



U.S. Department of Energy  
Office of Civilian Radioactive Waste Management



# Update on Corrosion Testing

Presented to:

**Nuclear Waste Technical Review Board**

Presented by:

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**Framatome Advanced Nuclear Power**

**Bechtel SAIC Company, LLC.**

**September 10, 2002**

**Las Vegas, Nevada**



# Outline

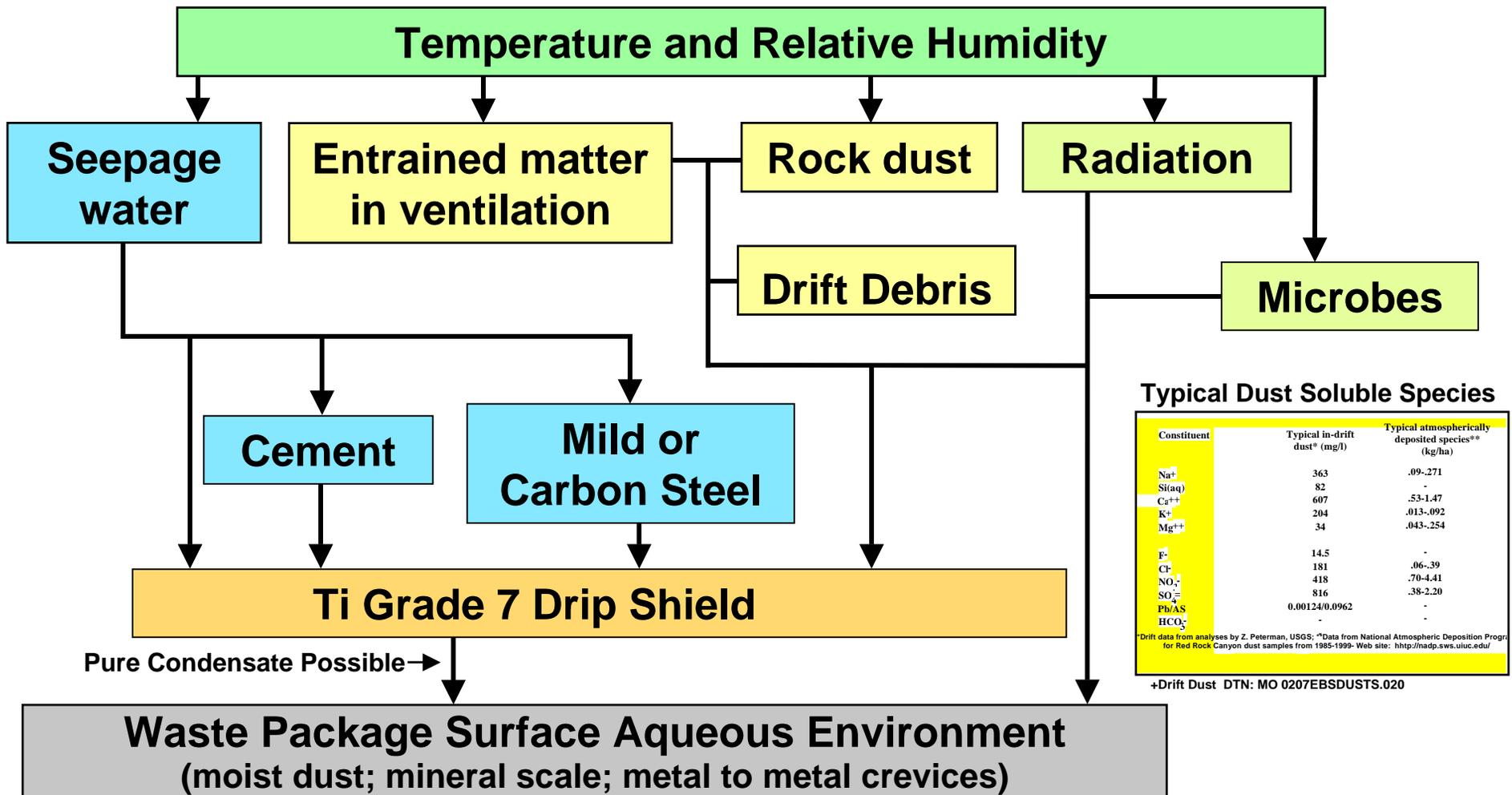
- **Expected Aqueous Environments**
- **Waste Package Corrosion Modeling Approach and High Temperature ( $\leq 150^{\circ}\text{C}$ ) Testing Status**
  - **Initial results from localized corrosion studies in  $\text{CaCl}_2$  with and w/o  $\text{NO}_3^-$** 
    - ◆ **Bulk brine solutions**
    - ◆ **Thin aqueous deliquescent brine films**
- **Summary**



# Expected Aqueous Environments



# Aqueous Environment Evolution



Typical Dust Soluble Species

Constituent	Typical in-drift dust* (mg/l)	Typical atmospherically deposited species** (kg/ha)
Na <sup>+</sup>	363	.09-.271
Si(aq)	82	-
Ca <sup>++</sup>	607	.53-1.47
K <sup>+</sup>	204	.013-.092
Mg <sup>++</sup>	34	.043-.254
F <sup>-</sup>	14.5	-
Cl <sup>-</sup>	181	.06-.39
NO <sub>3</sub> <sup>-</sup>	418	.70-4.41
SO <sub>4</sub> <sup>=</sup>	816	.38-2.20
Pb/As	0.00124/0.0962	-
HCO <sub>3</sub> <sup>-</sup>	-	-

\*Drift data from analyses by Z. Peterman, USGS; \*\*Data from National Atmospheric Deposition Program for Red Rock Canyon dust samples from 1985-1999. Web site: <http://nadrp.sws.uiuc.edu/>

+Drift Dust DTN: MO 0207EBSDUSTS.020

- Waste package shielded from seepage while drip shield intact
- Surface environments expected to exist as thin, aerated brine films
  - Formed through deliquescence of solubles in deposits



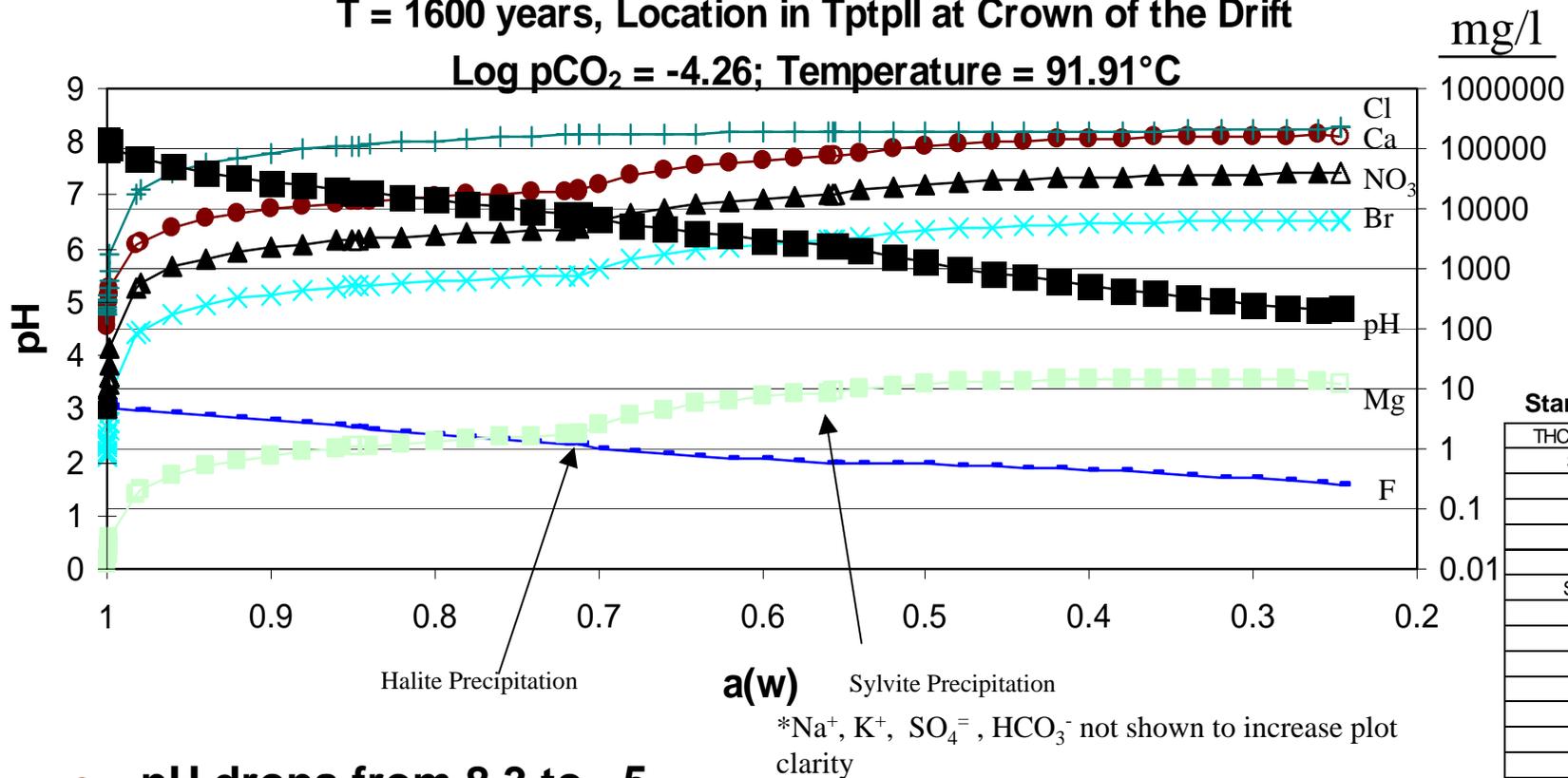
# Example Calculation Results for Evaporation of One Sample (high Ca content) Seepage Water Composition\*

Preliminary EQ6 Evaporation Run Results (Not yet documented)

Starting Composition Taken from THC Seepage Model Calculations (CAL-EBS-PA-0000013 REV 00)

T = 1600 years, Location in Tptpll at Crown of the Drift

Log pCO<sub>2</sub> = -4.26; Temperature = 91.91°C



**Starting Composition**

THC Model Results	Composition
Species	(moles/L)
Ca	2.75E-03
Mg	3.68E-04
Na	3.64E-03
Cl	4.18E-03
SiO2(aq)	7.46E-03
HCO3	6.06E-05
SO4	1.84E-03
K	4.19E-04
AlO2	2.47E-08
F	3.96E-04
HFeO2	1.11E-09
NO3	3.28E-04
pCO2 (v. frac.)	5.49E-05
pH	8.25

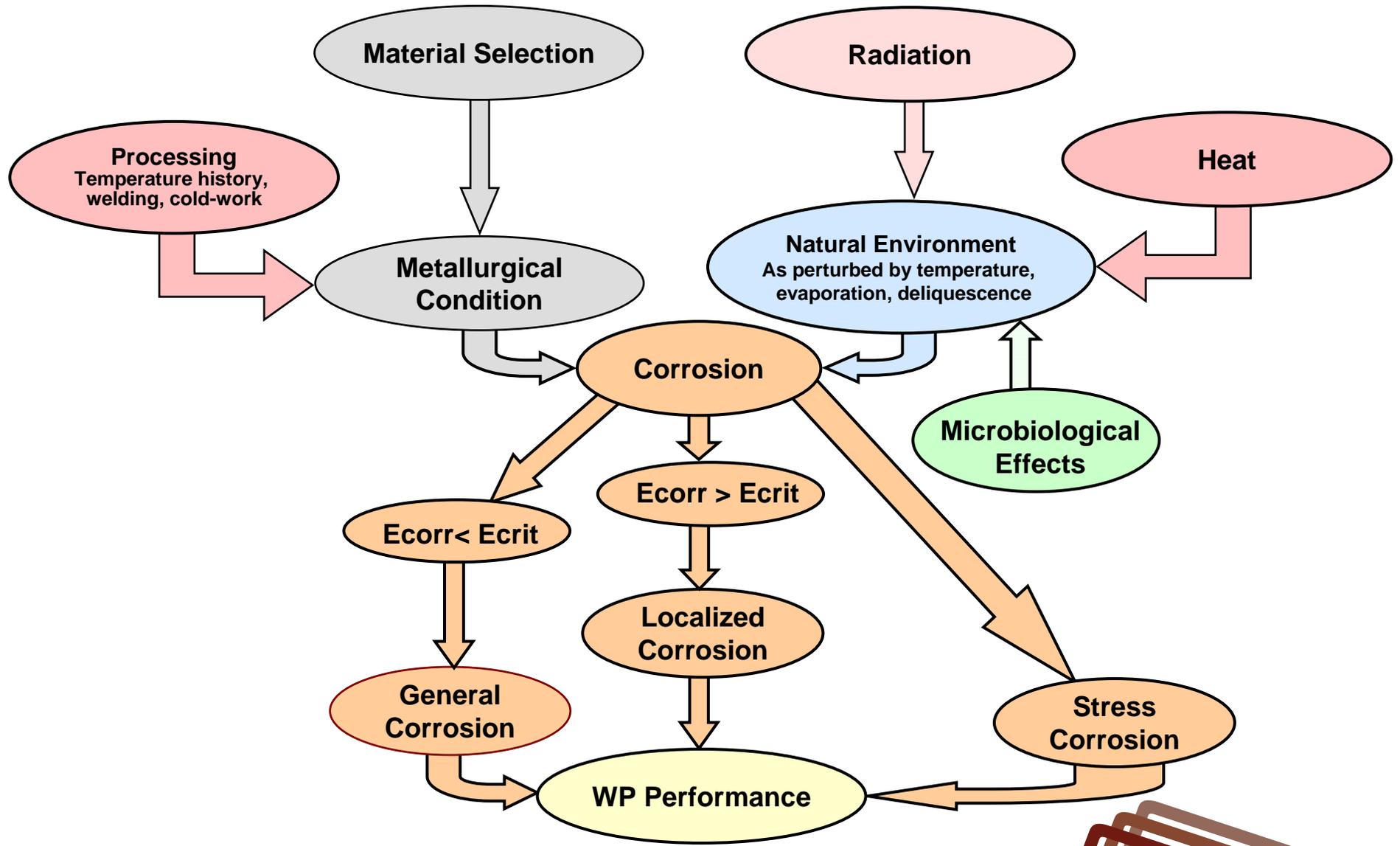
- pH drops from 8.3 to ~5
- Concentrated species include Cl<sup>-</sup>, Ca<sup>++</sup>, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup> and Mg<sup>++</sup>
- F<sup>-</sup> level drops because of CaF<sub>2</sub> precipitation



# Waste Package Corrosion Modeling Approach and High Temperature Testing Status



# Integrated Model for WP and DS



# Alloy 22 Localized Corrosion Susceptibility in Relevant Environments

- Localized corrosion can occur under very oxidizing conditions in concentrated chloride solutions when
  - Chloride to oxyanion molar ratio [  $\text{Cl}^- : (\text{NO}_3^- + \text{SO}_4^{2-})$  ]  $> \sim 5:1^*$
- These conditions lie outside the range of potential repository relevant aqueous conditions measured to date for which
  - $\text{Cl}^-$  : ‘Inhibitor’ ion molar ratios  $< 3:1$
  - $E_{\text{corr}} < E_{\text{crit}}$
  - Other potentially beneficial species (e.g. carbonate, silica/silicate) also often present

\*e.g. CNWRA results in NaCl with and w/o nitrate (D.S Dunn and C.S Brossia, Corrosion 2002, Paper No. 02548, April 2002), and UVa results in 5 M LiCl with and without nitrate and sulfate (B.A.Kehler et al, Corrosion 2001, Paper No. 01141, March 2001)

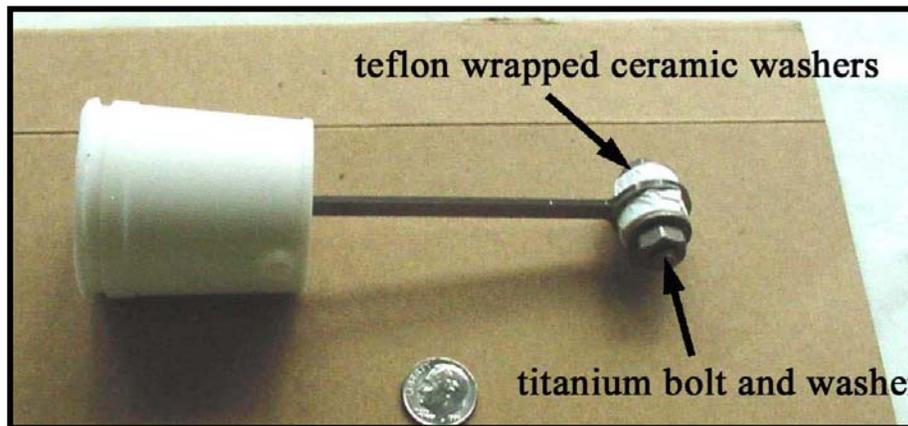
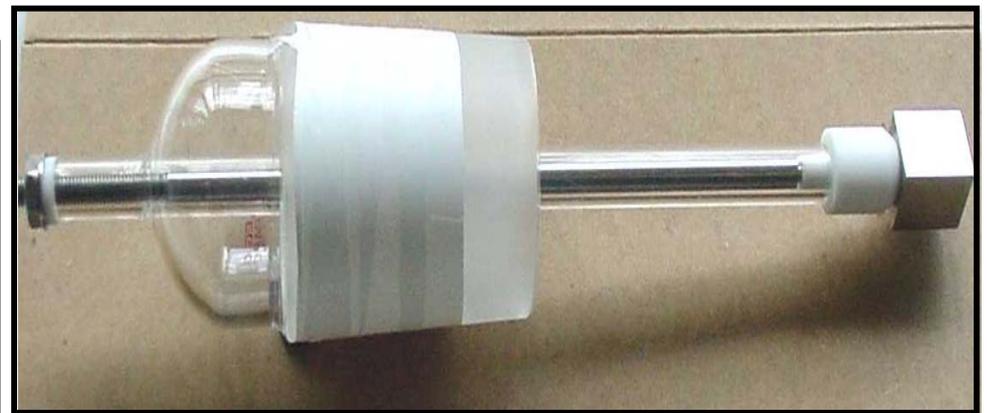
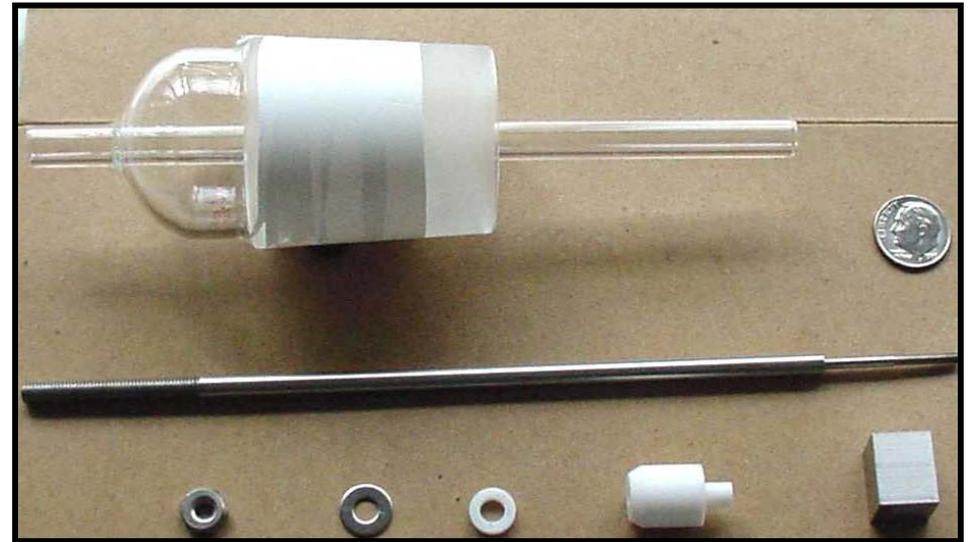
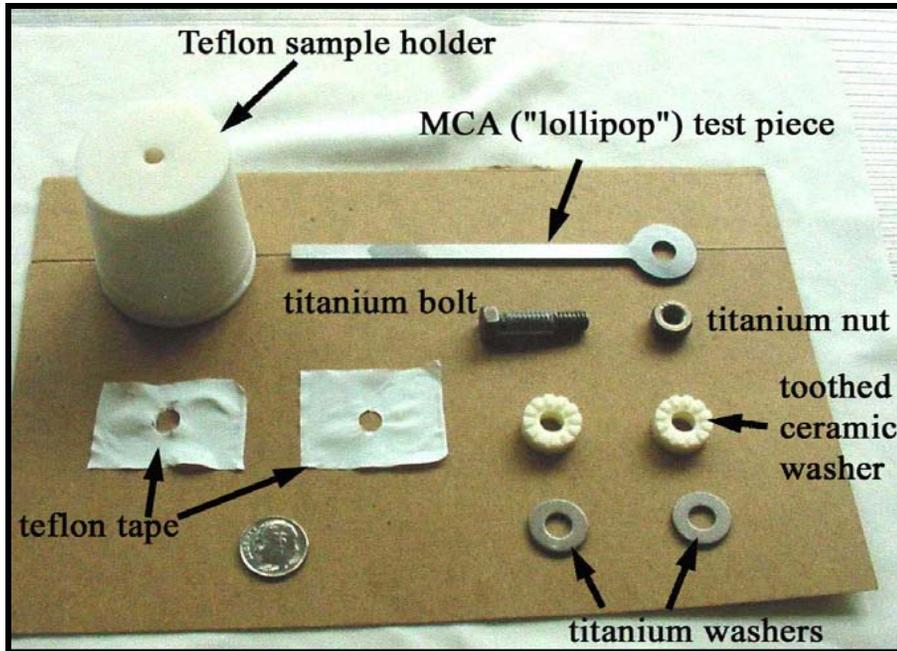


# Higher Temperature Alloy 22 Measurements

- **Initial tests in bulk environments**
  - **Electrochemical determination of critical potentials and corrosion potentials**
    - ◆ **Calcium chloride and calcium nitrate solutions up to 150°C**
- **Initial thin deliquescent surface film studies**
  - **Water chemistry changes and corrosion attack that may occur in thin films on surfaces exposed to high Ca content potential seepage waters at elevated temperatures**



# Crevice Corrosion Evaluation Specimen Types

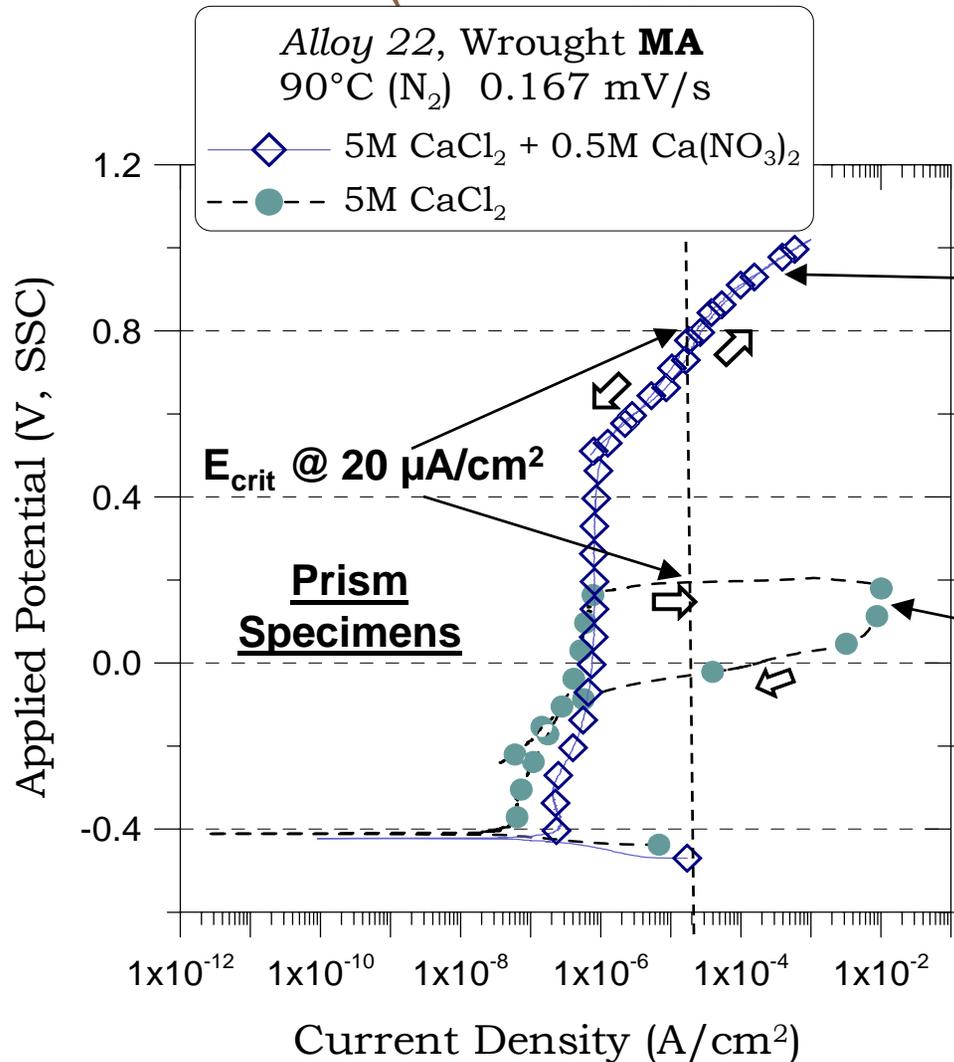


**Prism Specimen**

**Multiple Crevice Assembly (MCA)  
"Lollipop" Specimen**

# Benefit of Nitrate on Localized Attack in 5M CaCl<sub>2</sub> at 90°C

(Results documented in LLNL Scientific Notebooks)



5M CaCl<sub>2</sub> + 0.5M Ca(NO<sub>3</sub>)<sub>2</sub>



No Localized Attack

5M CaCl<sub>2</sub>



Localized Attack\*

\*Initiates at washer/metal interface and appears to propagate due to concentrated HCl formation

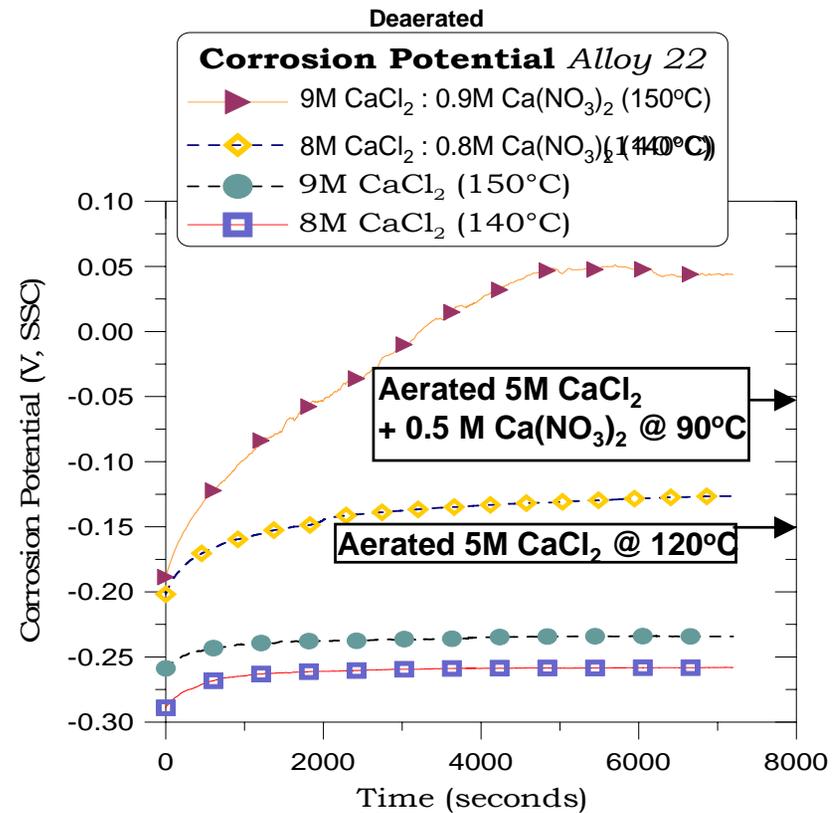
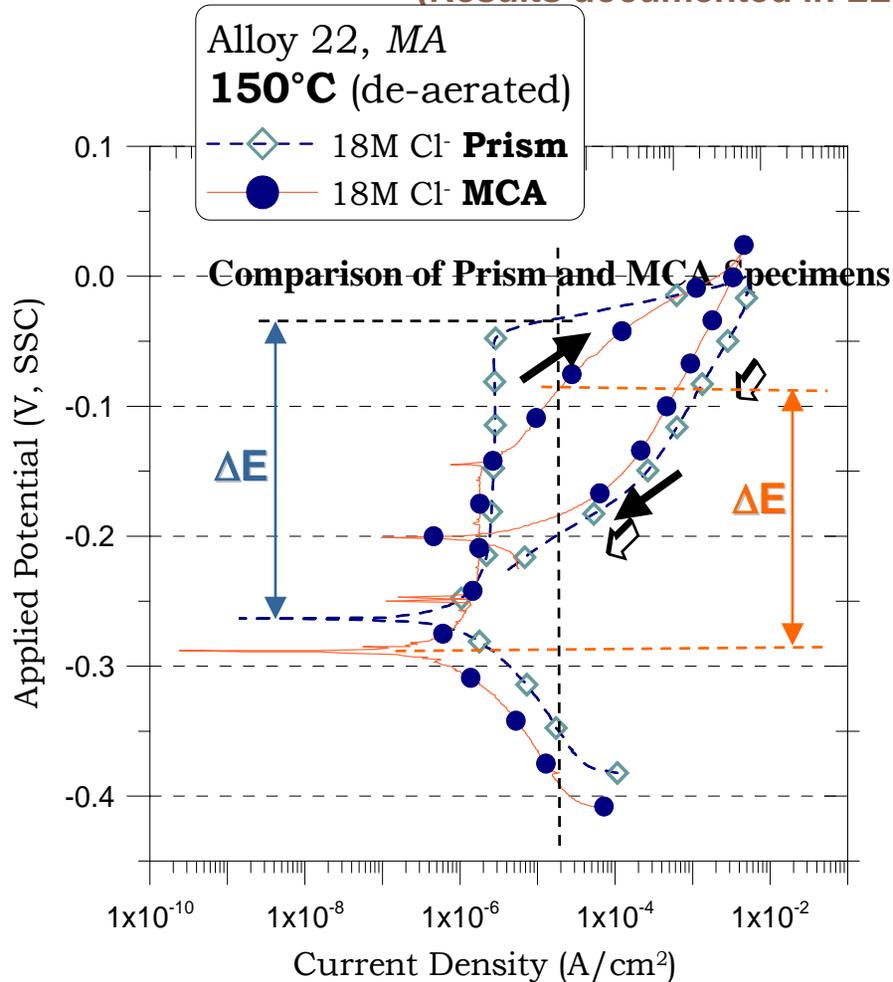
+ Initial creviced results based on critical breakdown potential,  $E_{crit}$  @ 20  $\mu$ A/cm<sup>2</sup> show 10:1 Cl/NO<sub>3</sub> addition inhibits crevice corrosion in 90°C CaCl<sub>2</sub>

+ Repassivation potential (more conservative) measurements with Tsujikawa technique now underway (S. Tsujikawa, Y. Hisamatsu: *Corr. Eng. (Jpn.)*, 29, 37 (1980))



# Cyclic Polarization and $E_{\text{corr}}$ in Concentrated $\text{CaCl}_2$

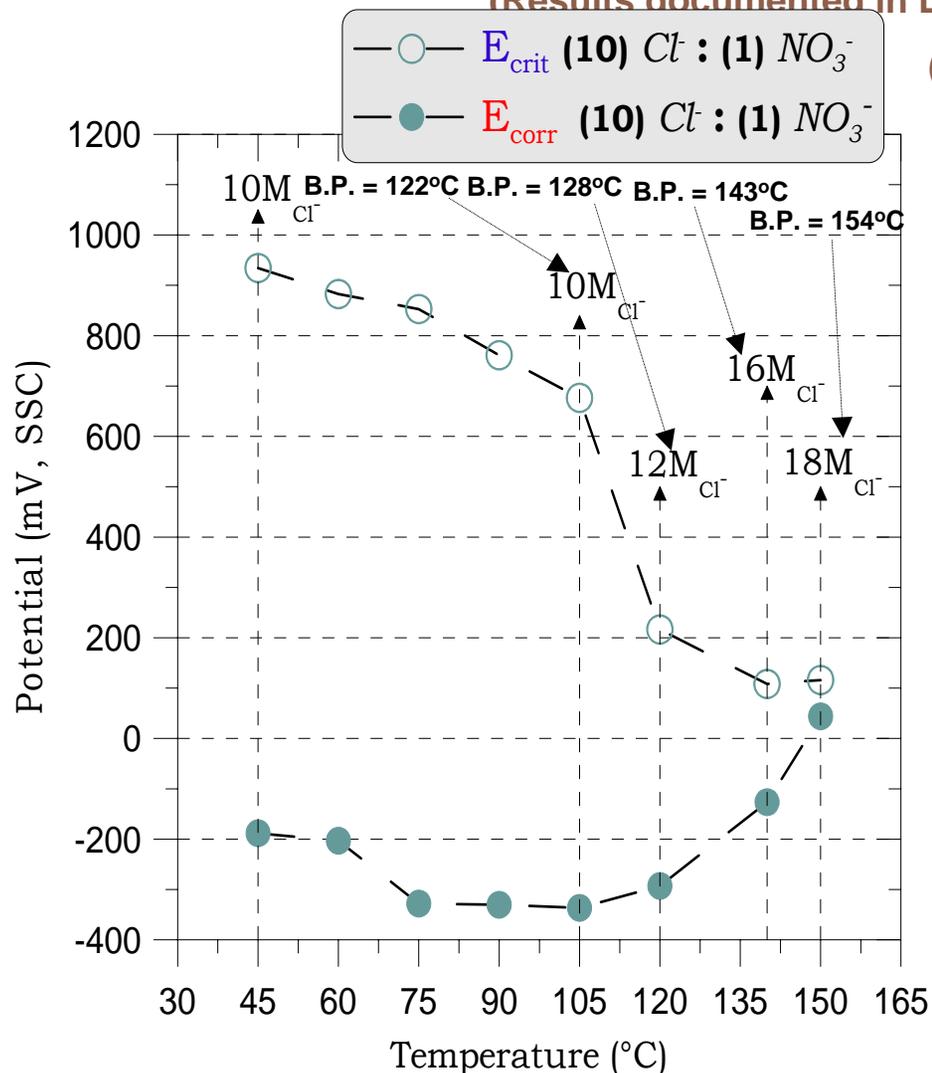
(Results documented in LLNL Scientific Notebooks)



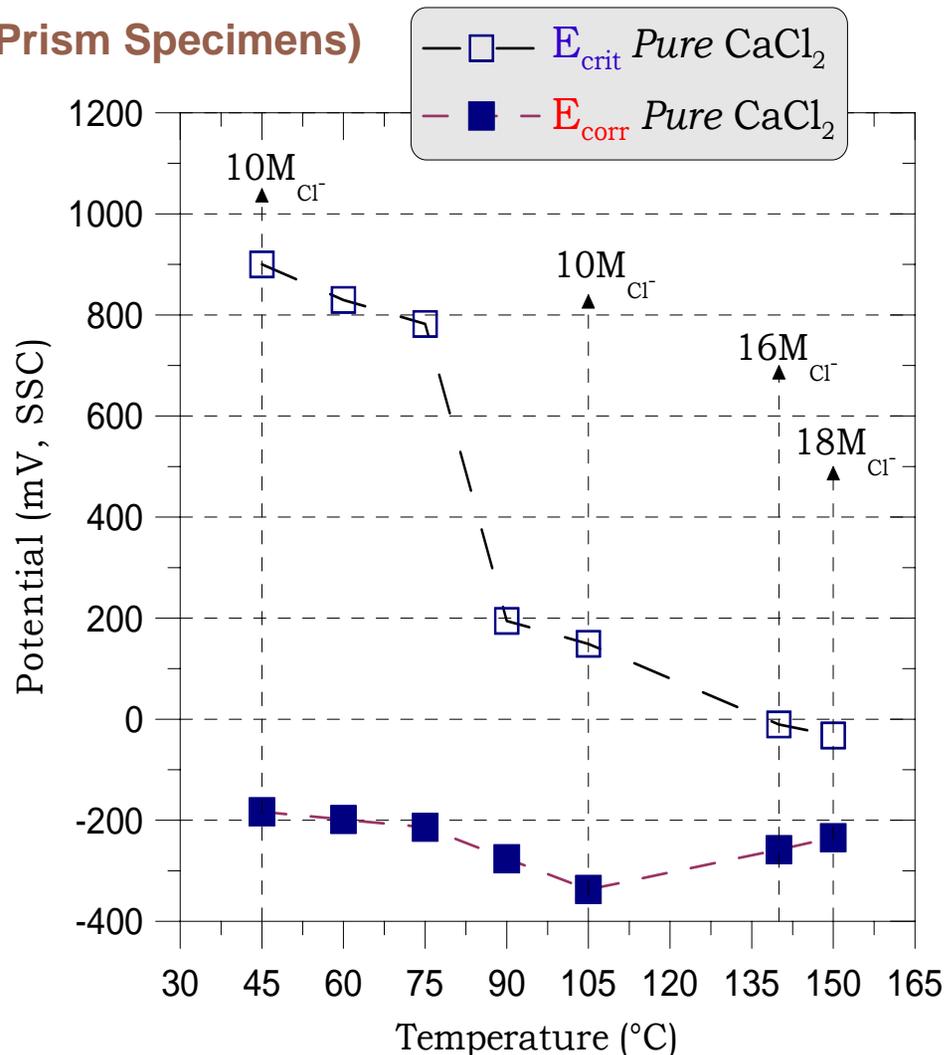
- For 9M  $\text{CaCl}_2$  (18M  $\text{Cl}^-$ ),  $\Delta E = (E_{\text{crit}} - E_{\text{corr}}) \cong 190\text{-}240$  mV  
- Similar for both Prism and MCA specimens
- Measured  $E_{\text{corr}}$  values plateau @  $\sim 50$  mV SSC for both aerated and deaerated  $\text{CaCl}_2$  solutions with and without 10:1  $\text{Cl}^-/\text{NO}_3^-$

# Alloy 22 Corrosion and Critical Potentials vs Temperature in Concentrated $\text{CaCl}_2$ Bulk Solutions with and w/o [10:1 ( $\text{Cl}^-$ : $\text{NO}_3^-$ )]

(Results documented in LLNL Scientific Notebooks)



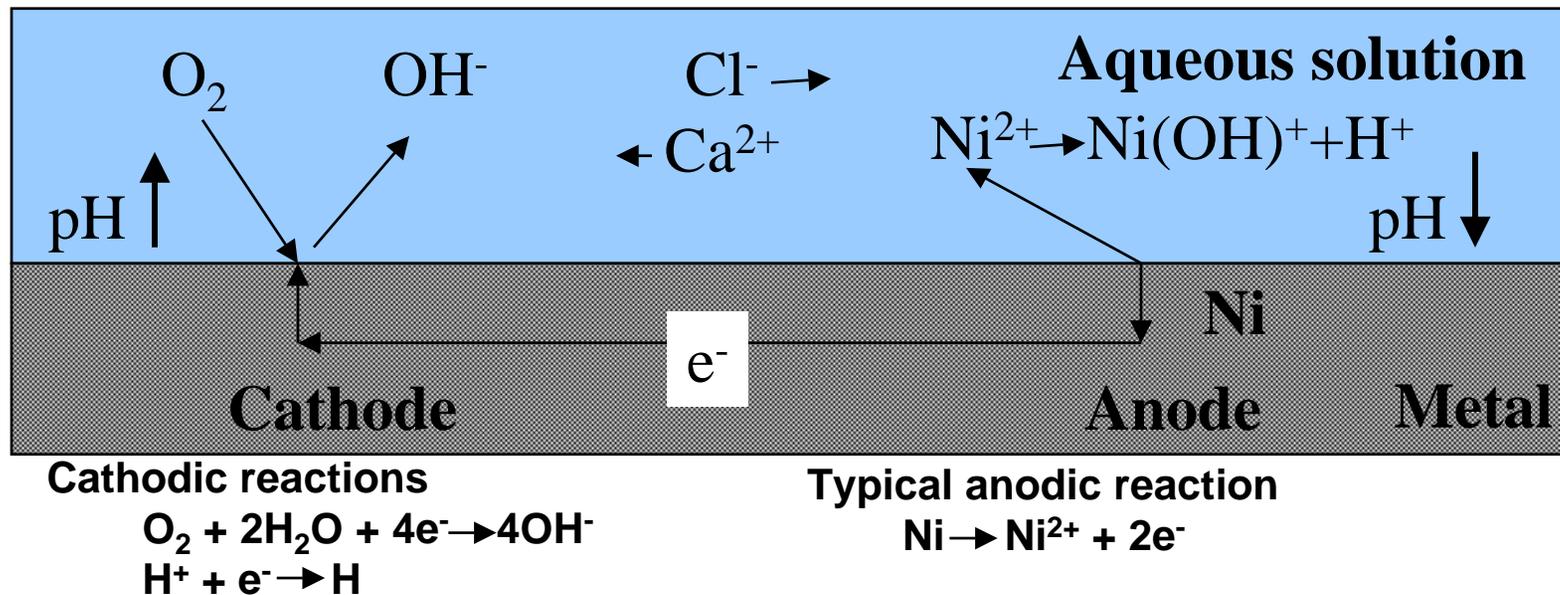
(Prism Specimens)



- Increase in  $E_{\text{corr}}$  when 10:1  $\text{Cl}^-/\text{NO}_3^-$  present leads to less margin at  $T > \sim 140^\circ\text{C}$
- Boiling point increases to  $154^\circ\text{C}$  for 9M  $\text{CaCl}_2$  (18M  $\text{Cl}^-$ )



# Corrosion in Thin Film Aqueous Solutions



- **In thin surface brine films, concentration changes due to limitations on diffusion, convection and water mass can**
  - **Increase pH at local cathodes leading to or accelerating**
    - ◆ **Precipitation of insoluble minerals, e.g. calcium hydroxide**
  - **Decrease pH at local anodes resulting in or accelerating**
    - ◆ **Acid gas volatility at higher temperatures, e.g. HCl↑**

# Thin Film Aqueous Corrosion Studies at LLNL

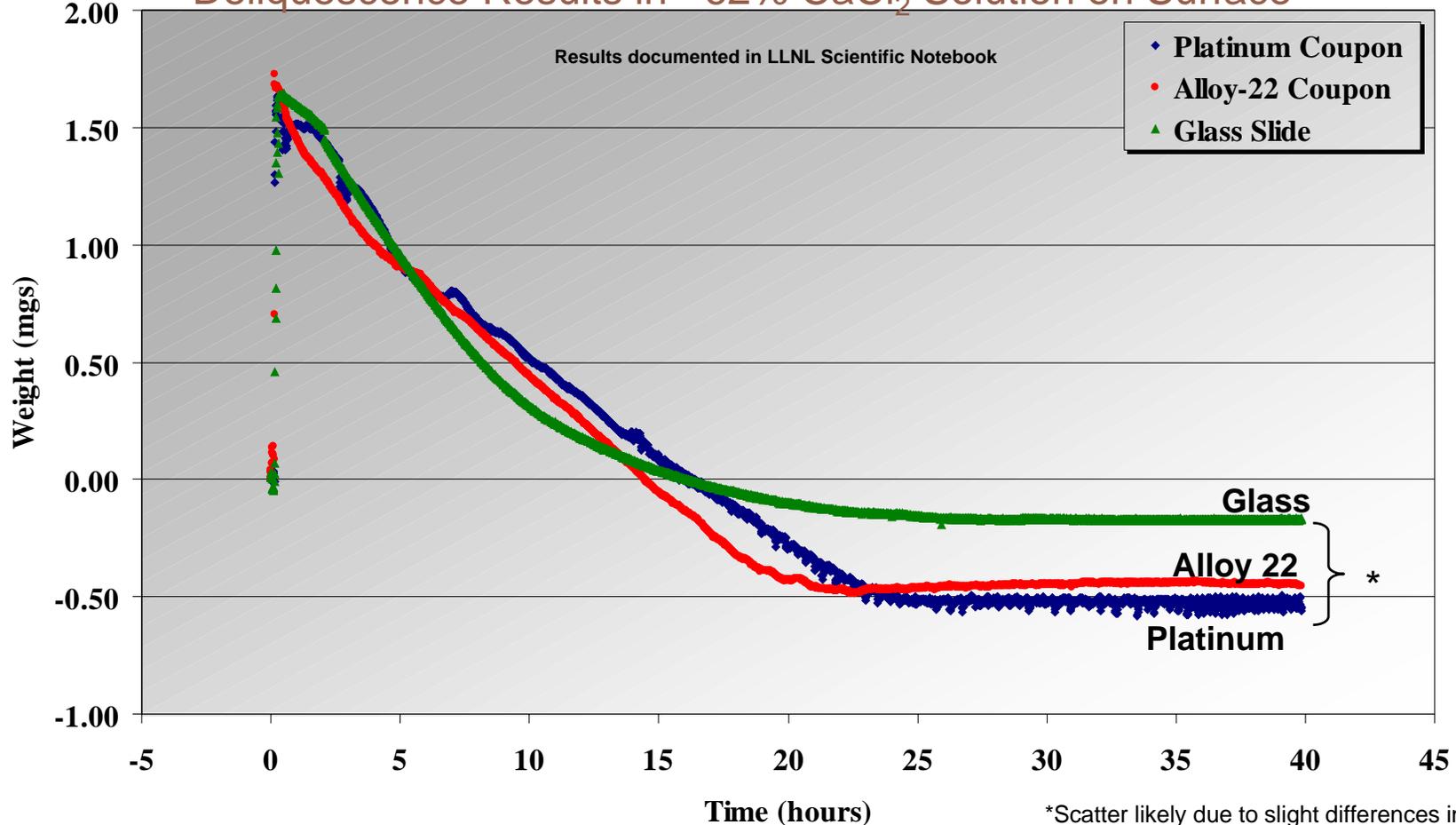
- **Custom thermogravimetric analyzer**
  - Controlled temperature and relative humidity (RH) in test cell
  - Continuous measurement of temperature, RH, and sample weight change as a function of time
- **Salt deposits were deposited as aerosols from an atomizer**
- **Tests so far**
  - Alloy 22 (also Pt & glass) +  $\text{CaCl}_2$  @ 150°C and 22.5% RH
  - Alloy 22 +  $\text{CaCl}_2$  @ 100°C and 22.5% RH
  - Alloy 22 +  $\text{CaCl}_2$  +  $\text{Ca}(\text{NO}_3)_2$  @ 150°C and 22.5% RH
  - Alloy 22 +  $\text{CaCl}_2$  @ 125°C and 22.5% RH



# Weight Change vs Time for $\text{CaCl}_2$ Coated Specimens

(150°C and 22.5% RH)

Deliquescence Results in ~62%  $\text{CaCl}_2$  Solution on Surface



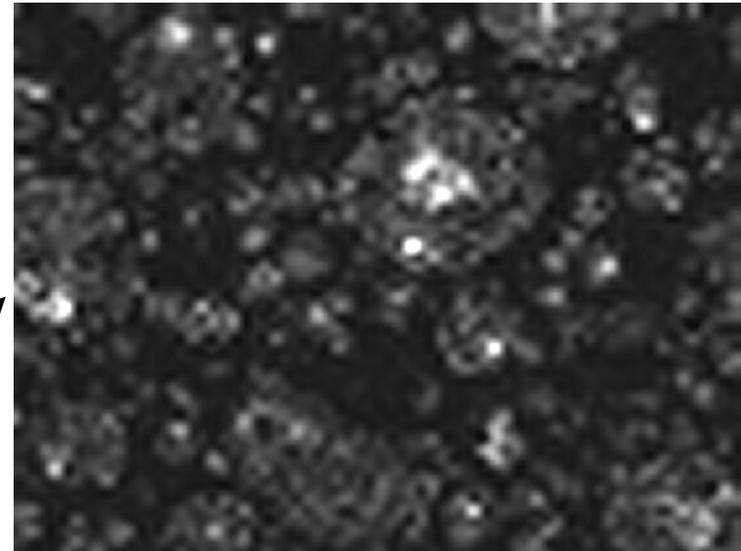
- Initial weight gain from deliquescence of  $\text{CaCl}_2$
- Weight loss due to volatilization of HCl leading to increased pH, precipitation of Ca and resultant water loss
  - Losses similar for Alloy 22 and controls
    - ◆ Within expected scatter

# CaCl<sub>2</sub> + Alloy 22 at 150°C

Pre-test specimen



Raman spectroscopy on selected areas



Post-test specimen



- **White, Ca containing precipitates formed by deliquescence**
- **Precipitates (analyzed only on Alloy 22) contain significant Cl**
  - EDS analysis indicates Ca:Cl atomic ratio ~1:1, consistent with HCl volatilization
  - Wet chemical analysis confirms ~1:1 ratio
- **No surface degradation observed visually after deposits removed**
  - Highly polished sample being tested to confirm absence of surface attack using SEM

# Summary

- **Waste package (WP) surface environment strongly influenced by Titanium Gr 7 drip shield (DS)**
  - Seepage waters diverted from WP while DS intact
  - Aqueous brines on WP will exist as thin deliquescent films
- **WP calculated to maintain corrosion resistance for regulatory period**
  - Even if DS fails, recent tests in bulk and thin film brines continue to confirm expected WP localized corrosion margin at temperatures approaching 150°C
- **A comprehensive materials testing program is continuing to LA and beyond to reduce remaining uncertainties in long-term degradation behavior**



# Backup



# Potentially Relevant Alloy Compositions

## Composition of Ni-Cr-Mo Alloys

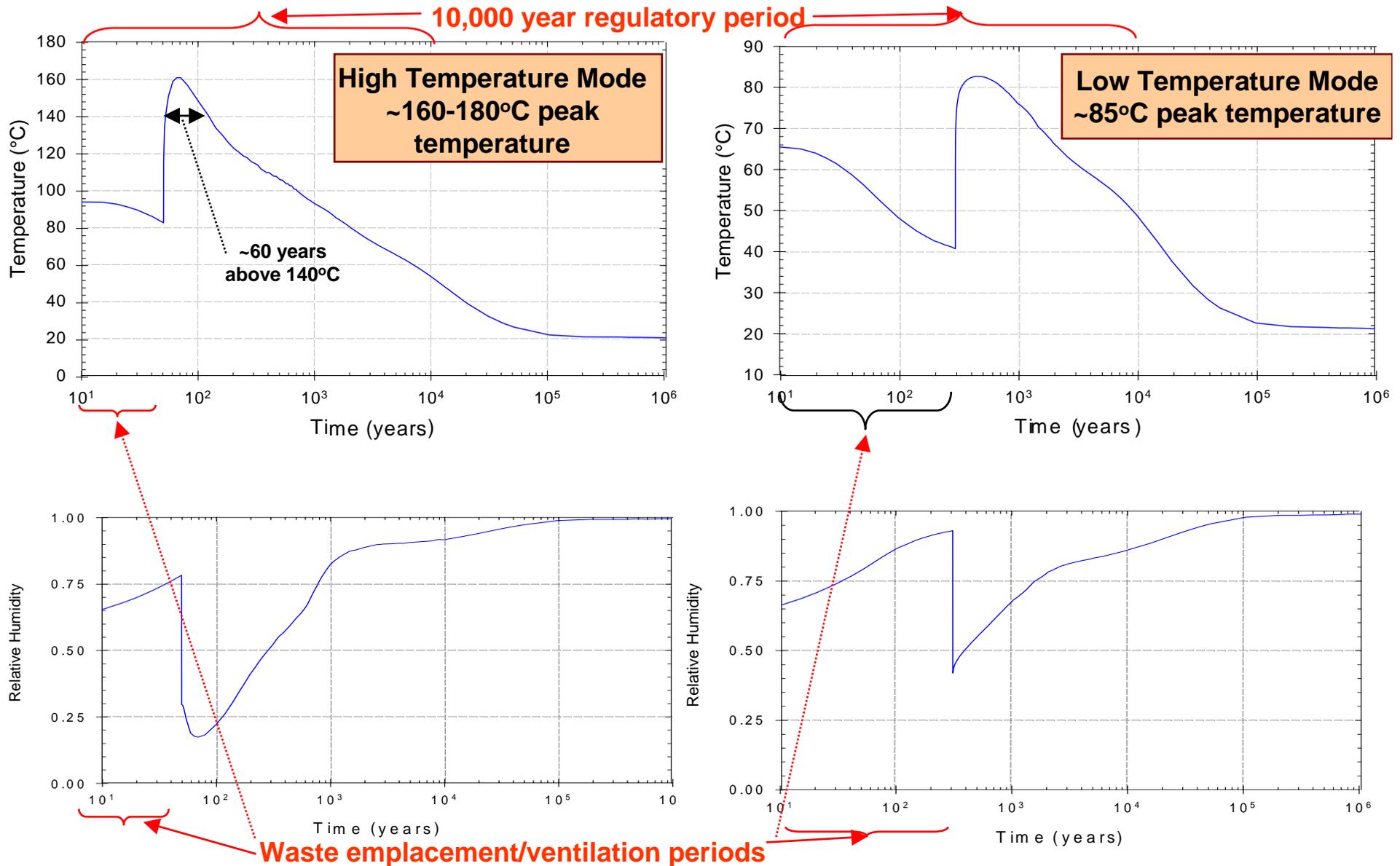
UNS No.	Alloy Name	Cr	Mo	W	Fe	Co	Mn	Si	C	P	S	Ni	Other
N06022	Hastelloy C-22	20.0-22.5	12.5-14.5	2.5-3.5	2.0-6.0	2.5 max	0.50 max	0.08 max	0.015 max	0.02 max	0.02 max	Rem	V: 0.35 max
N06455	Hastelloy C-4	14.0-18.0	14.0-17.0		3.0 max	2.0 max	1.0 max	0.08 max	0.015 max	0.04 max	0.03 max	Rem	Ti: 0.70 max
N10276	Hastelloy C-276	14.5-16.5	15.0-17.0	3.0-4.5	4.0-7.0	2.5 max	1.0 max	0.08 max	0.02 max	0.030 max	0.030 max	Rem	V: 0.35 max
N10002	Hastelloy C	14.5-16.5	15.0-17.0	3.0-4.5	4.0-7.0	2.5 max	1.00 max	1.00 max	0.08 max	0.040 max	0.030 max	Rem	V: 0.35 max
N06059	Nicofer 59	22.0-24.0	15.0-16.5		1.5 max	0.3 max	0.5 max	0.010 max	0.010 max	0.015 max	0.010 max	Rem	Al: 0.1-0.4
N06686	Inconel 686	19.0-23.0	15.0-17.0	3.0-4.4	5.0 max		0.75 max	0.08 max	0.010 max	0.04 max	0.02 max	Rem	
N06200	Hastelloy C-2000	22.0-24.0	15.0-17.0		3.0 max	2.0 max	0.50 max	0.08 max	0.010 max	0.025 max	0.010 max	Rem	Cu: 1.3-1.9

## Composition of Titanium Alloys

UNS No.	Grade	Intentional Elements	Residual Elements	Other
R52400	Grade 7	Pd: 0.12-0.25	C:0.03 max; Fe: 0.30 max; H: 0.015 max; N: 0.03 max; O: 0.25 max	
R52402	Grade 16	Pd: 0.04-0.08	C: 0.10 max; Fe: 0.30 max; H: 0.010 max; N: 0.03 max; O: 0.25 max	Other residuals: each 0.1 max; total 0.4 max
R56403 R56405	Grade 24	Al: 5.5-6.5; V: 3.5-4.5; Pd: 0.04-0.08	C: 0.10 max; Fe: 0.40 max; H: 0.015 max; N: 0.05 max; O: 0.20 max	Other residuals: each 0.1 max; total 0.4 max
R53400	Grade 12	Mo: 0.2-0.4; Ni: 0.6-0.9	C: 0.08 max; Fe: 0.30 max; H: 0.010 max; N: 0.03 max; N: 0.020 max; O: 0.25 max	



# Waste Package Surface Temperature and RH vs Time for Typical High and Low Temperature Operating Modes



\*OCRM "FY01 Supplemental Science and Performance Analyses, Vol. 2: Performance Analyses," TDR-MGR-PA-000001. July 2000, pp. 4F-36-37

# Path Forward on Susceptibility of Alloy 22 to Localized Corrosion in Bulk Solutions

- **Use different ratios of  $\text{Cl}^-/\text{NO}_3^-$** 
  - $\text{Cl}^-/\text{NO}_3^- = 10, 5 \text{ and } 1$
- **Vary the Initial  $\text{Cl}^-$  Concentration**
  - $[\text{Cl}^-] = 2 \text{ M}, 10 \text{ M}, 16 \text{ M}$
- **Vary the Microstructure**
  - **Base Metal (Wrought Mill Annealed), Aged Base, As-Welded and Aged Welded**
- **Different Surface Finish on the Specimens**
  - **Freshly Polished, Solution Grown Oxide Films, Furnace Grown Oxide Films, Laser Peened Surfaces, etc.**
- **Different Methods**
  - **Cyclic Polarization Test, Tsujikawa-Hitsamatsu Electrochemical (THE) Test, Constant Potential Test**



# Thin Film Corrosion Path Forward

- **Low RH sample holder for surface analysis**
  - Additional Raman spectroscopy
  - X-ray diffraction
- **Quantification of elemental composition of deposits**
  - Wet chemistry
- **Quantification of surface degradation**
  - Scanning electron microscopy (SEM)
  - Optical microscopy
- **Effect of different salt combinations; matrix has been developed**
  - for example,  $\text{NaCl} + \text{CaCl}_2$



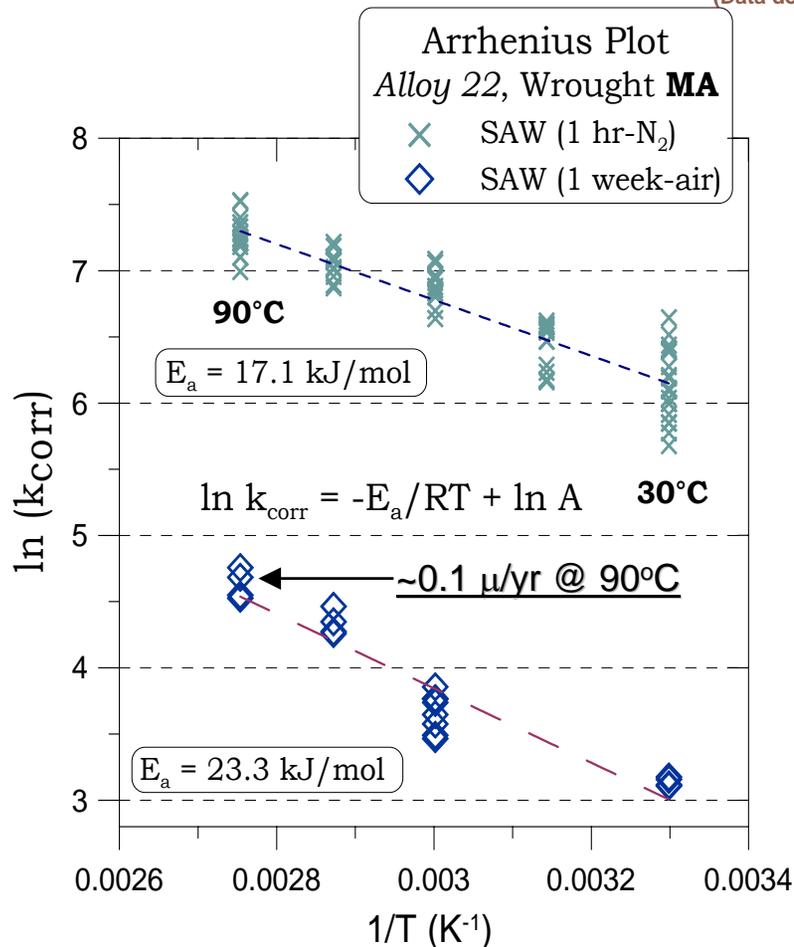
# Key Elements For License Application

- **Resolution of Key Technical Issues (KTI)**
  - Container Lifetime and Source Term
  - Evolution of the Near-Field Environment
- **Mechanistic basis for environment evolution on waste packages and drip shields**
- **Mechanistic basis for amount of corrosion per unit of deposited salt**
- **Bulk aqueous solution electrochemical studies and thin aqueous film studies complement each other to gain the mechanistic bases**

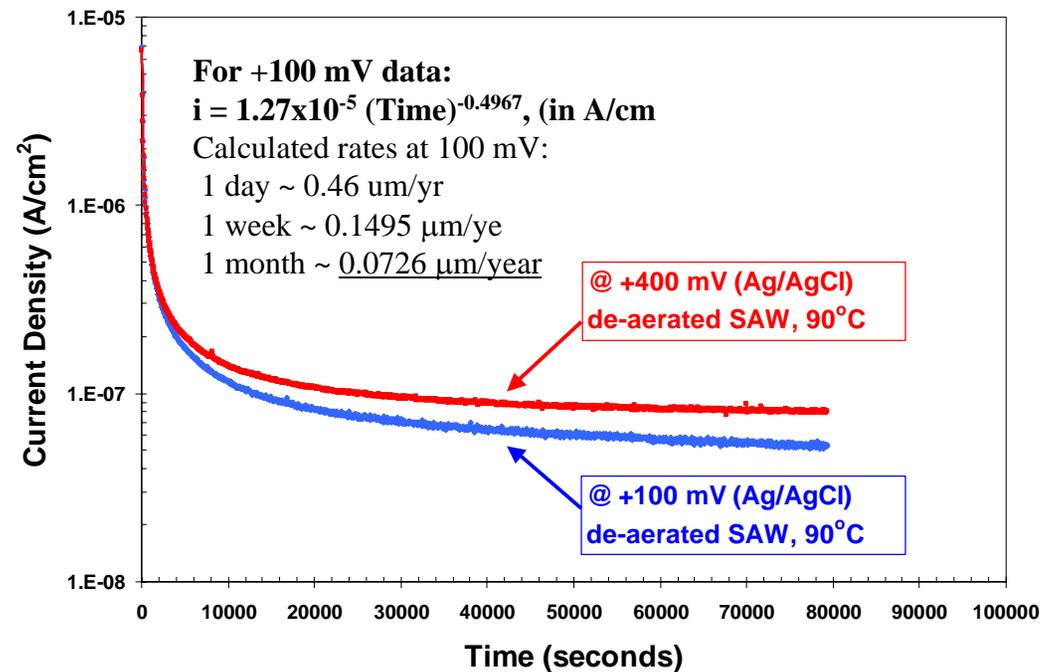


# Electrochemical Confirmation of General Corrosion Rates from Weight Loss Measurements

(Data documented in LLNL Scientific Notebooks)



## Passive Dissolution Rate Measured Potentiostatically in 90°C SAW



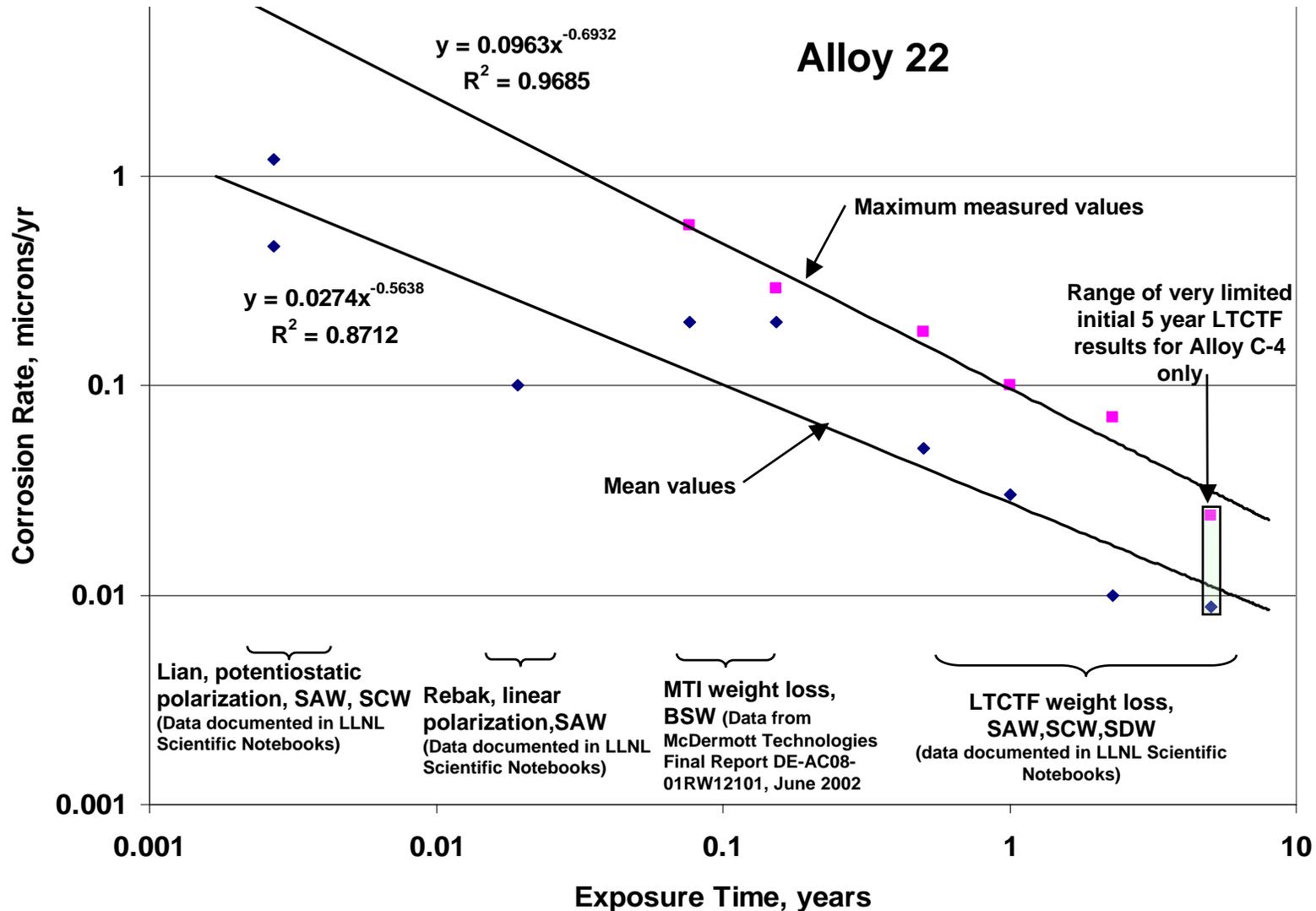
## Potentiostatic Polarization

- TSPA currently employs corrosion rates obtained from descaled weight loss measurements on 2 year exposed specimens from LTCTF  
+ Electrochemically measured rates consistent with rates measured by descaled weight loss



# General Corrosion Rate at 90°C vs Exposure Time

(Based on electrochemical and weight loss measurements)

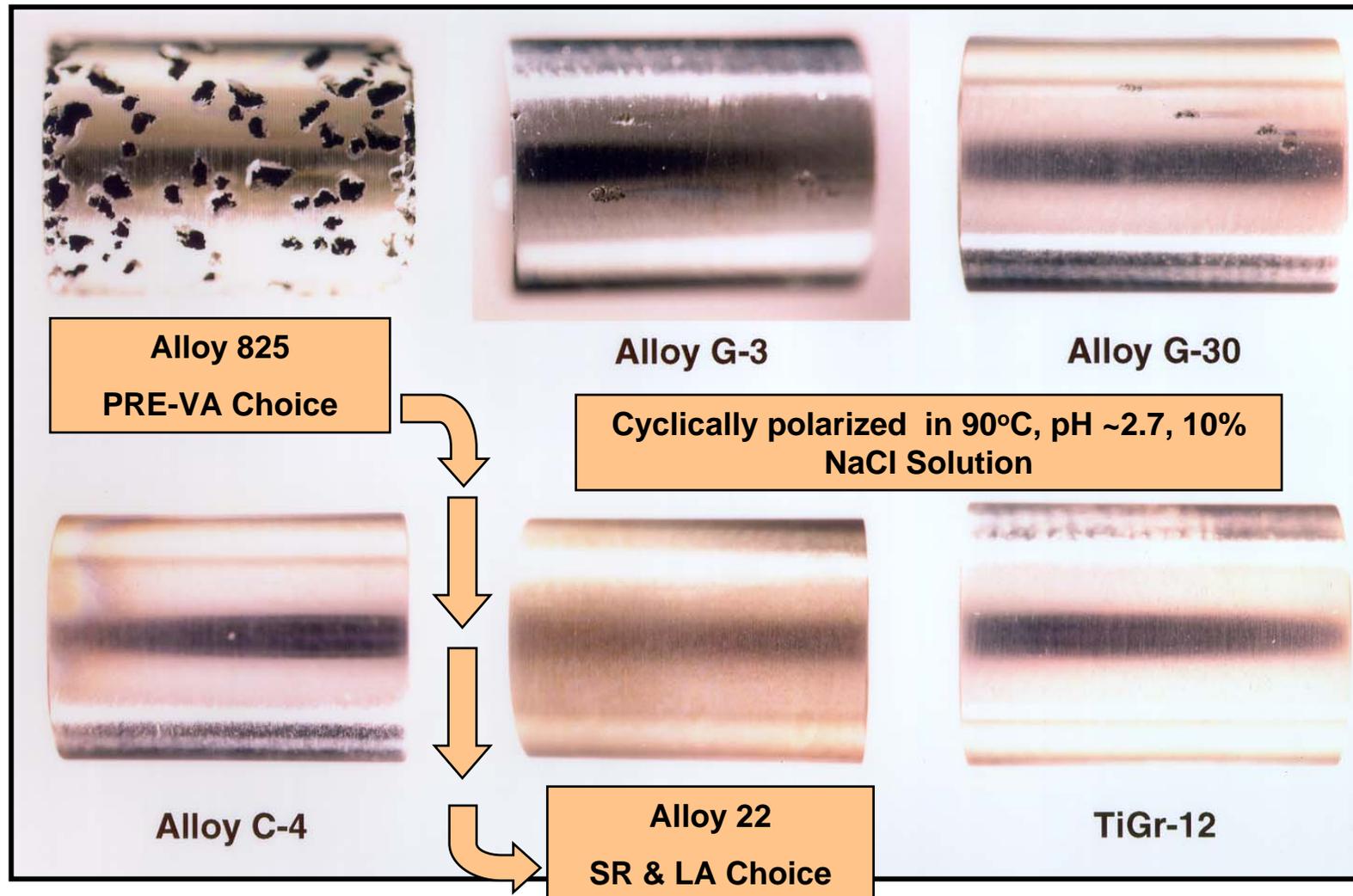


- Two-year LTCTF rate distribution currently used in TSPA
- Five-year exposed samples now under evaluation
  - Initial results consistent with expectations



# Pitting Susceptibility of Candidate WP Outer Barrier and DS Materials in Acidic NaCl Solution

Molar Ratio =  $\infty$



Results from A.K. Roy et al, "Localized Corrosion Behavior of Candidate Nuclear Waste Package Container Materials," Materials Performance, V. 37, 3, March 1998, p. 55

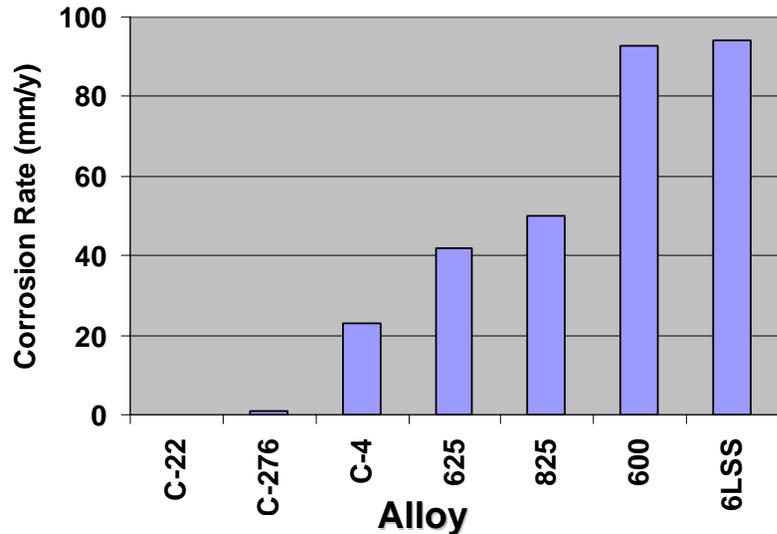


# Alloy 22: Exceptional Corrosion Resistance

Literature Results

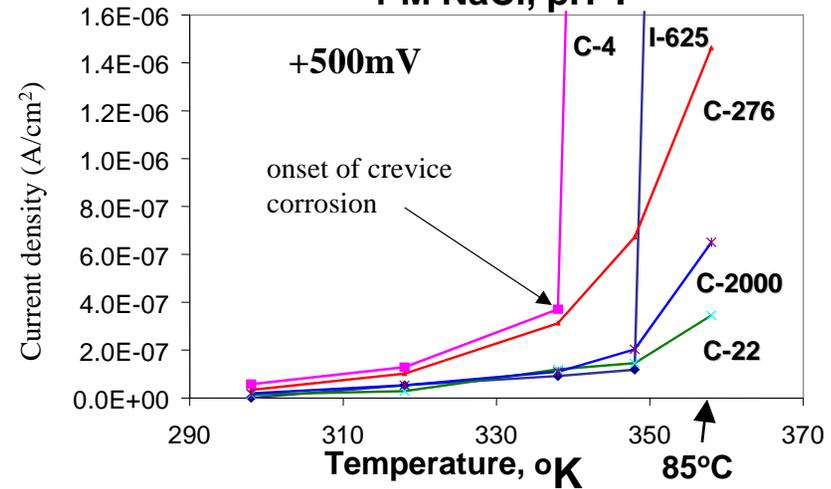
Boiling Green Death Solution

11.5% H<sub>2</sub>SO<sub>4</sub> + 1.2% HCl + 1% FeCl<sub>3</sub> + 1% CuCl<sub>2</sub>



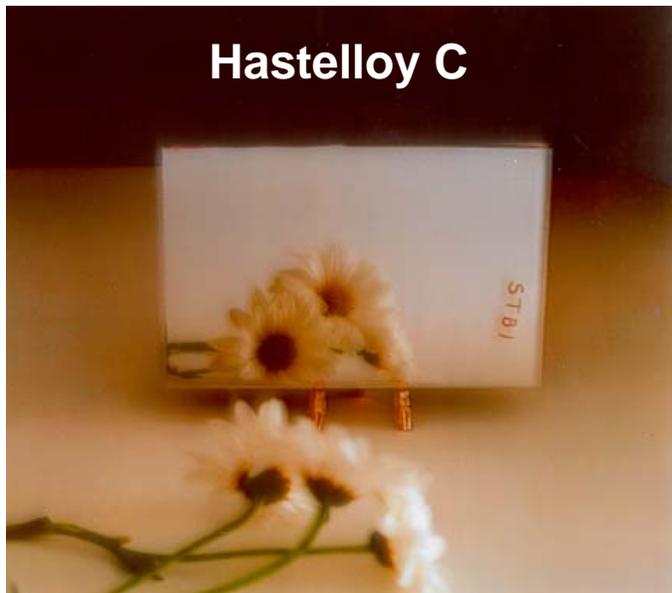
Potentiostatic Polarization at 500 mV, SSE

1 M NaCl, pH 1



Passive current vs temperature

\*A.C.Lloyd et al, Stainless Steel World, 2001



Hastelloy C

- A less resistant predecessor of Alloy 22 (16.5% Cr, 17% Mo, 4.5% W, 6% Fe, <0.15% C)
- Alloy C exposed at Kure Beach, North Carolina since 1941 (~50 years)
  - 250 meters from ocean
- Original mirror finish still intact after salt and debris washed from surface



YUCCA MOUNTAIN PROJECT

# Localized Corrosion Initiation: Current versus Future Models

- **TSPA-SR/SSPA/FEIS Model**

- **Process Model**

- ◆ **Based on potentiodynamic data**
    - ◆  $\Delta E = E_{crit} - E_{corr} = f[T, pH, \log(Cl^-)]$

- **Abstraction Model**

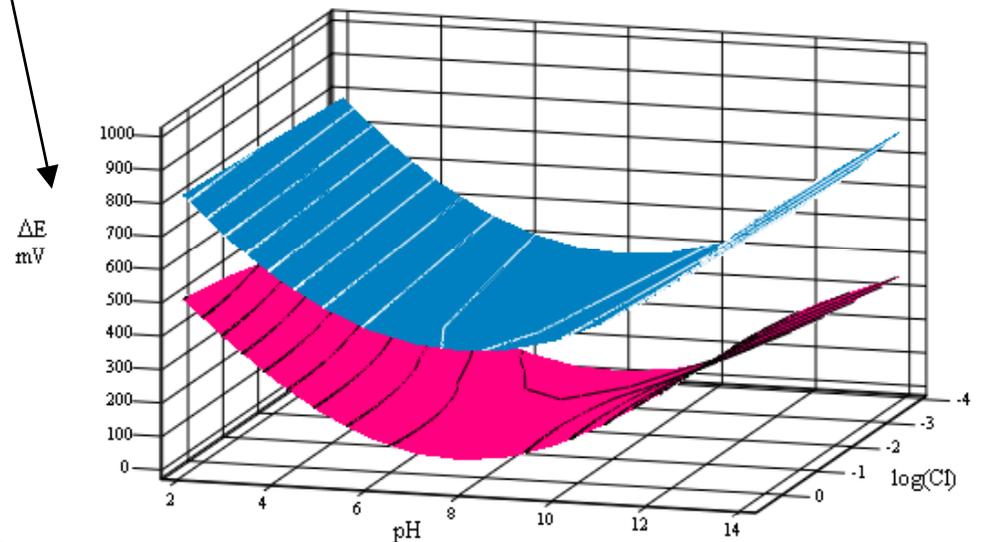
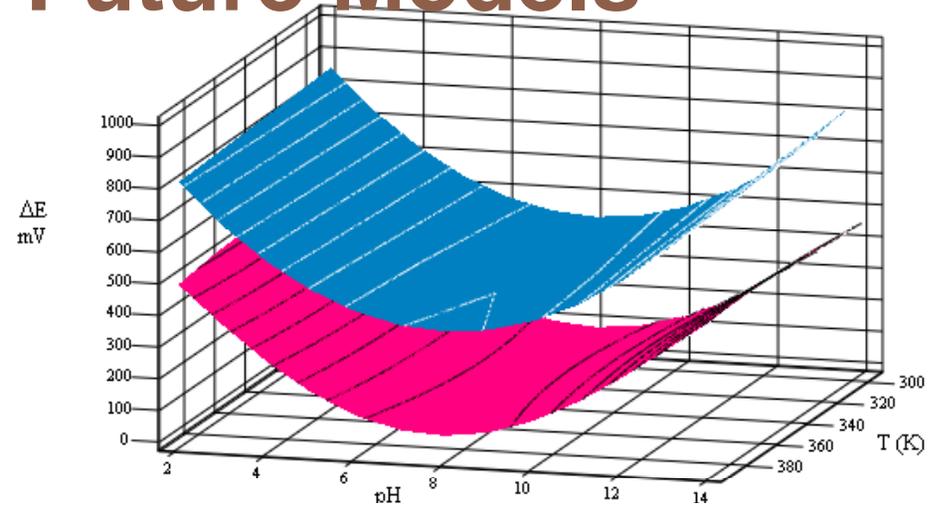
- ◆ **Implemented in TSPA Model**
    - ◆  $\Delta E = E_{crit} - E_{corr} = f[pH]$

- **TSPA-LA Model**

- $E_{crit}$  and  $E_{corr}$  Modeled Separately

- ◆ **Allows independent adjustments for MIC and Aging**

- $f[T, pH, \log(Cl^-), \log(Cl^-/NO_3^-)]^*$



\*Will incorporate inputs for most aggressive relevant cation(s) and anions



# Expected In-Drift Environmental Conditions

- Aqueous solutions in contact with waste package and drip shield will become thin aerated brine films through
  - Evaporative concentration of dilute seepage waters to dryness and subsequent deliquescence and/or
  - Deliquescence of hygroscopic salts present in dust deposits formed from particulates and aerosols introduced during construction and ventilation phases
- While drip shield remains intact, any aqueous films formed on waste package will result only from deliquescence of soluble species present in dust deposits
- In all cases  $Cl^-/NO_3^-$  Molar Ratio  $<3$

Constituent	J-13 Well Water (mg/l)	'Perched Water' (mg/l)	PTn Pore Water (mg/l)	1000X J-13* (mg/l)	~1000X Pore Water** (mg/l)
Pb/As					
HCO <sub>3</sub> <sup>-</sup>	128.9	147.0	74-220	24255	<45
Molar Ratio <sup>+</sup>	0.56	0.76	<2.7	0.58	1.17
pH	7.41	8.1	5.2-8.6	~10.3	6-6.5

•Basic brines (pH ~8-12) from carbonate dominated J-13 or perched waters  
 •Near neutral brines (pH ~5-7) from rock pore waters  
+HCO<sub>3</sub><sup>-</sup> and molar ratios from Ptn waters sampled from boreholes USW SD-6,7 and 9 ) (Range covers 9 samples) and CMWRA 2001-003, Table 2-1; Pb and As from Argonne National Laboratory trace element analyses, 5/89.

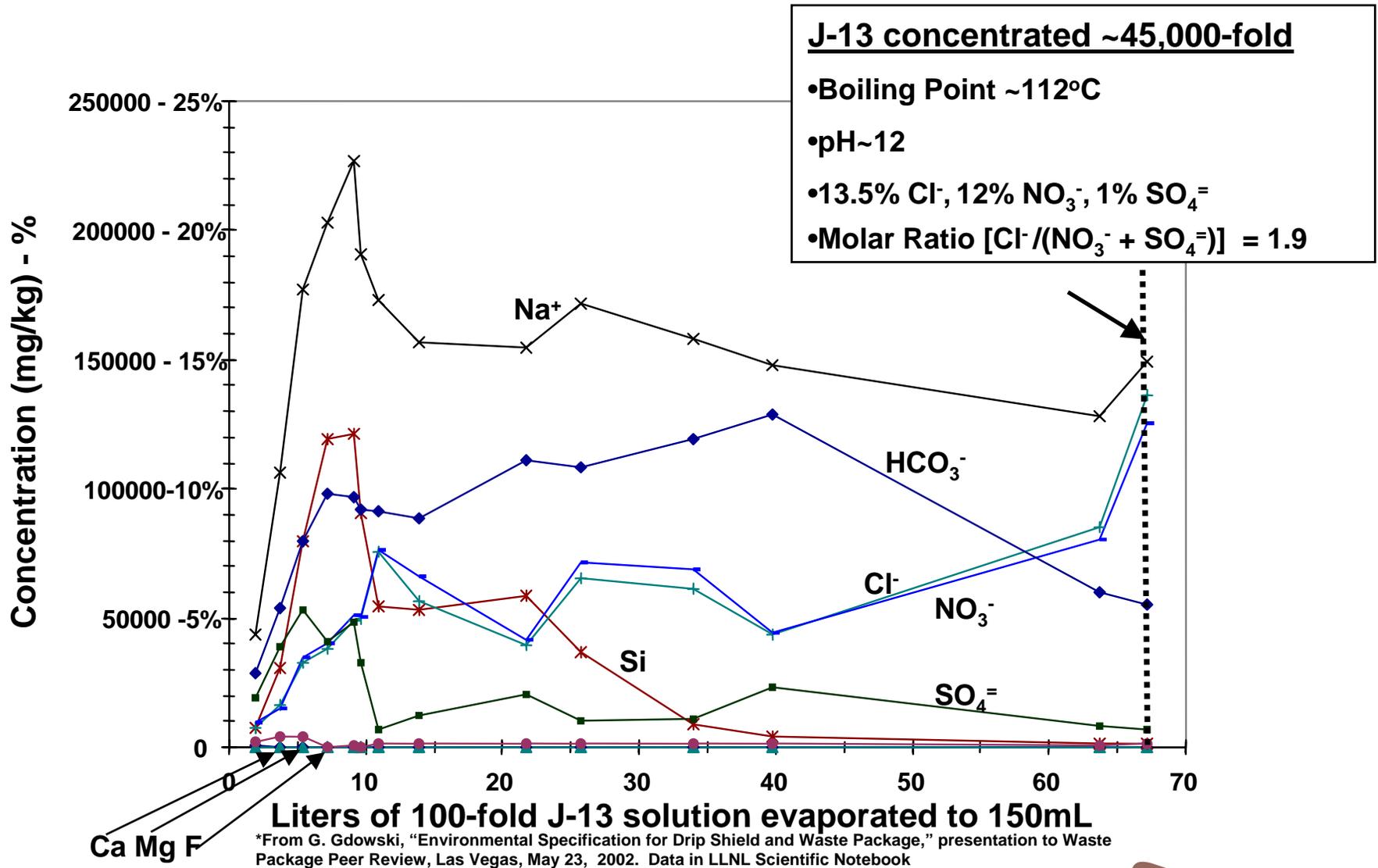
Constituent	Typical in-drift Dust+ (mg/l)	Typical atmospherically deposited species++ (kg/ha)	**
Na <sup>+</sup>	363	.09-.271	
Si(aq)	82	-	
Ca <sup>++</sup>	607	.53-1.47	
K <sup>+</sup>	204	.013-.092	
Mg <sup>++</sup>	34	.043-.254	
F <sup>-</sup>	14.5	-	
Cl <sup>-</sup>	181	.06-.39	
NO <sub>3</sub> <sup>-</sup>	418	.70-4.41	
SO <sub>4</sub> <sup>-</sup>	816	.38-2.20	
Pb/As	0.00124 / 0.0962	-	
HCO <sub>3</sub> <sup>-</sup>	-	-	
Molar Ratio	<0.27	0.15 - 0.33	

+Preliminary in-drift data from Zell Peterman, USGS; ++Atmospherically deposited species from Southwestern Nevada from National Atmospheric Deposition Program/National Trends Network; Site ID NV00, web site: <http://nadp.sws.uiuc.edu/>



# Brine Evolution by Evaporative Concentration at Boiling Point

(Simulated 100-fold J-13 Carbonate-Based Groundwater and Perched Water Starting Solution)



**High chloride, high nitrate basic brine formed**



# Principal test environments for general and localized corrosion measurements

(Data from J.C. Farmer, "General and Localized Corrosion of Waste Package & Drip Shield Materials", presentation to Waste Package Materials Performance Peer Review Panel, February 28, 2002 and from LLNL Scientific Notebooks)

**\*Long Term Corrosion Test Facility (LTCTF) Large tank environments**

**Other corrosion test bulk environments**

**Thermo-gravimetric Analyses**

Ion	Concentration (mg/L)						Water films	
	Simulated Dilute Water (SDW)*	Simulated Concentrated Water (SCW)*	Simulated Acidified Water (SAW)*	Basic Saturated Water (BSW)	Simulated Saturated Water (SSW)	Pure CaCl <sub>2</sub> (with and without nitrate)	Pure *CaCl <sub>2</sub> (with and without nitrate)	
K	34	3,400	3,400	81,480	141,600			
Na	409	40,900	40,900	231,224	487,000			
Mg	1	<1	1,000	---	---			
Ca	0.5	<1	1,000	---	---	1M - 9M	~220,000	
F	14	1,400	0	1,616	---			
Cl	67	6,700	24,250	169,204	128,000	2M -18M	~390,000	
NO <sub>3</sub>	64	6,400	23,000	177,168	1,313,000	0 - 2M	variable	
SO <sub>4</sub>	167	16,700	38,600	16,907	---			
HCO <sub>3</sub>	947	70,000	0	107,171	---			
Si	27 (60°C); 49 (90°C)	27 (60°C); 49 (90°C)	27 (60°C); 49 (90°C)	9,038	---			
Molar Ratio Cl/NO <sub>3</sub> +SO <sub>4</sub>	0.7	0.7	0.9	1.6	0.2	1- ∞	1- ∞	
pH	10.1	10.3	2.8	>12	6.7	5.8-6.4		
Temp. °C	25-90	25-90	25-105	25-105	25-120	30-150	≤ 150°C	

Environments evaluated cover range of relevant and accelerated concentrated brines, pH's, Cl<sup>-</sup>/NO<sub>3</sub><sup>-</sup> ratios and temperatures

\*Thin surface films

