LA-UR-11-02917

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Title: Corrosion Working Group Technical Meeting, April 26 to 27, 2011

Author(s): See attached list

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Intended for: Submission to Allen Gunter, Department of Energy, Savannah River

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Corrosion Working Group Technical Meeting
LANL
April 26-27, 2011

Abstract
A DOE packaging and storage standard (DOE-STD-3013) is being used for long-term storage of excess weapons-grade materials. Close to five thousand 3013 storage containers remain in long term storage at the Savannah River Site (SRS). An Integrated Surveillance Program based at SRS assures the safe long-term storage of these materials that were processed at Rocky Flats Environmental Technology Site (RFETS), Fluor Hanford Site, and SRS, Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL). As part of the surveillance destructive testing work, corrosion has been found in numerous 3013 containers and in shelf life studies. These presentations review the data and allow for technical discussions and hypothesis to develop.

Corrosion Working Group Technical Meeting
April 26 - 27, 2011
Research Park Building, TA-3 Bldg 4200
National Security Education Center, Suite 300, LANL

Goal is a focused technical small team meeting to
i) Evalutate and draw conclusions on DE results and shelf life surveillance results
ii) Review progess on the SCC Test Plan
iii) Determine with current data if the Program has a safe package for 50 year lifetime
Specific expectations:
1) annotated outline for SCC Test Plan Status
2) LANL / SRS draft report on H003328 ; Sampling Plan for SRS parts
3) Conditions for next set of LANL and SRS corrosion tests
4) Future EJ: Prioritization of 3013s wrt corroision
5) Gas Phase Corrosion - Can we say this is not a problem and the inner container is not at risk?
6) Recommendation on RH measurements for future DE

Tuesday, 4/26/11	**NOTE - Presentations should not fill the time slot - please leave time for discussions**		
8:00 AM	**Technical Basis, Data and Comment Resolution Review**		
8:00 AM	0:45	Status Shelf Life Corrosion work at LANL	Scott Lillard
8:45 AM	0:45	Status Shelf Life Corrosion work at SRS	John Duffey
9:30 AM	0:45	Pitting Analysis and Prediction of through wall pit; Discussion of SCC wrt pit and pit depths	Scott Lillard / John Mickalonis
10:15 AM	0:45	Cause of visible material fill lines in DE convenince containers	Kerry Dunn
11:00 AM	0:30	Relative Humidty changes in large scale containers	Josh Narlesky
11:30 AM	0:30	**Lunch (Working lunch can be arranged)**	
12:00 PM	0:45	RH observed after 5 years	Kirk Veirs
12:45 PM	0:45	Justification for continued RH / Temp measurements in DE	Beth Hackney
1:30 PM	0:45	Deliquescent Behaviour of salts: Iron Chloride - others?	Steve Joyce, Josh Narlesky
2:15 PM	0:30	High Temperture small scale planning and surrogate salts	John Berg
2:45 PM	1:00	**Open discussion**	All
3:45 PM	1:30	**Tour of Radiological Laboratory/Utility/Office Building (RULOB)**	
Wednesday, 4/27/08			
8:30 AM	1:00	Statistical Sample: Unusual and/or Corrosion Observations in EJ and Random Containers	Elizabeth Kelly
9:30 AM	2:30	Review and draw conclusions on DE results Present observations based on extent of corrosion; Develop a rating scale	Kerry Dunn Chip McClard
12:00 PM	0:30	**Working Lunch**	
12:30 PM	1:00	Future EJ Engineering Container Selection for DE, Prioritization of containers	Chip McClard, John Berg
1:30 PM	1:00	H003328 - Evaluation, Impact to Program, Sampling Plan @SRS	Laura Worl, Kerry Dunn
2:30 PM	1:30	Review of SCC Test Plan - Feed back on results, Test Plan revision?? including impact of Gas Phase Corrosion Conclusions on what conditions do we see films, pits, ..	John Berg and Scott Lillard

4:00 PM	1:00	**Open discussions,Action Items , Closing Remarks**	All

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Action items from 3013 Corrosion Working Group Meeting, April 26,27, 2011 LANL			
	Action Item	**Recommendation**	**Responsible ID**
1.	Report LAUR for basis of pit size and sampling Minimum pit size – 50 microns 5 years → grid and mapping; provides conservative value for 50 ext. Pit Size for crack – 1000 um	(need to confirm pit size for crack)	Scott Lillard
2.	Conceptual risk plot on SCC – update	Update	J. Berg
3.	Ranking: 0 – Nothing or wipe-able coating (IC and/or CC) 1 – CC Coating adherent 2 – CC < 50 micron 3 – CC > 50 micron 4 – IC coating adherent 5 – IC < 50 micron 6 – IC > 50 micron 10 – Inner Can Crack	Update Database; Generate Table -	K Dunn
4.	Harris GEV calculation – what were the parameters for the fit		J. Mickalonis
5.	SRNL Shelf Life tests – next loading	22-25% RH with tests in triplicate (not 3 different tests)	J. Duffey
6.	Database Information - RH and temperature of sensor in Summary Sheets and Database		K Dunn
7.	Continue to collect K-Area RH and Temperature collection in DE? Need to justify why we need it; why is it valuable? Specific parameters: RMC Line, Dry line; Hanford vs RFETS vs SRS	Provide 1 page technical basis to K Area for Justification of RH Measurements Hackney / Veirs	Hackney / Veirs
8.	Definition of Significant Corrosion What is our Confidence that we have seen at least 1	Today: 86% with Random With EJ included: 95%	E. Kelly

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	of the worst 5%?		
9.	EJ – - look at Pressure Bin for high moisture (undetected Cl) (John needs to look at TGA low temp for these items.) Items with weight gain. - Containers like 10DE#13, H003367 (significant corrosion - high ratio of water to Cl,; and F-)	Future MIS Call discussion	
10.	H003367 DE10 #13 – corrosion with no H2 in gas phase 0.22 moisture "ugly spots"	What were parameters causing corrosion?	
11.	Report on Corrosion for 11589 samples		Narlesky
12.	Report on MClx DQ		S. Joyce
13.	RH at 5 years (time of DE)		K. Veirs
14.	Updated / Status of Integrated SCC Plan with ref. to reports on work that is complete / updating remainder of tests		J. Berg, L. Worl
15.	Large Scale SCC cans – DE dates?		Lillard
16.	H003328 data to SRNL		Worl
17.	H003328 report – integrated with LANL/SRS		Worl / Dunn

3013 Cross Reference Table

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

DE Run No.	3013 ID	ISP BIN	Sample Type
2010-1	H004251	P & C	Judgmental
2	H002496	P & C	Judgmental
3	H003710	P & C	Random
4	H003655	P & C	Judgmental
5	H002447	P & C	Random
6	R610627	P & C	Random
7	H003900	P & C	Judgmental
8	H003650	P & C	Judgmental
9	H002567	P & C	Random
10	H002728	P & C	Random
11	H002786	P & C	Random
12	H003077	P & C	Random
13	H003367	P & C	Random
14	H003704	P & C	Random
15	R610785	P & C	Random
16	R610826	P & C	Random
17	R610853	P & C	Random
18	S001721	P & C	Random
2011-1	H003443	P&C	Judgmental
2	S002129	P&C	Judgmental
3	H002592	P&C	Random
4	H003337	P&C	Random
5	S001105	P&C	Judgmental
6	H003343	P&C	Judgmental

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

Status of SRNL Shelf Life Corrosion Studies

Jon Duffey

April 26, 2011

Corrosion Working Group Technical Meeting

April 26-27, 2011
Los Alamos, NM

EM Office of Environmental Management

SRNL Radioactive Test Matrix

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

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New Test Configuration

Use existing test container dimensions for existing heater slots

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

Limited volume for tear drop coupons only; no flat coupons

Solid contact and headspace

Glass container for visualization only

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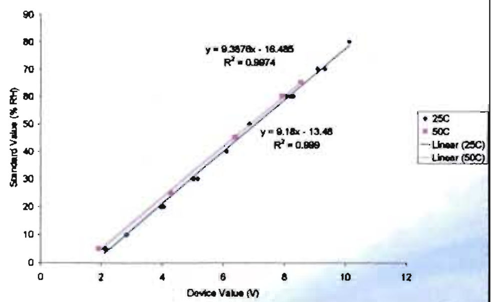
Sensor Calibrations

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

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

Additional calibration checks planned using saturated salt solutions



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Material Preparation for First Rad Test Series

Heated 52.051 g PuO_2 to >300 °C; cooled to <150 °C

Added 1.101 g chloride salt mixture (2.071%)

- Pre-weighed in Ar glovebox (< 400 ppm H_2O or < 1.5% RH)
- Transferred to Pu air glovebox in glass jar inside plastic jar with 4Å molecular sieve

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

Cooled to <150 °C, transferred to glass jar, placed in plastic jar with 4Å molecular sieve

Total mass before heating – 53.152 g; after heating – 53.007 g; loss - 0.145 g

Residue in crucible - <0.017 g

Mass prior to moisture loading (in helium glove bag) – 53.044 g (0.069% increase)

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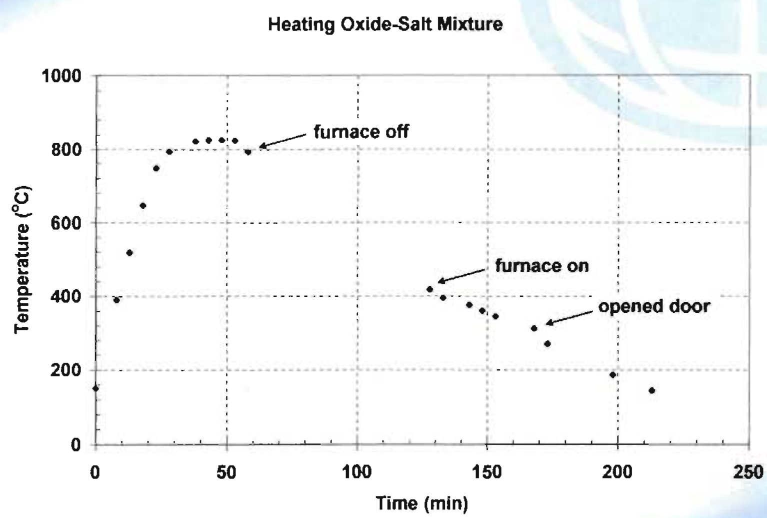
Material Preparation for First Rad Test Series



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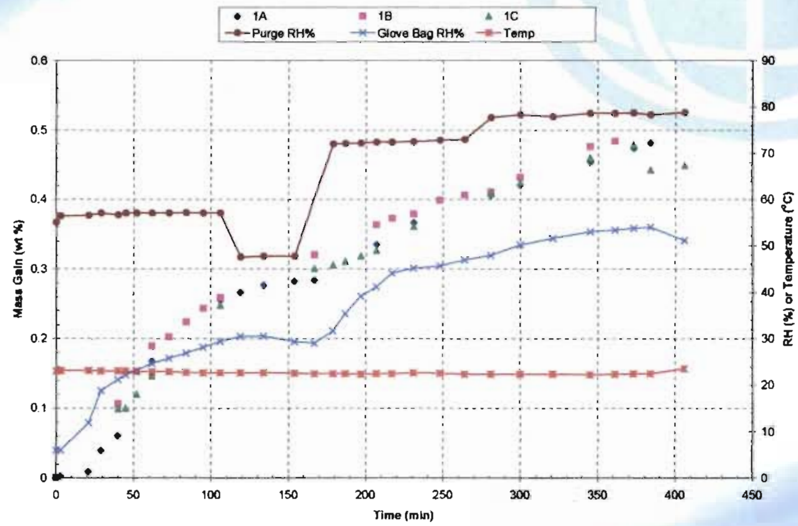
Series 1 Moisture Uptake



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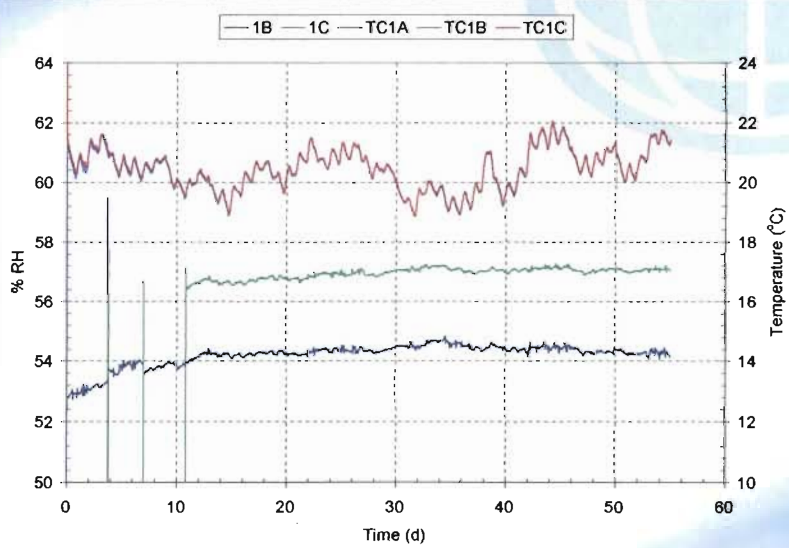
Series 1 %RH and Temperature Trends



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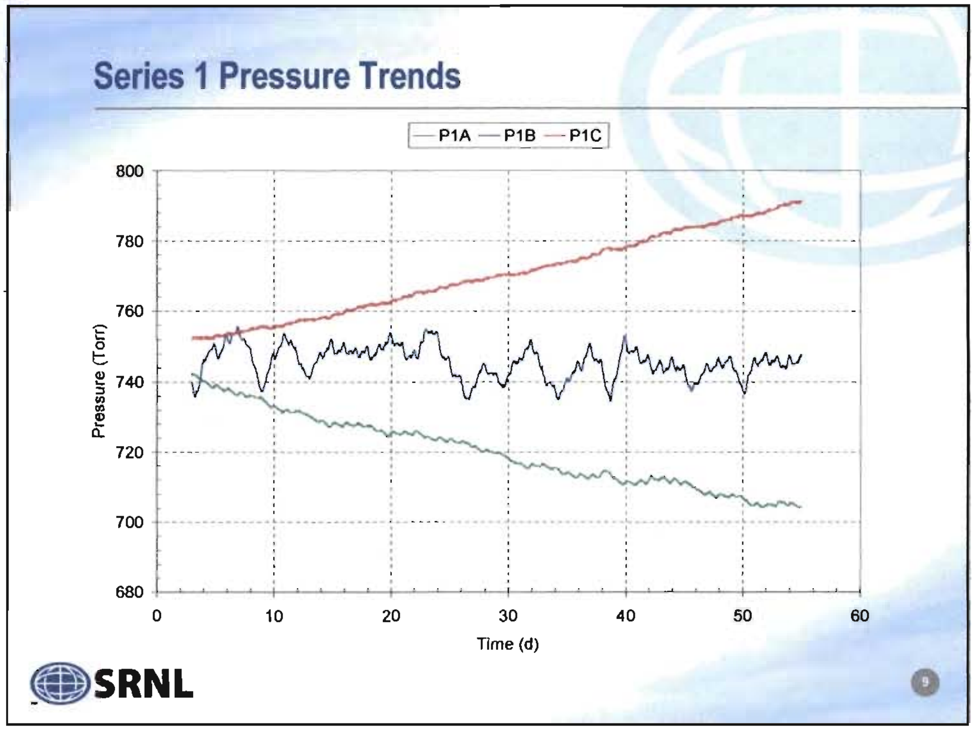
Series 1 Pressure Trends
P1A
P1B
P1C
800
780
760
740
720
700
680
Pressure (Torr)
0
10
20
30
40
50
60
Time (d)
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Role of HCl and Water Vapor in Corrosion

Steve Joyce C-PCS
Josh Narlesky MET-1
Corrosion Working Group Technical Meeting
April 26 - 27, 2011

Background

Observations of 1) corrosion in the headspaces above the plutonium-bearing material, 2) the formation of NH_4Cl solid in the head space, and 3) the lack of any elements other Cl and than those associated the stainless steel indicate the formation of HCl (g). In some cases, the relative humidity was fairly low (~10-20%). (Veirs et al. JNMM, 2010)

Several studies have shown that chloride-induced corrosion of stainless steels *will* occur at the deliquescent relative humidity of a covering salt. (NaCl, MCl_2 where M=Mg,Ca,Zn, Shoji et al., Boshoku Gijutsu, 1986; NaCl, MCl_2 where M=Mg,Ca, Prosek et al., Corrosion, 2009; ...)

Some residual processing salts such as $CaCl_2$ and $KCaCl_3$ have DRH in the range of 15 – 20% may be present in the bulk, but none detected in the head spaces. (Joyce et al. JNMM, 2010)

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Background

Little information on the corrosion of steels by HCl gas at low temperatures and low RH (high temperature corrosion presumed to occur by evaporation of metal chlorides).

Consider 3 possibilities:

1) Formation of HCl / water solutions
2) Formation of deliquescent metal chlorides from the elements of the steel
3) Formation of ultrathin water films at lower than bulk RH

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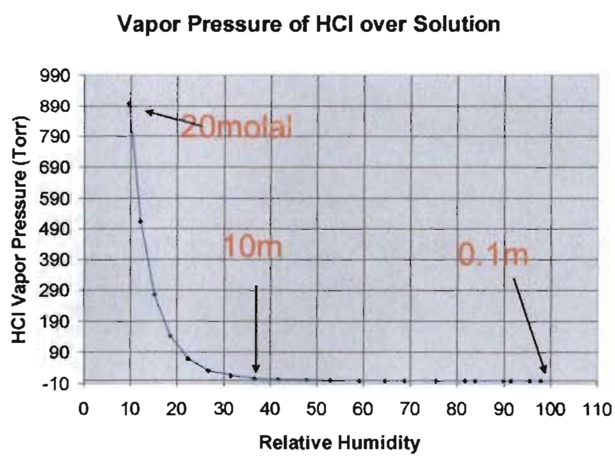
Role of HCl and Water in Corrosion (I)

HCl / pure water solutions can corrode stainless steels. Could such solutions form?

Based on both experimental data (Perry's Handbook) and thermodynamic modeling, the vapor pressure of HCl must be very high to form solutions at low RH. Adding Cl-salts pushes the curve up.



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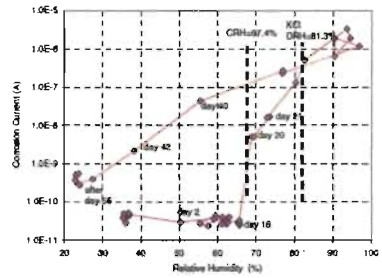
Role of HCl and Water in Corrosion (II)

HCl may react with the steel to form salts that do deliquesce at low relative humidities. Likely candidates are the chlorides of Fe, Cr, Ni, and Mn. Of these, $FeCl_2$ has been detected in the corrosion of mild steels by HCl/H_2O (80% RH) gas at RT and higher temperature corrosion of stainless steel with "dry" HCl using XRD.

Pabalan and co-workers observed the corrosion of carbon and stainless steels at low RH after cycling to higher RH (to deliquesce KCl) and postulated the role of the corrosion products in the low RH.



from Lietai Yang et al.
Mat. Res. Soc. Symp. Proc. Vol. 757, II4.14.1 2003

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Nickel Chloride, $NiCl_2$

Hydrate Formation: 0, 2, 4, 6

Dihydrate forms at 1.3% RH at 25°C (based on calculation)
Tetrahydrate: 25% RH
Hexahydrate: 41% RH
Hexahydrate stable up to 36°C

Deliquescence: 53% RH at 25°C for the hexahydrate
~50% RH above 40°C for the tetrahydrate

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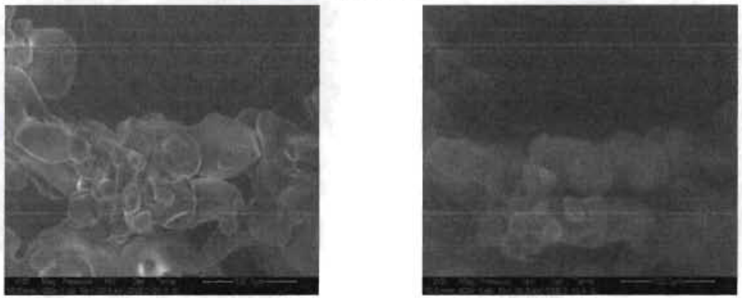
Nickel Chloride: $NiCl_2$

RH increased ->



DRH of 57% at 10°C
Measured stoichiometry at 30% RH as tetrahydrate using Spot-XRF

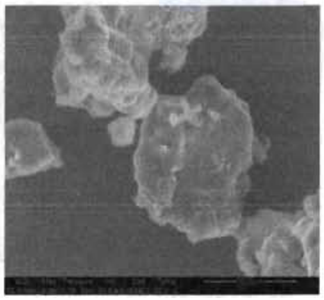
Manganese Chloride, $MnCl_2$

Hydrate Formation: 0, 1, 2, 4

Dihydrate forms at 2.6% RH at 25°C
Tetrahydrate: 22% RH
-reported to melt at ~50°C
-stable up to ~60°C

Deliquescence: 54-58% RH at 25°C for the tetrahydrate
~45% RH above 60°C for the dihydrate

Manganese Chloride: $MnCl_2$



DRH of 58% at 10°C
Measured stoichiometry at 10% RH as dihydrate using Spot-XRF

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Chromium Chlorides: $CrCl_2$ and $CrCl_3$

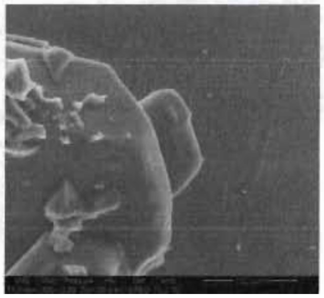
Hydrate Formation: 0, ?, 6 for $CrCl_3$
0, ?, 3 for $CrCl_2$

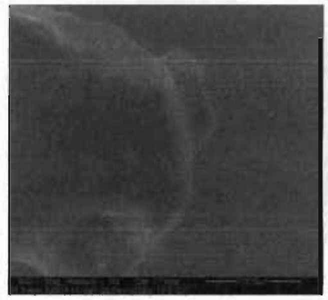
Little information on hydrate thermodynamics
- $CrCl_2$ reported as not stable w.r.t to oxidation to Cr (III)

Deliquescence: 42% RH at 25°C for the $CrCl_3$
31% RH at ~50°C for the $CrCl_2$

Slide 10

Chromic Chloride, $CrCl_3$





DRH of 45% at 10°C
Measured stoichiometry at 10% RH as hexahydrate using Spot-XRF

Ferrous Chloride: $FeCl_2$

Hydrate Formation: 0,1,2,4

Monohydrate forms at 0.1% RH at 25°C
Dihydrate: 1.7% RH
Tetrahydrate: 27% RH

Deliquescence: 55-60% RH at 25°C

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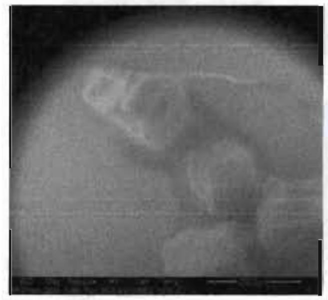
Ferric Chloride, $FeCl_2$



DRH of 60% at 10°C
Measured stoichiometry at 10% RH as dihydrate using Spot-XRF

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Ferric Chloride, $FeCl_3$

Hydrate Formation: 0, 2, 2.5, 3.5, 6, 10

The hexahydrate is the commonly available form, melts at ~37°C.

Scant literature on the thermodynamics of the hydrates.

Existing phase diagram indicates low melting point phases.

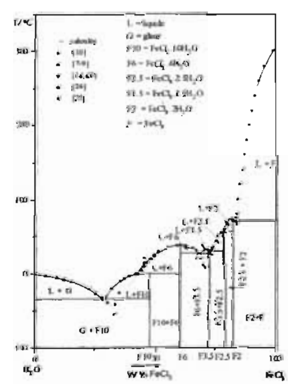

Fig. 4 Diagramme de phases du système binaire $FeCl_3$-H_2O

from *A. Atbir, A. Marrouche, H. Atif, L. Boukbir, M. El Hadek and R. Cohen-Adad, Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 849-860*

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Ferric Chloride, $FeCl_3$

Interpretation of deliquescence experiments is complicated by hydrolysis reactions.

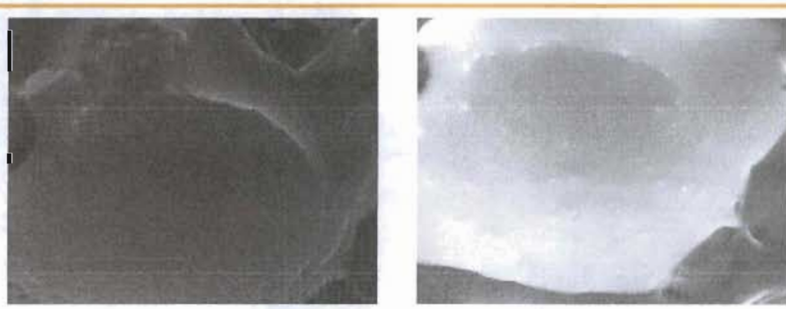
$$Fe^{3+} + H_2O + Cl^- \rightarrow Fe(OH)_3 + HCl$$

The HCl acidifies the solution (1M $FeCl_3$: pH = 2.2)

Other products observed such as FeOOH, Fe_2O_3, FeOCl, ...

Reported DRH values range from 5% to 48%

Ferric Chloride, $FeCl_3$



DRH of 10% at 20°C
Measured stoichiometry at 5% RH as dihydrate and at 10%RH as ~2.5 waters
Note: Bright dots observed are likely another phase indicating that hydrolysis is occurring

Ferric Chloride, $FeCl_3$

Microbalance Experiments: Reagent grade $FeCl_3*6H_2O$ at 20°C and 0.1%RH first converted to $3.5H_2O$, and then slowly to $2.5H_2O$. Increasing to 40°C resulted in a salt between the dihydrate and anhydrous. Increasing the RH to 0.25% RH led to an initial weight gain, followed by a weight loss, presumably through the liberation of HCl(g). The resultant material contain black- and rust-colored, water-insoluble materials, likely Fe_2O_3 and FeOOH.
Additional experiments show that the 3.5 hydrate melts at 27.5°C.

RH Probe Experiments: The RH above both the reagent grade $FeCl_3*6H_2O$ and a saturated solution were ~15% and 35% RH, respectively.

Ferric Chloride, $FeCl_3$

$FeCl_3$,. if present, may form solutions at low RH by either melting or deliquescence.

However, the conditions under which $FeCl_3$ solutions might occur are complicated by the hydrolysis and likely other factors such as the thermal and humidity history.

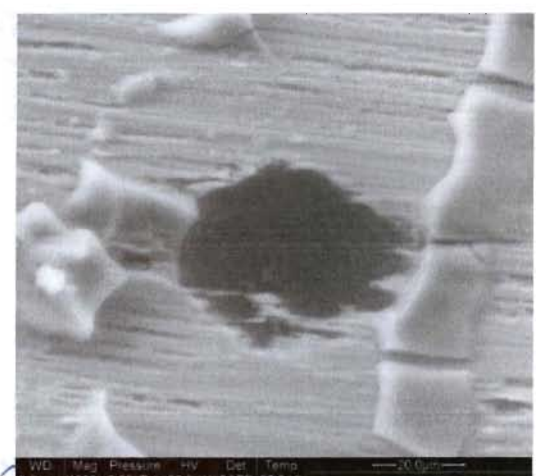
Corrosion of Stainless Steel by $FeCl_3$ Solutions

$FeCl_3$ is fairly corrosive due to the presence of both Cl^- and the oxidizing Fe^{3+} ions. It forms the basis of ASTM G48 “Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution”.

A drop of 6 wt% $FeCl_3$ was placed on 304 steel pieces for up to 3 days by which point only a solid was present (laboratory ambient between 20-30% RH).

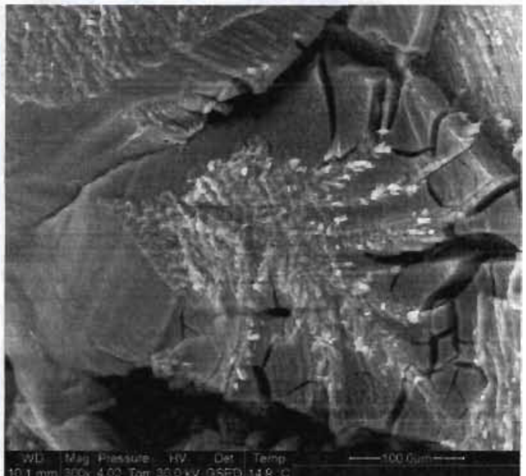
The residual salt and the steel piece were examined with SEM.

Corrosion of Stainless Steel by $FeCl_3$ Solutions



Pit exposed after removing the loose salt deposits.

Corrosion of Stainless Steel by $FeCl_3$ Solutions



The salts produced are heterogeneous physically and chemically.

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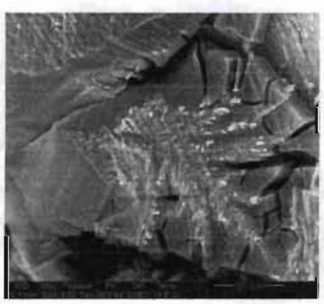
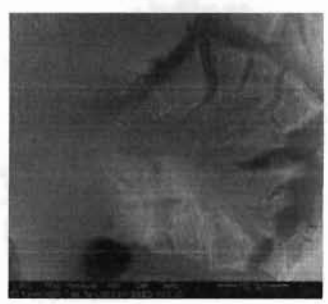
Corrosion of Stainless Steel by $FeCl_3$ Solutions





DRH of 61% at 10°C and 59% at 15°C
Consistent with $FeCl_2$ as well as $NiCl_2$ and $MnCl_2$
The Fe(III) is likely reduced to Fe(II).

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Role of HCl and Water in Corrosion (III)

HCl may not need bulk solutions to corrode steel.

- •Corrosion of SS tubing in process gas delivery is observed at RT in the semiconductor industry and water clearly plays a role (even at ppm levels, 100 ppm ~ 0.3% RH). Industry standard is to purge to 100 ppb. (Note that at very high gas pressures, solutions may form.)
- •Corrosion of iron artifacts. $FeCl_2*4H_2O$ corrodes at 22% RH but deliquesces at 60%. FeO(OH) with Cl impurity corrodes at 16% RH, and while it takes up water vapor, it does not deliquesce.
- •Numerous studies have shown that 3-5 layer thick water films can exist on salt surfaces and support conductivity.

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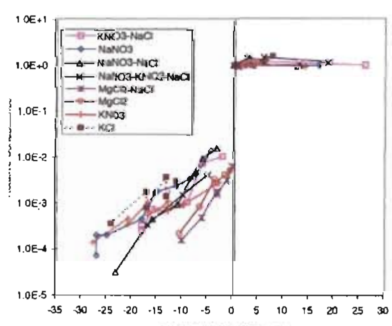
Role of HCl and Water in Corrosion (III)

IR of absorbed water on NaCl at 52% RH (DRH 74%)

Conductivity measured with STM on mica at 60% RH (insoluble)

Pabalan's RH probe based on conductivity



from Lietai Yang, Roberto T. Pabalan and Lauren Browning, **Mat. Res. Soc. Symp. Proc. Vol. 713 , JJ.11.4.1 2002**

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Role of HCl and Water in Corrosion (III)

Currently setting up experiments to study the behavior of SS exposed to ppm levels of HCl and low RH (10-20%) to determine if these environments are corrosive and to examine the surfaces using SEM and XPS to measure the extent and identify of the chlorides formed.

Destructive Examination (DE) Data Analysis

Elizabeth Kelly, LANL
Gary Friday, SRNL

Corrosion Working Group

LANL

April 26-27, 2011

DE Data Summary

- 69 DE's with data available (through 11DE#7)
  - One DE with partial info - container H003328 (10DE#19).
    - Hanford container with high moisture - opened at LANL
- 58 DE containers from the P&C Bin; 10 from the Pressure Bin and one from the Innocuous Bin.
- 38 of the 58 are from the random sample, 20 from Engineering Judgment (EJ) sample [two of these are Foreign Material Inspection (FMI)]
- Hanford P&C 34 (19 R/15 EJ); RFETS P&C 21 (18 R/ 3 EJ); SRS P&C 3 (1 R / 2 EJ)

Probabilities of Corrosion for P&C Bin from Random and EJ Samples

- *Two categories – Adherent coating and/or Pitting (Coating/Pitting) and Pitting (may also have coating) (p = proportion with corrosion)*

		Random			EJ		
	Corrosion Type	Sample Size	*n*	p/(95% LCL, UCL)	Sample Size	*n*	p
All Containers	Coating/Pitting	38	7	0.18 (0.085,0.32)	20	11	0.55
Hanford	Coating/Pitting	19	7	0.37 (0.18, 0.58)	15	11	0.73
RFETS	Coating/Pitting	18	0	0 (0, 0.15)	3	0	0.00
All Containers	Pitting	38	6	0.16 (0.066, 0.29)	20	8	0.40
Hanford	Pitting	19	6	0.32 (0.14, 0.53)	15	8	0.53
RFETS	Pitting	18	0	0 (0, 0.15)	3	0	0.00

- *EJ sample shows effective targeting of coating/pitting and pitting in all cases except possibly Hanford pitting.*
- *Hanford and RFETS significantly different.*

Factors Examined

- MISRepresented (Taxon)
- TotalActinides (%)
- StabTempCycle (Degrees C)
- PackagingEnv : C-Line or Dry (SPE or RFETS)
- MSH2OConcentration (Initial) (%)
- BET (m^2/g) (surface area per unit mass)
- AvgDensity (g/cc)
- H2 (Vol.%)
- Na Leach (μg/g)
- K Leach (μg/g)
- Mg Leach (μg/g)
- Ca Leach (μg/g)
- IonCl (μg/g)

What is the Single Most Important Factor for Predicting Corrosion in P&C Bin?

Factor	Proportion of Coating and/ or Pitting	Proportion of Pitting
H2 > 1%	0.85 (17/20)	0.65 (13/20)
PyroOx-HN-RF-ERScrap	0.70 (14/20)	0.50 (10/20)
Stabilization Temp = 750	0.60 (15/25)	0.44 (11/25)
C-Line	0.56 (18/32)	0.44 (14/32)
MS H20 > 0.1%	0.51 (18/35)	0.40 (14/35)
PyroOx-HN-RF-MiscOx*	0.60 (3/5)	0.60 (3/5)

Containers from PyroOx-HN-RF-ERScrap all have 750 stabilization temp and packaged in C line. These three factors are highly correlated.

* Sample size too small for conclusions, only 5 cases. All three of the containers from PyroOx-HN-RF-MiscOx with moisture > .1%, have coating and/or pitting. One of these is H003328 (highest moisture, opened at LANL) and the other is H003367 the low H2 case (H2 = 0.73).

(Note that Cl>3000, proportion of Coating and/or Pitting = 0.44 (18/41) and proportion of Pitting = 0.34 (14/41)

Exceptions – fit the bill, but no adherent coating or pitting

ID	DE Num	Surv Reason	MIS Represented	PG Cl%	PG F%	MS H2O	BET	Avg Density	H2	Na	K	Mg	Ca	IonCl
H003443	11DE-1	EJ	PyroOx-HN-RF-ERScrap	6.4	0	0.32	0.8	6.96	35	17100	30700	1565	302	60500
H002554	09DE-3	Random	PyroOx-HN-RF-ERScrap	6.1	0	0.22	1.07	6.76	19	20900	35900	1460	4.29	65650
H002509	09DE-6	EJ	PyroOx-HN-RF-ERScrap	6.3	0	0.26	1.35	7.04	34	17950	30400	1635	3.53	58350

Stabilization Temperature 950^0 C with Pitting (could have coating too)

ID	DENum	SurveillanceReason	Taxon	PGCI%	PGF%	Env	MSH2O	BET	Avg Density	H2	Na Leach	K Leach	Mg Leach	Ca Leach	IonCl
H003367	10DE-13	Random	PyroOx-HN-RF-MiscOx	1.44	2.86	C	0.22	0.81	6.04	0.73	2240	3090	6	7915	8355
H003371	11DE-7	Eng Judgement	PyroOx-HN-RF-MiscOx	0.00	1.18	C	0.274		6.97	14	694.5	1160	10.145	2665	3455
H002496	10DE-2	Eng Judgement (FMI)	ScrapOx-HN-Lo	0.91	3.69	C	0.17	0.49	6.06	1.2	588	538	9	5690	3465

Note that two of these have low H2 generation, yet still have corrosion

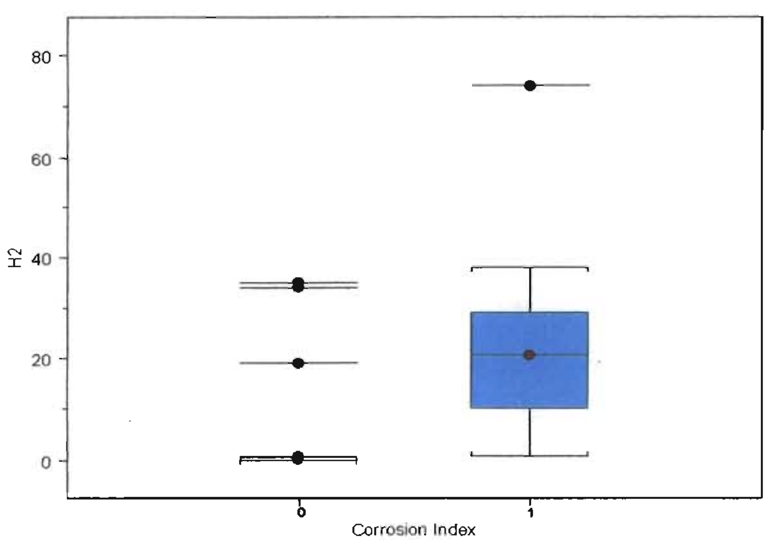
Corrosion Index

- 0 – no adherent coating or pitting
- 1 – adherent coating and/or pitting

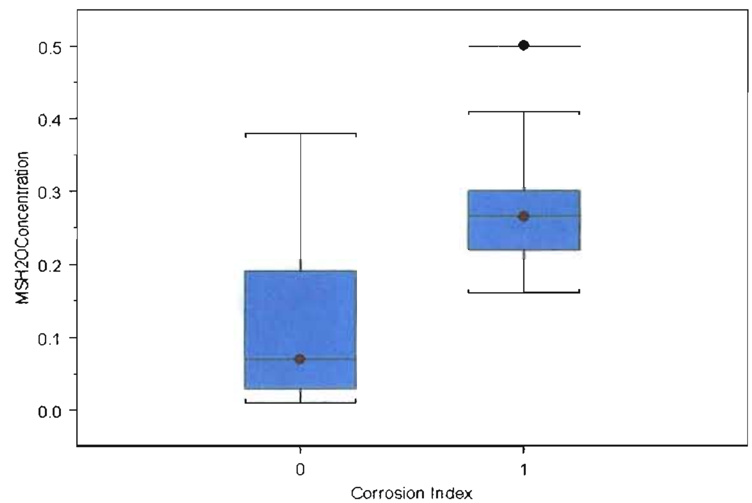
Factors Differing Between the Corrosion Index Groups

- H2
- MS H20
- Cl, Na, K, Mg
- BET
- Avg. Density effect

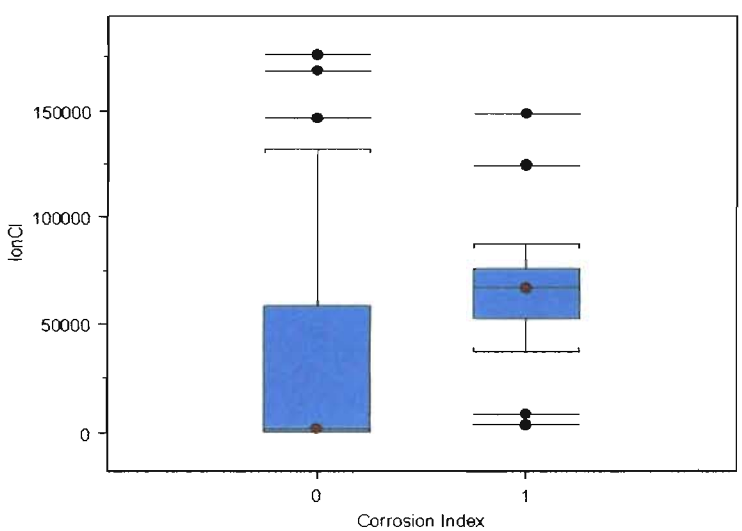
H2 (Vol. %)



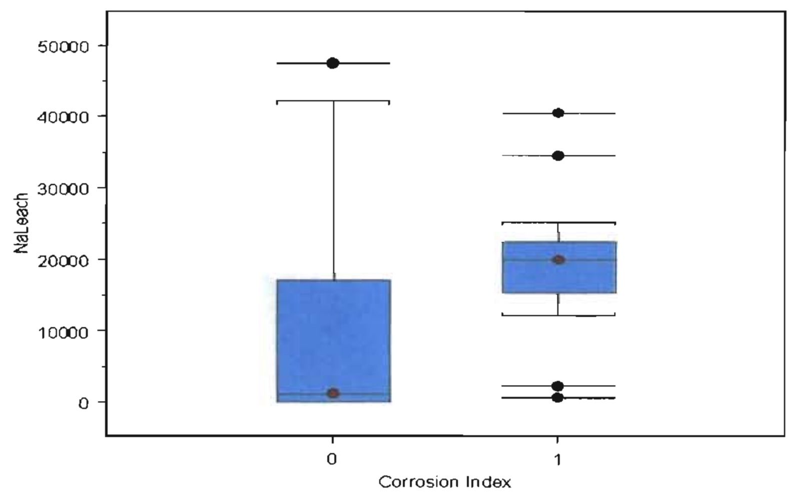
MS H20 Concentration (%)



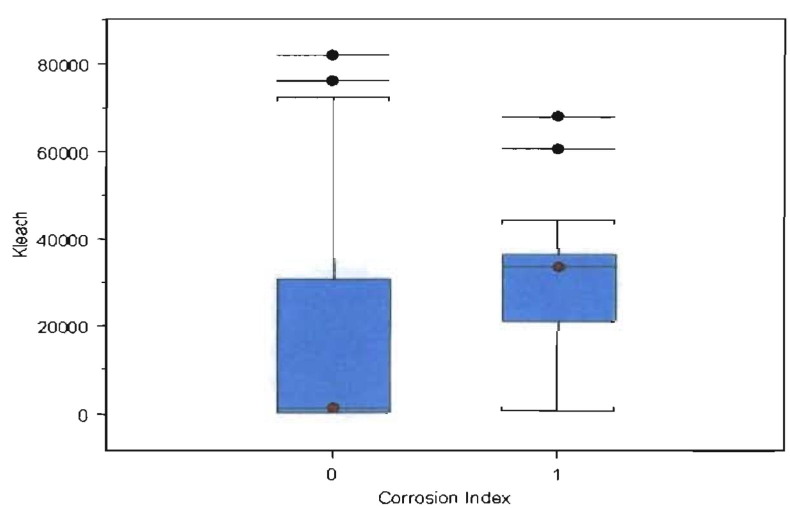
Cl (μg/g)



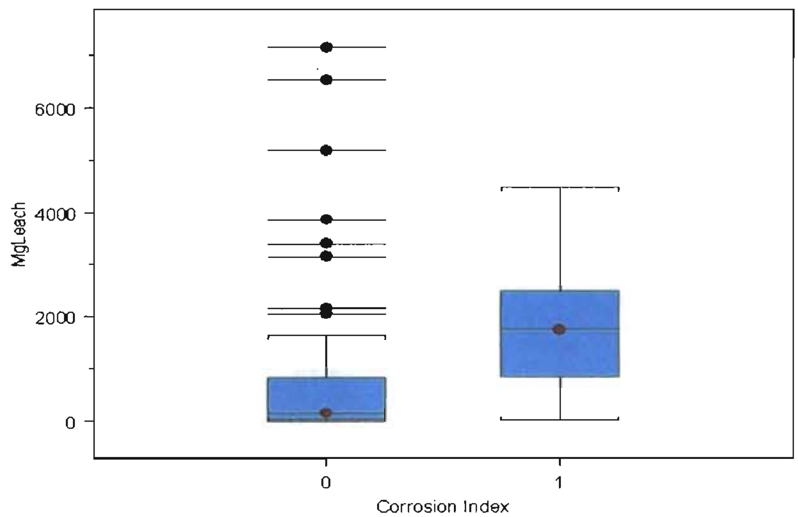
Na (μg/g)


50000
40000
30000
20000
10000
0
NaLeach
0
1
Corrosion Index

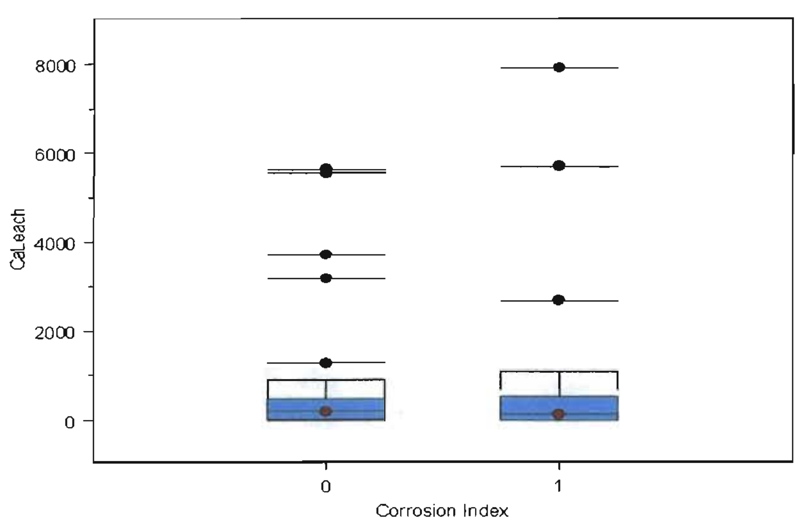
K (μg/g)


80000
60000
40000
20000
0
Kleach
0
1
Corrosion Index

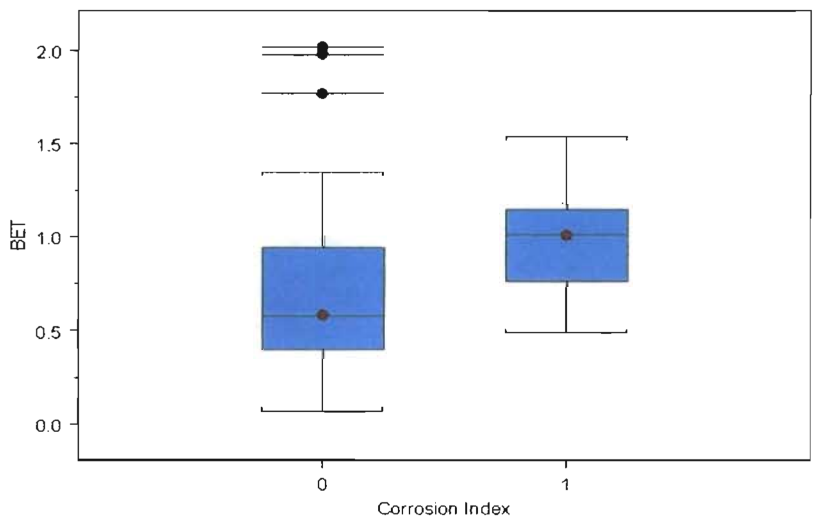
Mg (µg/g)


6000
4000
2000
0
MgLeach
0
1
Corrosion Index

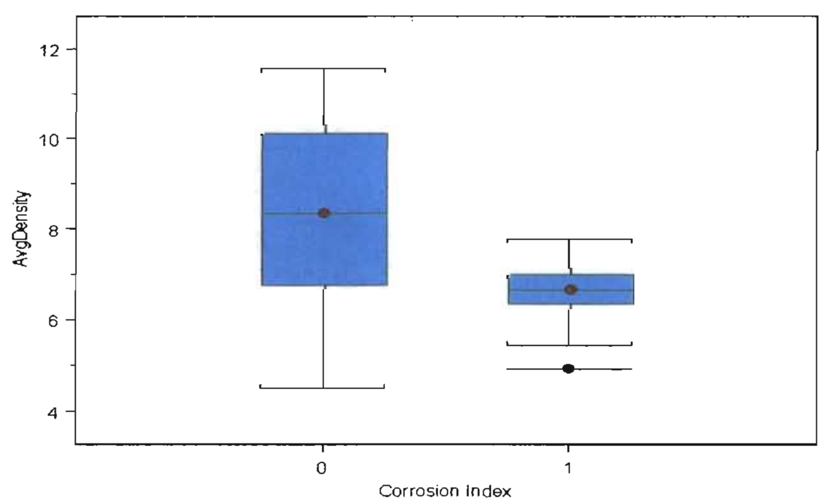
Ca (µg/g)


8000
6000
4000
2000
0
CaLeach
0
1
Corrosion Index

BET (m^2/g)



Avg. Density (g/cc)



No Significant Corrosion (*e.g., Based on modeling and expert judgment no corrosion of inner container in 50 years that could cause degradation of outer container*)

What can be said at this time based on random sample?

- 0/38 *
- 95% Confidence Interval for Probability of Significant Corrosion (CI) (0, 0.07);
- 99% CI (0, .11);
- 99.9% CI (0, .16)
- 86% probability that have seen one of the worst 5%

**Note 1/38 = 0.026 showed pitting on inner container 95% CI =(0.0012, 0.116), 99% CI = (0.00027, 0.159), 99.9% CI=(0.00003, 0.213)*

Issue for Statistical Statements about Corrosion

- Must be able to defend that when you destructively examine containers you can assess "significant corrosion degradation in 50 years" (however this is defined, e.g., *corrosion of inner container has a non-negligible probability of degrading the outer container)*
  - Related Issues
    - Defend that you can asses/bound what the depth of pits will be in 50 years
    - Defend that you can asses/bound what the extent of stress corrosion cracking will be in 50 years

Defense of Surveillance Efforts from Statistical Perspective

- Continue EJ sampling for P&C bin, since these results are assumed to be bounding.
- Continue random sampling to test EJ bounding assumption (e.g., no surprises) and to provide statistically-based conclusions.
- Perform studies to defend
  - Assumption that EJ sample is bounding
  - That "significant corrosion" in 50 years can be assessed/bounded when containers have DE

Kirk Question: *"What can we say about corrosion in Pressure Bin?"*

- In the past the argument has been that P&C bin results will bound Pressure bin results for corrosion.
- Ten containers examined to corroborate assumption.
  - No corrosion observed
  - Cannot make a statistical statement (sample not random)
  - Even if assume random have 0/10, which gives 95% CI (0, 0.24)
- *Key argument is that P&C results are bounding.*

Relative Humidity Changes in Large Scale Corrosion Containers

Joshua Narlesky

April 26, 2011

Status

- 6 containers loaded; 2 available slots

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

Relative Humidity for Deliquescence and Hydrate Formation

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

Moisture Absorption Observations

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

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

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

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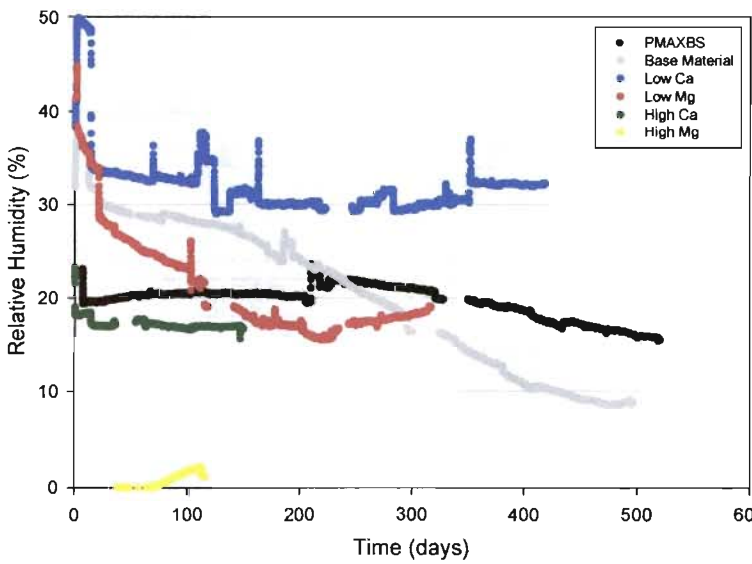
Storage Conditions (first 30 days)

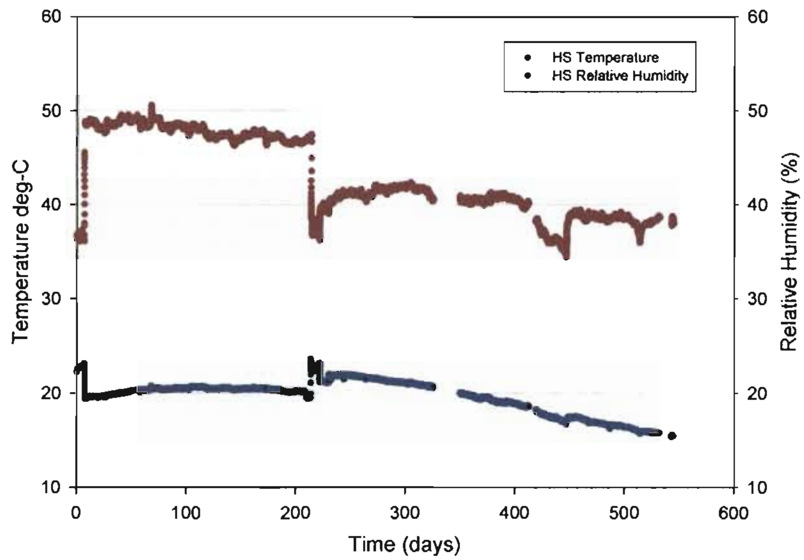
Material	wt% Moisture	Condition	Headspace Temp °C	Headspace RH (%)	Sidewall Temp °C	Sidewall RH (%) (calc.)
PMAXBS	0.09	Bare 3013	36	23	41	18
		Insulated	49	20	47	22
Base Material	0.05	Bare 3013	30	35	29	37
		Insulated	36	31	33	37
Low Ca	0.28	Bare 3013	30	49	32	44
		Insulated	39	34	35	42
Low Mg	0.28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

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

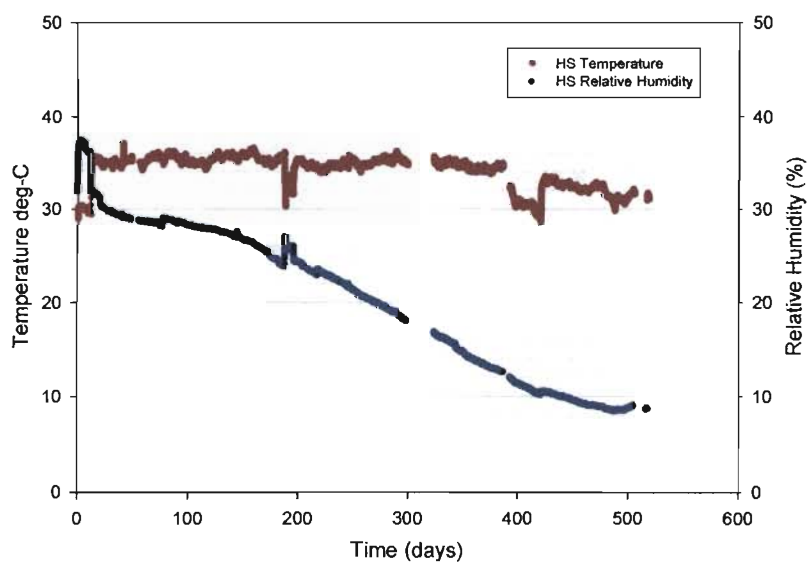
Relative Humidity



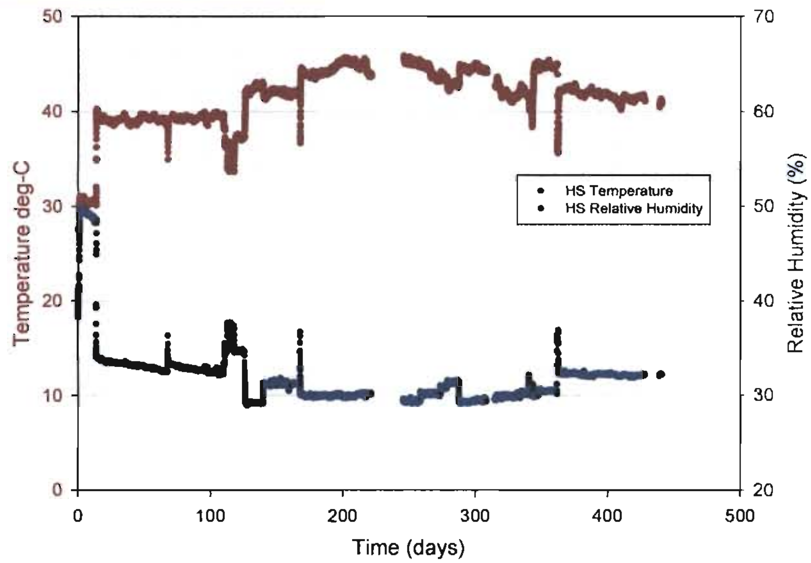
PMAXBS (0.09 wt% H_2O)



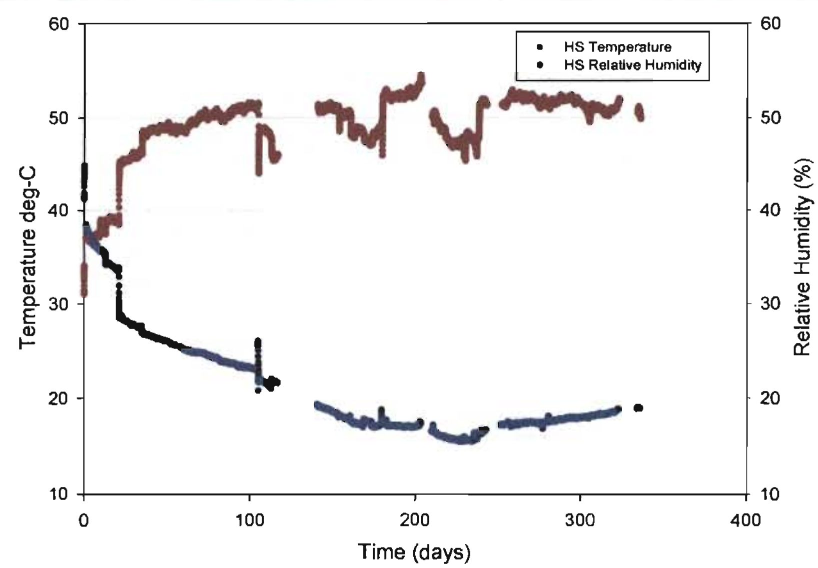
Base Material (0.05 wt% H_2O)



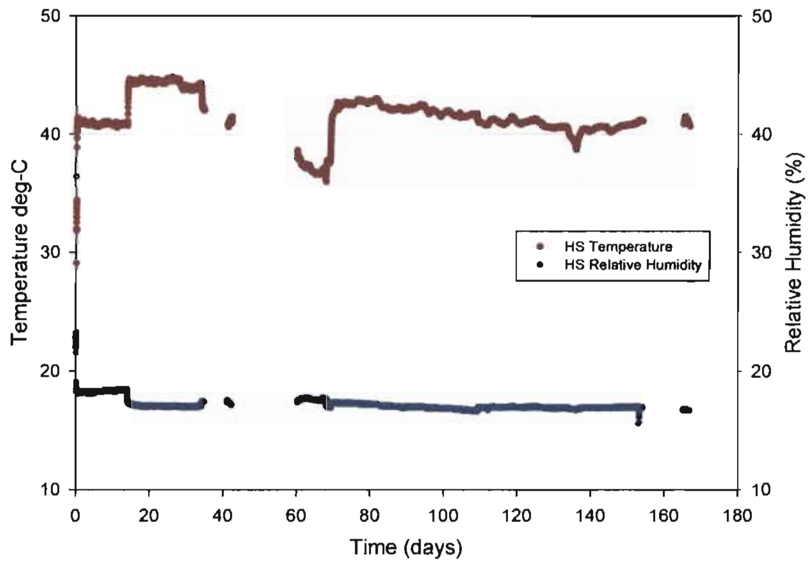
Low Ca (0.28 wt% H_2O)



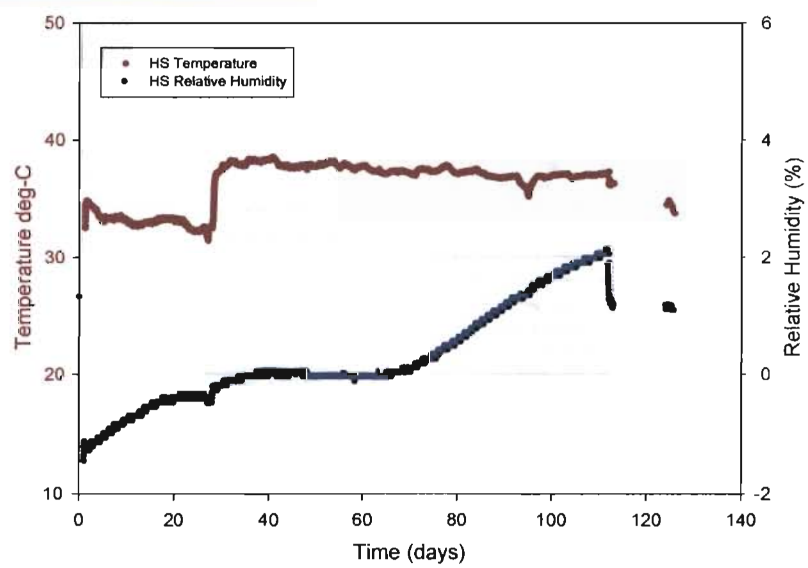
Low Mg (0.28 wt% H_2O)



High Ca (0.39 wt% H_2O)



High Mg (0.55 wt% H_2O)



Conclusion

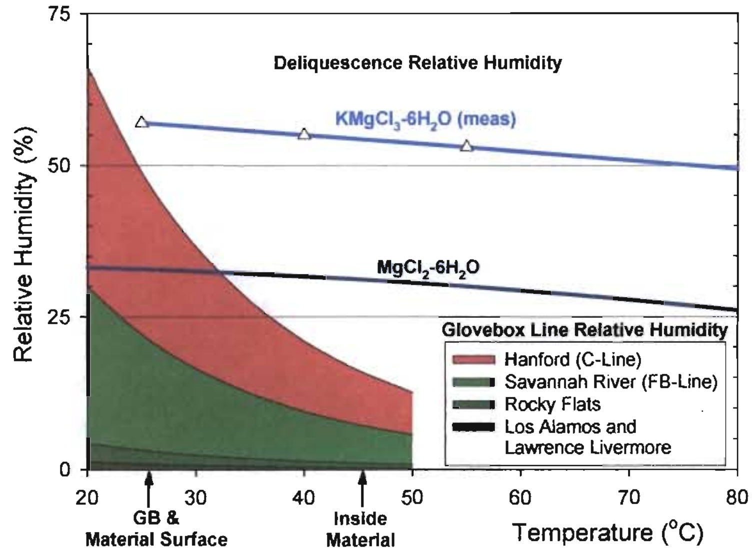
- Corrosion is possible where liquid phases are present
- Where do we expect liquid phases?

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

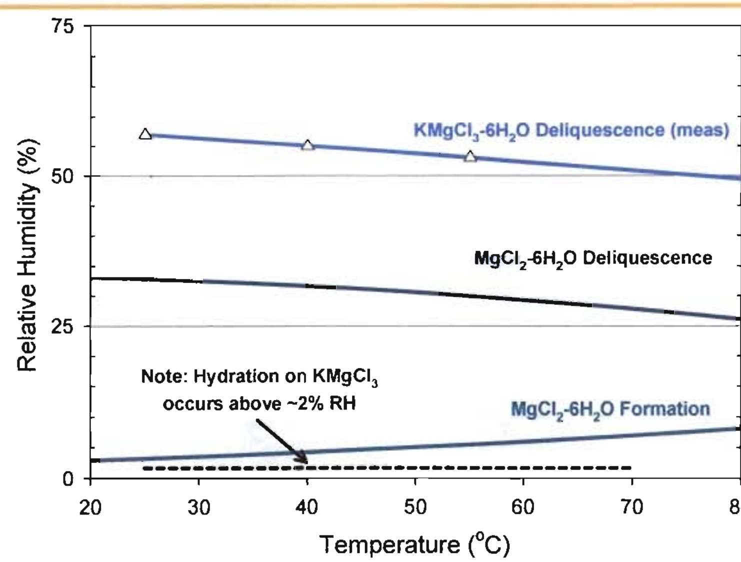
- Liquids phases possible even for short exposure to high RH
- Gas generation: O_2 being generated in all materials with AEC added

Additional Information

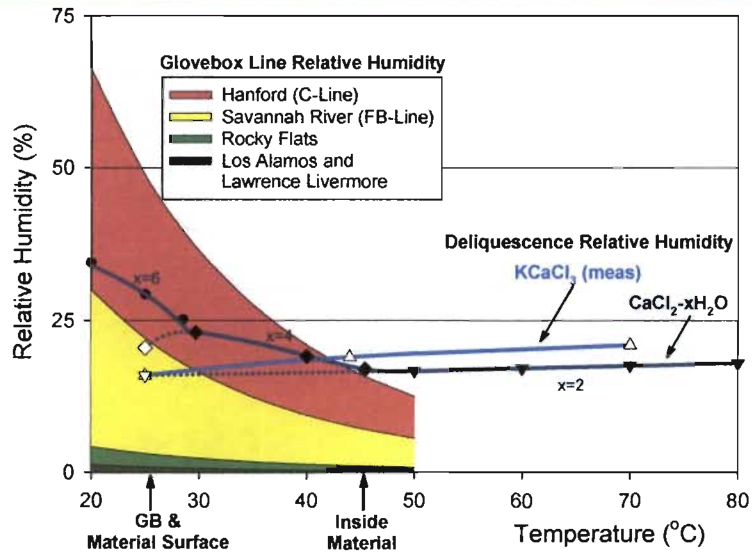
Magnesium Chloride Salt Behavior During Packaging



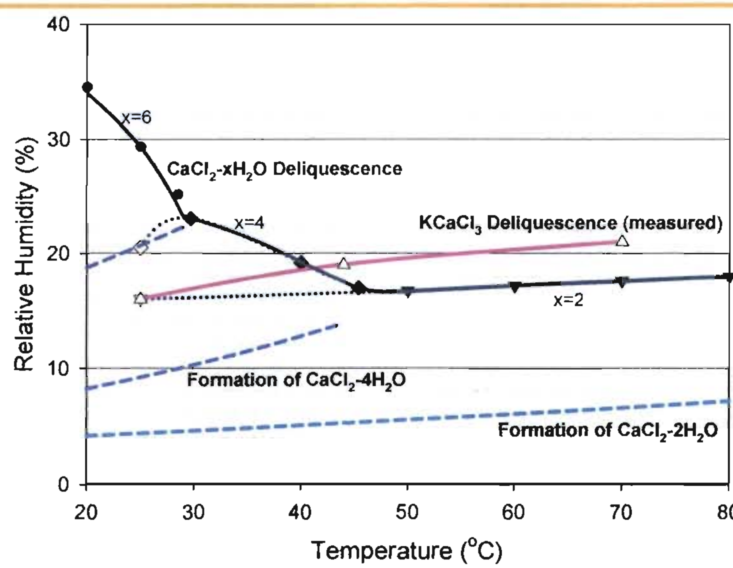
Hydration behavior of magnesium chloride salts



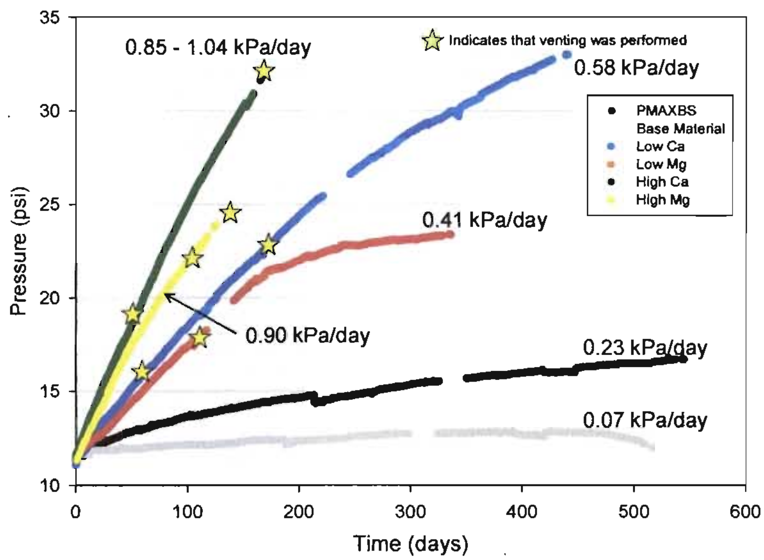
Calcium Chloride Salt Behavior During Packaging



Hydration behavior of calcium chloride salts



Total Pressure



H003328 Summary

86% PuO_2, with soluble ions of 3.3%Cl, 0.03%Mg, 0.3%Ca, 0.7%Na, 1.4%K
Package Moisture (TGA): 0.48-0.53%

Seven years later…
Moisture: Center top - 0.34% (TGA) and 0.24% (M/S)
Wall top - 0.50% (TGA) and 0.44% (M/S)
RH (Headspace): 22.9%, Centerline temp: 60.4 ^0C
Inner can pressure: 43.4 psia
Headspace gas: 75% H_2, 11% N_2, 14%He, trace O_2
Specific Surface Area: 0.83 m^2/g

Initial DE of H003328 Hanford High Water Can

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

Ted Venetz, Hanford Site
Suzanne Clarke, DOE-RL

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

Hanford Can H003328

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

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

Processing Flow Diagram

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

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

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

Hanford Assembly

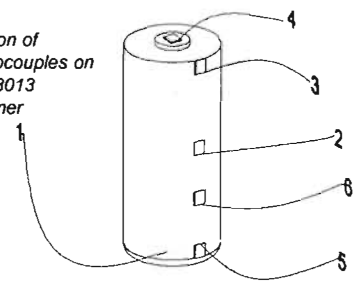
NDE: *Temperature of 3013 container in a 9975*

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

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

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

Location of thermocouples on outer 3013 container



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

Analytical equations yield conservative wall temperatures in this test.

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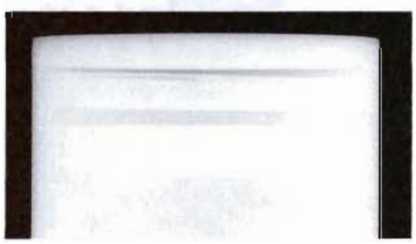
NDE: *Radiography*



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

Variations Hanford vs. LANL include:

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

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Gas Sample

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

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

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

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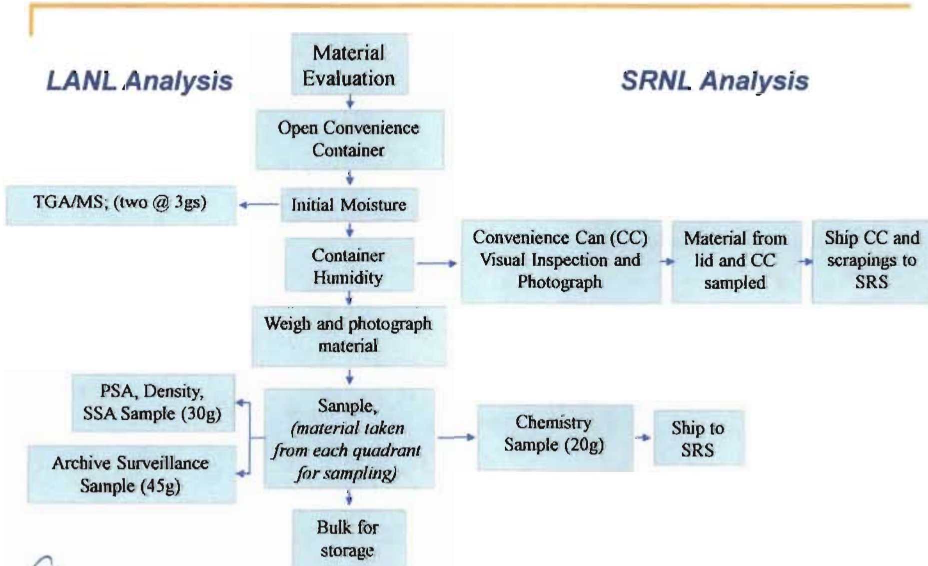
Material Evaluation



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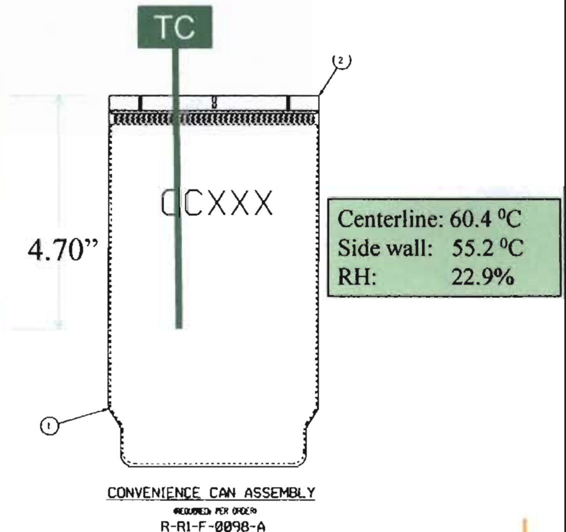
Cutting the outer and inner 3013 container and initial measurements were time sensitive.

3013 Container Cutting Equipment

Relative Humidity and Temperature readings



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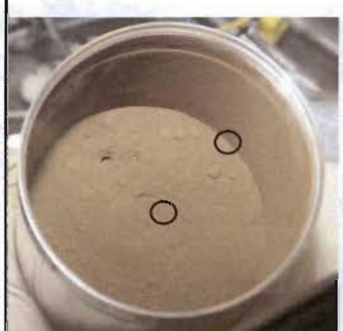
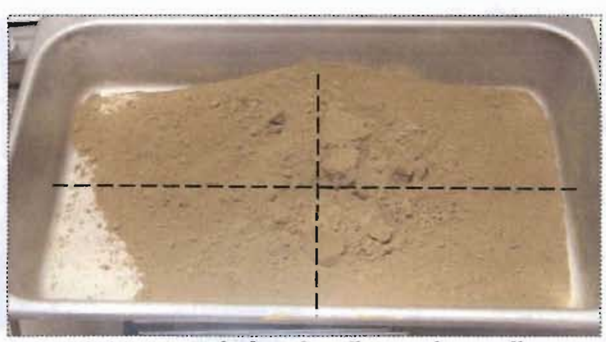
H003328 Material Images and Sampling

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



Oxide in Hanford CC



Oxide in pan before leveling and sampling

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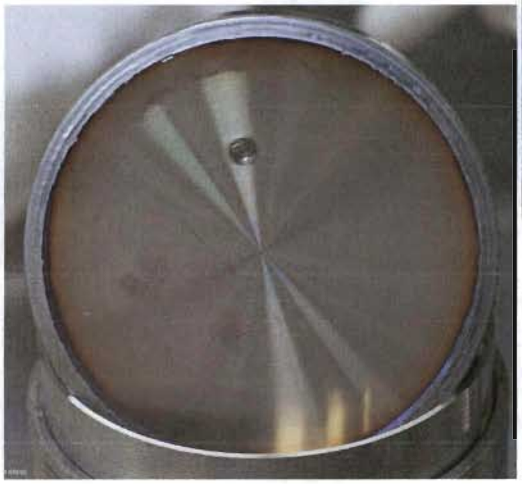
Outer 3013 Images



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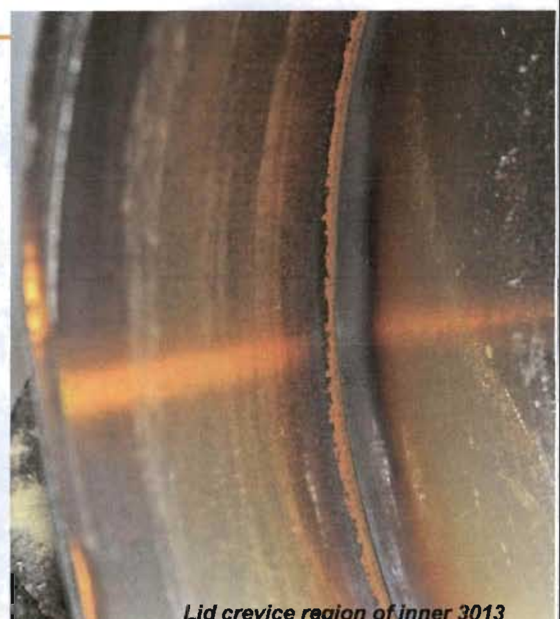
Inner 3013 Images

Inside lid image

Bottom of inner 3013



Lid crevice region of inner 3013

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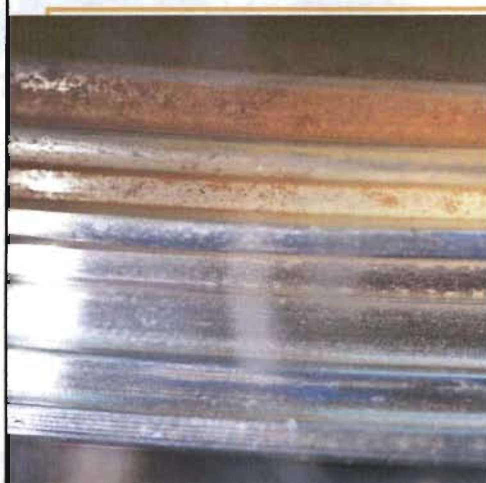
Convenience Can Images: outside lid showing filter

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

Convenience Can: inner images



Lid thread region

Bottom of CC lid

Convenience Can

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

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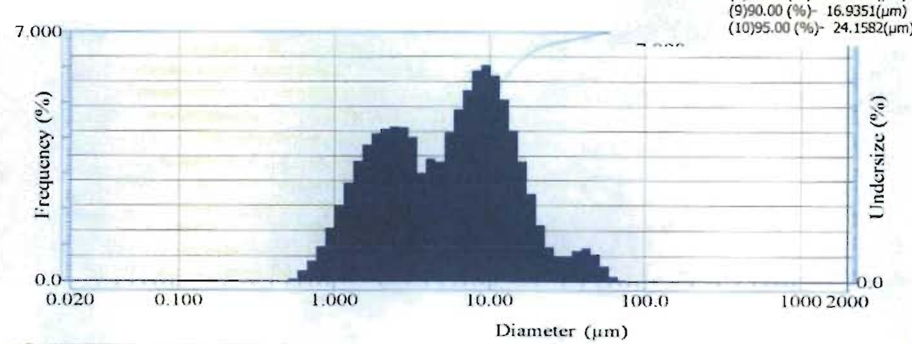
Particle Size Analysis

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

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

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



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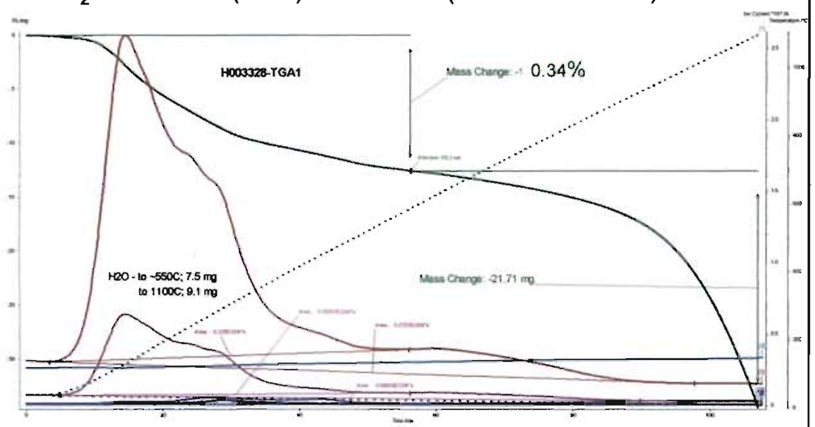
H003328 TGA-MS

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

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

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



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Summary

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

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

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

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

Binh V. Nguyen

Taken From Binh's MIS Talk

3013 Surveillance and Monitoring Program Review

766-H Room 2138

3013 Containers Collected To Date (FY09 to present)

- **One Rocky Can** (R610806)
- **Three SRS Cans** (S001721, S002129, S001105)
- **23 Hanford Cans** (H003119, H002195, H004251, H002496, H003710, H003655, H002447, H00390, H003650, H002567, H002728, H002786, H003077, H003367, H003704, H003443, H002592, H003337, H003343, H003371, H003526, H003565, H003625)
- **Three not completed in FY11** (1 Hanford, 1 Rocky and 1 LLNL)

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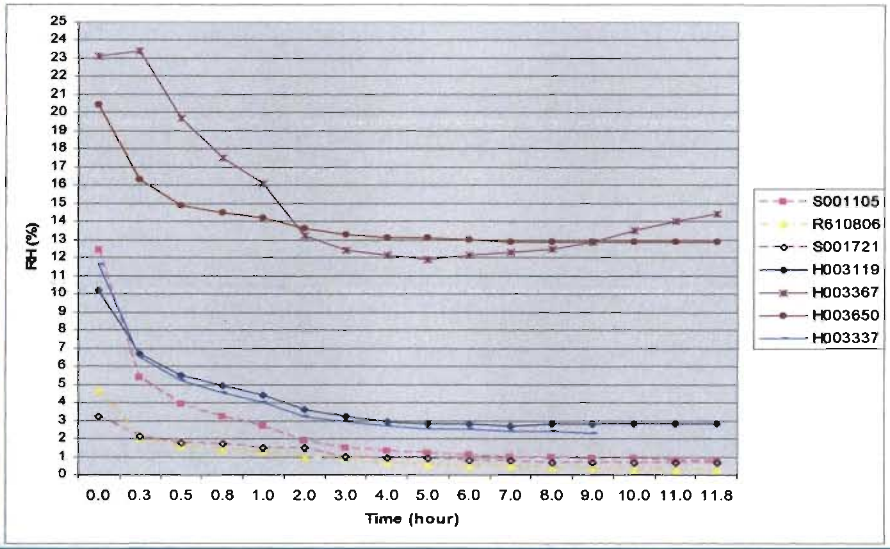
Relative Humidity Over Time



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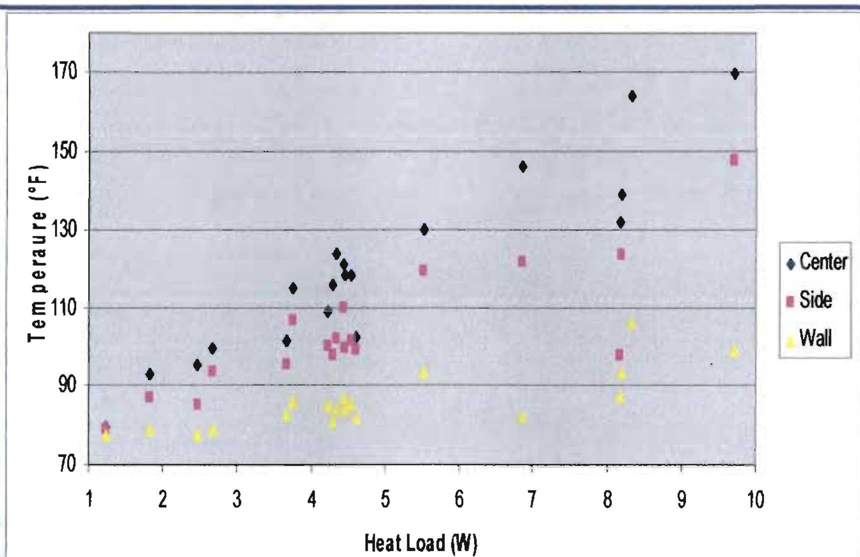
Temperatures vs. Heat Load



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Data (1 of 2)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
R610806	8.2	0.3	138.6	123.4	93.6
S001721	8.3	0.7	164.2	n/a	106.1
S002129 (6)	9.6	1.0	154.3	136.2	98.1
S001105	9.7	0.8	169.9	147.7	99.1
H003119	5.5	2.8	129.8	119.1	93.6
H002195	8.2	n/a	131.8	97.8	87.2
H004251	3.8	3.7	115.1	106.5	86.0
H002496	2.5	12.1	95.2	85.1	77.4
H003710	4.5	5.3	118.0	99.5	84.2
H003655	4.5	3.1	118.4	101.3	85.5
H002447	4.8	5.3	n/a	n/a	n/a
H003900	3.7	5.7	101.4	95.2	82.6
H003650	4.6	12.9	102.5	99.1	81.8

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Data (2 of 2)

3013 ID	Heat Load (W)	Humidity (% RH)	Center (°F)	Side (°F)	Wall (°F)
H002567	1.2	11.8	79.2	78.8	77.5
H002728	4.4	4.2	123.8	102.0	84.1
H002786	4.3	3.2	115.7	97.4	80.9
H003077	6.9	4.1	146.4	121.7	82.4
H003367	2.7	14.4	99.5	93.6	78.8
H003704	4.4	3.1	120.8	109.9	86.9
H003443	4.2	8.0	108.8	100.1	84.9
H002592	1.8	11.6	93.1	87.0	79.0
H003337(9)	3.3	2.3	108.1	98.6	81.2
H003343	3.7	1.2	112.4	85.6	76.5
H003371	3.0	11.7	107.0	96.2	77.3
H003526	4.3	4.2	112.6	103.1	83.2
H003565	4.6	1.4	123.7	110.1	87.3
H003625	4.6	3.6	119.4	112.2	92.4

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Engineering Judgment

Recap and discussion of criteria for future selections

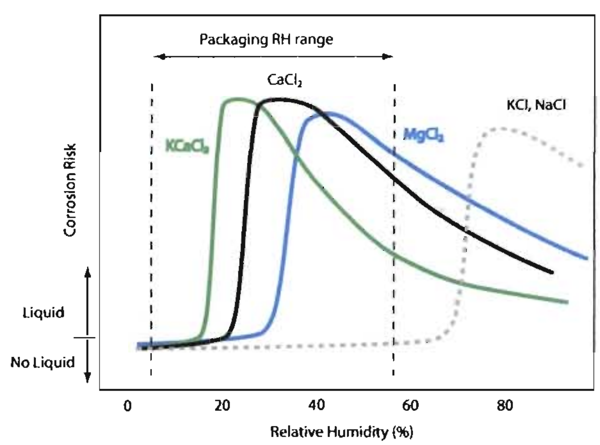
EJ selection for FY10 and FY11

- Of the six containers selected for DE based on engineering judgment in 2010, three containers were selected based on their contained material having the highest measured moisture at packaging (H003328 [opened at LANL], H003900, and H003650). A fourth container was selected based on having been packaged in a glovebox atmosphere with the highest relative humidity among ten containers with the highest moisture content (H003655). Two additional containers were selected based having similar packaging histories to containers in which foreign objects were found in previous surveillances (H002496, H004251). In addition, 16 containers identified as having the potential for foreign objects based on weight discrepancies had NDE.
- In 2011 there were 13 containers selected as part of the P&C random sample and five containers selected based on engineering judgment (Table 5). Engineering judgment selection of containers for DE in FY2011 sought to identify containers likely to be at the greatest risk for internal corrosion based on packaging conditions and material composition that could have led to formation of liquid water films or droplets within the container (Table 5). The relevant packaging data available for this selection process are the total moisture and total chloride content. A high ratio of moisture to chloride was deemed to be the highest risk based on shelf-life studies. Two containers were selected based on having the highest such ratios from the Hanford and SRS packaging campaigns (H003343 and S001105). Two additional containers were selected based on high moisture but undetected chloride under the assumption that chloride is probably present but below the detection threshold of prompt gamma (H003371 and S002129). A fifth container (H003443) was selected based solely on having the highest total moisture at the time of packaging of the containers remaining in the field surveillance program.

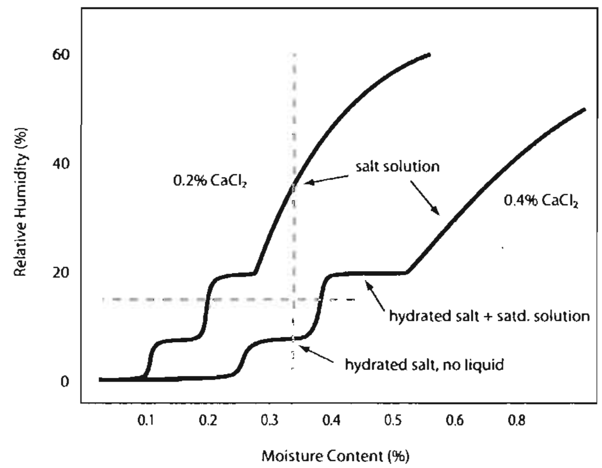
Criteria for Future Selections

- Continued focus on corrosion potential.
  - Moisture, salt content
- Do we need a larger sample of from previous criteria?
  - Size of the population of containers meeting the selection criteria.
- Update criteria based on DE findings since last selection.
- New criteria?
  - Could consider features in TGA in moisture range?

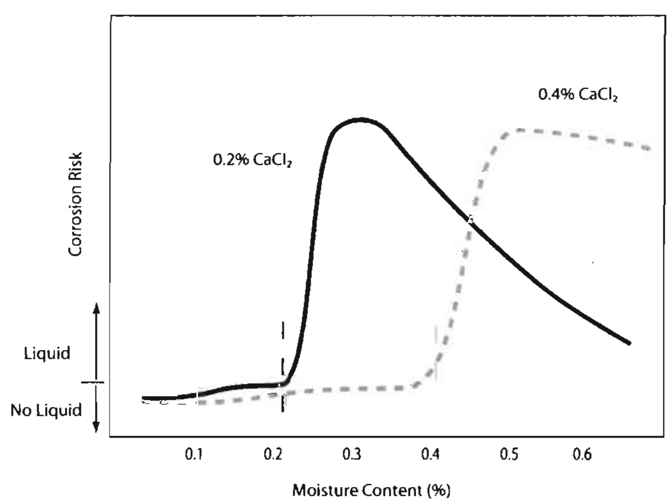
Conceptual model of risk vs. packaging RH for different impurities



Packaging RH limit vs. moisture limit



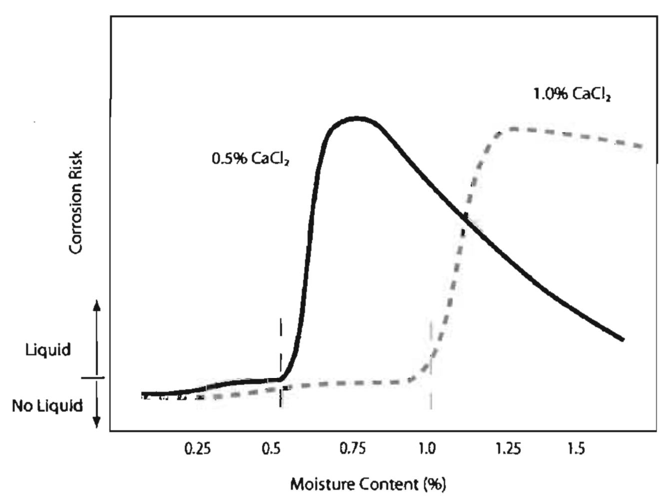
Effect of salt content on risk



H003328 Cl mass balance

	molar mass	observed mass fraction	soluble (leach)	mole/kg matl	Cl:metal as salt	moles Cl as salt per kg
Ca	40.08	0.0101	3440	0.085828343	2	0.171656687
K	39.1	0.012	13500	0.345268542	1	0.345268542
Cl	35.45	0.0317	32000	0.902679831		
Na	22.99	0.007	7600	0.330578512	1	0.330578512
Mg	24.3	0.0035	310	0.012757202	2	0.025514403
Fe	55.8	0.0083	0	0	3	0
Ni	58.7	0.0033	16	0.000272572	2	0.000545145
Cr	52	0.0025	500	0.009615385	3	0.028846154
H2O	18	0.005	0.005	2.77778E-07		
					Total:	0.902409443
					Mass fraction CaCl2:	0.00952523

Revised figure showing 1% $CaCl_2$ seen in H003328



Capabilities and cold testing of high-temperature shelf-life apparatus

John Berg

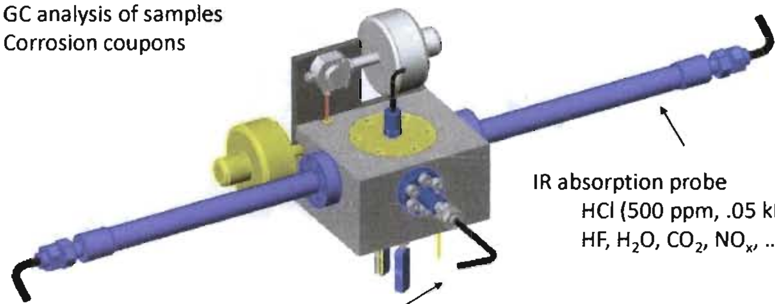
Capabilities

- Heated, nearly isothermal vessel.
- In-situ FTIR for headspace gas monitoring.
  - Detection thresholds for H2O, HCl, CO2, CO etc.
- GC analysis after withdrawing samples, similar to current large and small scale, except need to move the sample.
- Currently in cold testing with hydrated salts.

High-temperature shelf-life experiments:
Study effects of reactive gases generated in the headspace

T and P logging
GC analysis of samples
Corrosion coupons

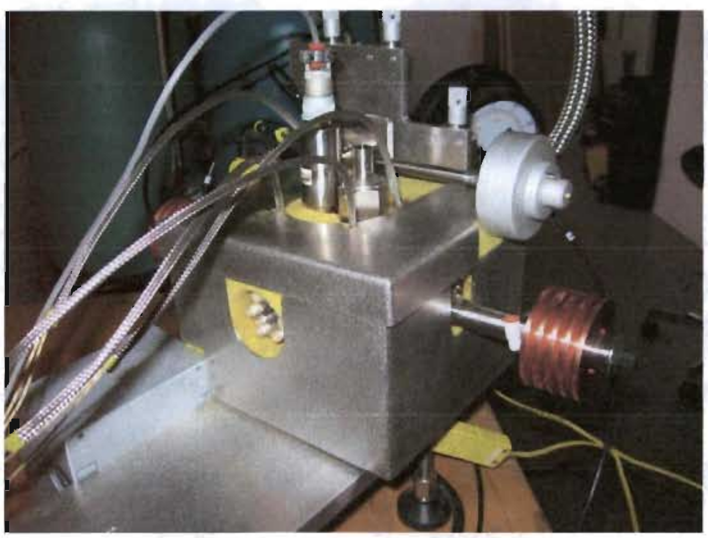
Cell heated to 200 °C
Max. P ~ 250 psig
25 ml volume, ~ 40 g samples



IR absorption probe
HCl (500 ppm, .05 kPa), HF, H_2O, CO_2, NO_x, ...

Raman scattering probe
H_2 (1 kPa), O_2, N_2, CO_2, H_2O, ...

High-temperature shelf-life experiments:
Study effects of reactive gases generated in the headspace



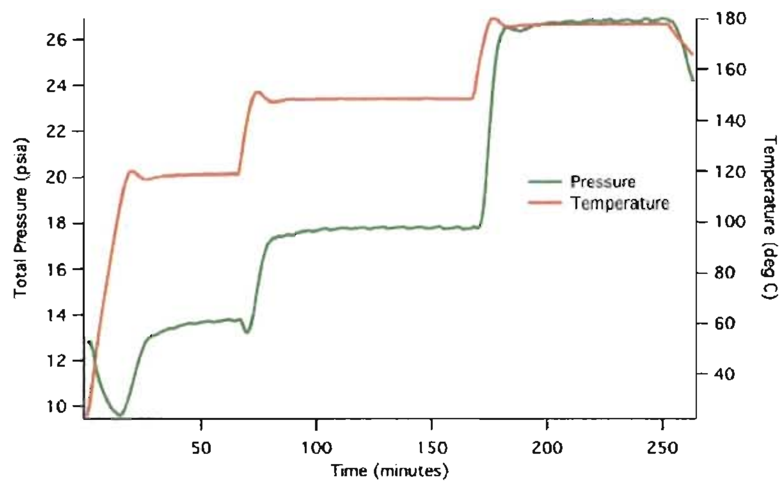
What can we learn?

- Differences in salt behavior in confined space compared with published studies in flowing gas.
- Temperature effects and temperature cycling effects on salt phases as manifested by P(H2O).
- Moisture removal at controlled temperature followed by temperature cycling to observe P(H2O).

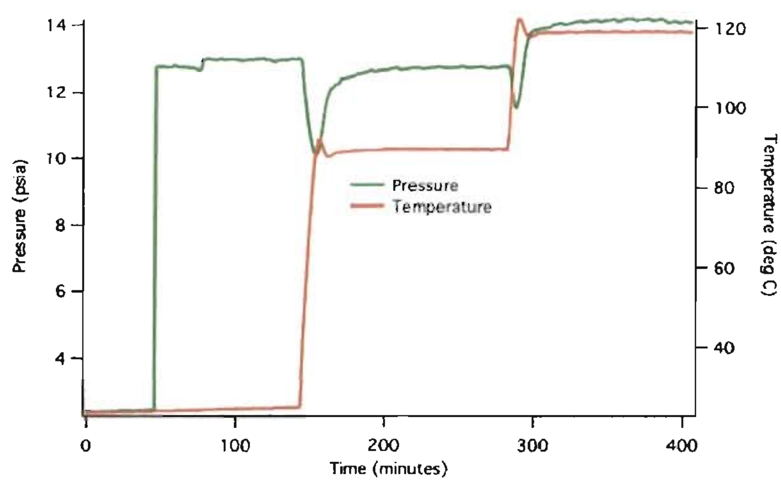
Recent experiments

- $MgCl_2 \bullet 6\ H_2O$
- $MgCl_2 \bullet 6\ H_2O + H_2O$(liquid)
- $MgCl_2 \bullet 4.5\ H_2O$
- $CaCl_2 \bullet 1.7\ H_2O$
- $KMgCl_3$

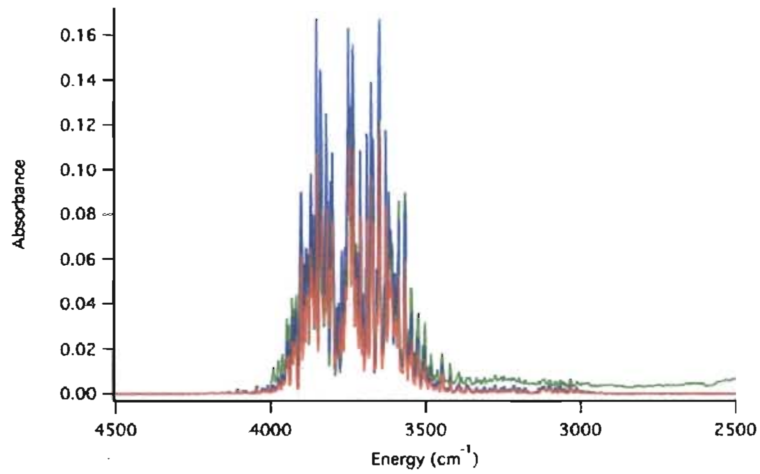
P vs. T over $CaCl_2 \bullet 1.7\ H_2O$



P vs. T over $CaCl_2 \bullet 1.7\ H_2O$



FTIR spectrum of gas over $MgCl_2$•$6H_2O$ at 80 ⊕C.



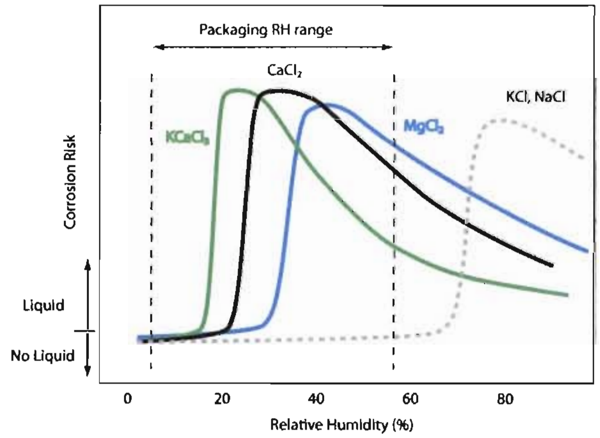
Corrosion Test Plan

Update

Test Plan List of Critical Questions

- What is the RH inside the 3013 container, given its process/loading history, e.g. RH_{INT}?
- What is the threshold RH that will support SCC, e.g. RH_{SCC}?
- What containers have the residual stress exceeding K_{SCC}?
- 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)?

Conceptual model of risk vs. packaging RH for different impurities



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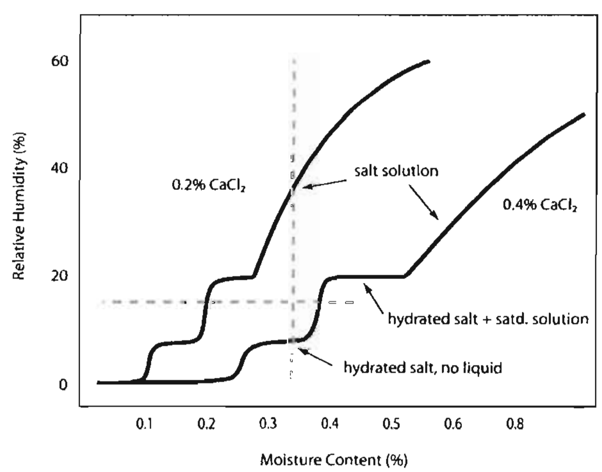

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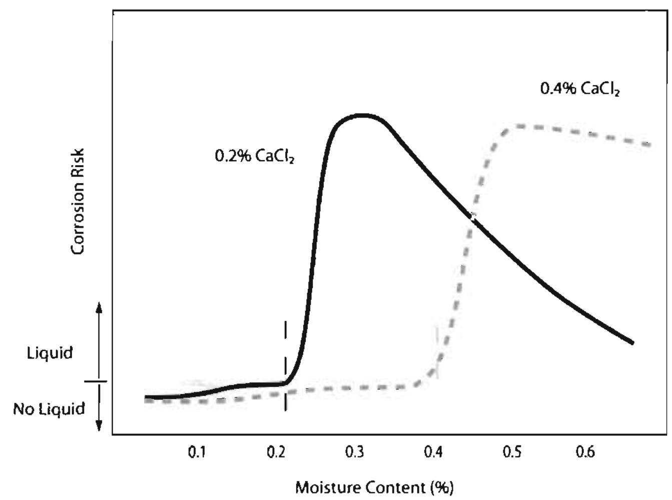

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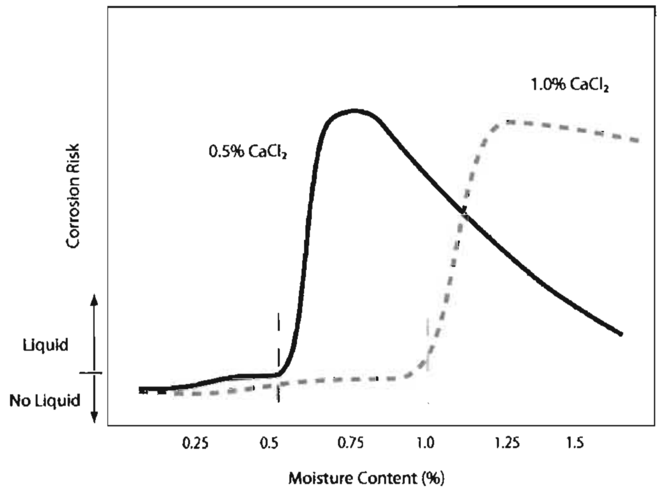

Add/Change Critical Questions?

- DE observations of corrosion
  - Pitting and coatings, but no SCC observations to date.
  - Likelihood of through-wall pit in <50 years.
  - Refine correlation with stabilization and packaging conditions.
  - Observed corrosion may have occurred early in storage period.
    - How and why does the RH at the container wall change in storage?
- How important is it to understand salt hydration and hydrolysis chemistry?
  - Possible liquid formation at very low RH.
  - Arresting of pit growth when salt dries.
- Do we have a mechanism for inner-can corrosion that explains the rare observation?

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We Put Science To Work

Pit Analysis and EV Prediction for FY09 DE2

Phil Zapp, Steve Harris and John Mickalonis

April 26, 2011

3013 Surveillance and Monitoring

Corrosion Working Group Meeting - LANL

FY09 DE2 – Closing Details

Item/Event	ID/Date&Time
3013 Serial Number	H004111
9975 Serial Number	04744
BTCC Number	H7609
Stabilization End Date	11/26/2003 17:38
BTCC gross wt after storage	12/1/2003 0:24
BTCC gross wt after sampling	12/1/2003 10:20
Boat staged for transfer	12/1/2003 9:49
Date BTC welded	12/3/2003 1:20
Inner can leak rate test	12/3/2003
Helium backfill of outer can	12/9/2003 22:33
Outer can welded	12/9/2003 22:45
Outer can leak rate test	12/10/2003
Date NDE surveillance performed	9/20/2006
9975 leak rate test	8/1/2007
9975 shipping date	Info not in database

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2

FY09 DE2 – DE Processing

Inner can lid was found with a ring of corrosion near around the circumference of the inside surface.

Four samples sectioned from inner container lid and sidewall at 0°, 90°, 180°, and 270°.

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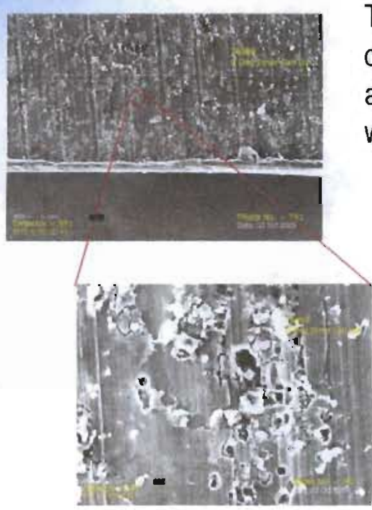
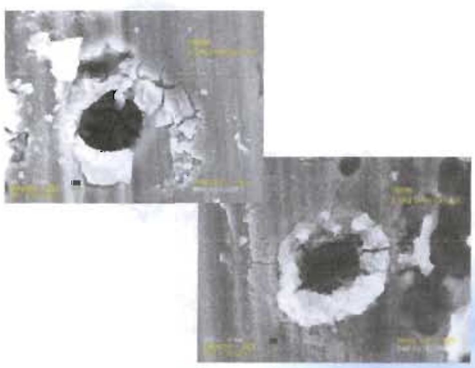
3

FY09 DE2 – SEM Observations



The ring feature on the inside of the inner container lid was further examined by SEM and the presence of small coalesced pits was observed.



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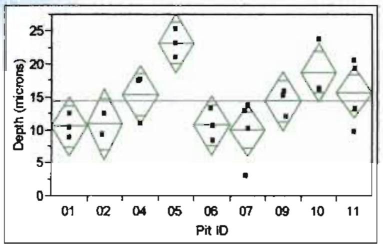
FY09 DE2 – Pit Depths



A total of 11 pits were examined with pit depths being measured on 9 pits only.

Measurements were made by focusing on the top edge of the pit and then focusing on the bottom.

Pit ID	# of Data Points	Mean	Std Dev
01	3	10.4667	1.85562
02	2	10.8000	2.26274
04	3	15.2667	3.78197
05	3	23.1000	2.10000
06	3	10.6333	2.40278
07	4	9.8750	4.88970
09	3	14.3000	2.10000
10	3	18.6667	4.35928
11	4	15.6250	5.16228

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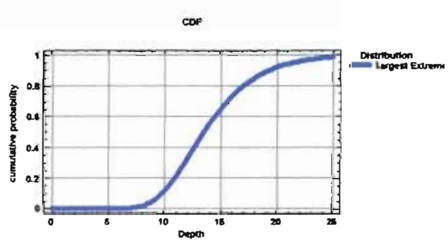
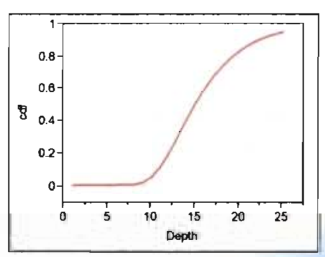
FY09 DE2 – Pit Distributions



The data fit to several distribution functions due to the small number of data points.

For the AFR data, a cumulative distribution of all three classis EV distributions was used.



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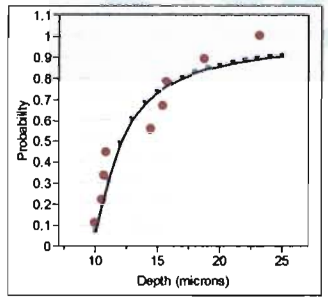
FY09 DE2 – GEV Cummulative Distributions

$$F(x) = \exp\left\{-\left[1 - k(x-u)/\alpha\right]^{1/k}\right\}, \quad kx \le \alpha + uk$$



U – location parameter (-0.878)

K - shape parameter (5.16)

α - scale parameter (0.859)

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FY09 DE2 – GEV Cummulative Distributions

Mean pit depth for GEV:

$$\mu_{\max} = (u + \alpha/k)t^b - \frac{\alpha M^{-k} t^b}{k}\Gamma(1+k), \quad k \ge -1$$

p^{th} percentile for pit depth:

$$x_p = (u + \alpha/k)t^b - \frac{\alpha t^b}{k}\left[-\frac{\ln(p)}{M}\right]^k$$

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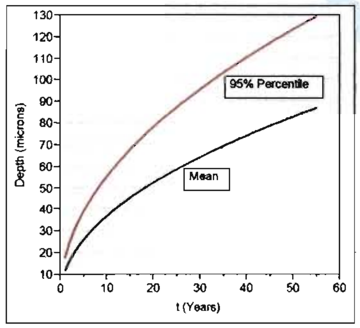
8

FY09 DE2 – 50 Year Prediction



3013 Wall Thickness – 1, 670 μm

AFR 50-year prediction – 264 μm

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9

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We Put Science To Work

H003328 – Evaluation, Impact to Program, Sampling Plan at SRS

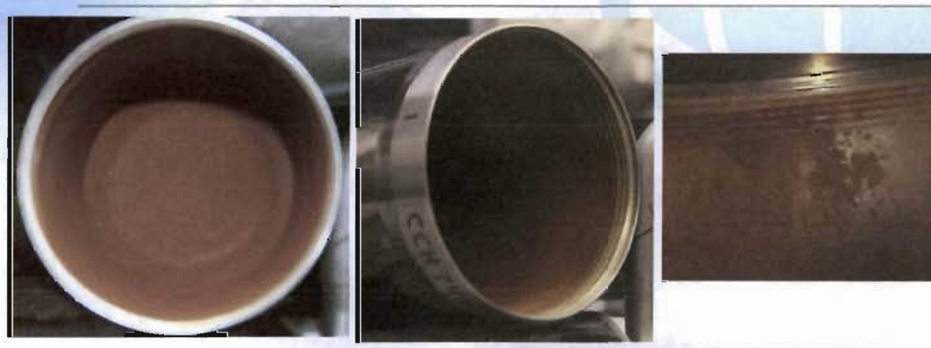
Kerry Dunn & Laura Worl

April 27, 2011

Corrosion Working Group Technical Meeting, April 26-27

EM Office of Environmental Management

H003328 – Convenience Container Visual



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2

H003328 – Inner Container Visual

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Tests Already Requested

Convenience Container

- SEM stub – placed on lid or body
- Scraped coating collected for XRD and SEM

Inner Container

- SEM stub – placed near inside near weld interface
- Scraped "debris" collected for XRD and SEM

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Proposed Cutting and Tests – Convenience Container

Convenience Container

- Section representative sample from:
  - Top portion of container
  - Bottom portion of container
  - Lid
- Perform SEM
  - Pitting, EDX of film, EDX of pit debris
  - Clean sample and re-do SEM work

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5

Proposed Cutting and Tests – Inner Container

Inner Container

- Obtain 4 sections from welded region of lid at 0°, 90°, 180° & 270°
- Take 2 of the sections and examine, as is, in SEM looking for:
  - Pitting/SCC
  - Buildup composition
- Take 2 of the sections and cut away opposite side with weld so that the piece can be pulled apart
  - Examine down into crevice with optical microscope and/or SEM looking for corrosion, especially SCC

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6

Humidity Calibration of Miniature Sensors

Juan G. Duque
Rhonda McInroy
David M. Harradine
C-PCS, LANL
Corrosion Working Group

Vaisala

Sensirion

Objective: Provide a calibration of miniature humidity sensors being used in both full scale 3013 containers and small scale experiments. The aim is to develop a fit, which correlates the humidity between different sensors to enable the replacement of costly sensors with less expensive ones.

Experimental Method:

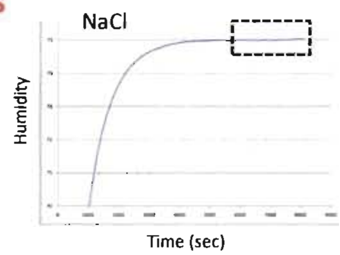
1. Calibrate sensor with known salts solutions
2. Examine how changes in temperature affects humidity measurements with different sensors
3. Use the salt solution results to calibrate the temperature measurements

Extract sensor correlation

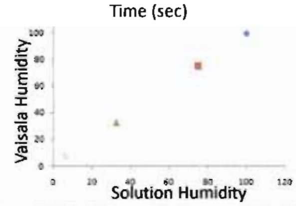
1. Implement in real life experiments

Vaisala Calibration as a function of salts

1. Extract humidity and temperature average values of the salt solution after it reaches steady state
   NaCl, MgCl2, NaOH, LiCl, LiBr

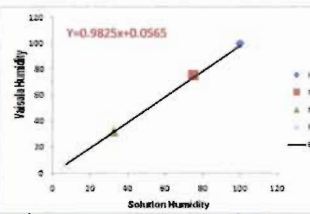


2. Use empirical formula to calculate the predicted humidity at given experimental temperature
   Humidity = $2.84E^{-5}T^3 - 2.65E^{-3}T^2 + 3.96E^{-2}T + 7.55E^1$
   formula changes depending on salt solution



3. Compared experimental results with empirical calculation

	Solution	Experimental Vaisala Humidity	Calculated Humidity
H2O	100.00	99.57	99.78
NaCl	75.30	74.69	75.26
MgCl2	32.77	32.02	31.84
NaOH	7.00	6.30	6.32
LiCl	11.00	10.86	10.80
LiBr	5.50	5.31	5.24



Very good agreement between experimental and empirical observations

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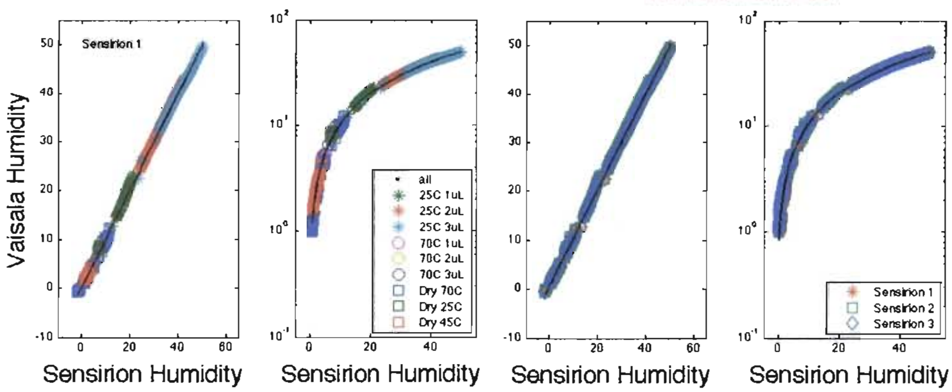
Temperature Dependence on Different Sensors

Humidity measurements were obtained at 25 and 70°C in a sealed humidity chamber with one vaisala sensor and three sensirions. At each temperature, the humidity was changed by adding different aliquots of water into the chamber (1 uL, 2 uL and 3 uL). The humidity was also collected in a dry chamber (ambient humidity) at 25, 45, and 70°C.

3 different sensirion



Overall we can see a very good overlap of the collected humidity at all temperatures indicating the lack of temperature dependence between the two sensors

Very good overlap of the humidity measured using the three different sensirion sensors

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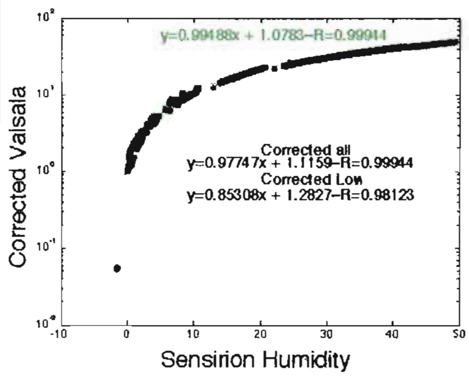
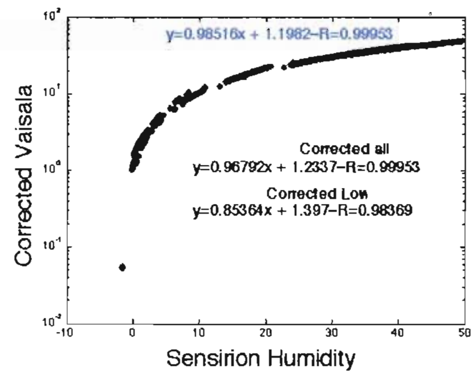
Data Correlation Using the salt data





Green, and blue dots and equations correspond to the humidity data collected in the absence of salts before the vaisala response was normalized to the response obtained with the salt solutions.
In black we can see the data after the vaisala is normalized to the values obtained with the salts. The data was fitted using all of the points and up to humidity 6 (low).

The normalization was obtained using the average of the fitting resulting on:

Humidity < 6	y= 0.853362 x + 1.339809
Humidity > 6	y= 0.972694 x + 1.174813

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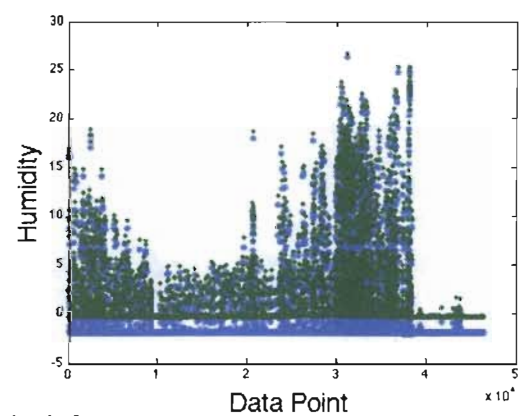
Implementation in real life experiments

Equations which will be use to normalized humidity data collected in standard 3013 storage containers.

Humidity < 6	y= 0.853362 x + 1.339809
Humidity > 6	y= 0.972694 x + 1.174813



In blue we see the humidity before normalization and in green after normalization.

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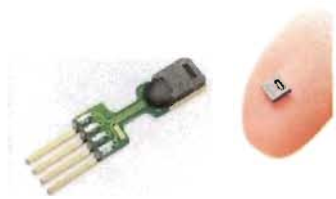
Conclusions

- We have usefully obtain a calibration between the sensirion and the vaisala sensors
- The sensor response do not show any significant temperature dependence

Vaisala



Sensirion

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Humidity at Long Times (years)

D. Kirk Veirs – responsible party

Significant contributors over the years:

Los Alamos: David Harradine, Max Martinez, John Berg, Josh Narlesky, Stephen A. Joyce, Scott Lillard, Laura Worl, Juan Duque, Rhonda McInroy

SRS: Jon Duffey, Binh V. Nguyen, Chip McClard, Ron Livingston, Lance Travers

MIS Program
Corrosion Working Group Meeting
Los Alamos, CA
April 26, 2011

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Why is it surprising that water survives so long?

- 2.5 kg of weapons grade material results in ~150 MegaJoules of radiation energy deposited into the material after 5 years.
- ~150 kiloJoules of energy is sufficient to decompose all the water (0.5 wt%) into H_2 and O_2.
- What we observe is typically less than 10% of the available water is converted into H_2 so we have a process that is less than 0.01% efficient.
- Observations of H_2 over time suggest that the H_2 plateaus. If the water decomposition is reflected in the H_2 gas present, then we expect the RH to remain virtually constant over the remaining 45 years of container life.

IS THIS A PROBLEM?

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RH observations

- Large Scale at Los Alamos with RH sensors
- Small Scale at Los Alamos:
  - At DE with Vaisala RH meter.
  - New capability with RH sensors in lid of container (now operational)
- SRS at DE with Vaisala RH meter.
  - Also with temperature measurements at wall, in material near wall, and centerline temperature

Material measurements

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

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SRS DE observations

- Remove convenience container lid and replace with lid containing a Vaisala meter at the top and two thermocouples located at the centerline and about 1.3 inches from wall and 2.7 inches from bottom.
- A stick-on thermocouple at the same height gives the boundary temperature.

•We need temperatures as well as RH in order to calculate the RH at various locations within a container.

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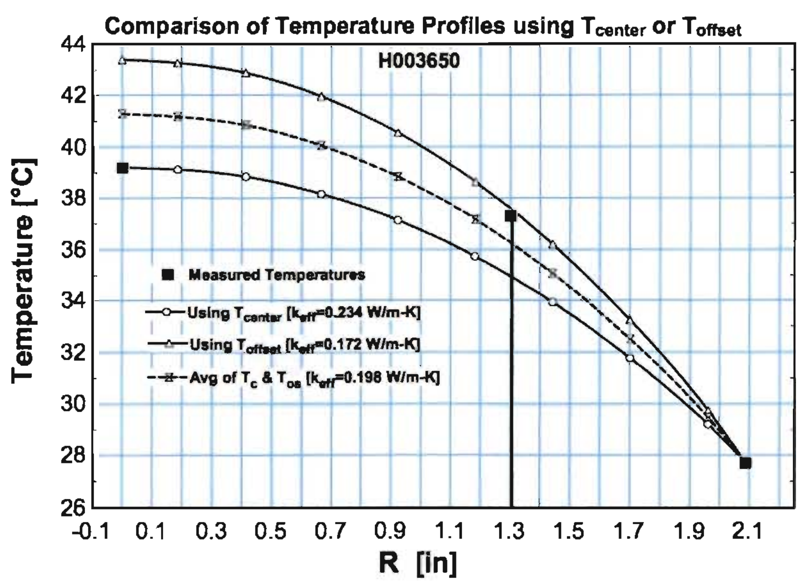

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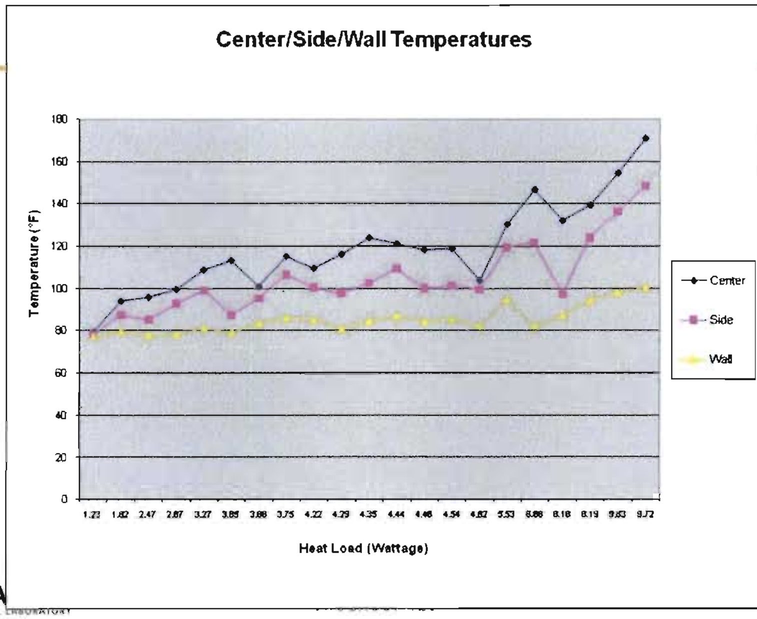

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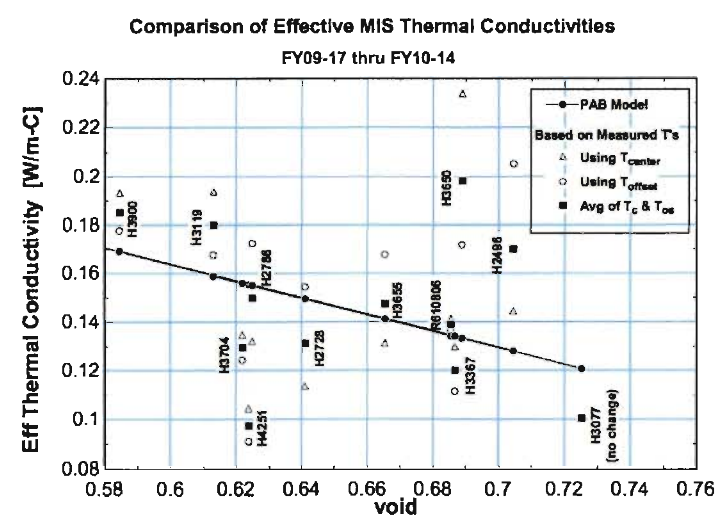

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SRS Humidity measurements

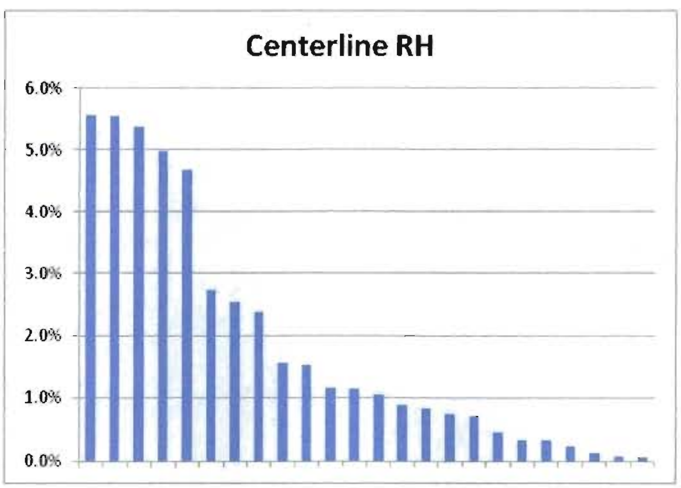
- The Vaisala measures temperature and RH. We use these to calculate the water vapor pressure.
- In a static system the water vapor pressure should be uniform throughout the container.
- With the temperatures at the two bounding conditions – the centerline and the wall temperature – the RH at these two locations can be calculated.

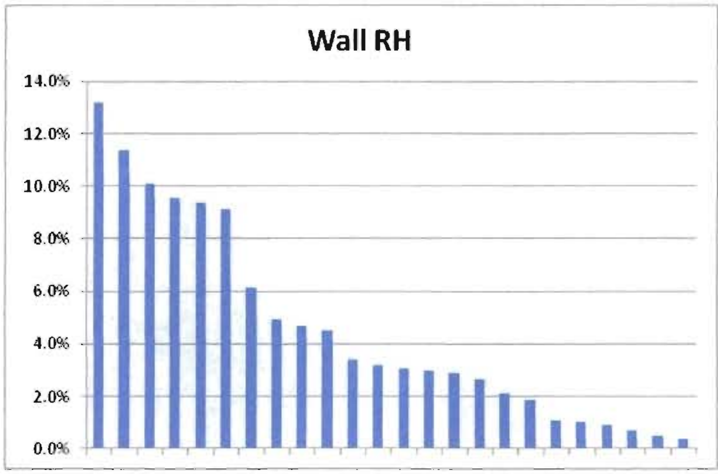
SRS DE calculated RH at Centerline and Wall

Year	DE	Containe	data	Water VP (kPa)	T_center line (C)	T_wall (C)	RH CL	RH W
FY11	DE07	H003371	X	0.53	42.6	26.7	5.0%	13.2%
FY10	DE13	H003367	X	0.44	37.5	26.0	5.5%	11.4%
FY10	DE02	H002496	X	0.37	35.1	25.2	5.4%	10.1%
FY10	DE08	H003650	X	0.41	39.2	27.7	4.7%	9.5%
FY11	DE18	H003328	X	0.72	60.2	36.9	2.5%	9.4%
FY11	DE03	H002592	X	0.36	33.9	26.1	5.6%	9.1%
FY11	DE01	H003443	X	0.30	42.9	29.6	2.7%	6.1%
FY09	DE18	H003119	X	0.32	54.3	34.2	1.5%	4.9%
FY10	DE03	H003710	X	0.22	47.8	29.0	1.5%	4.7%
FY10	DE07	H003900	X	0.20	38.6	28.1	2.4%	4.5%
FY10	DE12	H003077	X	0.15	63.6	28.0	0.4%	3.4%
FY10	DE10	H002728	X	0.15	51.0	28.9	0.9%	3.2%
FY10	DE04	H003655	X	0.15	48.0	29.7	1.0%	3.1%
FY10	DE01	H004251	X	0.15	46.2	30.0	1.1%	3.0%
FY11	DE08	H003526	X	0.14	44.6	29.2	1.1%	2.9%
FY10	DE11	H002786	X	0.11	46.5	27.2	0.8%	2.6%
FY10	DE14	H003704	X	0.11	49.3	30.5	0.7%	2.1%
FY11	DE04	H003337	X	0.08	42.3	27.3	0.7%	1.9%
FY11	DE09	H003565	X	0.05	50.3	30.0	0.3%	1.1%
FY11	DE06	H003343	X	0.04	45.0	26.2	0.3%	1.0%
FY09	DE17	R610806	X	0.06	59.2	34.2	0.2%	0.9%
FY11	DE02	S002129	X	0.05	67.9	36.7	0.1%	0.7%
FY11	DE05	S001105	X	0.04	76.6	37.3	0.1%	0.5%
FY10	DE16	S001721	X	0.03	73.4	41.2	0.1%	0.4%

SRS DE calculated RH at Centerline and Wall

Year	DE	Container data		Water VP (kPa)	T_center line (C)	T_wall (C)	RH CL	RH W	Containers with pitting
FY11	DE07	H003371	X	0.53	42.6	26.7	5.0%	13.2%	
FY10	DE13	H003367	X	0.44	37.5	26.0	5.5%	11.4%	←
FY10	DE02	H002496	X	0.37	35.1	25.2	5.4%	10.1%	←
FY10	DE08	H003650	X	0.41	39.2	27.7	4.7%	9.5%	←
FY11	DE18	H003328	X	0.72	60.2	36.9	2.5%	9.4%	
FY11	DE03	H002592	X	0.36	33.9	26.1	5.6%	9.1%	
FY11	DE01	H003443	X	0.30	42.9	29.6	2.7%	6.1%	
FY09	DE18	H003119	X	0.32	54.3	34.2	1.5%	4.9%	
FY10	DE03	H003710	X	0.22	47.8	29.0	1.5%	4.7%	←
FY10	DE07	H003900	X	0.20	38.6	28.1	2.4%	4.5%	
FY10	DE12	H003077	X	0.15	63.6	28.0	0.4%	3.4%	
FY10	DE10	H002728	X	0.15	51.0	28.9	0.9%	3.2%	←
FY10	DE04	H003655	X	0.15	48.0	29.7	1.0%	3.1%	
FY10	DE01	H004251	X	0.15	48.2	30.0	1.1%	3.0%	
FY11	DE08	H003526	X	0.14	44.8	29.2	1.1%	2.9%	
FY10	DE11	H002786	X	0.11	46.5	27.2	0.8%	2.6%	←
FY10	DE14	H003704	X	0.11	49.3	30.5	0.7%	2.1%	
FY11	DE04	H003337	X	0.08	42.3	27.3	0.7%	1.9%	
FY11	DE09	H003565	X	0.05	50.3	30.0	0.3%	1.1%	
FY11	DE06	H003343	X	0.04	45.0	26.2	0.3%	1.0%	
FY09	DE17	R610806	X	0.06	59.2	34.2	0.2%	0.9%	
FY11	DE02	S002129	X	0.05	67.9	36.7	0.1%	0.7%	
FY11	DE05	S001105	X	0.04	76.6	37.3	0.1%	0.5%	
FY10	DE18	S001721	X	0.03	73.4	41.2	0.1%	0.4%	





Some generalizations

- From the LANL observations during loading of large-scale containers, the RH within a container is considerably below the RH of the atmosphere.
- All materials observed to date have significant water that survives within containers for long periods of time.
- The RH in the containers are always less than the RH at the time of packaging.
- Pits have been observed in containers with RH that is too low to have deliquesced salts.
- Plateaus in the RH suggest that the RH is pinned by a common phase. The phases have yet to be identified.

Studies of Ca-Rich Surrogate Material Using Teardrop Specimens

Scott Lillard, MST-6

Josh Narlesky, Kirk Veirs MET-1

Laura Worl IMP-2

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SCC Test Plan Milestone

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

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SRS Results

Table 7. Summary of Corrosion Observations

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

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Slide 3

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Surrogate Composition vs. SRS 4a

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

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

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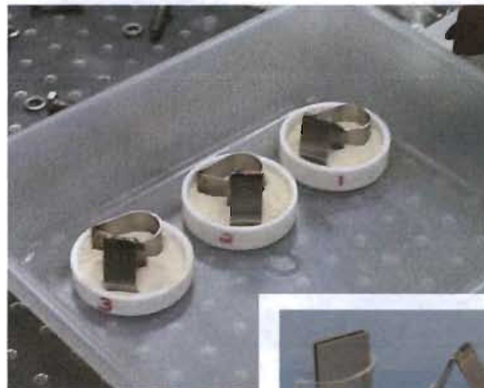
Slide 4

Surrogate / Teardrop Experiments

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



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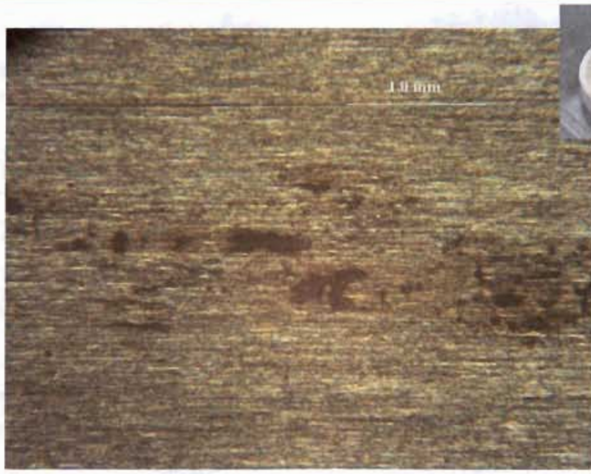
Experimental – cont.

Results

- Upon removing samples from chamber large (4mm) patches of oxide salt remained on sample .... larger patches deeper in material.
- All Patches were associated with pitting corrosion.

Sample #17 Side config, saltline/air interface



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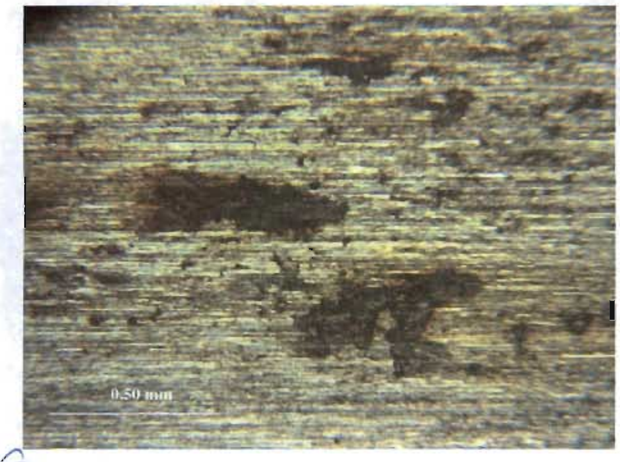
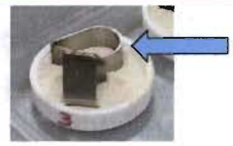
17 Side config, saltline/air interface





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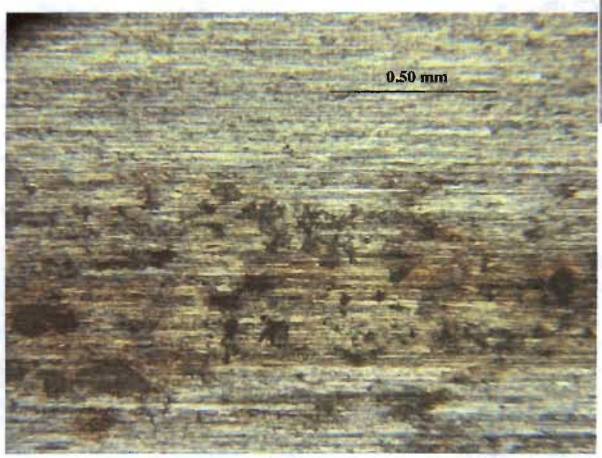
17 Side config, saltline/air interface



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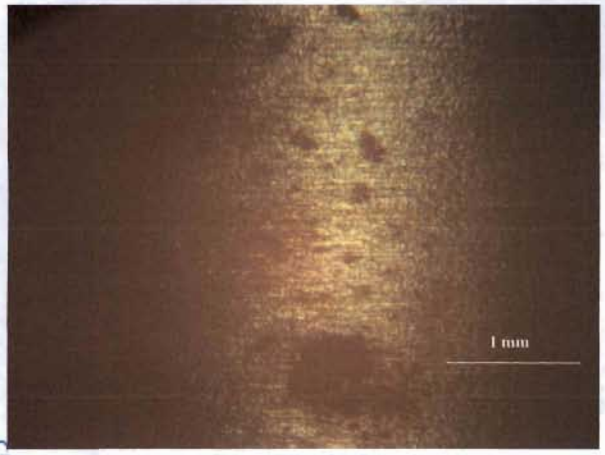
Sample #32 Up config, near weld location 1



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Slide 11

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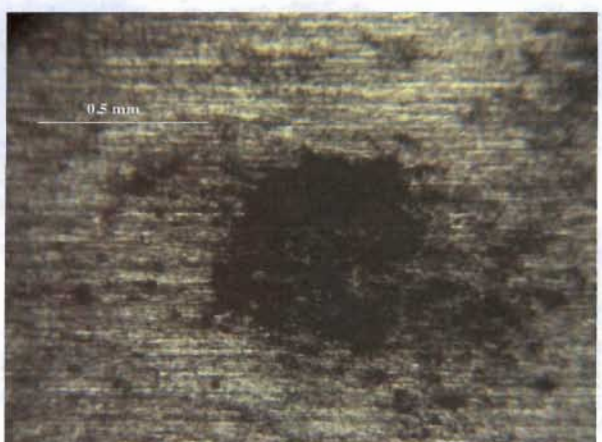
Sample #32 Up config, near weld location 1



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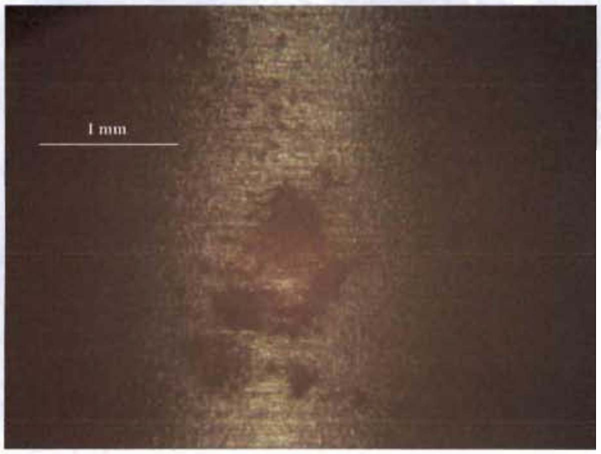
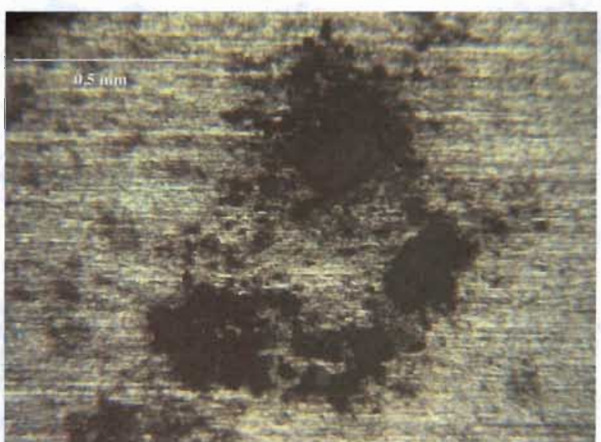
Sample #32 Up config, near weld location 2



Sample #32 Up config, near weld location 2



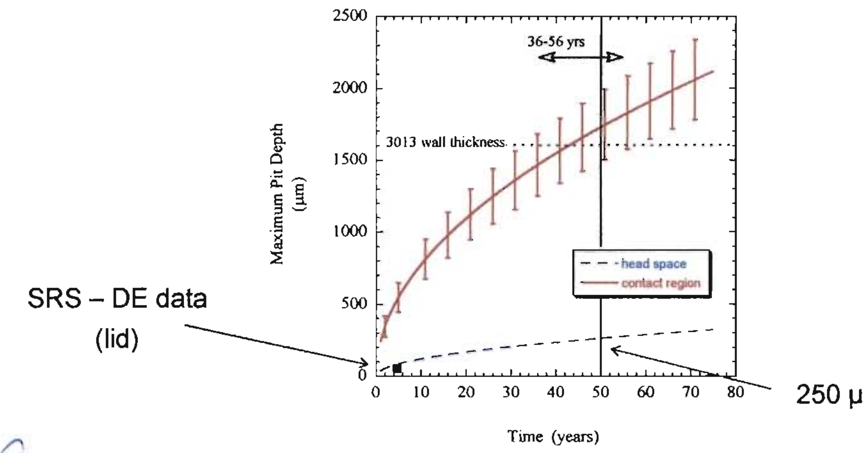
Points for Discussion

- We can easily grow pits comparable to those observed in the SRS Series 4a cans .... though no cracking has been observed for exposure periods up to 60 days.
- Pits are located through out contact region including salt line ... larger pits appear to be associated with locations deeper in the salt/oxide.
- Future work will look at the influence of lower %RH.

UNCLASSIFIED

Extroplation of Pit depths from DE data (Zapp data)

Comparison of Zapp data ARF-223 Projections



Data and Results for Fit Parameters

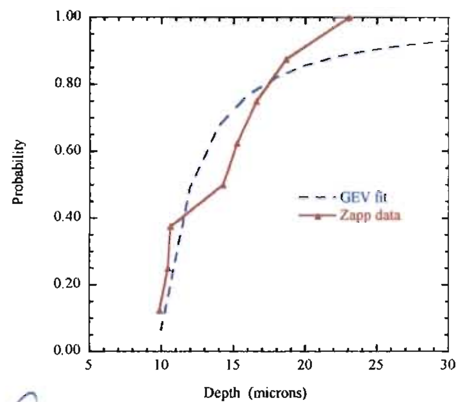
- **Zapp data (microns):**

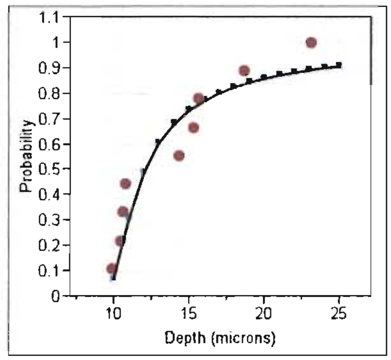
10.4667 +/- 1.85
10.8000, 2.26
15.2667, 3.78
23.1000, 2.10
10.6333, 2.40
9.8750, 4.89
14.3000, 2.10
18.6667, 4.36
16.6250, 5.16

$$GEV(u,\alpha,k) = \exp\left\{\left[1-k(x-u)/\alpha\right]^{1/k}\right\} \quad kx \le \alpha + uk$$

GEV parameter	LANL – maximum likelihood estimates / standard error	Harris Consulting - unknown
α	1.880 / 0.87	0.859
k	-0.873 / 0.71	-0.878
u	11.26 / 0.39	5.16

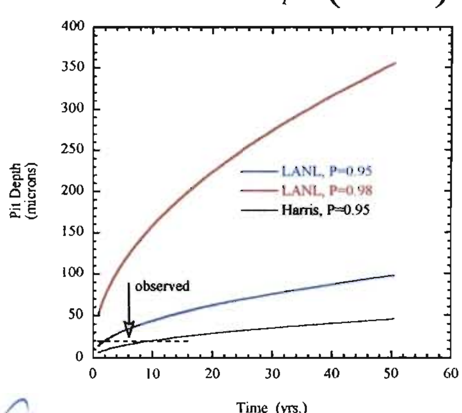
Comparison of GEV fits LANL/Harris



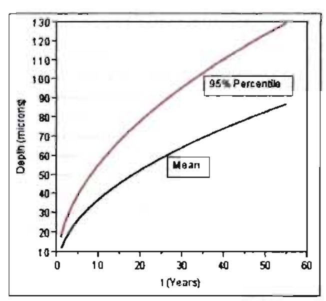


Projected Pit Depths

$$x_p = \left(u + \alpha / k\right)t^b - \frac{\alpha t^b}{k}\left[-\frac{\ln(P)}{M}\right]^k$$



•avrg of 3-4 repeats (?)



Points for Discussion

- Areas from which pit depths are taken e.g. using a grid and taking the maximum depth from each grid location
- Use of "master curves" for which future DE data from similar cans (salt composition) can be compared to.
- How do we handle small, non-through wall cracks if observed?