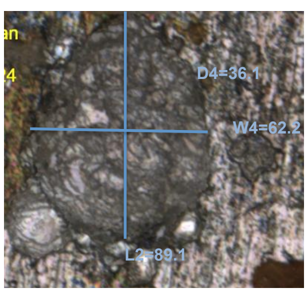


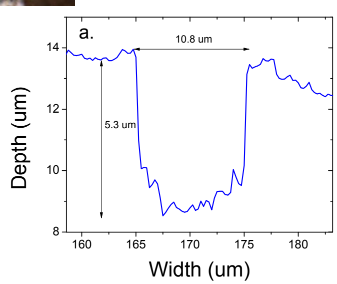
Pits much smaller than droplet

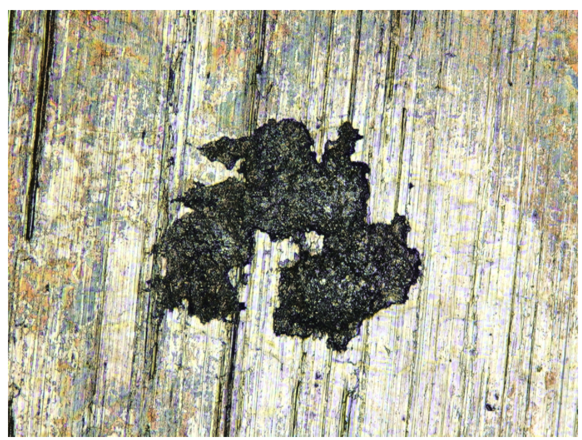


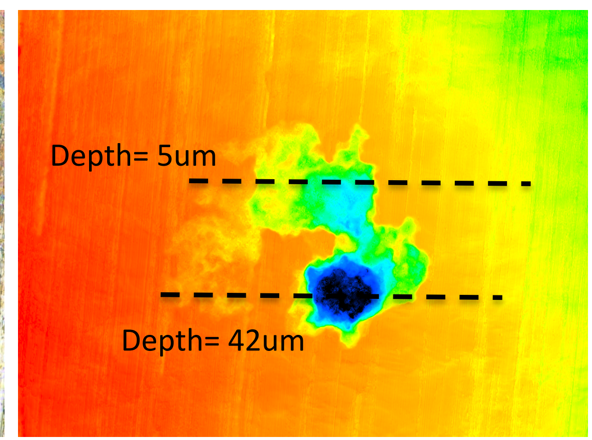
Shown by J. Berg

Irregulars in shape, diameter, depth





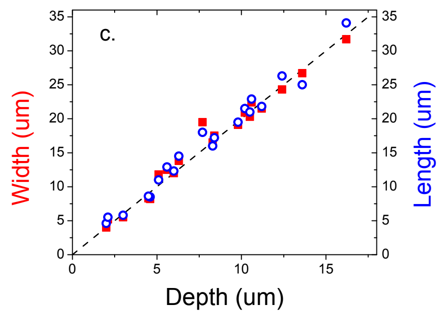


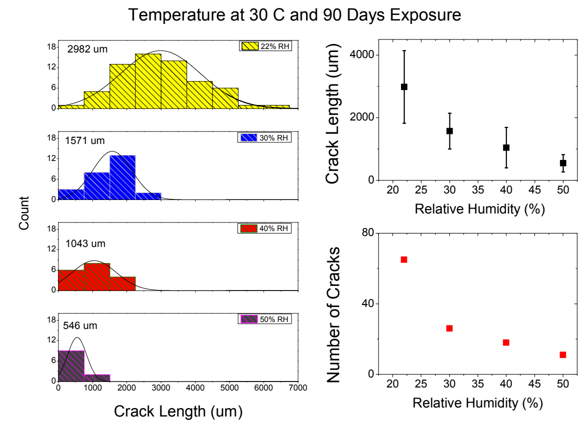


100's um in size

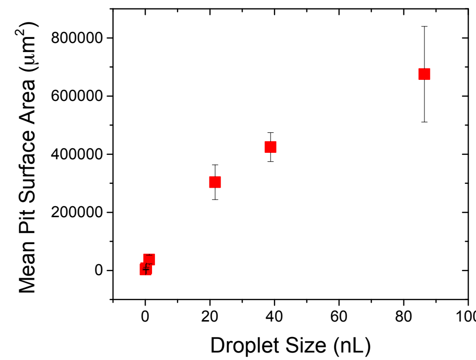
Conclusions

1. Quantitative information on pits and cracks

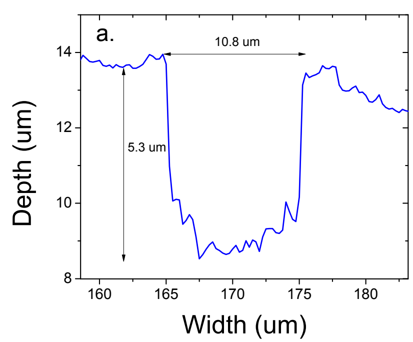


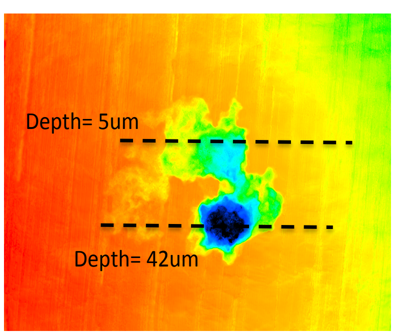


1. Dependence on Temperature, RH and size
   SCC worst at 22% RH
   Higher tem more aggressive corrosion



2. Direct information on pit





LA-UR-14-21867

Los Alamos NATIONAL LABORATORY EST.1943

Selection of 3013 Containers from K-Area for DE and for Disposition

3013 Surveillance and Monitoring Annual Program Review

March 24 – 27, 2014

FY13/FY14 DE Sample Selection

- Original FY 13 DE proposal – 7 random, 2 Engineering Judgment (EJ)
- Random - highest moisture based on 2011 random sample (*2011 Update, LA-UR-11-04417*)
  - EJ – H001236 (cats and dogs, high moisture) and S002277 (high moisture and Cl)
  - MIS WG letter to Allen Gunter, June 18, 2012
- Only one DE in 2013 - EJ item H001236
  - MIS WG letter to Allen Gunter, April 2, 2013

FY13/FY14 DE Sample Selection (con't)

- Remainder of FY13 moved to FY14 and an EJ item added
  - Added EJ item R610996 was packaged during the same work shift as R610960 (FY12DE8). Destructive examination data for R610960 showed anomalously high water vapor and H_2 and anomalously low N_2 in the headspace, as well as high moisture content in the material.
  - MIS WG letter to Allen Gunter, August 19, 2013

FY14 DE's (Are FY13 DE's moved forward - based on 2011 Random Sample)

Selection of FY14 3013 Destructive Examination Surveillance Samples for the Integrated Surveillance Program

Surv Year	Surv Type	ISP Bin	Selection Type	Site (Packaged)	Surveillance Comment	3013 Container ID
2014	DE	Pressure and Corrosion	Judgmental	RFETS	Stabilized during same work shift as R610960 (FY12 DE8).	R610996
		Pressure and Corrosion	Judgmental	SRS	High moisture by TGA-MS with positive Cl by prompt gamma	S002277
		Pressure and Corrosion	Random	Hanford	Random Sample with highest moisture from best available data	H003064
						H003307
						H003052
						H003898
						H004219
						H004024
				SRS		S002116
FY14 Total						9

Random Sample Changed in January, 2013 (*2013 Update*, *LA-UR-13-21195)*

- LANL went from 160 P&C to 8 in the total population and LLNL went from 111 to 109, so random sample changed

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**	

- **FY14/FY13 random DE items no longer highest moisture items in random sample**

Sample Section and Prioritization of DE's in FY15 and Beyond

- FY15-FY25
  - 73 more containers
    - 33 Hanford, 21 RFETS, 7 SRS, 11 LLNL, 1 LANL
  - 7 random per year until FY25, 3 in FY25
  - EJ to be determined
- Prioritized of random sample by moisture content based on 2013 (current) random sample

Selecting Containers for Disposition Based on Risk

- Priority 1 (442 containers) all from P&C bin
  - Rocky Flats material packaged at Hanford C-line and SRS (regardless of whether chlorine was detected)
  - Other containers packaged at Hanford C-line and SRS with detectable chlorine
  - Excludes previously DE'd containers

Selecting Containers for Disposition Based on Risk (con't)

- Priority 2 (135 containers) all from Pressure bin
  - Hanford materials produced from impure solutions and packaged in C-line: Filtrate (F), Cats and Dog(C&D), Critical Mass Laboratory (CMLs)
  - Excludes purified nitrate (PN)
  - Excludes previously DE'd containers

Disposition Priority Containers and DE

- 577 containers on disposition priority list
- 40 containers in future DE random sample
  - Includes seven random containers from 2014
  - (8 containers in DE random sample, not on priority disposition list)
- 351 containers MOXable
- Removing DE and MOXable containers,186 left on disposition priority list
  - 57 of these are under IAEA surveillance

Prompt Gamma Update

Joshua Narlesky & Elizabeth Kelly

March 26, 2014

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Outline

- Overview
- FY13 Analyses
- Results for new calibration models
- Summary

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*

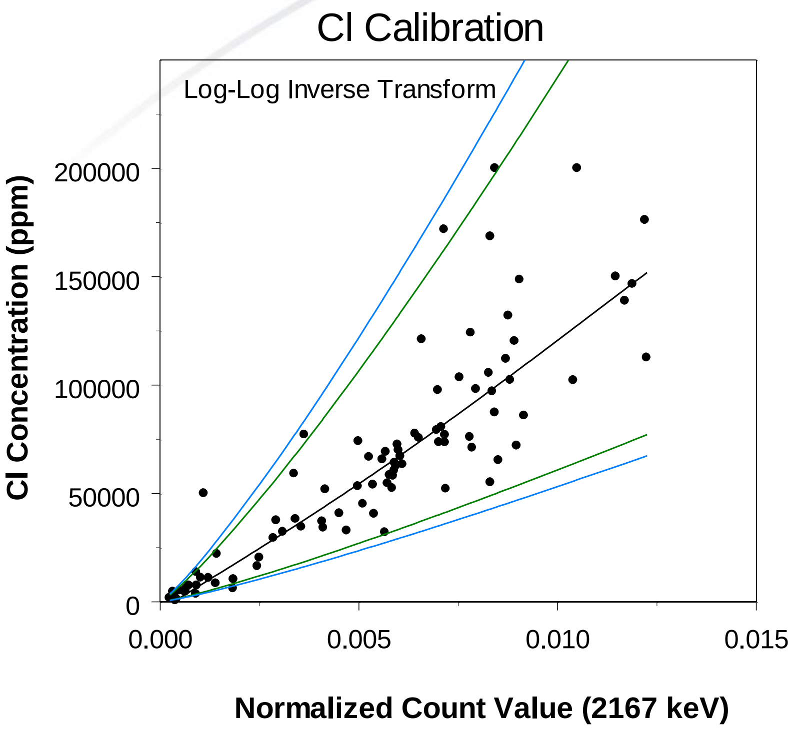
Element	Isotope Detected	Isotopic Abundance (%)	Element $LLD_{60\ min}$ (%)	Semi-Quantitative Analysis
Li	^{7}Li	92.5%	0.026%	No
Be	^{9}Be	100.0%	0.008%	**Yes**
B	^{10}B	19.9%	0.046%	No
N	^{14}N	99.6%	No data	No
O	^{18}O	0.2%	13.0%	No
F	^{19}F	100.0%	0.200%	**Yes**
Na	^{23}Na	100.0%	0.014%	**Yes**
Mg	^{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

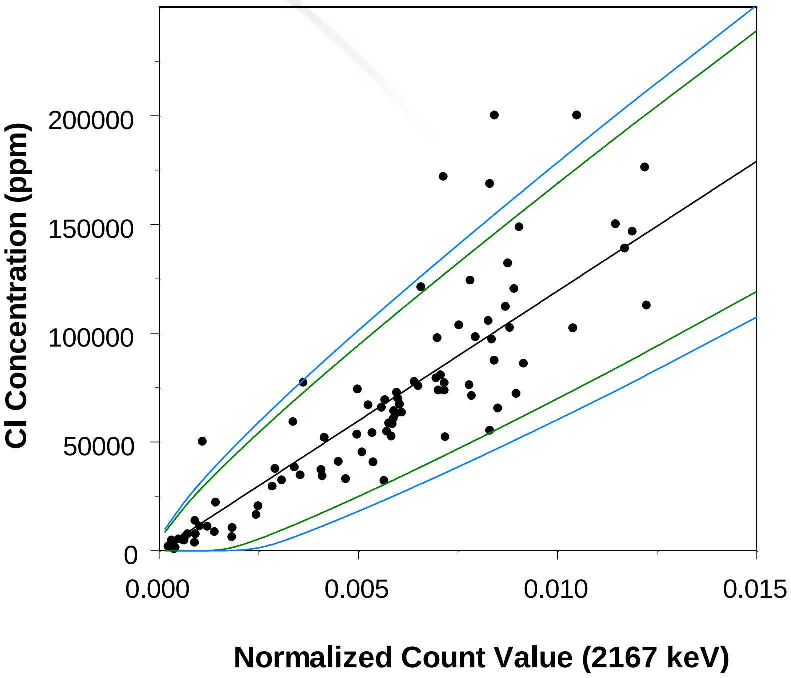
Analyses in FY13

- ARIES material
  - Pure oxides
  - Analyses completed: 48
  - Impurities: Be detected in 3 containers (all originated in to same blend lot)

Calibration: Old vs New



Inverse transform (power function)



New Model (WLS)

Status of new calibration

- Completed work to refine models and reduce uncertainty
  - Added new data for fluorine model
  - Review of diagnostic plots
  - Identified sources of variability in data
    - Materials with high U or undissolved solids
    - Correction for Na interference applied to Mg data
  - Identification and removal of outliers
  - Selection of best model(s) for use in database
- Final report nearly complete
  - Model(s) and conditions
  - Details for implementation in database
  - Supplementary information: models for other peaks based on relative intensity

Results

Element (Model)	Sensitivity (cts/ppm)	Maximum Range (wt%)	Uncertainty range at 1 wt%	Uncertainty range at 5 wt%	Uncertainty range at 10 wt%
Cl (WLS)	9.10E-08	17.6	0.0 – 2.3	2.0 – 8.0	5.8 – 14.2
Cl (MOX)	1.10E-07	8.0	0.0 – 2.0	2.7 – 7.3	n/a
Cl (Log-Log)	--	17.6	0.5 – 2.0	2.5 – 10.2	4.9 – 20.2
Mg (WLS; all)	3.61E-07	32.7	0.0 – 2.3	2.0 – 8.0	5.8 – 14.2
Mg (WLS; Cl)	5.39E-07	3.7	0.5 – 1.5	n/a	n/a
Mg (WLS; No Cl)	3.54E-07	32.7	0.0 – 2.4	2.0 – 8.0	5.7 – 14.2
Mg (Log-Log)	--	32.7	0.3 – 3.3	1.5 – 16.3	3.1 – 32.8

Results

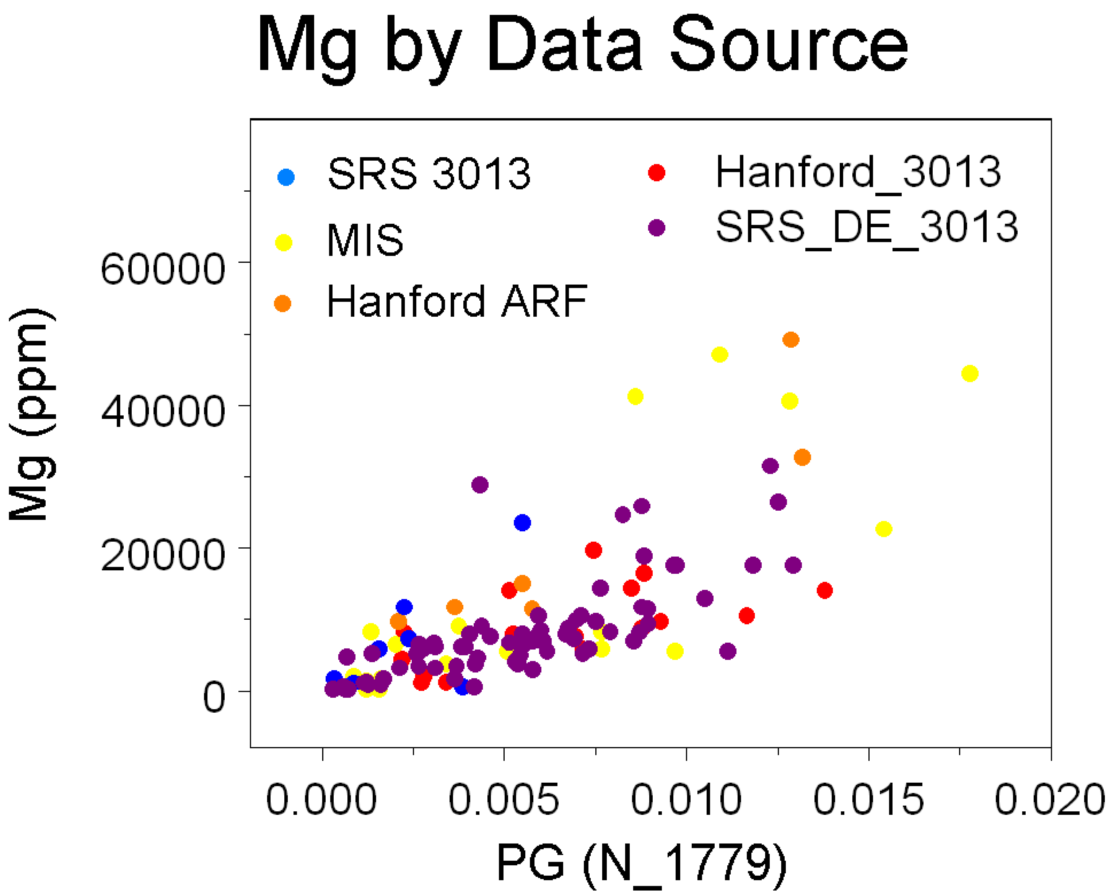
Element (Model)	Sensitivity (cts/ppm)	Maximum Range (wt%)	Uncertainty range at 1 wt%	Uncertainty range at 5 wt%	Uncertainty range at 10 wt%
Al (WLS)	8.28E-07	4.0	0.2 – 1.8	n/a	n/a
Be (WLS)	1.53E-05	1.1	0.6 – 1.4	n/a	n/a
F (WLS)	1.08E-06	22.9	0.0 – 2.0	2.7 – 7.3	6.6 – 13.3
P (WLS)	3.84E-07	2.1	0.5 – 1.5	n/a	n/a
K (WLS)	7.34E-08	7.8	0 – 2.2	2.5 – 7.5	n/a
Na (WLS)	3.98E-06	5.2	0.4 – 1.6	3.7 – 6.3	n/a

Summary

- New calibration equations were developed using WLS
- New method and new data (113→ 166 data points)
  - Includes analytical chemistry from DE through FY12
  - Additional data for F from 3013 DE
- Reduced uncertainty for high concentrations
- Next steps
  - Update detection limits—related to sensitivity
  - Complete report
  - Update database—minimal impact to existing analyses and binning

Additional Slides

Sources of Variability for Mg



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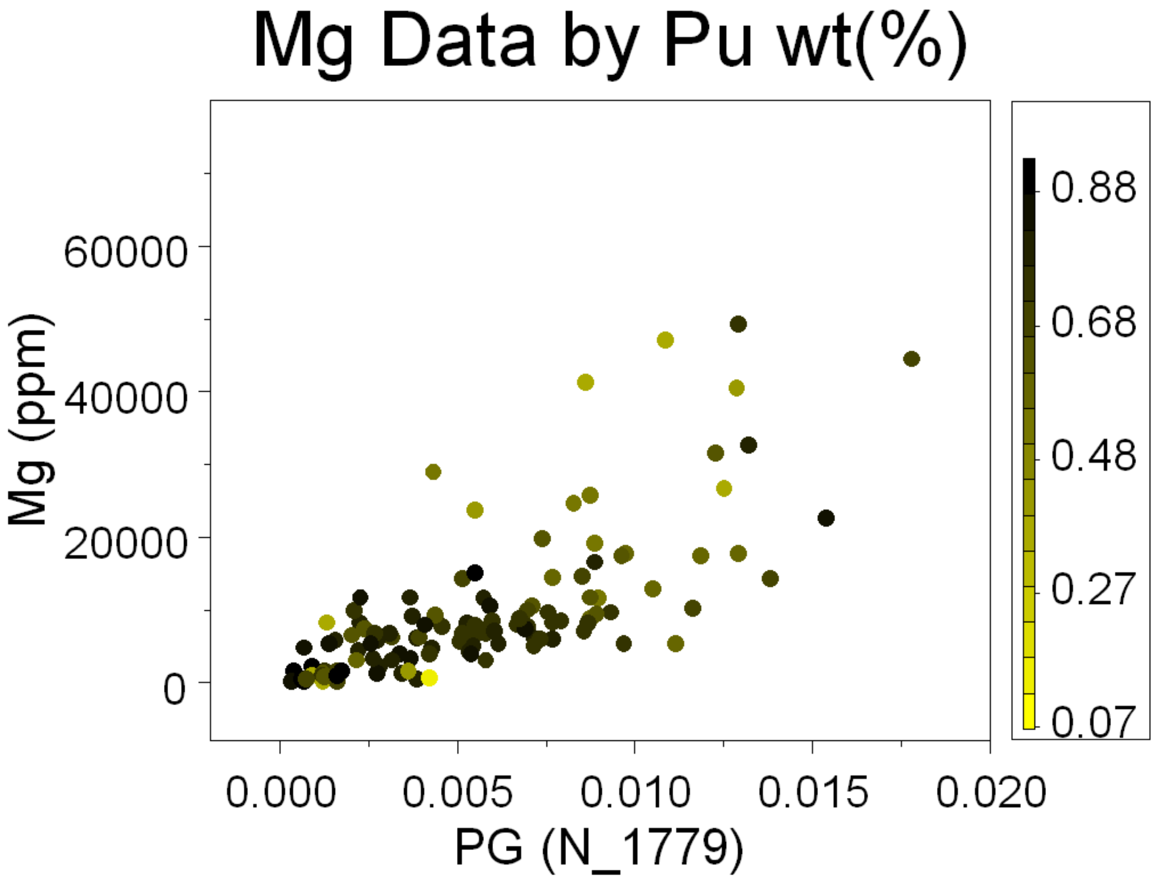
Sources of Variability for Mg



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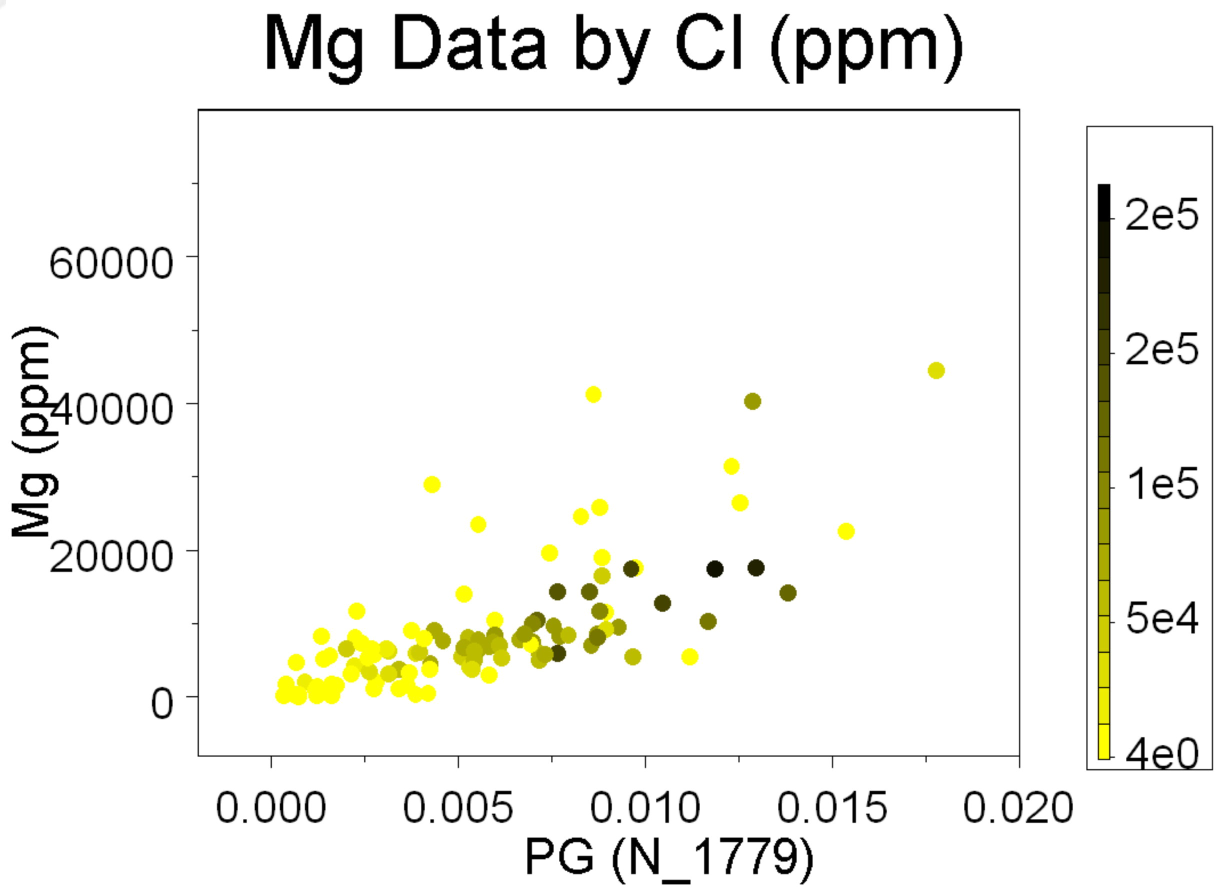
Sources of Variability for Mg



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)

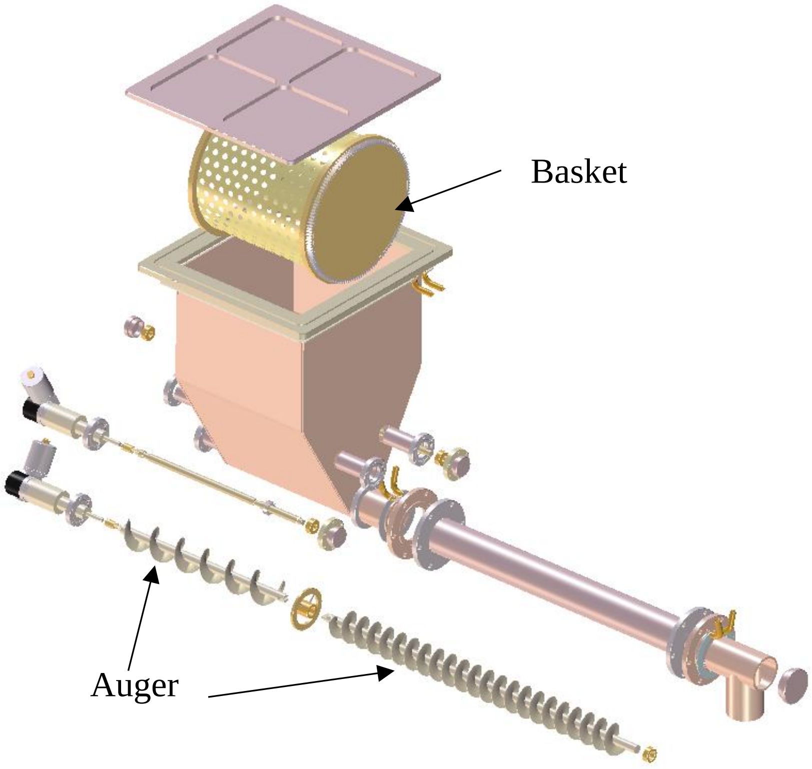
Ron Livingston (SRS)

MIS Program Review, SRS, February 2013

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

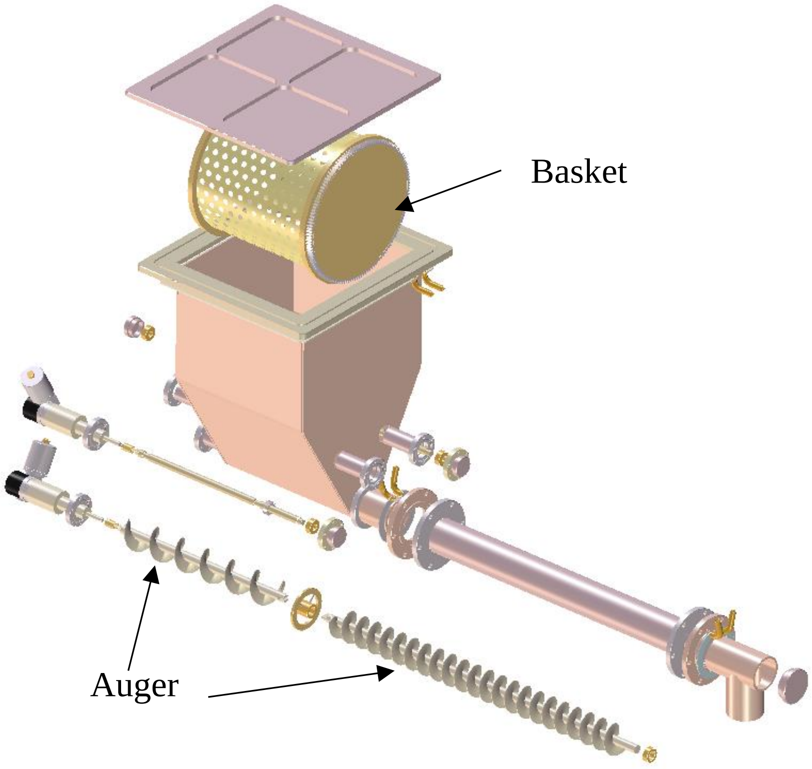
LANL ARIES Direct Metal Oxidation System (DMO-2)

- 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



Steps to Technical Equivalency Document

- **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.**

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.

Concluded that 650 °C will meet stabilization objectives subject to the following controls:

- Limited to specific feed material and process equipment.
- Maintain a minimum material temperature of 650°C for a minimum of two hours.
- Flowing gas mixture of 75% O_2 and balance an inert gas.
- Prohibit exposure of stabilized oxide to glovebox atmosphere greater than 15% RH.
- Moisture measurement by TGA in an inert carrier gas or by a related method with added moisture detection capability such as TGA-MS in an inert carrier gas. (Not LOI).
- Testing of initial production runs and periodic sampling of subsequent runs to verify negligible residual reactivity after stabilization.

Concluded that 650 °C will meet stabilization objectives

It is recommended that the required minimum sustained stabilization temperature for DMO oxide be lowered from 950 °C to 650 °C as doing so will not compromise the ability to achieve stabilization objectives. This conclusion applies subject to the following controls:

- Feed material and process equipment shall fall within the scope of this document (see section 1.2).
- The stabilization operation shall maintain a minimum material temperature of 650°C for a minimum of two hours.
- The stabilization process shall take place under a flowing gas mixture consisting of approximately 75% O_2 by volume, with the balance being an inert gas.
- Post-stabilization handling procedures shall prohibit exposure of stabilized oxide to glovebox atmosphere greater than 15% RH.
- Post-stabilization moisture measurement shall be performed by TGA in an inert carrier gas or by a related method with added moisture detection capability such as TGA-MS in an inert carrier gas.
- The first three product lots stabilized to 650 °C shall be tested to verify negligible residual reactivity after stabilization. Subsequent batches shall be sampled and tested periodically to confirm that the process continues to produce oxide with negligible residual reactivity. SSA shall also be measured on the first three production lots.

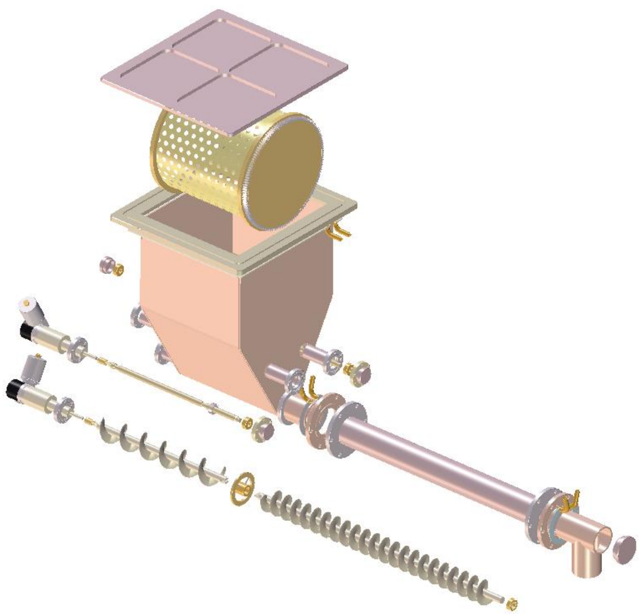
Concluded that 650 °C will meet stabilization objectives

Subject to the following controls:

- Limitations on feed metal shapes.
- Flowing gas mixture consisting of approximately 75% O_2 by volume, with the balance being an inert gas.
- Post-stabilization handling < 15% RH.
- Post-stabilization moisture measurement shall be performed by TGA gas or TGA-MS in an inert carrier gas.
- First three product lots tested for residual reactivity after stabilization. Subsequent batches shall be sampled and tested periodically.

Independent Review of LANL DMO Equivalency

Ted Venetz
Review Team Lead
Washington River Protection Solutions



Independent Review Team

- Established by DOE/SR , Chairman of the Integrated Surveillance Program, in June 2013

- Members
  - Beth Hackney,
  - Savannah River Nuclear Solutions

  - Laura Worl,
  - Los Alamos National Laboratory

  - David Riley,
  - Lawrence Livermore National Laboratory

  - Ted Venetz,
  - Washington River Protection Solutions

- All long time MIS Working Group Members with extensive experience with DOE-STD-3013.

Initial Revision

- Received Primary Document from SRS AMNMSP on 7/25/2013
- LA-UR-13-23120, technical basis supported by LA-UR-13-20802, Stabilization Tests
- No team involvement in document preparation
- Site Visit August 27-28th
- Examined equipment, controls, procedures
- Provided initial comments and met with authors and facility staff to develop path forward
- Submitted 24 comments back to AMNMSP on 9/11/2013

Initial Revision Comments

- 16 essential comments in key areas
- Additional specificity of DMO process conditions
  - Packaging RH, oxidizing gas
  - Not rely on "20 points"
- Better Definition of feed envelope
  - "Plutonium metal parts taken from surplus pits"
- Product sampling to ensure material produced is the same as that tested in the technical basis
  - Initial process verification and periodic process verification
- Moisture measurement by TGA/MS or TGA inert
- Testing and Equivalency is specific to LANL DMO-2 and DMO-3 process and does not include muffle furnace oxidization and massive metal (buttons)

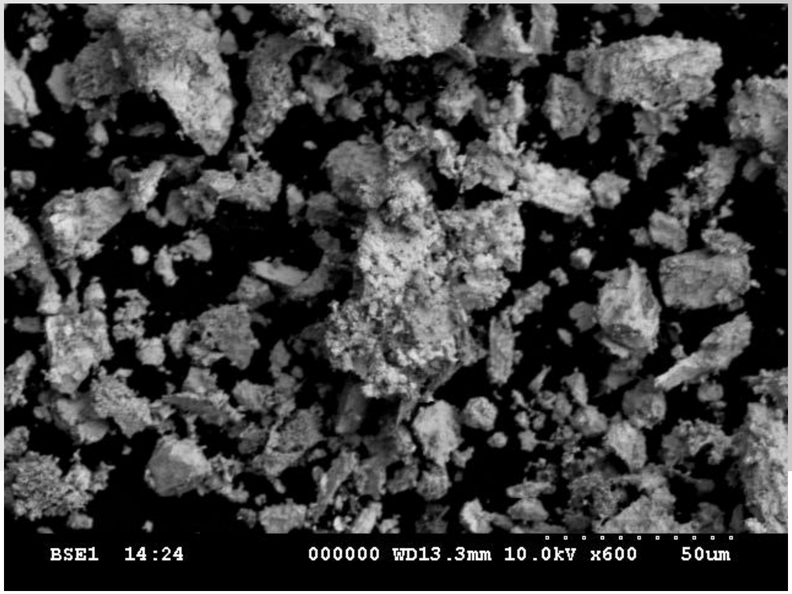
Final Revision

- Team worked closely with authors to address issues
- LA-UR-14-20201 issued to capture Thermal and Physical Properties of ARIES Produced Oxide
- Final Revision of Equivalency Document received from LANL 2/7/2014
- Comment Resolution Table received 2/12/2014
  - Team feels all comments satisfactory addressed
- Issues to be addressed in "20-points" document
  - Equivalency states initial process verification on first three batches
  - Periodic requirements to be worked out with receiver site

Concluding Remarks

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

Thanks to team members, LANL staff , document authors, and DOE/SR.



Oxide Production Update Status and Path Forward

Steve McKee

3013 Surveillance and Monitoring Annual Review

MET-1

March 26, 2014

Plutonium Science and Manufacturing
Los Alamos National Laboratory

Outline of presentation topics

- TA-55 paused operations
- LANL Oxide Production
- Material Storage
- Process Qualification
- 3013 Packaging

Authors of this work

- PITD – **Wendel Brown**, Alonso Archuletta, **Ernie Montoya**, Anthony Martinez
- DMO – **Larry Peppers**, Jennifer Butler, Alexis Perry, John Valdez, Aaron Martinez, **Kenny Martinez**, Xavier Martinez
- Oxide Processing – **Dave Wayne**, **Liz Bluhm**, David Medina, Judy Roybal, Daniel Garcia, Richard Salazar
- Packaging – **Jane Lloyd**, **Scott Breshers**, **Curtis Emms**, **Harry Majors**, Daniel Garcia, Kenny Hansel, Timmy Lopez
- NDA – **Tracy Wenz**, **Gary Herrera**, Lyn Foster, **Walt Hansen**
- Ops Support – **Minnie Martinez**
- Eng – **Troy Harden**, **Vince Trujillo**, **Yvette Valdez**, **Kurt Weisbrod**, Diego Jaramillo, **Tim Renshaw**
- Quality – **Mark Swoboda**, Russ Klement, Karen Haynes, Mark Haines, Dan Stewart, Jennifer Elson
- Greg Powell and many others…

(red) > 15 years on the project

(blue) > 10 years on the project

(green) > 5 years on the project

TA55 paused operations…

To/MS: LANL- All
From/MS: Charles F. McMillan, A100
Phone/Fax: 7- 5101/Fax 5- 2679
Symbol: DIR-13-161

Date: June 27, 2013

SUBJECT: PAUSE IN PF- 4 PROGRAMMATIC OPERATIONS

Because of the nature and importance of the work we do, we must regularly assess all aspects of our operations to ensure we are executing our procedures and operational processes appropriately. Based on reviews with facility operations staff at PF- 4, and findings from recent assessments, I have decided to temporarily pause programmatic activities effective this afternoon. As I shared at our last all - employee meeting, it's very important for employees to raise concerns, and it's just as important for leaders to respond and take action. That's exactly what I'm doing and what I expect of others…

- Current resumption schedule and oxide production (published 14 February 2014):
  - "cold" equipment activities – end of April 2014 start
    - "cold" is defined as operational without plutonium
  - "hot" equipment activities – early June 2014 start
    - "hot" is defined as operational with plutonium
  - return to "normal" programmatic operations – August 13, 2014 start
    - "normal" is defined as the new world order…
    - expectation is much lower limits for SNM as operations resume with changes at a later date…

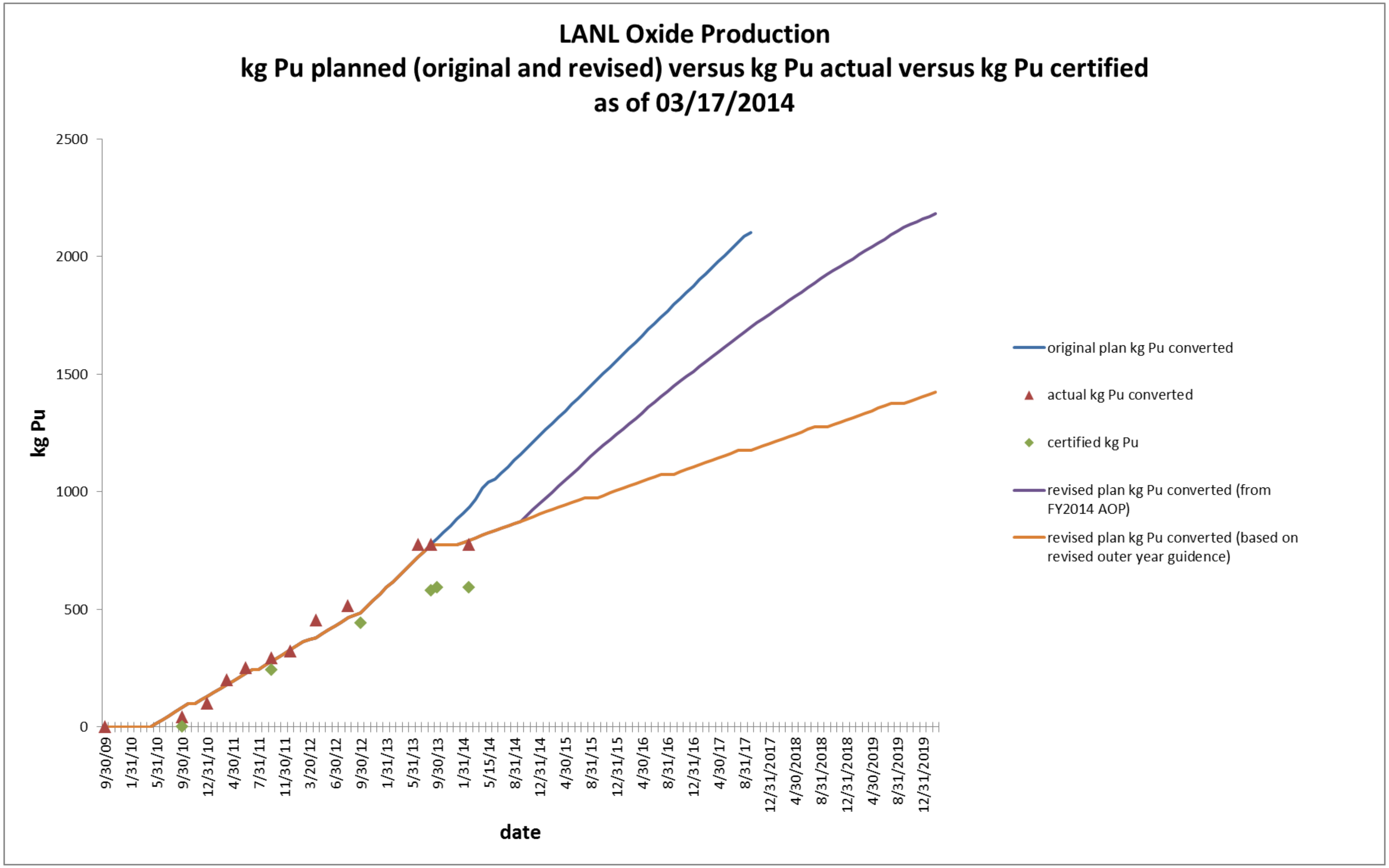
…has impacted LANL Oxide Production

	Annual Target kg Pu Converted to Certified Oxide	Cummulative Target kg Pu converted to Certified Oxide	Actual kg Pu converted to Certified Oxide	Cummulative Actual kg Pu converted to Certified Oxide
2011	200	200	242	242
2012	150	350	200	442
2013	150	500	150	592
2014	100	600	0 YTD	592 YTD
2015	100	700		
2016	100	800		
2017	100	900		
2018	100	1000		
2019	100	1100		

LANL Oxide Production

BLEND LOT	kg Pu (theoretical)			kg Pu (actual)	status	AC Report Complete	CoA prepared	CoC prepared	QPA-PQ review and approval	MOX Services approval	LASO review (if required)	metric designation
38-M	12.7						3/18/2014	3/18/2014	4/11/2014	4/22/2014	na	
40	12.7						7/24/2014	7/24/2014	8/14/2014	9/12/2014	na	requires AC sample shipped to PNNL and CGD process complete for tritium by 6/30
51	12.7						3/18/2014	3/18/2014	4/11/2014	4/22/2014	na	
52	12.7						3/18/2014	3/18/2014	4/11/2014	4/22/2014	na	redo prompt gamma for 2 cans
53	12.7					7/14/2014	7/24/2014	7/24/2014	8/14/2014	9/12/2014	na	AC sample arrives at SRNL by 5/1/14
54	12.7					7/14/2014	7/24/2014	7/24/2014	8/14/2014	9/12/2014	na	AC sample arrives at SRNL by 5/1/14
marggie 1	4.6						TBD	TBD	TBD	TBD	na	no AC but blend material from archive samples to achieve homogeneity
marggie 2	12.7					TBD	TBD	TBD	TBD	TBD	n/a	complete blend / sampling / packaging #55
marggie 3	12,7					TBD	TBD	TBD	TBD	TBD	na	complete mill / blend sample on #56, augmented with polished oxide material
total	**93.5**	**76**	**51**								na	
56	0					FY2015	FY2015	FY2015	FY2015	FY2015	na	
57	0					FY2015	FY2015	FY2015	FY2015	FY2015	na	
58	0					FY2015	FY2015	FY2015	FY2015	FY2015	na	

LANL Oxide Production



LANL Oxide Production

- All planned shipments of 3013 packages from LANL to SRS are currently on hold –
  - from 50 USC CHAPTER 42, SUBCHAPTER III: PROLIFERATION MATTERS.

> If, after January 1, 2014, the Secretary determines that the MOX production objective has not been achieved because of a failure to achieve milestones set forth in the most recent corrective action plan under this subsection, the Secretary shall suspend further transfers of defense plutonium and defense plutonium materials to be processed by the MOX facility until the Secretary certifies that the MOX production objective can be met.

  - DOE legal has indicated that sample shipments <u>can</u> continue from LANL to SRNL.

- Impacts to oxide production over the next few years.

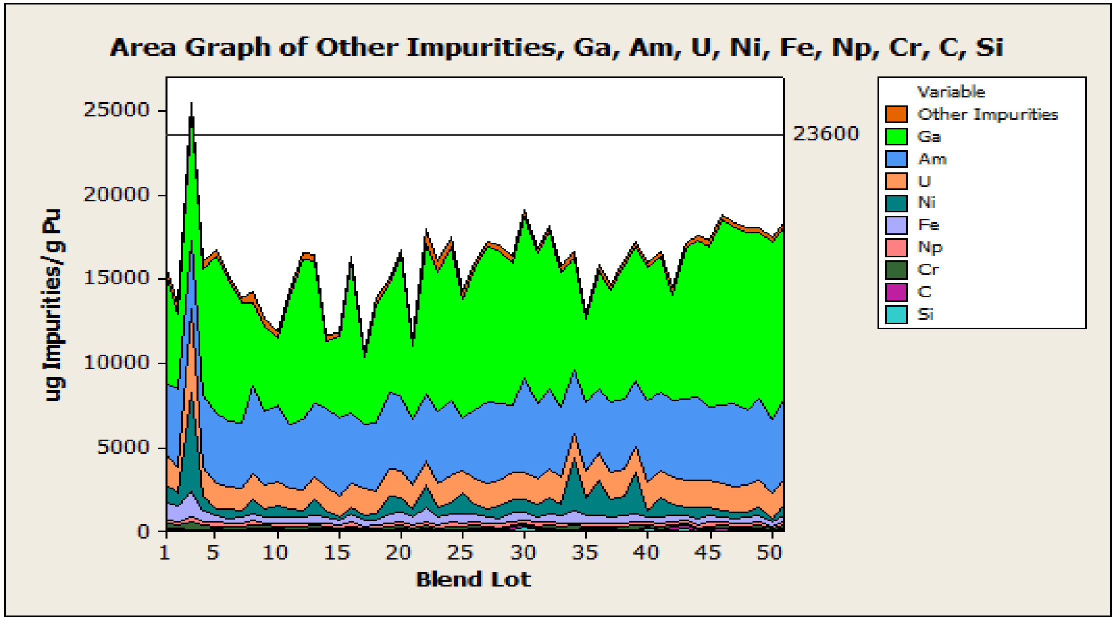
Material Storage

- Currently, the project has in inventory 107 containers of plutonium oxide in 3013 containers (< 450 kg Pu as oxide).
  - 53 containers (222 kg Pu) in the "ready-to-ship" category.
  - 39 containers (164 kg Pu) through review and awaiting weld report.
  - 9 containers (38 kg Pu) awaiting review and/or weld report.
  - 6 containers (25 kg Pu) awaiting AC data

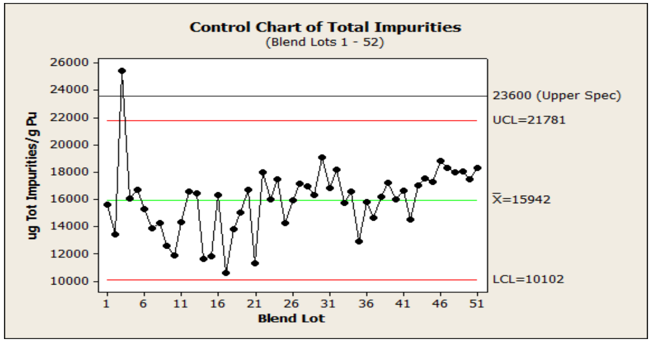
Material Storage

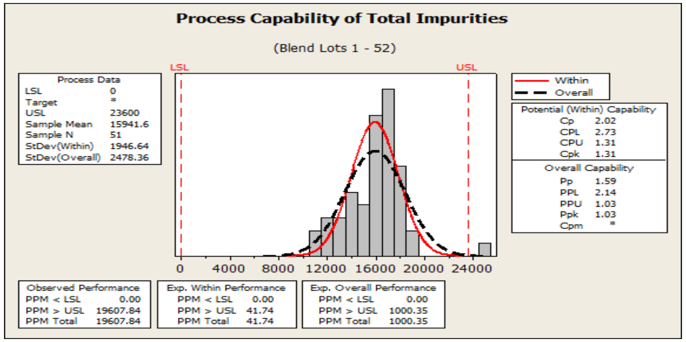
- Discussions with NPI-2 indicate that as of 2/24/2014, there are available 180 locations within the vault that can be used to store 3013 containers.
  - Equates to > 7 years production at 100 kg per year (5 years at 150 kg per year).
    - Additional analysis required in order to balance product storage with feed material storage and other programs.
  - This does not mean that there remains 180 open spaces. There are more that require material shuffling or reconfiguration in order to store 3013 contains (for example, there exists a quantity of 5 gallon locations presently available that could be used for 3013 containers).
    - Ability for MR&R to free up space…?
  - Additional storage could possibly be available if the loading density of floor safes is analyzed with additional engineered controls.
    - This effort will require criticality reviews and engineering to support modifications should the analysis support a change in the number of 3013 containers permitted in a floor safe.

Process Qualification



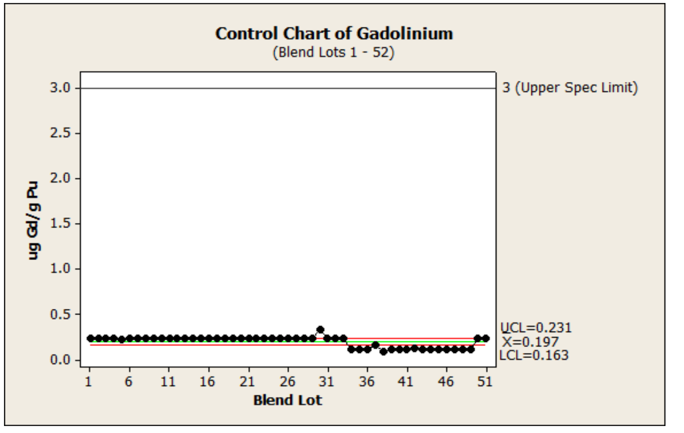
- Graph illustrating the relative contributions of 9 major impurities compared to the other 35 impurities that were measured in Blend Lot #'s 1-52.
- Expected failure rate for the sum of all measured impurities is < 0.1%.
- Of the 44 impurity elements measured, there are 9 that are major contributors to the total impurity concentration: Ga, Am, U, Ni, Fe, Np, Cr, C and Si.



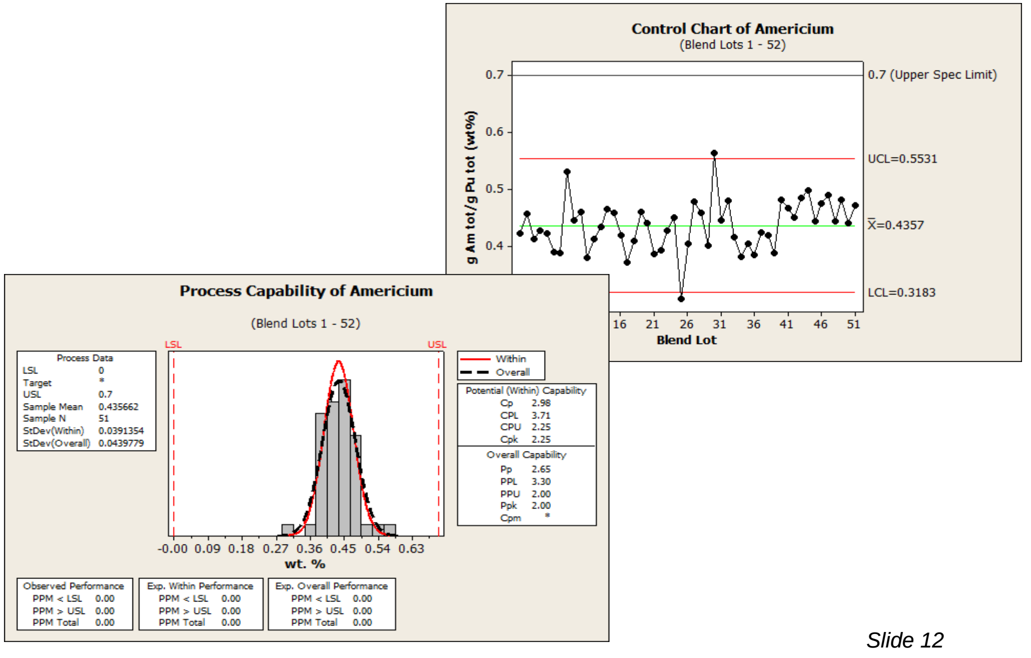


Process Qualification

- Analysis allows for the elements to be grouped into similar categories:
    1. Elements with concentrations typically below the detection limit (19);

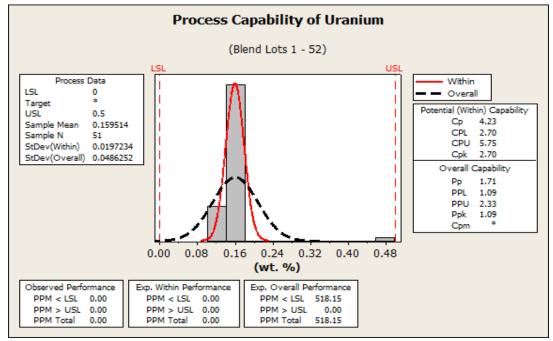


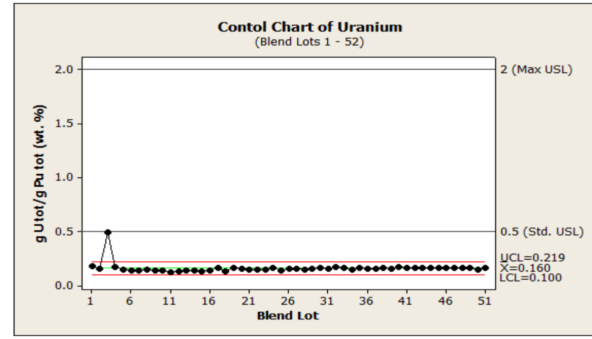
    2. Elements with a predicted failure rate of < 0.1% but have no observed failures to date and no outliers near the maximum content (16);



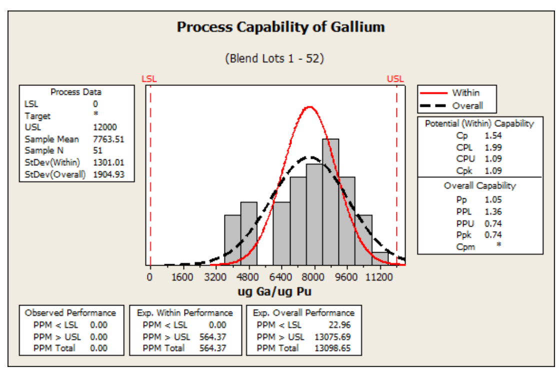
Process Qualification

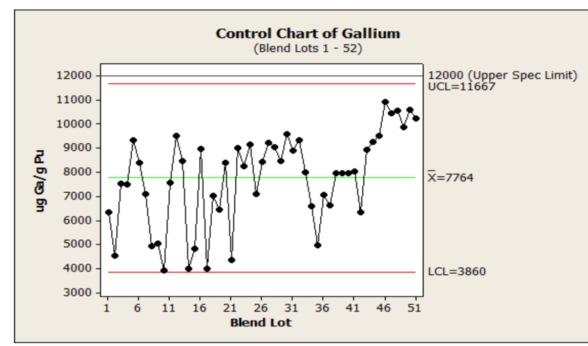
3. Elements with a predicted failure rate of < 0.1% but have experienced a failure or have an outlier near the maximum content (7); and





4. Elements with a distribution such that the predicted failure rate could be greater than 0.1% (2).





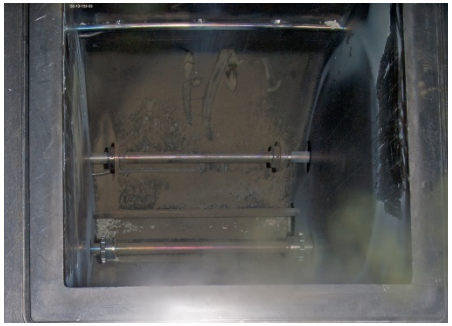
Process Qualification

- Ed Moore and Tommy Edwards of SRNL have come up with virtually identical groupings of elements using the same data and applying a nonparametric approach (using the EPA software) versus our probability approach (using a statistical software package).
  - Differences in groupings are with Be, F + Cl, Ni, P and N
- Technical basis for sampling frequency will require more justification.
- Influence of pit feed needs to be further documented and studied more.
  - Currently, we have stated that changes to the 2MT pit campaign and this analysis may require additional data to support basis.
- Need to establish that 3013 equivalency of lower calcination temperature will not have an impact to this analysis.

Process Qualification

- Basis proposed initially for only DMO-produced materials.
    - Additional data needed to extend to muffle furnace.
- Single feed versus multiple feed families:
    - Single feed is a Blend Lot comprised of a single pit family.
    - Multiple feed is a Blend Lot that is either multiple pit families **or** the oxide is recycled through DMO.
- Understanding of outliers…
    - Ex: “abnormal” processing, such as multiple recycle through DMO or mill/blend impacts Fe, Cr and Ni.
    - Ex: gallium sublimation of Ga_2O_3 during the oxidation step may contribute to the variability in the Ga control chart?

uncalcined PuO_2 in TGA crucible courtesy Dave Wayne



white film photo looking inside DMO oxidation furnace courtesy Larry Peppers

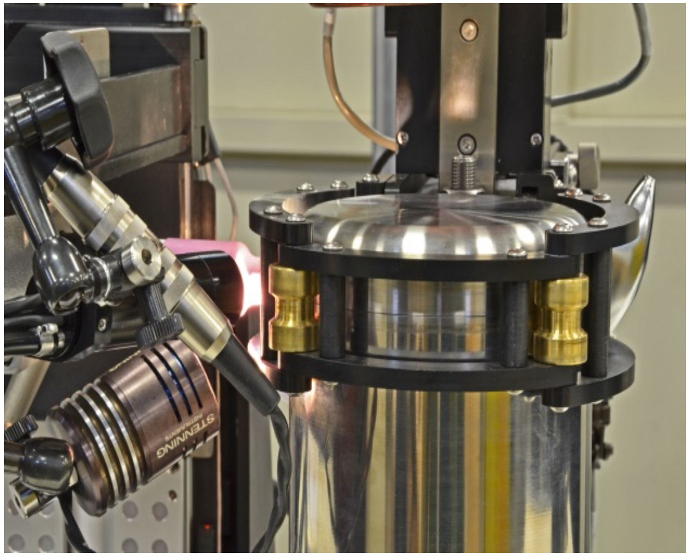
Impacts of 3013 equivalency

- Stabilization temperature (calcination temperature) reduced from 950°C to 650°C.
  - Elimination of reactive materials – potential for the persistence of reactive metal (incomplete oxidation) will be periodically tested.
  - Reduce corrosion products (Fe, Cr, Ni) into the product material.
- Overall, expectation is that there will be no change to the properties of the product material with the equivalency.
  - Calcination has minimal impact on the physical characteristics of the product because they have already been determined in the oxidation phase of metal-to-oxide conversion.
  - Surface area driven by Pu metal temperature in the oxidation step.
  - Particle size and percentage of material < 5µ show minimal change with changes in oxidation temperature. Might show some impact with the lowering of the calcination temperature.

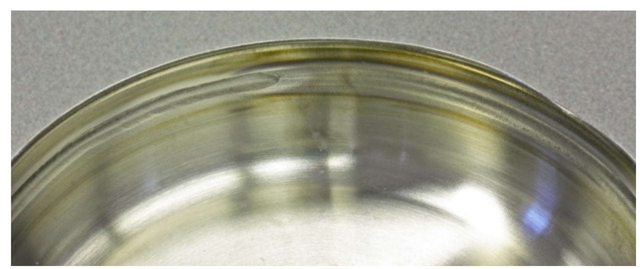
Packaging

- Replacement of the manual inner- and outer-can welding stations.
    - Systems approaching their service lifetime.
        - Inner can has been in operation since 1998.
        - Outer can has been in operation since 2003.
- The procedure qualification record and the welding procedure specification for these welds will not be altered.
    - Verification weld (dummy can) for the outer can will be performed and subjected to full volumetric radiographic examination and metallographic examination in accordance to section 1.d of G-ESR-G-00035.
    - If there are other requirements that we must meet prior to the use of these welders for production welds, please let us know.

Packaging

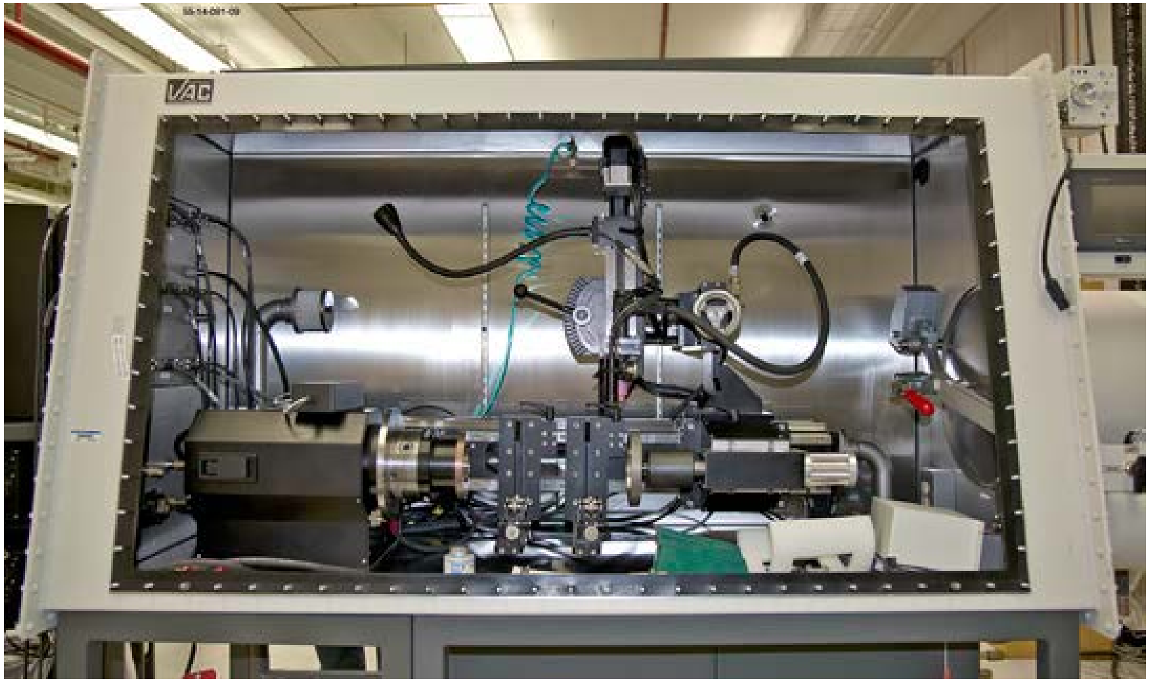


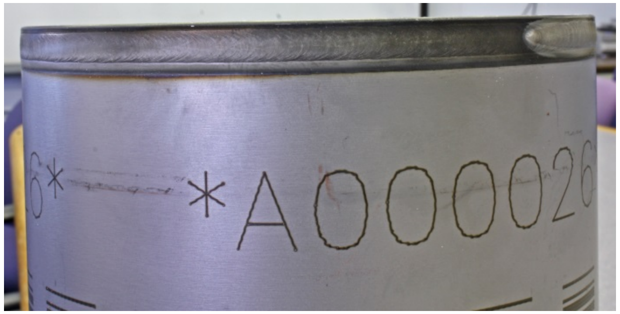
weld face
courtesy Scott Breshers

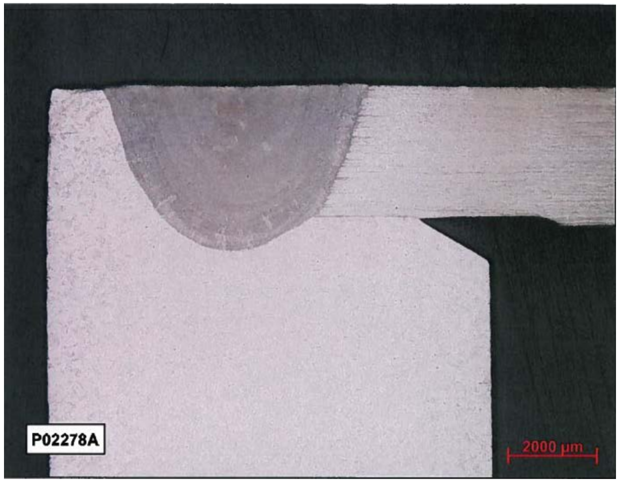


weld root
courtesy Scott Breshers

Packaging

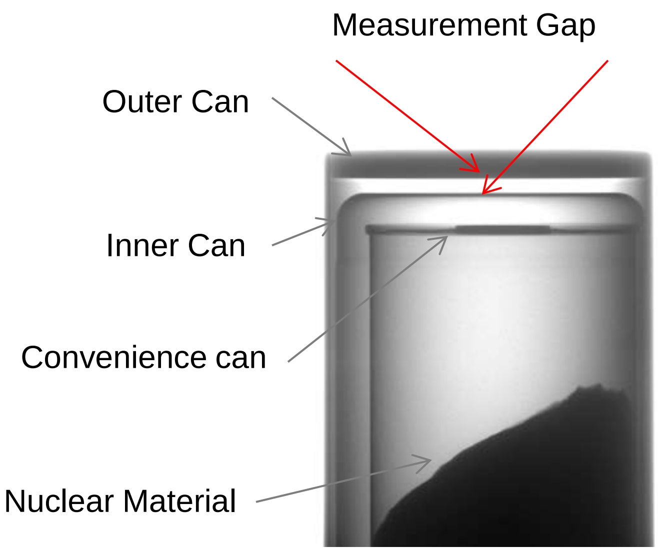




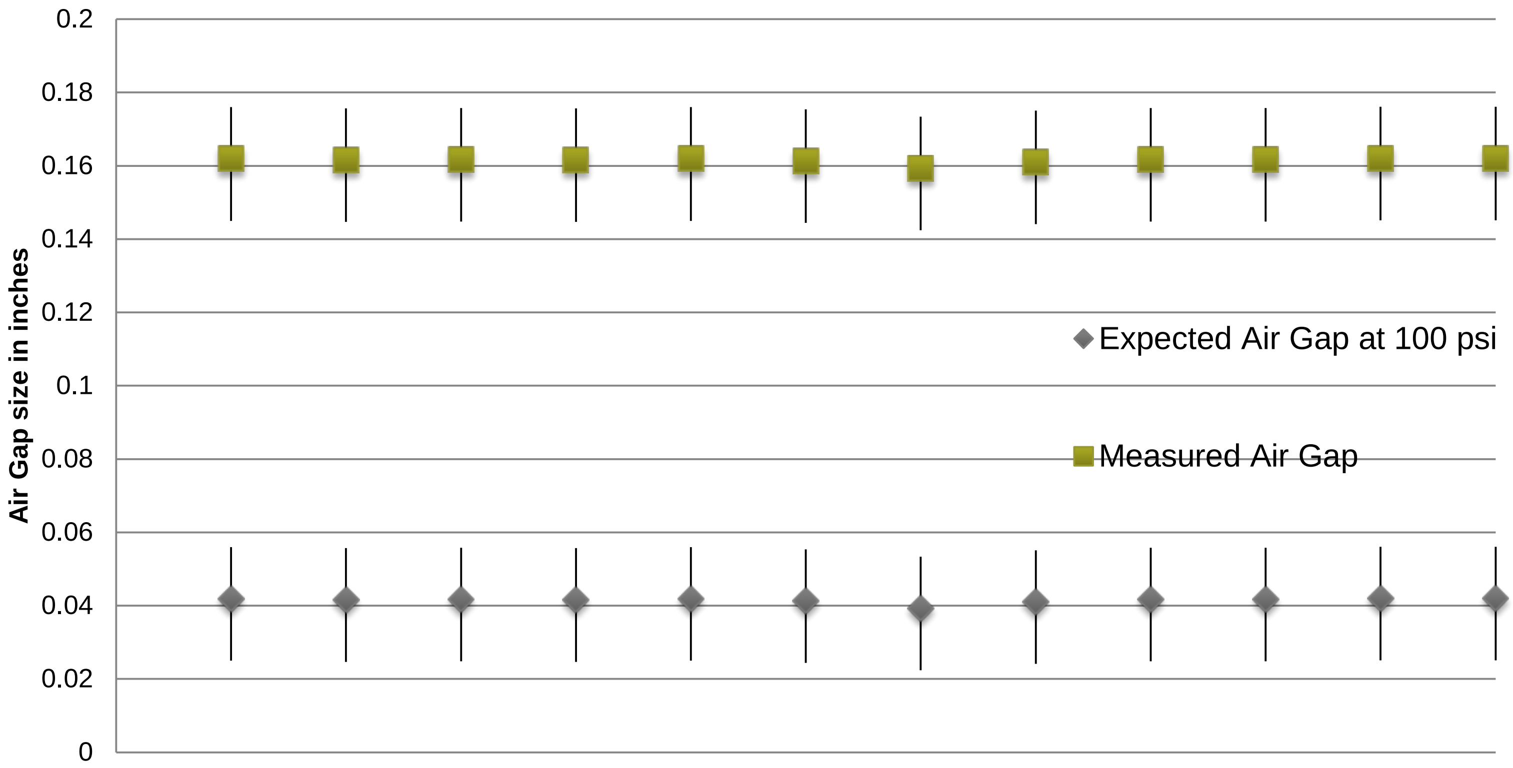


weld face and metallography
courtesy Scott Breshers

ARIES OP 3013 Package



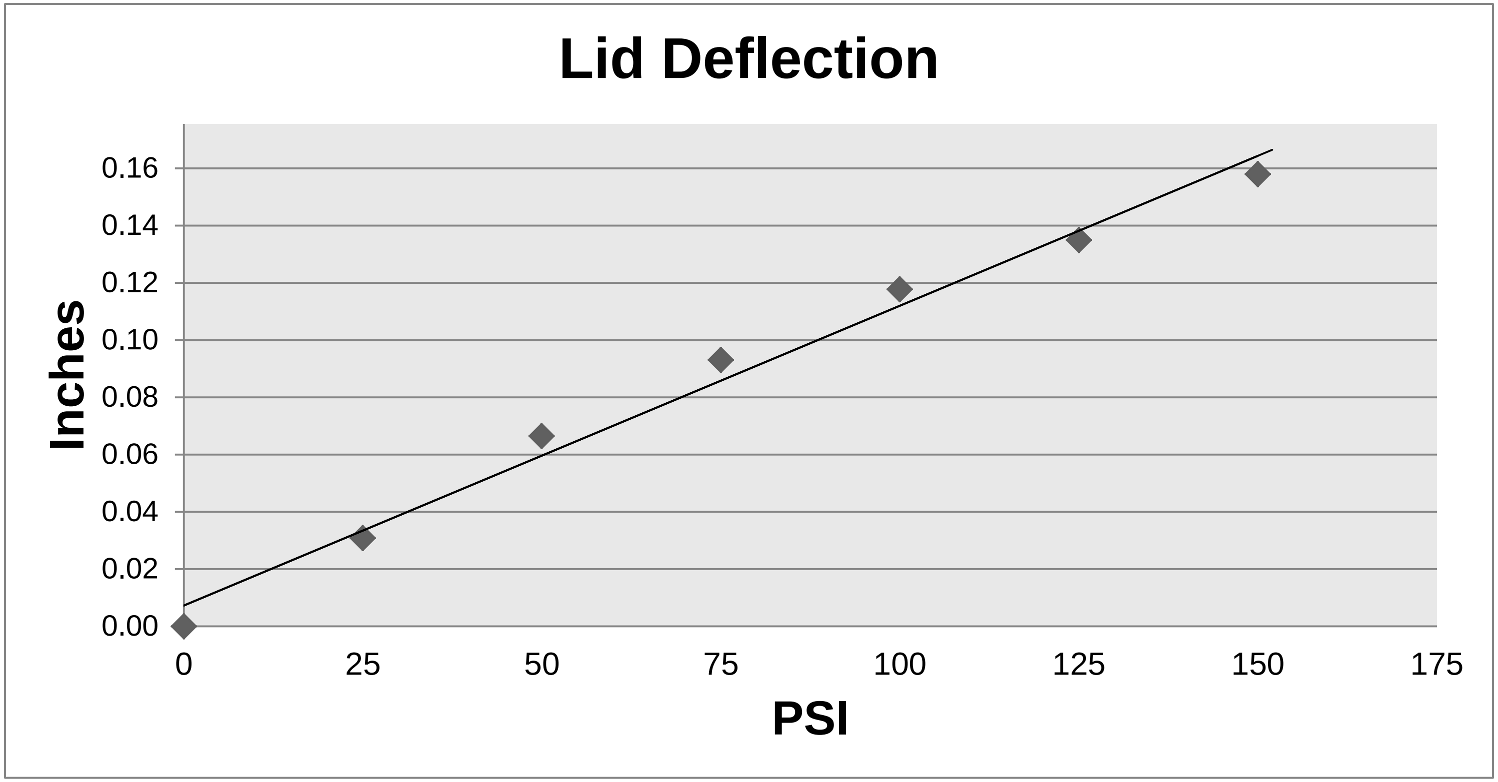
Measured Gap Data



Gap data for radiographic images for 134 ARIES OP Containers
Measured 134 cans x 12 angles = 1608 measurements

Measured baseline values vs expected at 100 psi

Inner Can Lid Deflection vs Pressure



IN CLOSING

- Will resume operations later this year and begin to make oxide.
  - Rate at which we make oxide is a variable…
  - Where it will go is a variable…
  - What will we do with it is a variable…
- Our operational pause has allowed us to look at the data that we have collected over the past three years.
  - Process is under control…
  - …but when the process is <u>not</u> under control we can look at the data and determine what the problem is.
  - 100% inspection by chemical analysis isn't value added.
- Continue to make investments in equipment to reduce single-point failures as budget permits.

Status of LANL's M441.1-1 container – the SAVY-4000

**D.K. Veirs, Murray Moore, Laura Worl,
Paul Smith, Jon Teague**

**3013 Surveillance and Monitoring Program Review
March 25-26, 2014
Savannah River Site**

OUTLINE

- SAR status
- Surveillance and Lifetime Extension
- Filter testing
- O-ring testing
- Water shedding membrane

SAR Status

- Revision 0 submitted Jan. 2011
- Comments received May 10, 2011 with request to respond by June 2011.
- Revision 1 submitted Mar. 2012.
  - "I expect another round of comments."
- Revision 2 submitted 4-25-13
- Revision 3 submitted 2-10-14
- 3-12-14 Energy Solutions performing a final peer review of the Safety Evaluation Report which authorizes use at LANL.

Los Alamos NATIONAL LABORATORY EST. 1943

Safety Analysis Report for the SAVY 4000 Container Series

LA-CP-12-?

Revision 1

February 29, 2012

Luke L. Anderson, Michael W. Blair, E. Jeanne Hamilton, Elizabeth J. Kelly, Murray E. Moore, Paul H. Smith, Timothy A. Stone, Jonathan G. Teague, D. Kirk Veirs, Eric Weis and Tresa F. Yarbro

OFFICIAL USE ONLY

Shelf-Life Surveillance

Statistical approach to achieve a high level of confidence of detecting aging effects

- **Identified 24 Worst Case Materials to package into SAVY Containers**
  - **Two items from each of 11 IDCs (Item Description Codes) that had many items with high calculated dose.**
  - **Preferred high beta/gamma in remarks field, smaller containers, and items already identified for repackaging**
- **Containers to undergo both NDE and DE; one set of 4 will undergo annual NDE for 5 years and then DE**

Shelf-Life Surveillance Evaluations

NDE to ensure container integrity and opportunity to validate SAR compliance with regard to internal packing configuration, authorized contents, and proper closure

- Collect LANMAS data, visual inspection of outside, weight, contamination surveys
- Inner package – visual on o-ring, inner container, bagout bag, liquids present
- He leak test container, Shore M hardness of O-ring
- Filter testing for % penetration and pressure drop

DE of O-rings allows comparison to Lifetime Extension Studies

- Compression Set, Tensile, TGA, FTIR

Testing equipment in PF-4 for SAVY and Hagan containers

He leak tester

Filter test rig

Repackaging

								Hagan Unpacking Information							SAVY Packaging Information					
Item	DMT	IDC Short	IDC Short Desc	Project	Project Description	1st Packing Date	Hagan Category and Size	Hagan Filter Serial # (Manufacture Month and Year & LANL Sequential Unique Number)	Hagan Body Serial #	Internal Shield Present & type?	Hagan Condition	Bagout Bag Condition	Inner-Most Container	Last B/G @ contact w inner-most (mr/hr)	SAVY Lid Serial #	SAVY Body Serial #	1st Packing Date	Inner-Most Container	Is Shield present & type?	As packaged weight of New Container (g)
CAXBL128D	52	R83	PROCESS RESIDUE, MSE Salt	345	MATLS STAGING & DISPOSITION- NON-NS	7/7/2004	SNMC-2 3Q	8/02 LANL-813	030142	no	good	discolored slightly	no entry	no entry	111103026L	111103026B	1/22/2013	stainless steel slip lid	Yes- External	nothing entered
GBS005	52	R65	PROCESS RESIDUE, ER Salt	345	MATLS STAGING & DISPOSITION- NON-NS	12/14/2004	SNMC-2 8Q	4/02 A-28	04/02-08028	no	good	good	Paint Can	200.0	041208025L	041208025B	3/5/2013	Paint Can	Yes- External Pewter	15477.0
GBS059	52	R65	PROCESS RESIDUE, ER Salt	345	MATLS STAGING & DISPOSITION- NON-NS	12/14/2004	SNMC-2 8Q	4/02 A-207	04/02-08010	no	good	good	Paint Can	370.0	041208004L	041208004B	3/5/2013	Paint Can	Yes-External Pewter	14827.0
INCA-20	54	R47	PROCESS RESIDUE, Incinerator Ash	345	MATLS STAGING & DISPOSITION- NON-NS	12/16/2004	SNMC-1 8Q	4/99 LANL-429	05/99 NMC 08000-305	no	good	good	stainless steel slip lid	3000.0	041208043L	041208043B	3/26/2013	stainless steel slip lid	Yes- External Pewter	9875.0
INCA-21	54	R47	PROCESS RESIDUE, Incinerator Ash	345	MATLS STAGING & DISPOSITION- NON-NS	12/8/2004	SNMC-1 8Q	4/99 LANL-405	04/02-08145	no	good	good	stainless steel slip lid	1800.0	041208009L	041208009B	3/26/2013	stainless steel slip lid	Yes- External Pewter	10501.0
ORF633956XBLC	52	N50	NON-COMBUSTIBLE, MgO	345	MATLS STAGING & DISPOSITION- NON-NS	12/2/1999	SNMC-3 8Q	2/99 LANL-83	080208	no	good	* good. There is a 2nd bag over bagout bag	stainless steel slip lid	280.0	041208038L	041208038B	1/31/2013	stainless steel slip lid	Yes- External Pewter	12170.7
PCS68B1	52	R71	PROCESS RESIDUE, Salt	345	MATLS STAGING & DISPOSITION- NON-NS	4/7/2008	SNMC-2 8Q	4/02 A-134	08/06-08077	no	good	good	Paint Can	no entry	041208028L	041208028B	1/31/2013	stainless steel slip lid	Yes- External Pewter	10614.9
PHX5R4	54	C80	COMPOUND, Tetrafluoride	345	MATLS STAGING & DISPOSITION- NON-NS	10/11/2006	SNMC-2 3Q	8/05 LANL-2282	08/05-03282	no	good	nothing entered	no entry	no entry	121103052B	121103052B	3/25/2013	hermetically sealed - welded	no	3131.0
POX4275C1	52	R78	PROCESS RESIDUE, Sweepings/Screenings	345	MATLS STAGING & DISPOSITION- NON-NS	8/16/2005	SNMC-1 5Q	7/02 LANL-393	06/02-05183	yes- lead	good	good	no entry	180.0	091205182L	091205182B	3/7/2013	stainless steel slip lid	Yes- External Pewter	6786.0
RBXS5657-1A	56	C21	COMPOUND, Dioxide	345	MATLS STAGING & DISPOSITION- NON-NS	4/14/2004	SNMC-2 5Q	7/02 LANL-515	06/02-05305	no	good	discolored. Some black substance in can and on bag	stainless steel slip lid	700.0	041205026L	041205026B	2/5/2013	stainless steel slip lid	Yes- External Pewter	6883.1
SLTF3123A	52	R42	PROCESS RESIDUE, DOR Salt	345	MATLS STAGING & DISPOSITION- NON-NS	5/5/2005	SNMC-1 3Q	8/99 LANL-1178	07/02-03184	yes- lead	good	good	no entry	150.0	121103062L	121103062B	3/7/2013	stainless steel slip lid	Yes- Exernal Pewter	6786.0
SWPVTB15	52	R71	PROCESS RESIDUE, Salt	345	MATLS STAGING & DISPOSITION- NON-NS	5/2/2007	Cert05-H3Q	08/02 LANL-897	08/05-03300	no	good	good	stainless steel slip lid	70.0	111103001L	111103001B	2/5/2013	stainless steel slip lid	Yes- External Pewter	5016.5

Repackaging

13	VTB-16C1	52	R78	PROCESS RESIDUE, Sweepings/Screenings	345	MATLS STAGING & DISPOSITION- NON-NS	8/9/2005	SNMC-2 5Q	4/02 A-164	04/02-05164	yes- lead	good	good	stainless steel slip lid	280.0	021205029L	021205029B	2/5/2013	stainless steel slip lid	Yes- External Pewter	8195.8
14	XBLC9413	52	N50	NON-COMBUSTIBLE, MgO	345	MATLS STAGING & DISPOSITION- NON-NS	10/6/1999	SNMC-3 8Q	2/99 LANL-80	080207	yes- lead	good	nothing entered	stainless steel slip lid	220.0	none given	041208055B	2/5/2013	stainless steel slip lid	Yes- External Pewter	12349.0
15	XBLS25	56	R83	PROCESS RESIDUE, MSE Salt	345	MATLS STAGING & DISPOSITION- NON-NS	5/24/2005	SNMC-3 8Q	10/99 LANL-1932	080234	no	good	good	Paint Can	1400.0	041208031L	041208031B	3/12/2013	Paint Can	Yes- External Pewter	12872.0
16	XBSOX153	52	R42	PROCESS RESIDUE, DOR Salt	345	MATLS STAGING & DISPOSITION- NON-NS	11/13/2006	SNMC-1 5Q	3/06 LANL-296	03/06-05296	no entry	good	good	no entry	no entry	091205175L	091205175B	3/12/2013	stainless steel slip lid	Yes- External Pewter	8652.0
17	HNN5502CP	52	M74	METAL, Alloyed Metal														3/22/2012			
18	NAB183-2	52	M44	METAL, Unalloyed Metal	311	NEST- LANL											121103013B	6/27/2012	food pack can		4940.0
19	PMP328CF	52	M44	METAL, Unalloyed Metal				Non-Standard													
20	PHX3F	54	C80	COMPOUND, Tetrafluoride	345	MATLS STAGING & DISPOSITION- NON-NS	4/5/2014	SNMC-1 3Qt									121103121B	4/3/2013			4701.4
21	CXLOX082911	52	C21	COMPOUND, Dioxide	362	PLUTONIUM SUSTAINMENT-LANL											031105052B	1/18/2012	stainless steel slip lid	Yes- External Pewter	6735.0
22	PBO	54	C21	COMPOUND, Dioxide	650	MATERIAL IDENTIFICAITON AND SURVEILLANCE										031105028B	031105028B	1/10/2012	stainless steel slip lid	Yes- lead lined & external pewter	
23	ROTRB9C2	52	R26	PROCESS RESIDUE, Filter Residue	345	MATLS STAGING & DISPOSITION- NON-NS									100.0		031105010B	8/2/2011	stainless steel slip lid	Yes- lead lined & external pewter	8911.1
24	TKS1C1	52	R26	PROCESS RESIDUE, Filter Residue	345	MATLS STAGING & DISPOSITION- NON-NS											031105059B	8/29/2011	stainless steel slip lid	Yes- External Pewter	8232.2

Repackaging

- **Hagan containers inspected – no evidence of any corrosion, pressurization, or damage**
- **Hagan O-rings sent for DE**
- **Hagan filters will be tested**

Lifetime Extension – O-ring

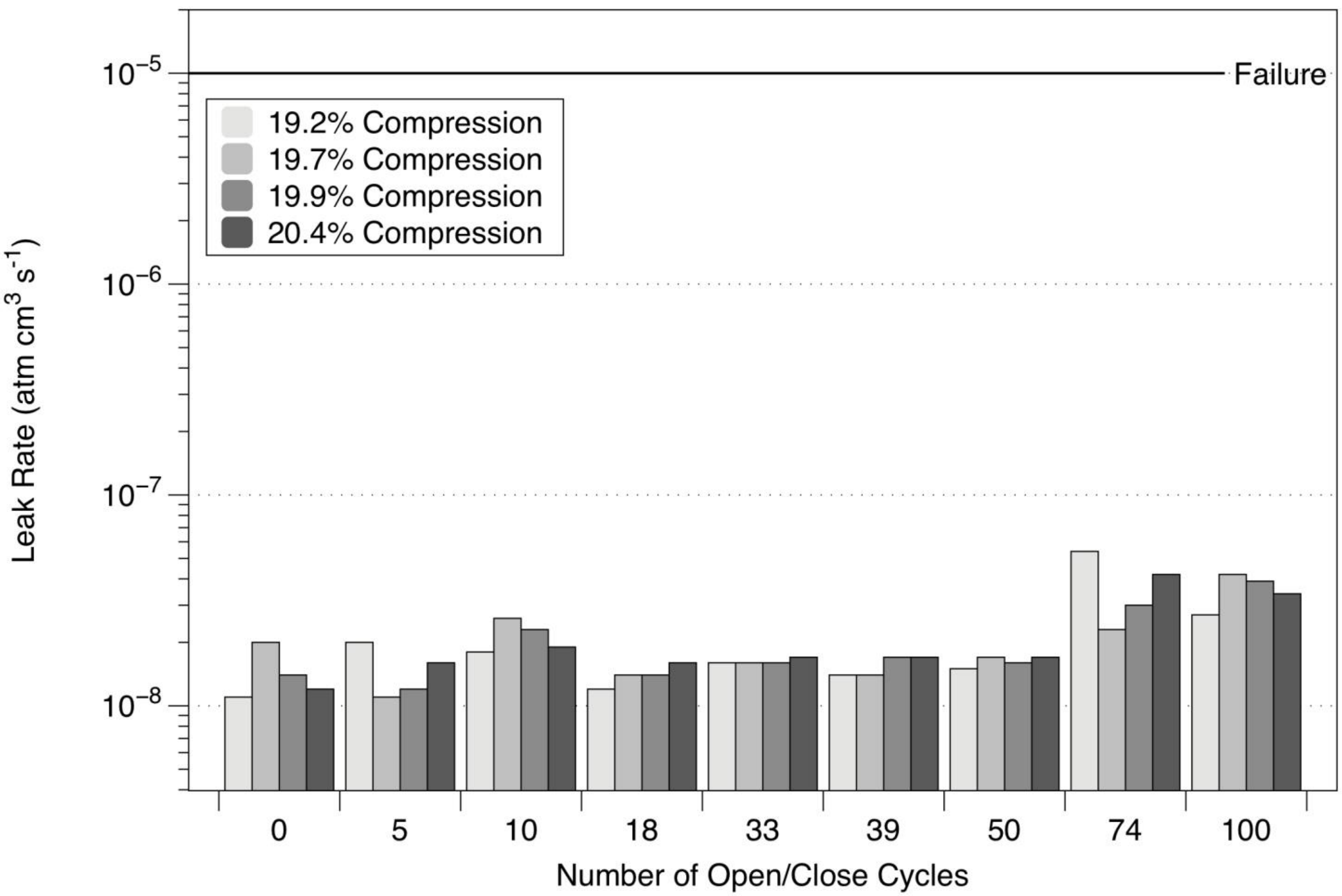
Commercial Parker Durometer 50 O-ring

- **Durability Study (Complete)**
- **Thermal Accelerated Aging**
- **Oxygen Consumption (not started)**
- **Radiation at Temperature (not started)**

Durability Study

- **Effect of opening and closing on leak rate**
- **Effect of cleanliness – hairs and dirt**

Effect of opening and closing



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Effect of cleanliness - hair

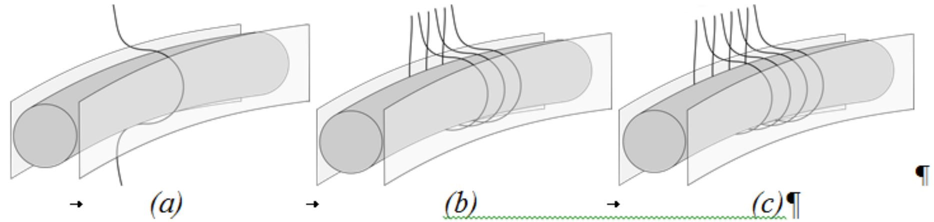
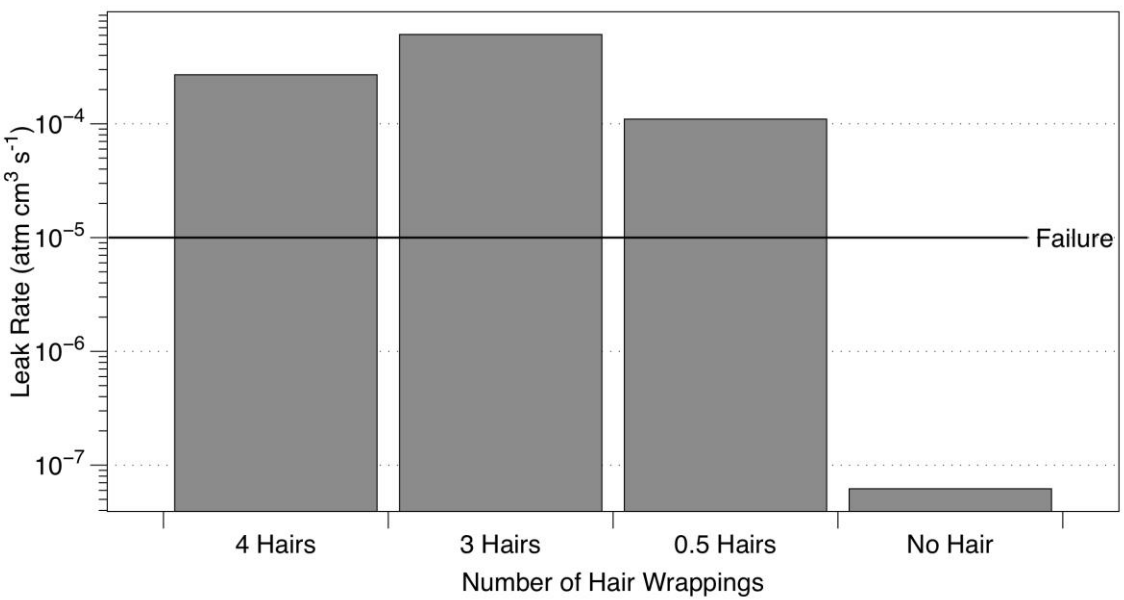
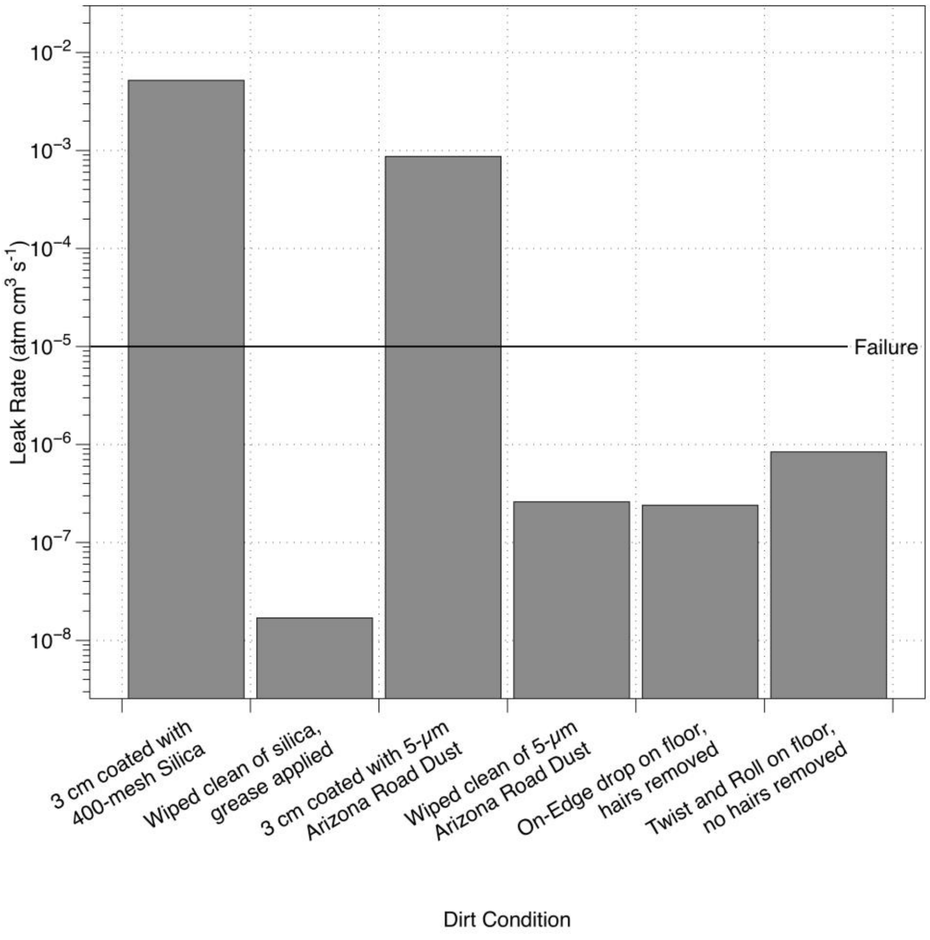


Figure 3. Wrapping of hair around O-rings. (a) one-half wrap. (b) three wraps. (c) four wraps.



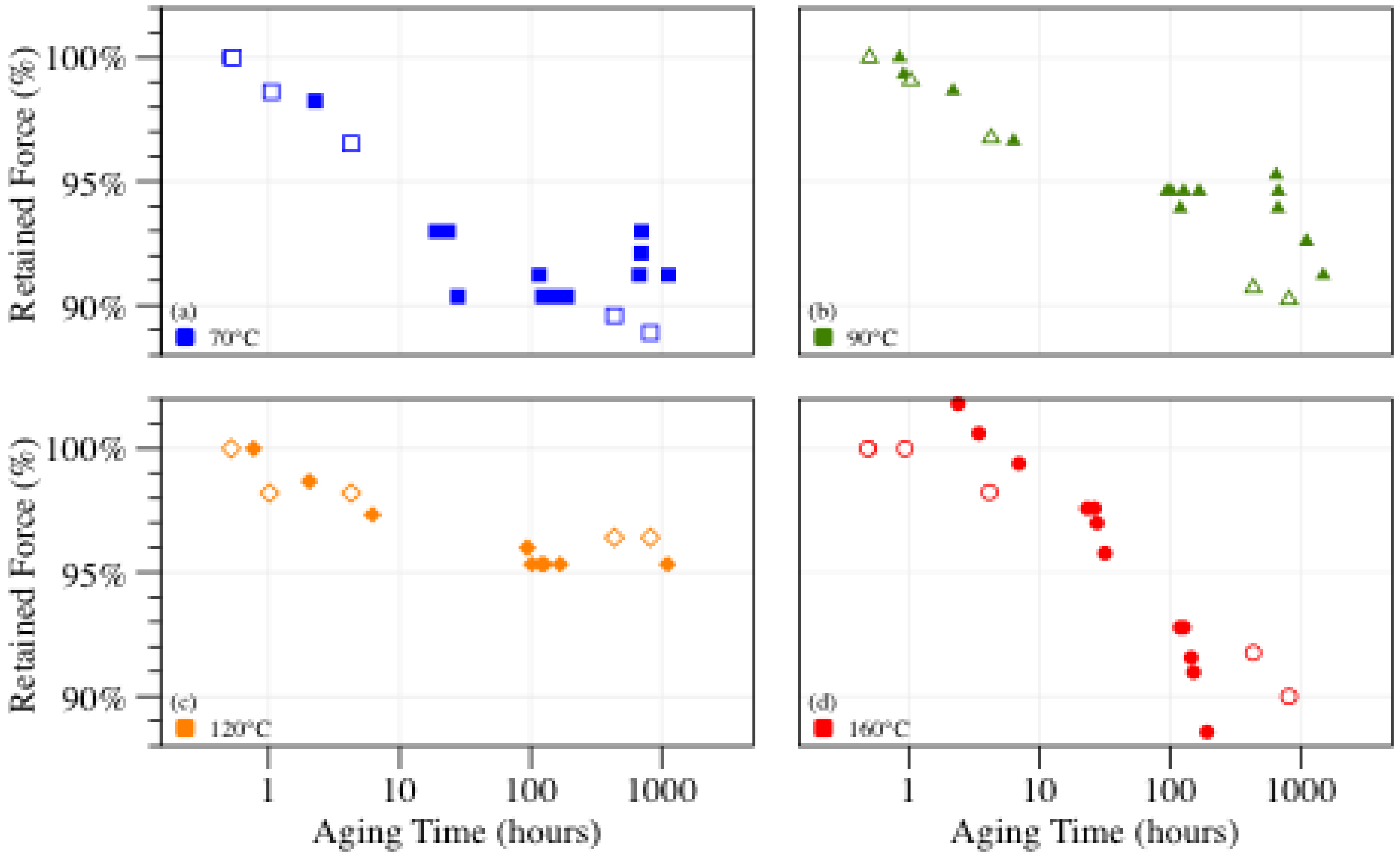
Cleanliness - Dirt

- Cleaning o-rings works



O-Ring Testing – Accelerated Aging

Tests show a very slow loss at high temperature inconsistent with 70 Durometer data



Filter Testing

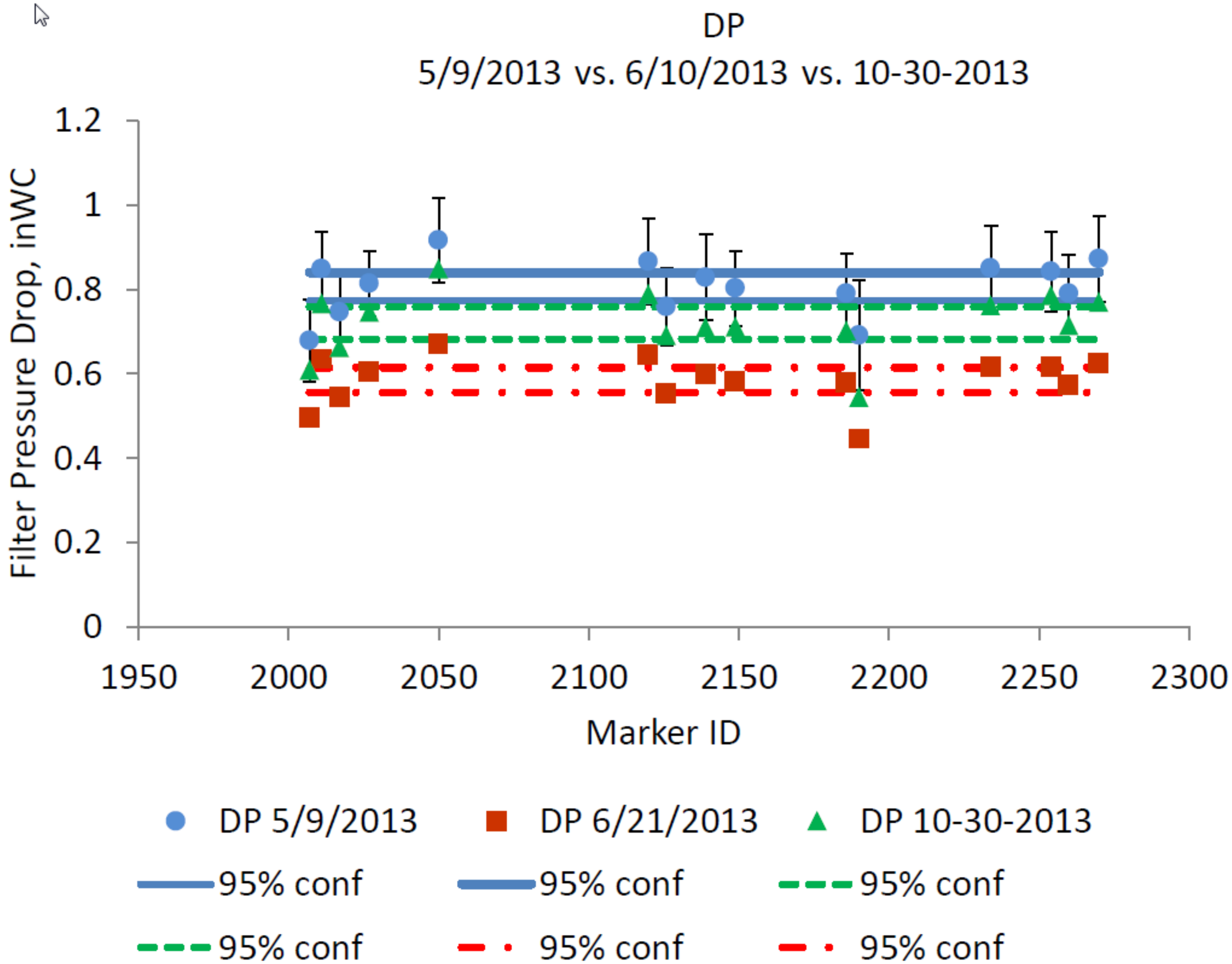
- Filter testing rig for PF-4 is complete and awaiting Procedure Authorization.
- No standards for filter testing at the low flow rates filters will be used at.
- Set of 15 Hagan lids used as reference to compare results from NucFil and LANL testing equipment.
- Significant differences in initial tests resulted in test rig modifications and re-definition of flowrate from Standard Liter Per Minute to Actual Liter Per Minute.
- New results show %Penetration to be equivalent but Pressure Drop is still statistically different

Comparison of pressure drop data

Blue – NucFil

Red – LANL1

Green – LANL 2



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Water Resistant Membrane

- **The Water Resistant Membrane was not originally part of the critical components.**
- **Crit Safety now credits the water resistant membrane.**
- **Membrane does let water through at long times.**
- **Radiation dose is highest for membrane and it is the least resistant material.**
- **A test plan to understand the aging of the water resistant membrane is under development.**

Radiation dose calculations

For the conservative assumptions we made, the water resistant membrane is closest to its criteria at 40 years. New results due to slightly different configuration.

Material of Construction	Radiation Damage Criteria
Viton®	5×10^{7} rads
316L Stainless steel	10^{22} neutrons cm^{-2}
Alumina and silica	$> 10^{10}$ rads
Teflon® (PTFE)	5×10^{6} rads

Exposure Time	Absorbed dose O-ring (rad)	Absorbed dose Membrane (rad)
1 hour	0.56	12
1 year	4.9×10^{3}	1.1×10^{5}
5 year	2.5×10^{4}	5.3×10^{5}
40 year	2.0×10^{5}	4.2×10^{6}

Tests on water penetration of membrane

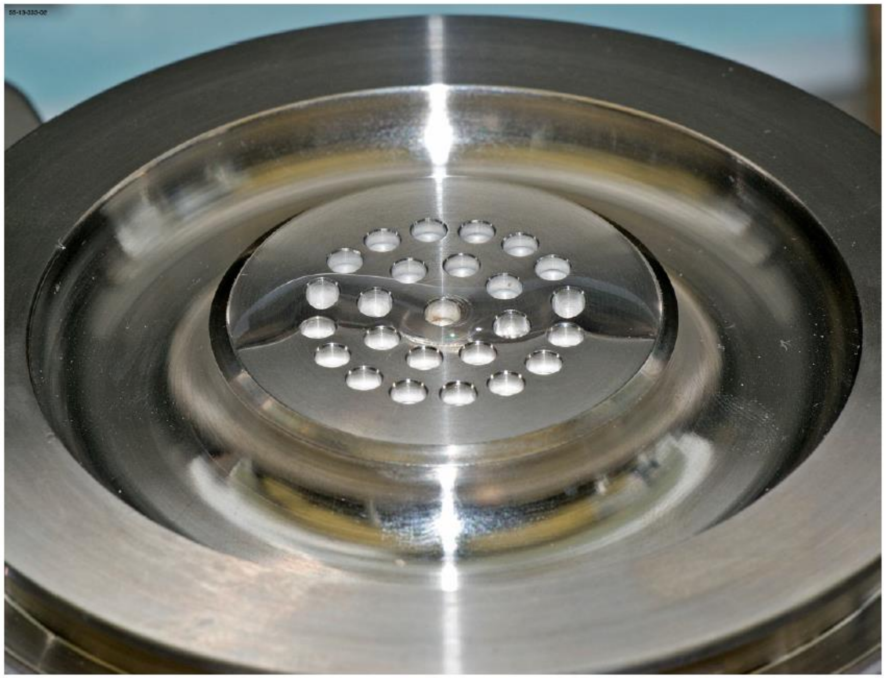
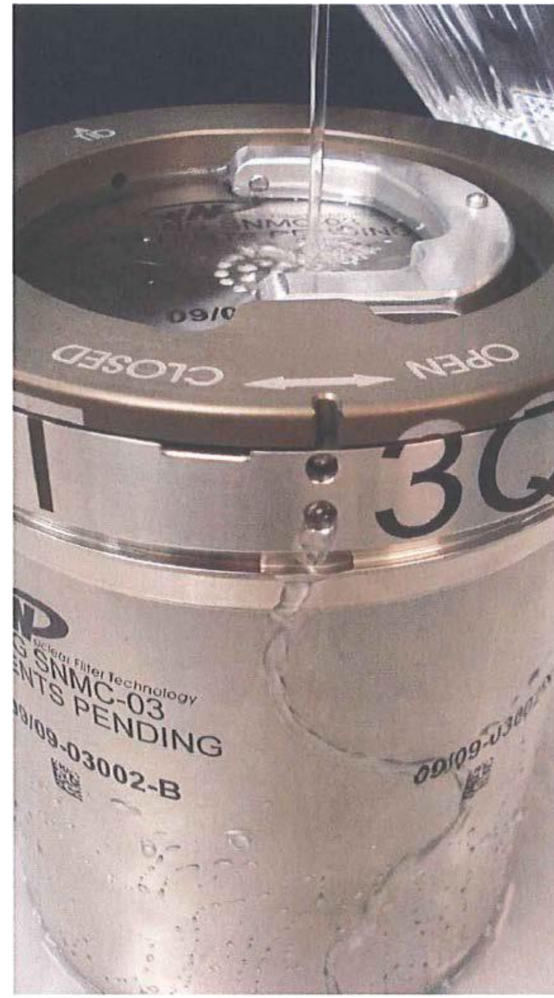


Figure 11. Liquid water is seen on the filter of a SAVY-4000 container after two hours exposure to six inches of water column.



Implementing the DOE M 441.1-1 Nuclear Materials Packaging Manual at Lawrence Livermore National Laboratory

3013 Surveillance and Monitoring Annual Program Review
Savannah River Site, Building 766H Room 2138
March 25, 26 2014

David Riley
Nuclear Material Transfer Manager – Nuclear Weapon Engineering

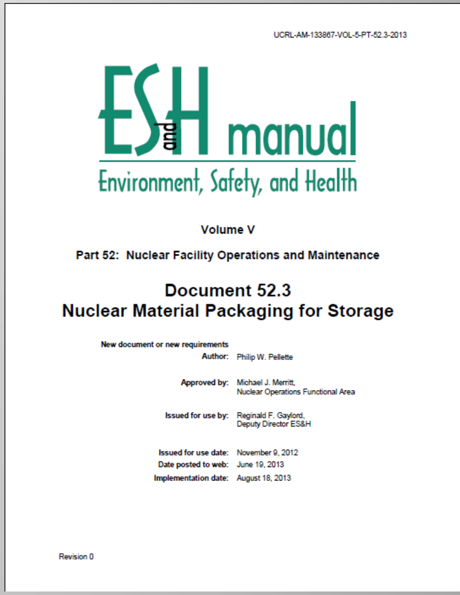
Lawrence Livermore National Laboratory

LLNL-PRES-DRAFT

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

LLNL has incorporated the DOE M441.1-1 into site documentation

- Incorporated requirements into site-wide document – ES&H Manual Document 52.3
- Have implementation plan
  - Updated Annually
- Plan is to package all programmatic materials by end of FY14


UCRL-AM-133867-VOL-5-PT-52.3-2013

ES and H manual
Environment, Safety, and Health

Volume V

Part 52: Nuclear Facility Operations and Maintenance

Document 52.3
Nuclear Material Packaging for Storage

New document or new requirements
Author: Philip W. Pellette

Approved by: Michael J. Merritt, Nuclear Operations Functional Area

Issued for use by: Reginald F. Gaylord, Deputy Director ES&H

Issued for use date: November 9, 2012
Date posted to web: June 19, 2013
Implementation date: August 18, 2013

Revision 0

Most DOE M 441.1-1 materials are in the Plutonium Facility

- Only a couple of items outside of Pu Facility
- Pu Facility has a number of items in vaults
- ~ 100 Programmatic containers
  - Store in SAVY containers
- ~ 300 Waste container (items <10% Pu)
  - Will not store in SAVY containers because will package as waste shortly

Current use of SAVY containers

- Storage of high heat materials
  - Storage and transfer
  - 40 SAVYs currently in use
- In the process of placing other programmatic materials into SAVY containers

Procedures for the use of SAVY containers

- Receiving containers that are purchased under LANL QA program
- Procedures we use are similar to the LANL procedures
- Surveillance of containers meet DOE 441.1-1 requirements

Concerns associated with use of SAVY containers due to tight o-ring

- The SAVY containers are difficult to open
- Requires handler to “hug” the container
- Results in additional dose during loading and unloading high dose materials (neutrons)
- Propose the use of lower durometer o-rings or smaller cross section.