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

Development and Implementation of the Localized Corrosion Model

Presented to:
Nuclear Waste Technical Review Board

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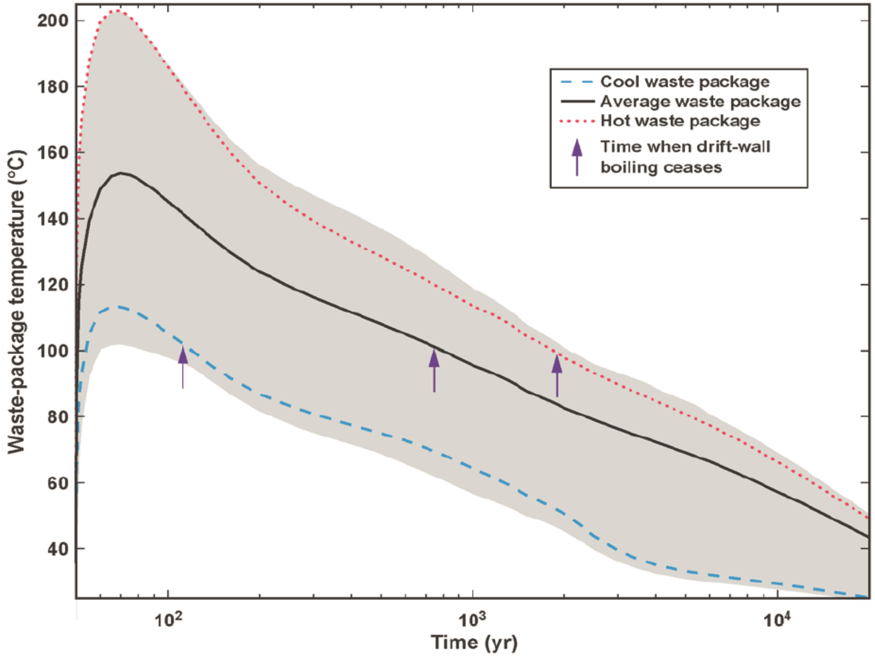
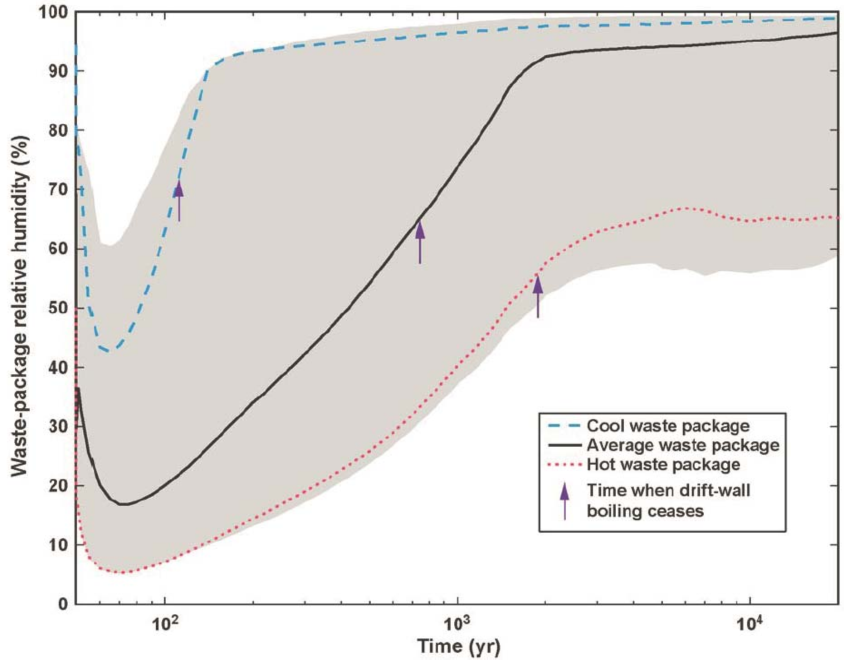
Outline

- In-drift exposure conditions
- Localized corrosion (LC) model for seepage conditions
  - Initiation model
  - Propagation model
- LC model for dust deliquescent conditions
- Conclusions

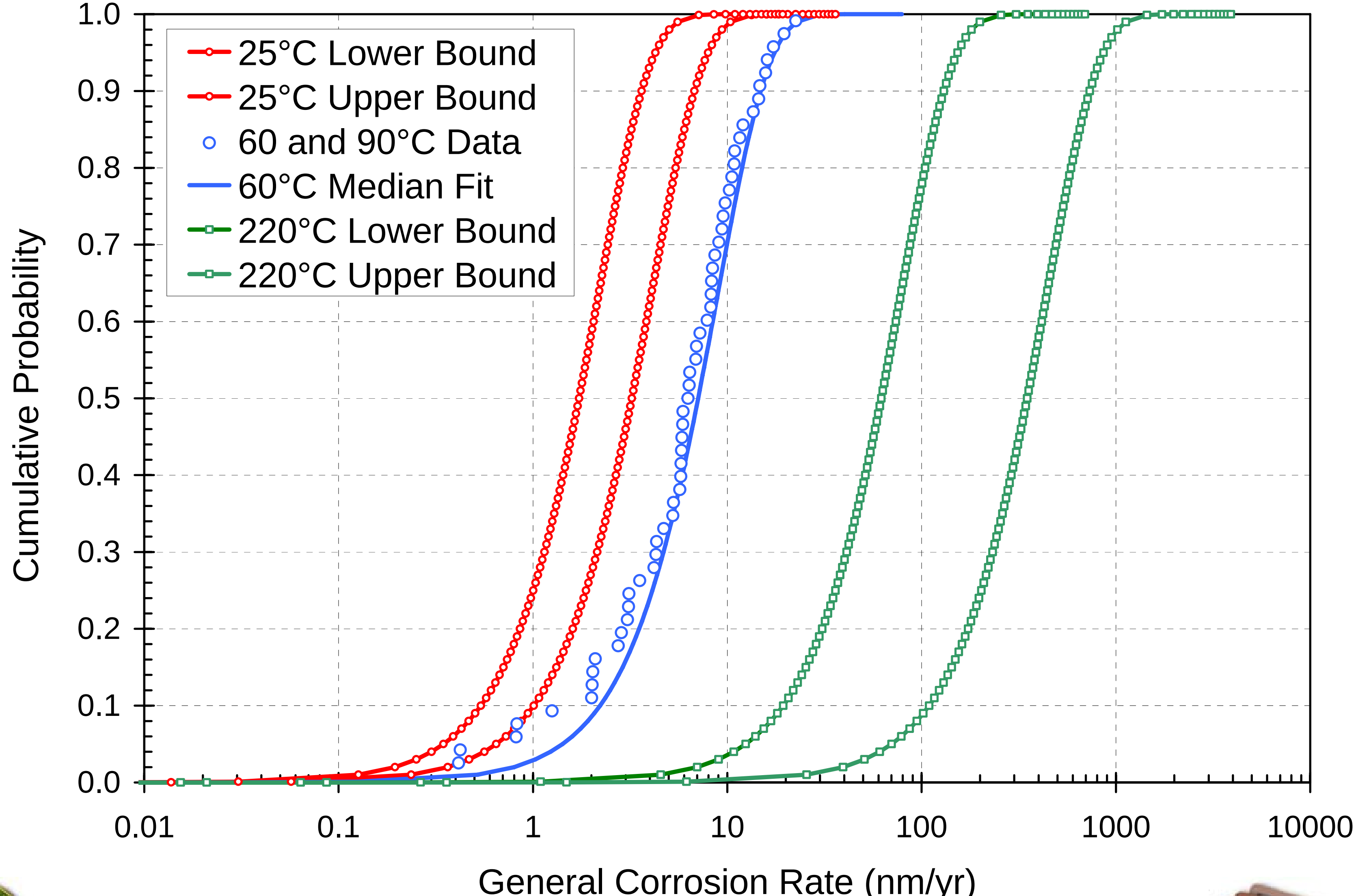
In-Drift Exposure Conditions





Ion	SDW (mg/L)	SCW (mg/L)	SAW (mg/L)	SSW (mg/L)	BSW-12 (mg/L)
K^+	34	3400	3400	142,000	67,620
Na^+	409	40,900	37,690	48,700	105,840
Mg^{2+}	1	<1	1000	0	0
Ca^{2+}	0.5	<1	1000	0	0
F^-	14	1400	0	0	1470
Cl^-	67	6700	24,250	128,000	130,830
NO_3^-	64	6400	23,000	1,313,000	1,395,600
SO_4^{2-}	167	16,700	38,600	0	14,700
HCO_3^-	947	70,000	0	0	0
Si	27 (60°C), 49 (90°C)	27 (60°C), 49 (90°C)	27 (60°C), 49 (90°C)	0	0
pH	9.8 to 10.2	9.8 to 10.2	2.7	5.5 to 7	12

General Corrosion Modeled to Always Occur

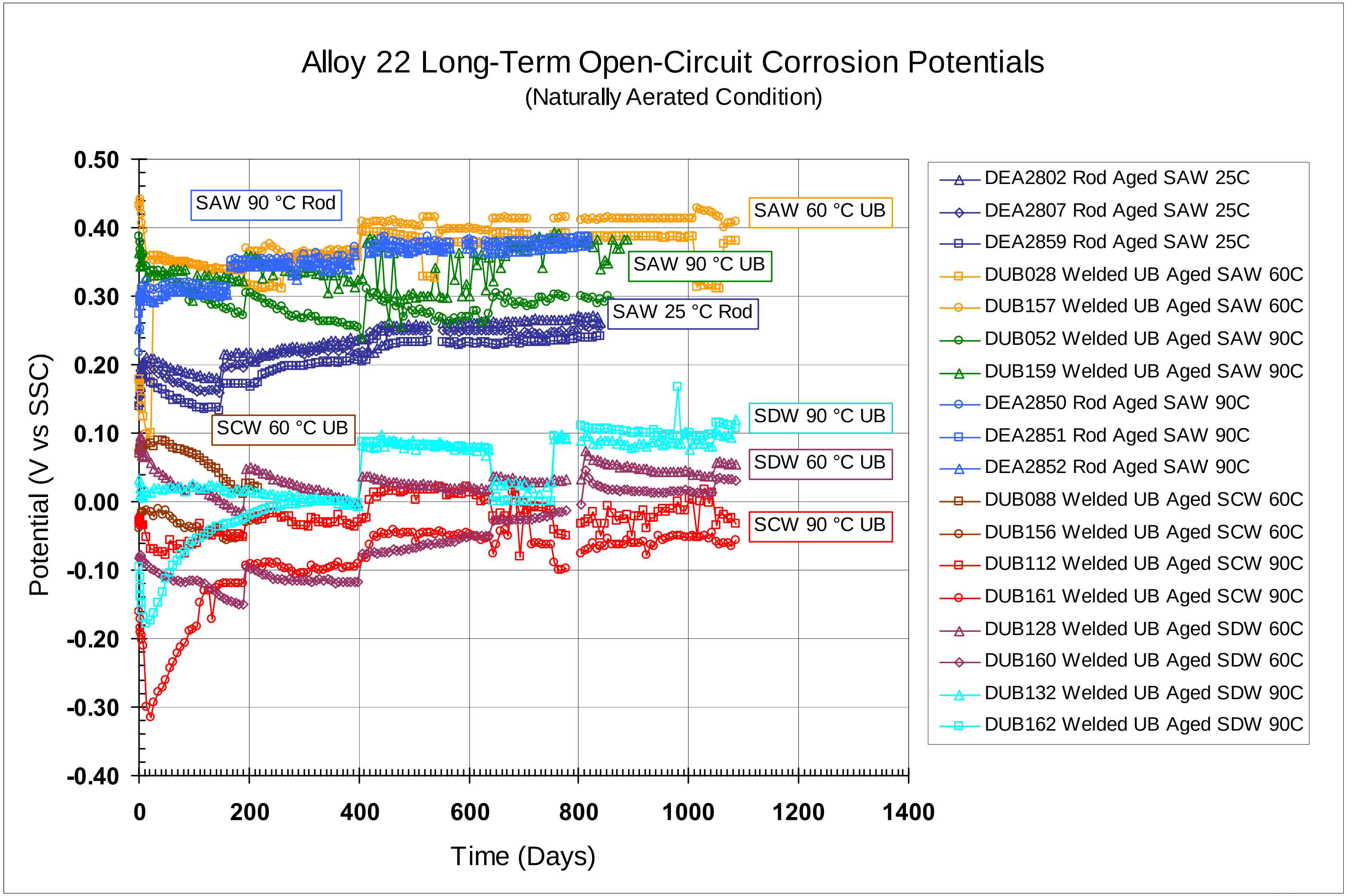


LC Model for Seepage

- Model based on comparison of long-term corrosion potential with crevice repassivation potential
  - If $E_{corr} \geq E_{rcrev}$ model initiates LC
  - Model applied to T<105°C
    - Maximum possible seepage temperature
  - If seepage occurs RH<77% model initiates LC to account for potential salt separation
  - Entire waste package surface may be subject to crevice corrosion
    - Crevice corrosion thresholds less than pitting thresholds
- Model fit to experimental data and accounts for associated uncertainty

Long-Term Corrosion Potential

- **Corrosion potential tends to increase with time**



Corrosion Potential (E_{corr}) Model

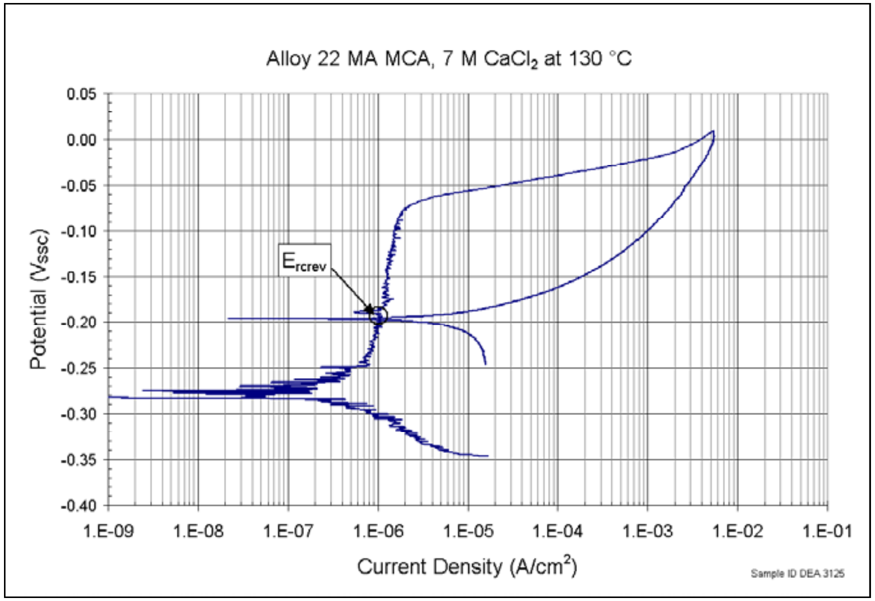
- E_{corr} determined by long-term tests (>300 days)
- Over 55 test conditions are available

T	25°C to 155°C
pH	1 to 13
NO_3	0 to 18 molal
Cl	0 to 36 molal
NO_3/Cl	0 to 100

$$E_{corr} = c_o + c_1 T + c_2 pH + c_3 [Cl^-] + c_4 \log\left(\frac{[NO_3^-]}{[Cl^-]}\right)$$

Crevice Repassivation (E_{rcrev}) Model

- E_{rcrev} obtained from cyclic polarization
- Over 90 test conditions are available
  - T 25°C to 160°C
  - pH 1 to 13
  - NO_3 0 to 13 molal
  - Cl 0 to 36 molal
  - NO_3/Cl 0 to >1000



$$E_{rcrev} = E^{o}_{rcrev} + \Delta E^{NO_3^-}_{rcrev}$$

$$E^{o}_{rcrev} = a_o + a_1 T + a_2 pH + a_3 \log([Cl^-]) + a_4 T \times \log([Cl^-])$$

$$\Delta E^{NO_3^-}_{rcrev} = b_o + b_1 [NO_3^-] + b_2 \frac{[NO_3^-]}{[Cl^-]}$$

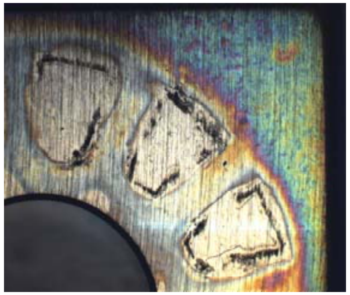
Cyclic Polarization: Na and K Brines at 110°C

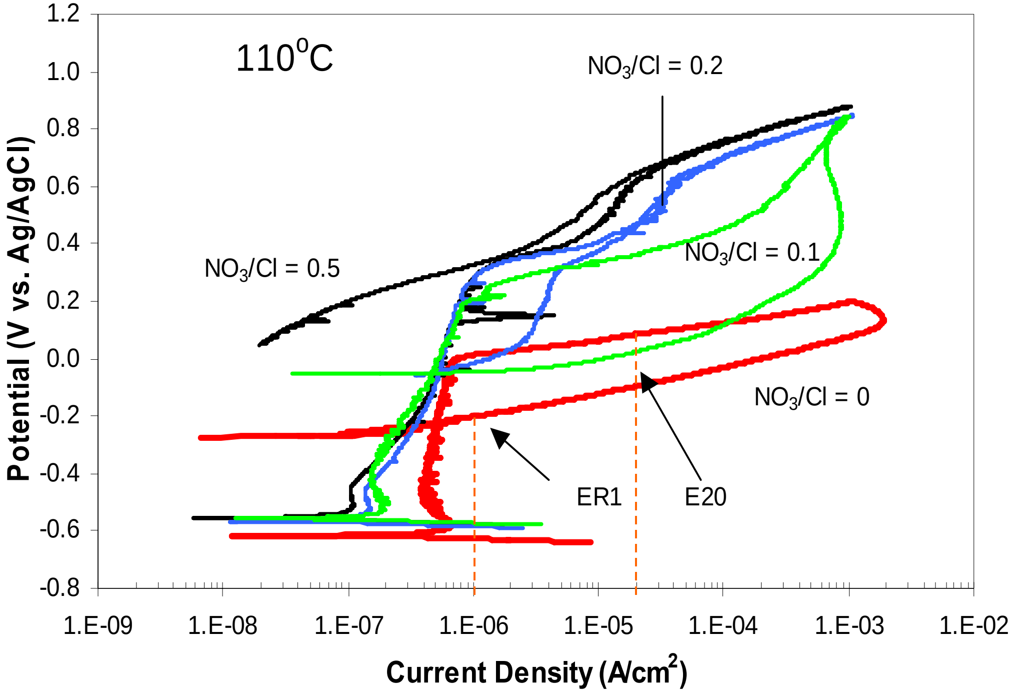
Increase in NO_3/Cl ratio results in shrinking of the hysteresis loop, and drives crevice attack deeper under the crevice former

$NO_3/Cl = 0$

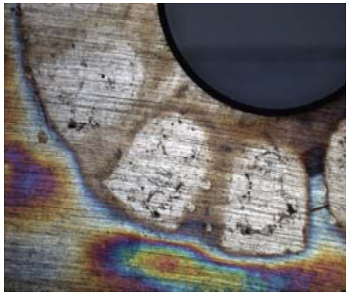
$NO_3/Cl = 0.1$

$NO_3/Cl = 0.2$





$NO_3/Cl = 0.3$

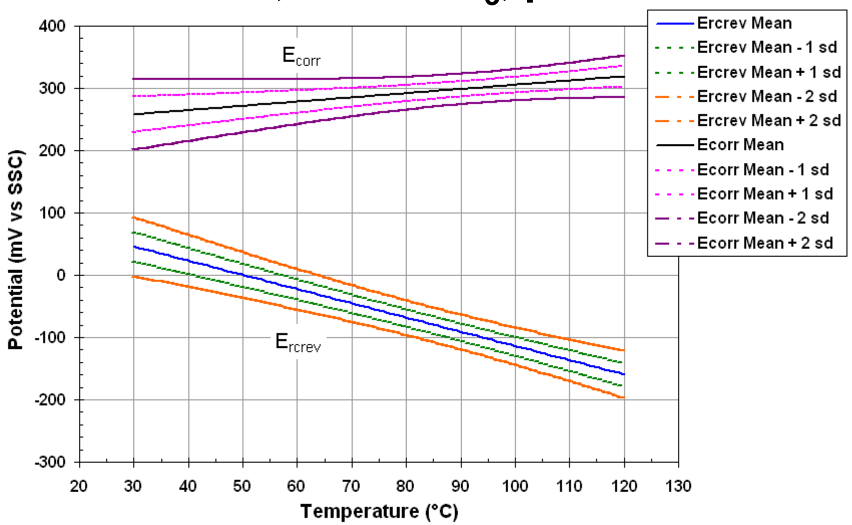


$NO_3/Cl = 0.5$

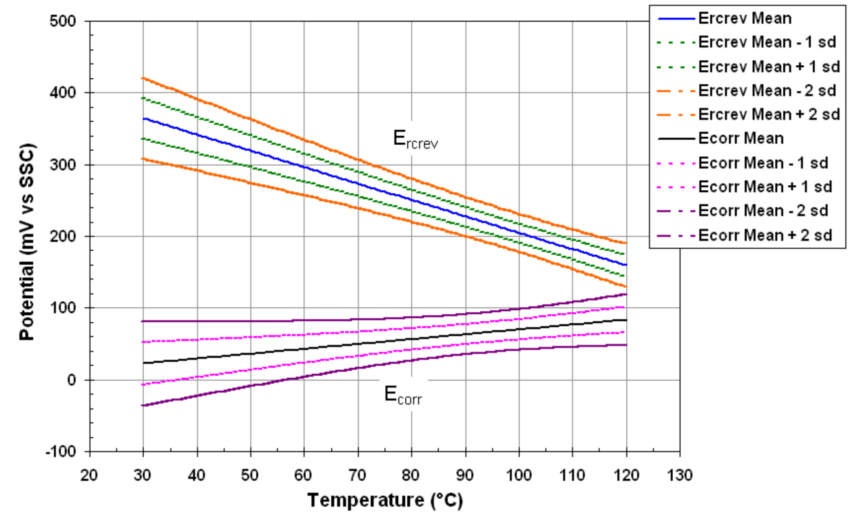
$NO_3/Cl = 1$

LC Initiation Model

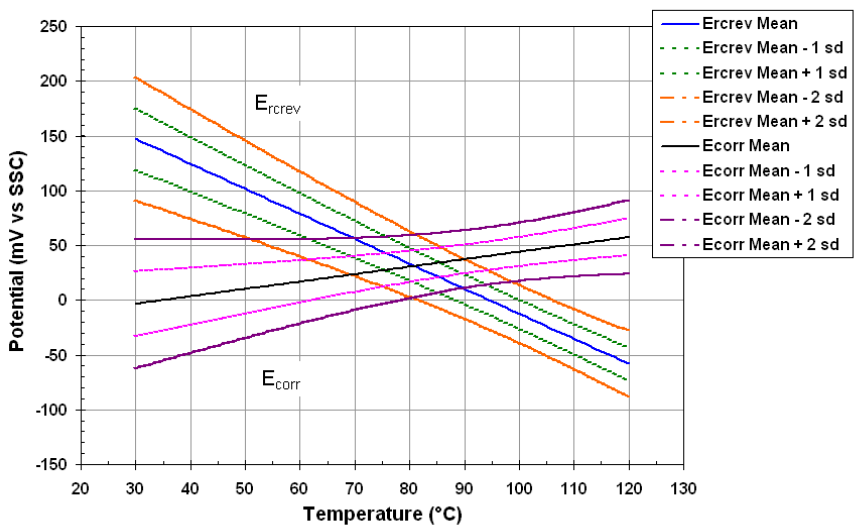
10 m Cl, 0.5 m NO_3, pH 3



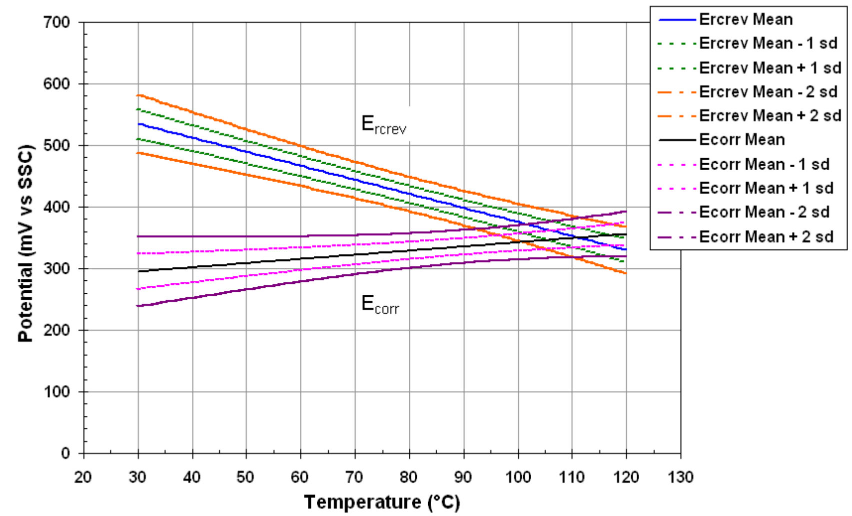
10 m Cl, 2.5 m NO_3, pH 7



10 m Cl, 0.5 m NO_3, pH 7



10 m Cl, 5.0 m NO_3, pH 3

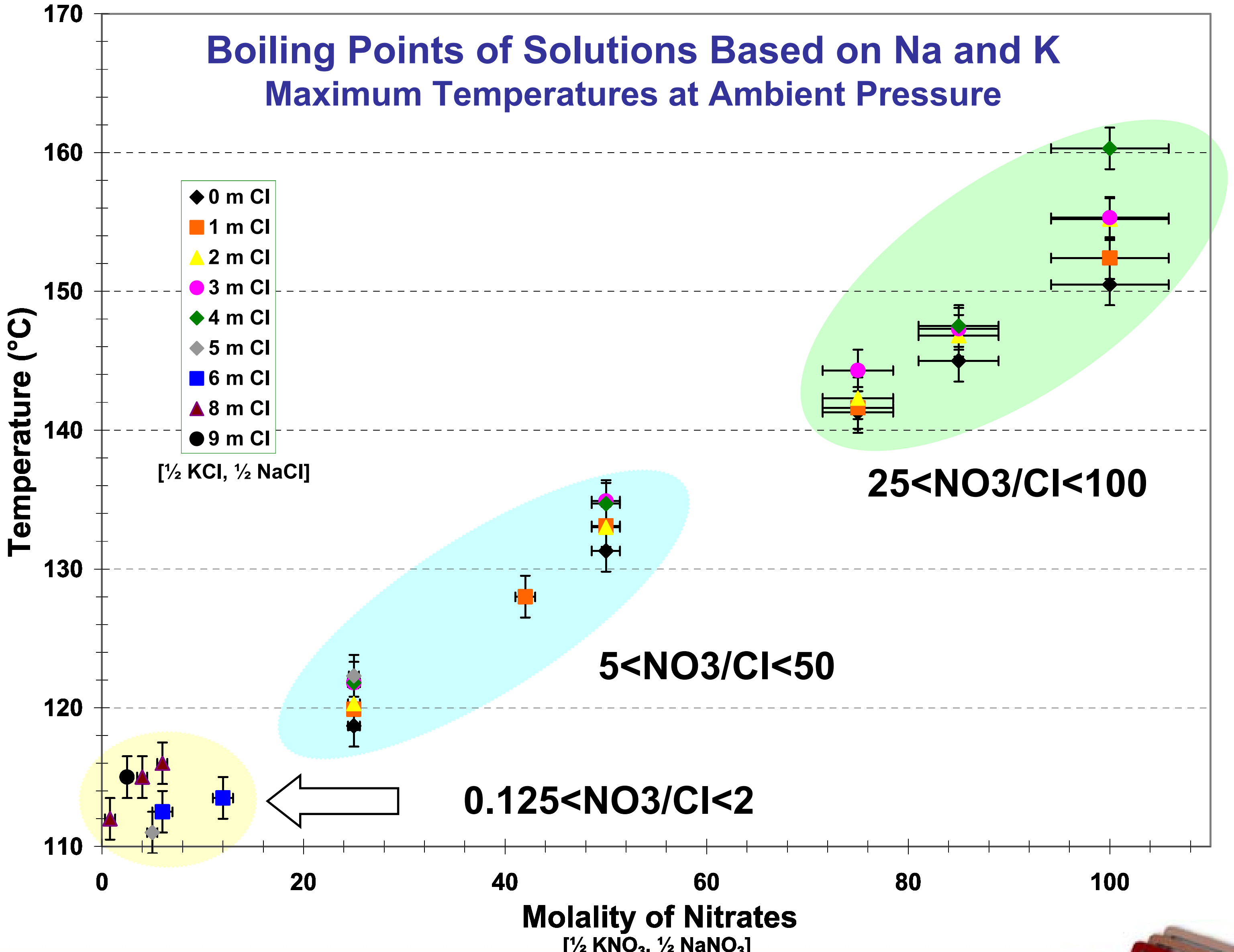


LC Propagation Model Seepage Conditions

- **Once LC initiates linear corrosion rate applied until penetration occurs (no stifling)**
- **Rate 12.7 to 1,270 µm per year**
  - **Log uniform**
- **Based upon testing in highly aggressive solutions**

Percentile	Corrosion Rate (µm/yr)	Type of Solution
0^{th}	12.7	10% $FeCl_3$ solution ~ 75°C
50^{th}	127.0	Concentrated HCl >100°C
100^{th}	1,270.0	Concentrated HCl >150°C

Deliquescent Solution Chemistries



LC Model Dust Deliquescent Conditions

- T>105°C liquid can only exist as a result of salt deliquescence
- LC due to deliquescence is screened out on basis of low consequence
  - *Analysis of Dust Deliquescence for FEP Screening* (ANL-EBS-MD-000074 REV 01)
- 5 questions must all be 'yes' for LC to occur

(1) Can multiple-salt deliquescent brines form at elevated temperature?

- Yes

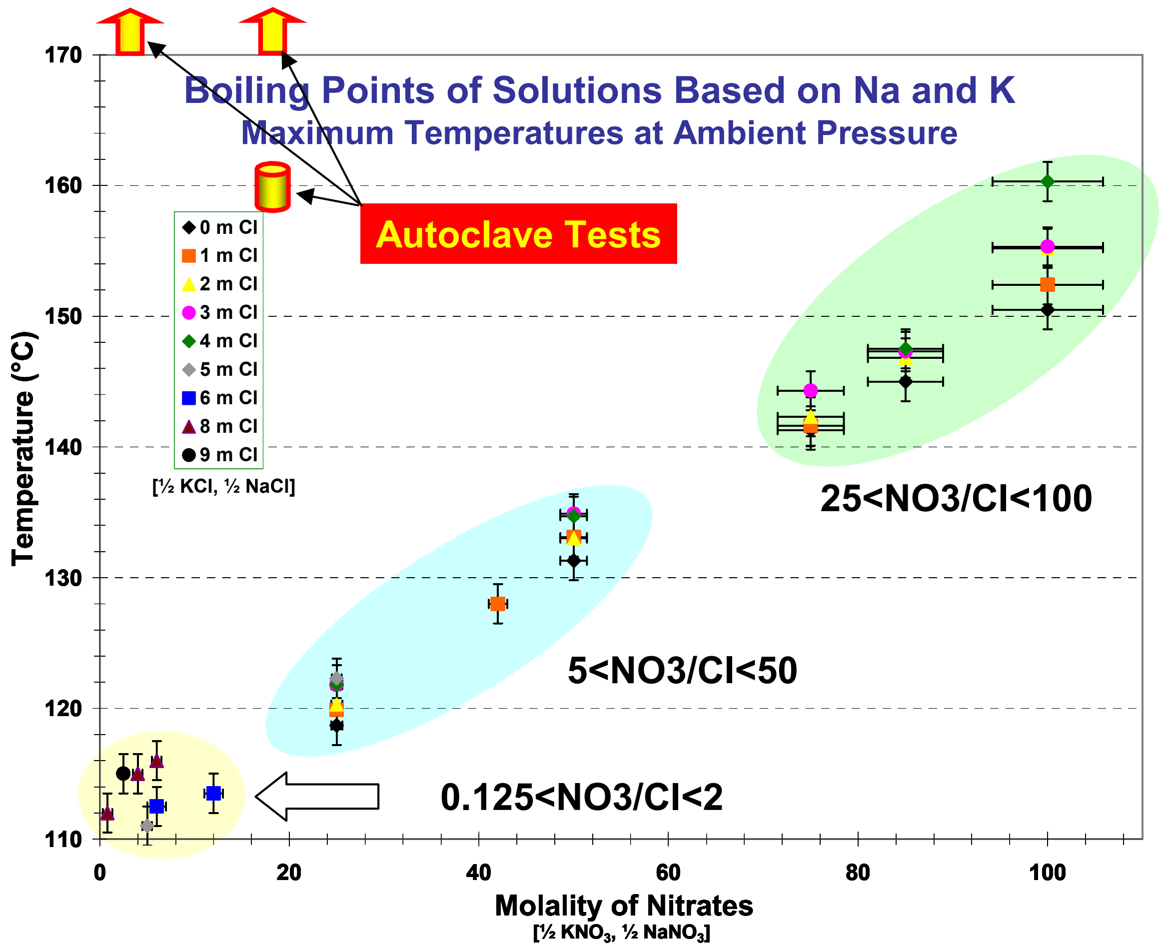
(2) If brines form at elevated temperature, will they persist?

- Sometimes

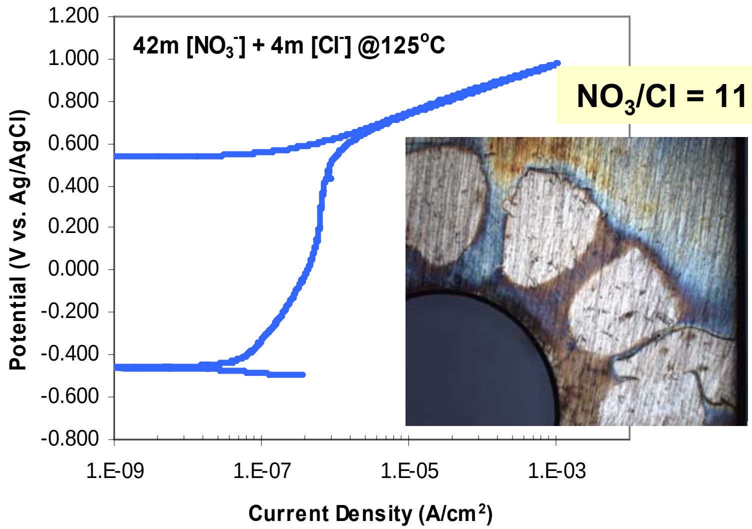
LC Dust Screening Arguments (cont.)

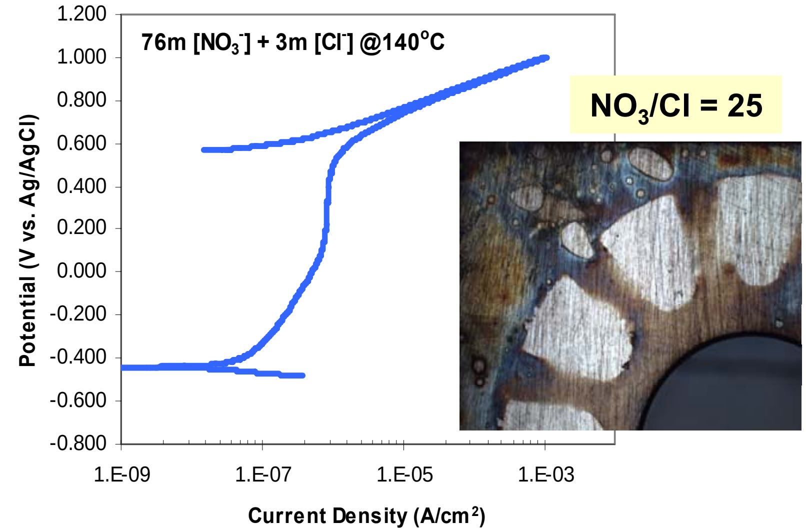
(3) *If deliquescent brines persist, will they be corrosive?*

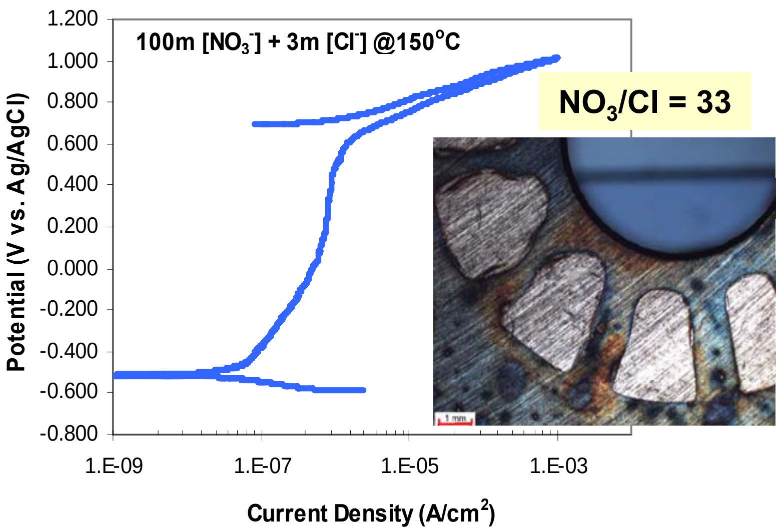
– **No** - not under repository-relevant conditions

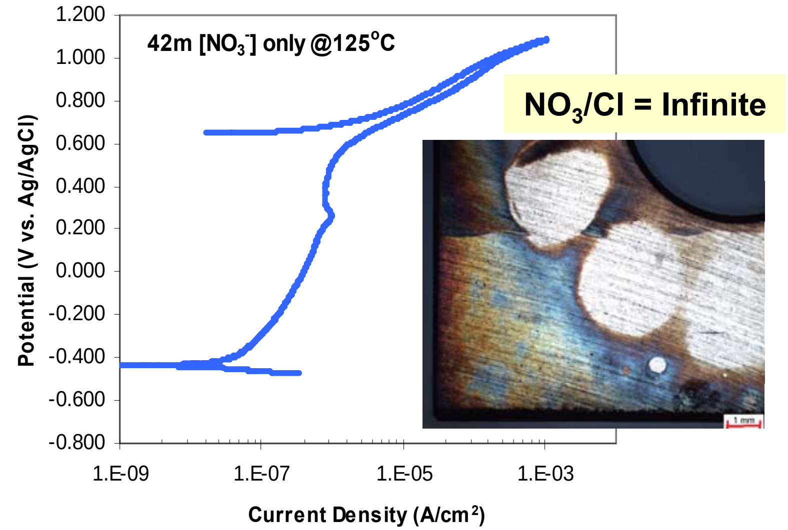


LC Dust Screening Arguments (cont.)







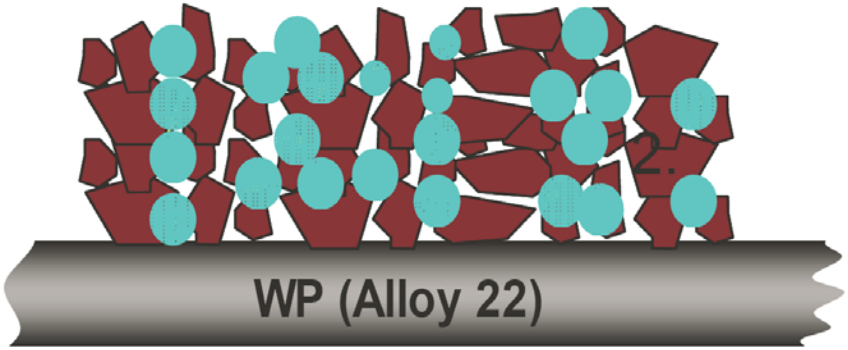


High NO_3 brines inhibit localized corrosion

LC Dust Screening Arguments (cont.)

(4) If deliquescent brines are potentially corrosive, will they initiate LC?

- **No - not under repository-relevant conditions**
- **Max brine volume ~1.8 μL/cm² at 120°C or ~18 μm thick**
- **Much of the brine will be held in dust by capillarity and not contact the waste package (WP) surface**
- **Small-scale and rapid mass transport will hinder establishment of chemical gradients**
  - **i.e., separation of cathode and anode**



Isolated droplets

LC Dust Screening Arguments (cont.)

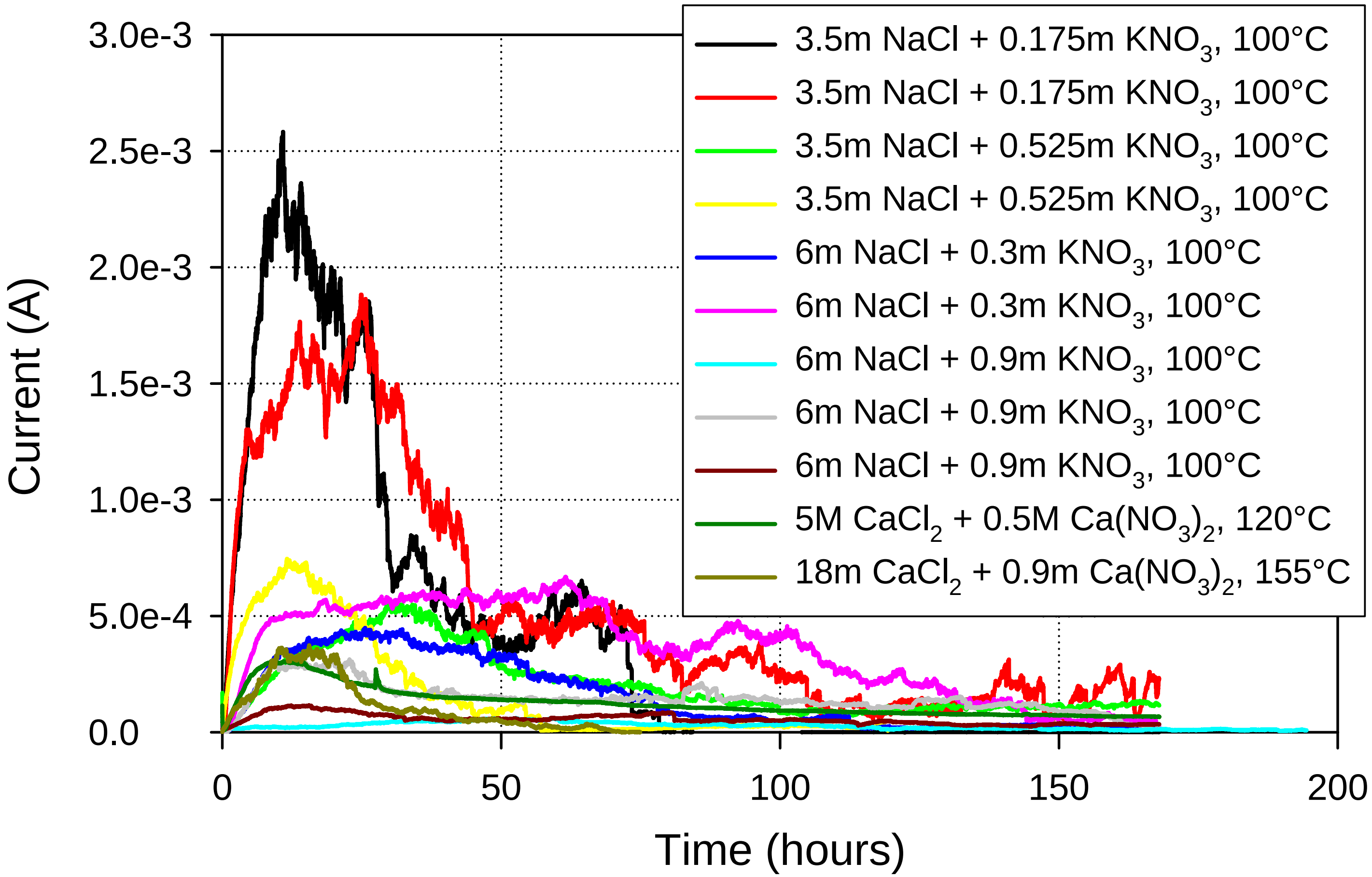
(5) Once initiated, will LC penetrate the WP outer barrier?

- No

- Crevice penetration rates follow a power law, $D = At^n$
  - He and Dunn 2006; Hunkeler and Boehni 1983; McGuire et al. 1998; EPRI 2002; Frankel 1998; Newman and Franz 1984
- Experimental results (He and Dunn 2006; Kehler and Scully 2005) indicate that the depth of attack may be limited
- Limited brine volumes and sequestration in corrosion products
  - Limits amount of Cl available for reaction
- Corrosion products can also limit the extent of crevice corrosion

LC Dust Screening Arguments (cont.)

(5) Once initiated, will LC penetrate the WP outer barrier? (cont.)



LC Dust Screening Arguments

(1) Can multiple-salt deliquescent brines form at elevated temperature? **Yes**

(2) If brines form at elevated temperature, will they persist? **Sometimes**

(3) *If deliquescent brines persist, will they be corrosive?*

- No, not under repository-relevant conditions

(4) If deliquescent brines are potentially corrosive, will they initiate LC?

- No, not under repository-relevant conditions

(5) Once initiated, will LC penetrate the WP outer barrier? **No**

- **On this basis, LC due to dust deliquescence is screened out due to low consequence**

Conclusions

- **LC model based upon experimental data is implemented for seepage conditions (T<105°C)**
  - **LC is unlikely in nitrate containing neutral brines**
- **LC due to dust deliquescence is screened out on the bases of low consequence**