U.S. Department of Energy

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

Effects of Dust Deliquescence on Localized Corrosion of the Waste Package Outer Barrier (Alloy 22)

Presented to:
Nuclear Waste Technical Review Board

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Focus

- **Can deliquescent brines support localized corrosion at high temperatures in repository environments?**
- **If initiated will localized corrosion stifle?**

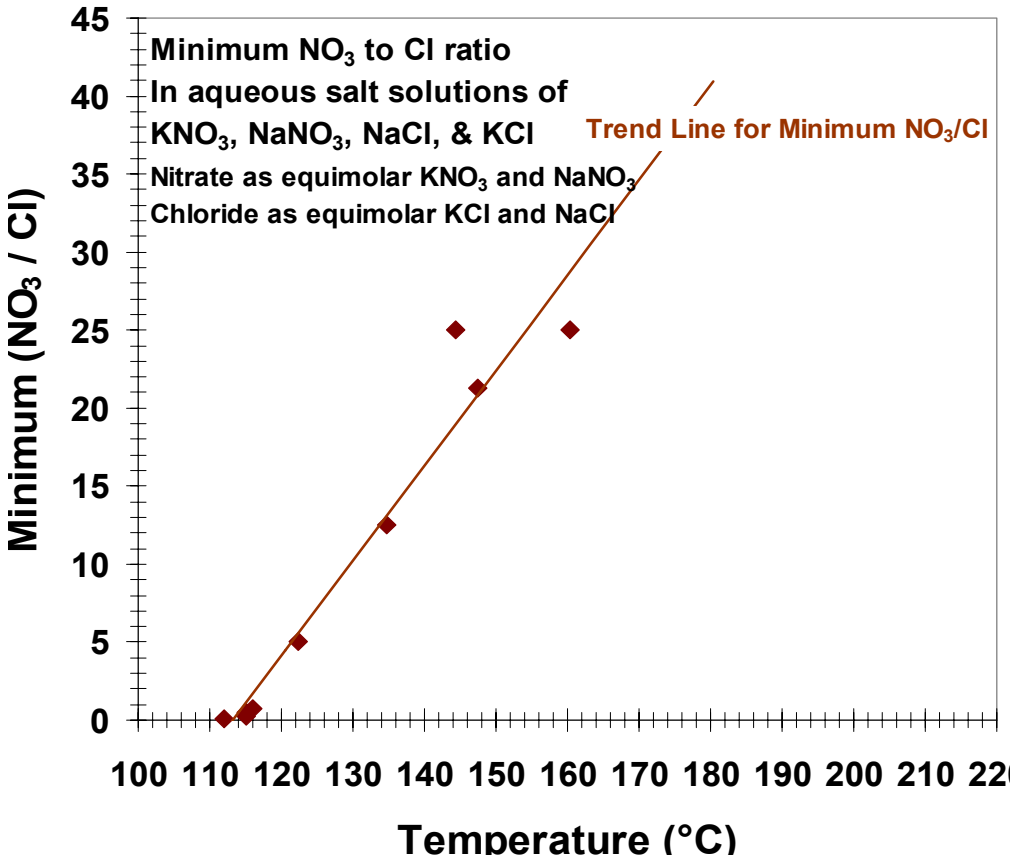
Testing Objective

- **Evaluate the bounds of Alloy 22 localized corrosion resistance**
  - **In simulated dust deliquescent environments (at 1 atm)**
  - **In environments not possible in the repository at very high temperature and pressure (using autoclaves) (> 1 atm)**
    - **Autoclaves provide high temperature and high pressure environments (~14 atm) which allow for greater [Cl^-] and lower [NO_3^-] to [Cl^-] ratios than possible in the repository at 1 atm.**
    - **Allows investigation of the effect of extended exposure time**
  - **No limitations on solution volume or amount of reactants**

- **Types of tests**
  - **Cyclic polarization and immersion tests at 1 atm and elevated temperatures**
  - **Autoclave immersion tests (liquid and vapor phase) at elevated temperatures and pressures**

Minimum NO_3^- to Cl^- Ratios Increase with Temperature

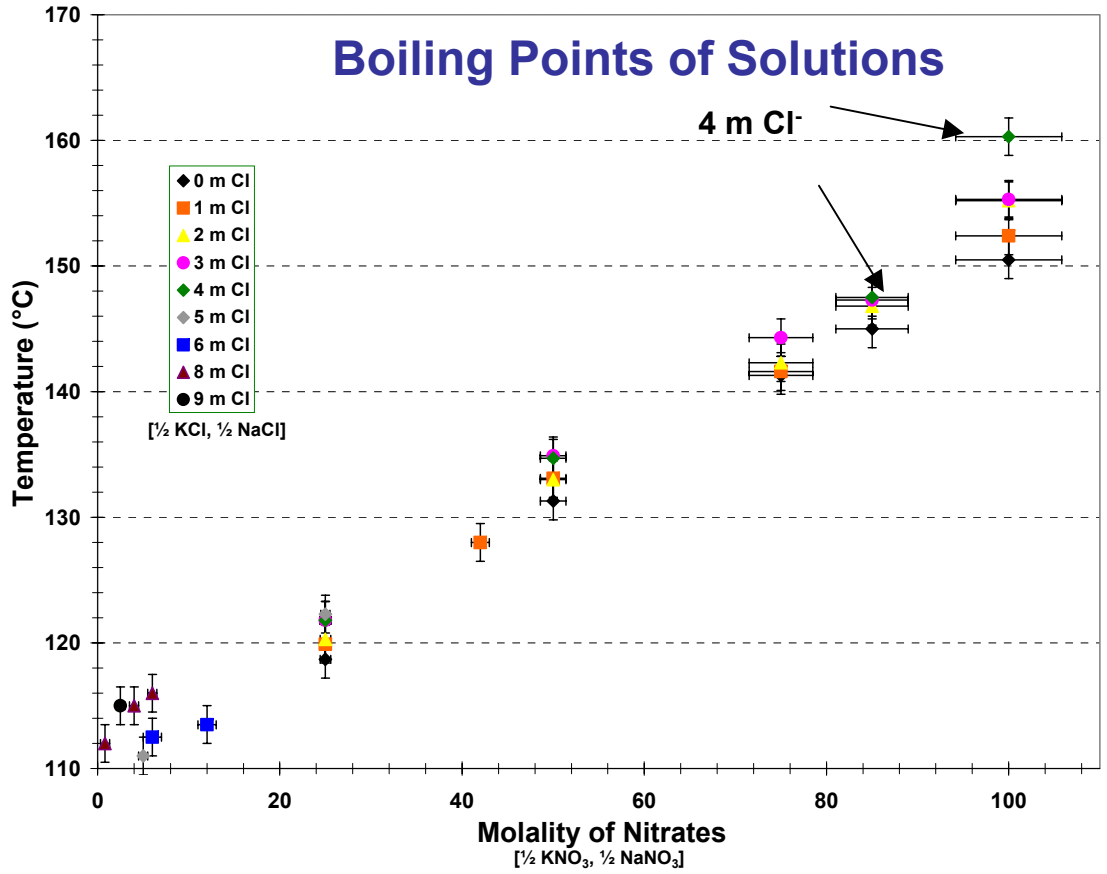
- **Minimum NO_3^-/Cl^- ratios increase with temperature**
  - **At 120°C, the minimum ratio is about 3 and increases to about 25 at 160°C**
  - **The higher the [NO_3^-] the less likely it is that LC* will occur**



*LC: Localized Corrosion

There is an Abundance of NO_3^- in Na^+, K^+, NO_3^-,Cl^- Brines at Elevated Temperature

- **Maximum solubility of Cl^- in NO_3^- brines is ~9 m at zero nitrate and decreases to ~4 m as temperature reaches 160°C**
- **Deliquescent brines are nitrate rich and chloride poor**
- **Deliquescent brines are not expected to promote LC***



*LC: Localized Corrosion

Behavior of Alloy 22 in NO_3^-/Cl^- Deliquescent Environments (Conducted at 1 Atmosphere)

Testing Conditions

Aim: To Investigate Resistance of Alloy 22 in Deliquescent Brines

- ***Conditions:***
  - **Temperature: 110 to 150°C**
  - **Chloride: 0 to 8 molal (Cl^- added as equimolal Na^+, K^+)**
  - **Nitrate/Chloride ratio: 0 to 100 (NO_3^- equimolal Na^+, K^+)**
  - **Deaerated solutions**
  - **These represent deliquescent brines**
  - **Have unlimited solution volume or amount reactants**
  - **Atmospheric pressure (bench top)**
- **OCP* Monitoring (24 hrs), Cyclic Polarization of Alloy 22 Multiple Crevice Assembly (MCA)**

*OCP: Open Circuit Potential

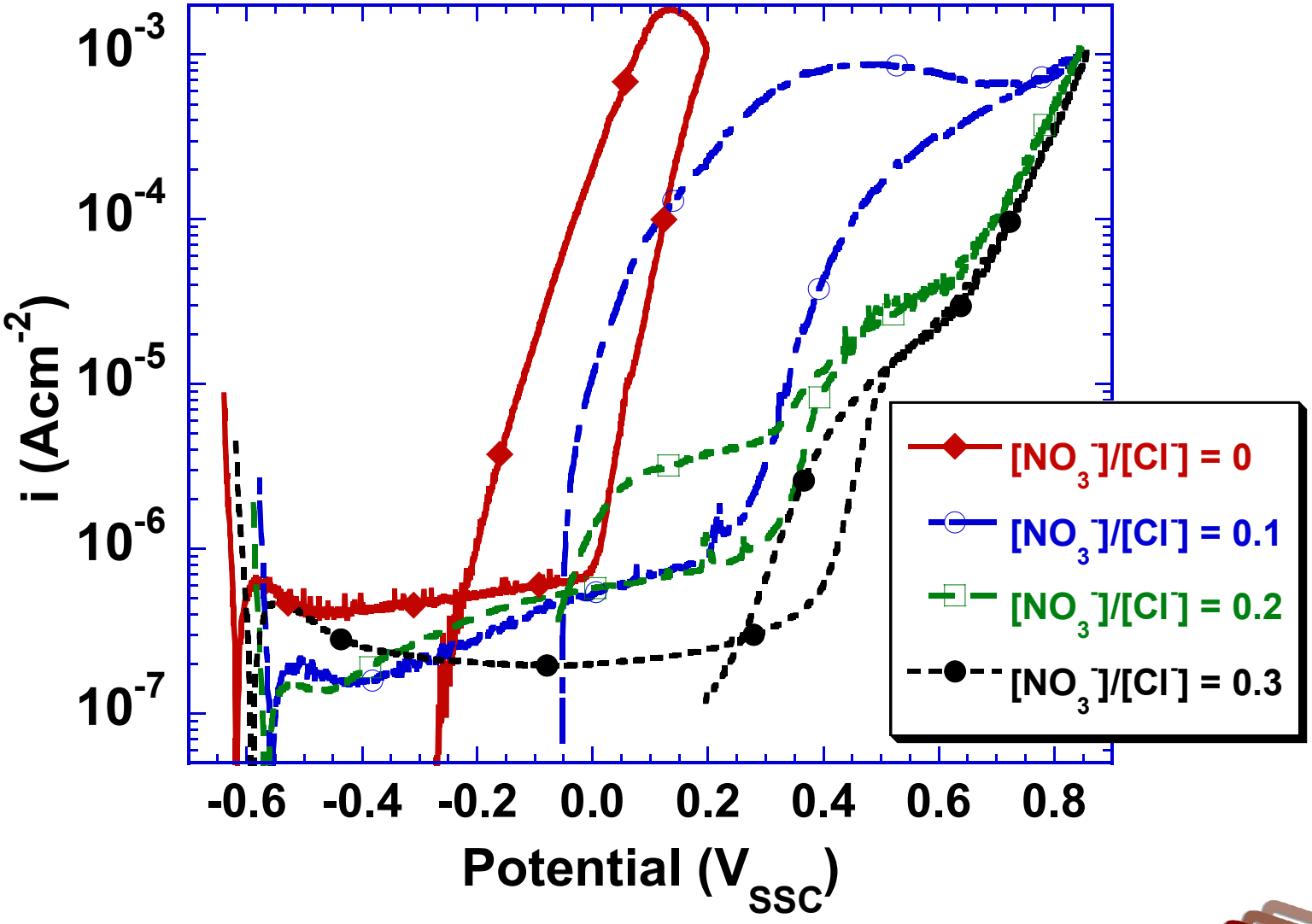
Simulated Aqueous Dust Deliquescent Environments

All salts added as equimolal concentrations of Na^+ and K^+ salts

$[Cl^-]$ (Molal)	$[NO_3^-]$ (Molal)	$[NO_3^-]/[Cl^-]$ (Ratio)	Temperature (°C)
8	0	0	110
8	0.8	0.1	110
8	1.6	0.2	110
8	2.4	0.3	110
8	4	0.5	110
6	6	1	110
4	42	10.5	110, 125
2	42	21	110, 125
1	42	42	110, 125
0	42	undefined	110, 125
3	76	25.3	140
1	72	71	140
1	100	100	150

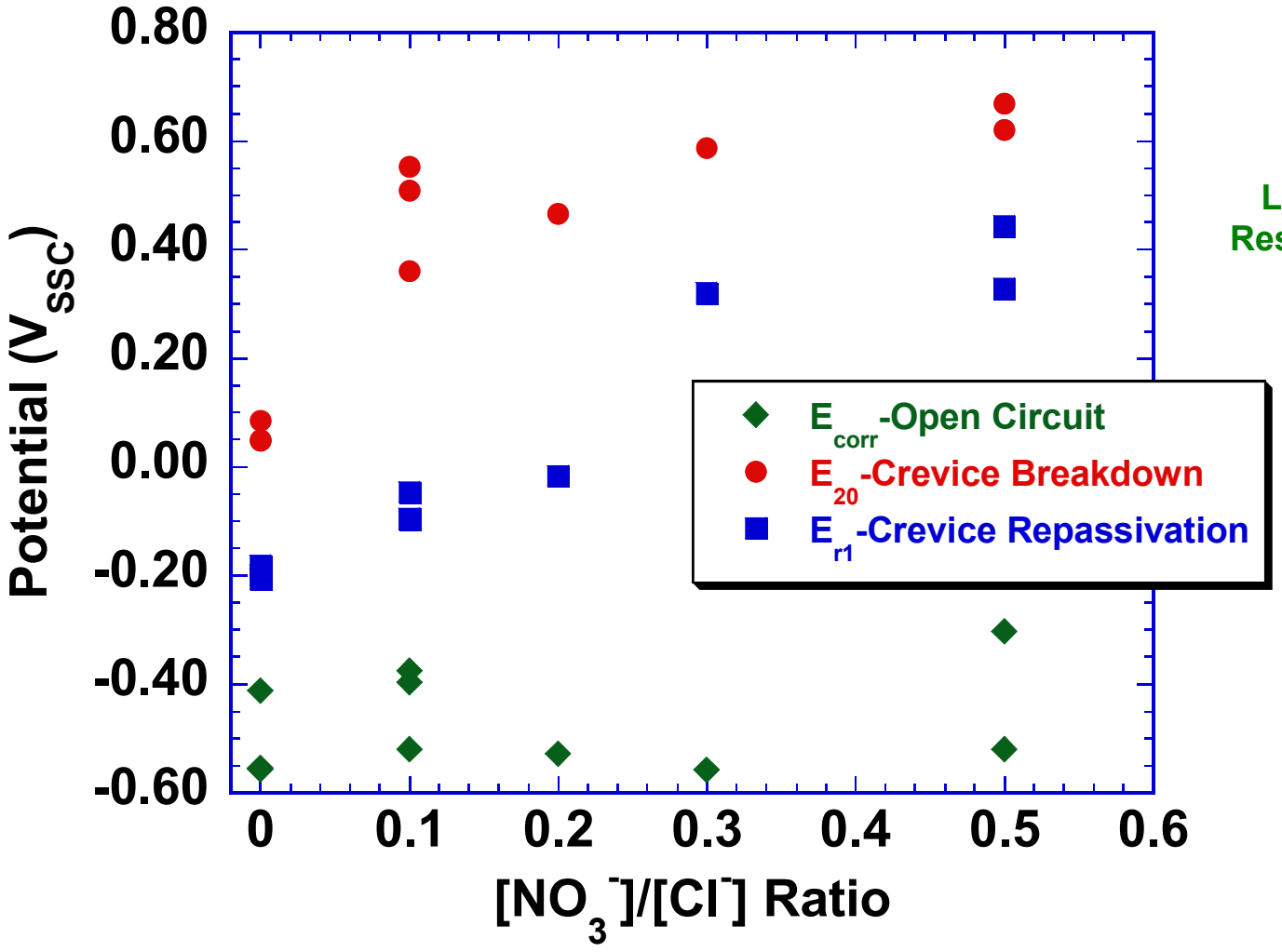
Passive Region Lengthens with NO_3^- Increase

Alloy 22 in 8.0 Molal [Cl^-] at [NO_3^-]/[Cl^-] Ratios of 0, 0.1, 0.2 and 0.3 at 110°C



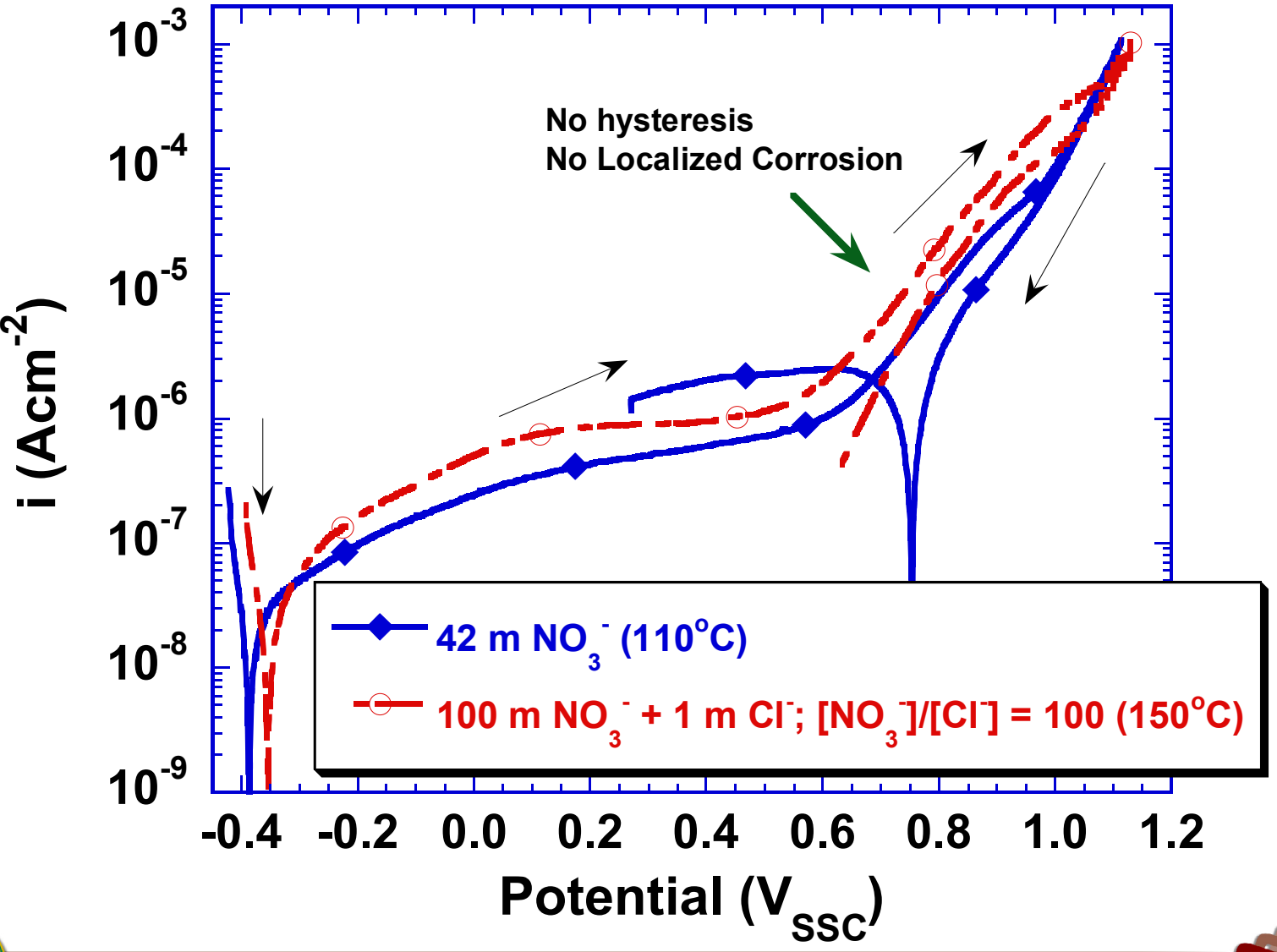
E_{20} and E_{r1} Rise with $[NO_3^-]/[Cl^-]$ Ratio at Constant Temperature in Cyclic Polarization Tests

E_{corr}, E_{20} and E_{r1} As a Function of $[NO_3^-]/[Cl^-]$ Ratio at 8.0 Molal $[Cl^-]$ at 110°C



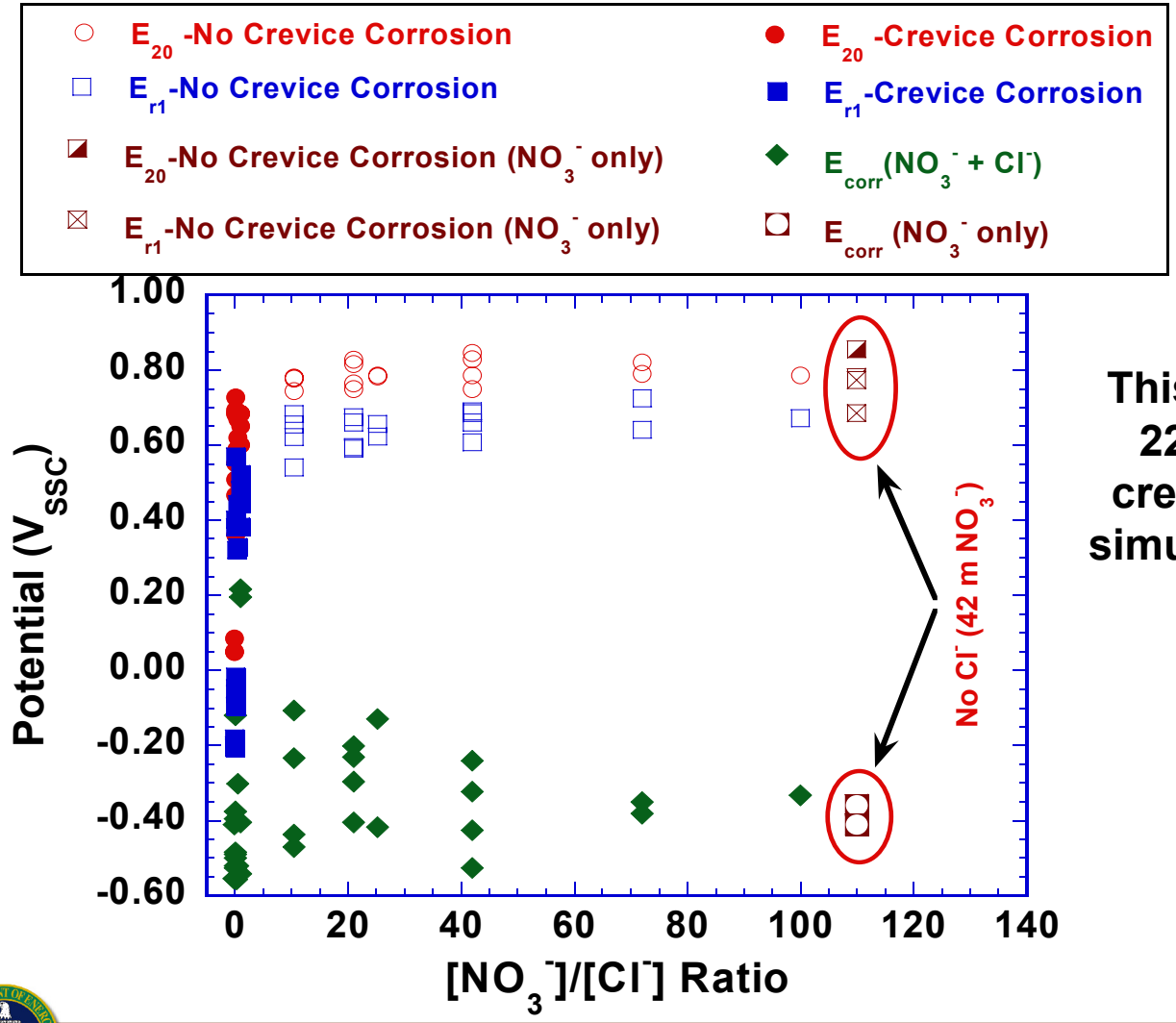
Localized Corrosion Resistance Improves as $[NO_3^-]$ Increases

Abundant Nitrate Inhibits Localized Corrosion at High Temperature



Corrosion Resistance Improves with Increase in $[NO_3^-]/[Cl^-]$ Ratio in Cyclic Polarization Tests

E_{corr}, E_{20} and E_{r1} As a Function of $[NO_3^-]/[Cl^-]$ Ratio at 0 - 8.0 Molal $[Cl^-]$ at 110 - 150°C



This data shows that Alloy 22 is highly resistant to crevice corrosion in these simulated dust deliquescent environments

Behavior of Alloy 22 in Non-Repository Environments (Autoclave) NO_3^-/Cl^- Tests

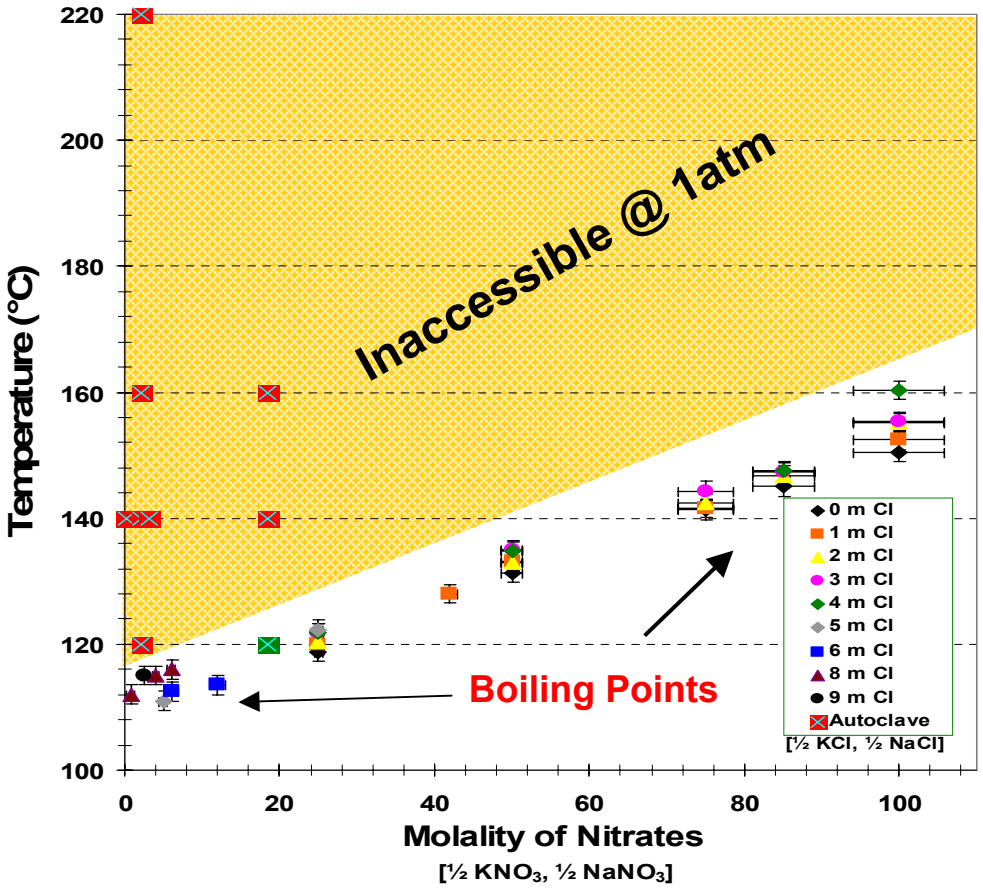
Autoclave Experimental Conditions

Temperature (°C)	NO_3^-/Cl^-	NaCl (m)	$NaNO_3$ (m)	KNO_3 (m)	Total Molality
120-220	0.05	6.4	-	0.3	6.7
120-220	0.3125	6.4	-	2.0	8.4
120-220	0.5	6.4	-	3.2	8.4
120-160	6.7	2.7	3.4	15.1	21.2

- **Aim: Investigate behavior of Alloy 22 at very high temperature**
  - ***Non-creviced*** **foil specimens immersed in liquid and vapor phase**
  - **120°C - 220°C, 8 months, NO_3^-/Cl^- of 0.05 and 6.7**
    - **Generally, these environments cannot exist except at high pressure and are not possible in the repository (autoclave pressure ~14 atm)**
    - **Environments used to probe limits of LC susceptibility of Alloy 22**
  - **Deaerated solutions**
  - **Internal pressure in autoclave approximately ~14 atm**
  - **Foils were 2 mils (~51 µm) thick (approximate thickness of human hair)**

Autoclave Experiments

- Allows for higher [Cl^-] and lower [NO_3^-]/[Cl^-] ratios than possible at 1 atm in Na/K-based electrolytes
- No limitations on solution volume or amount of reactants
- Allows investigation of the effect of extended exposure time



Autoclave Experiments Result

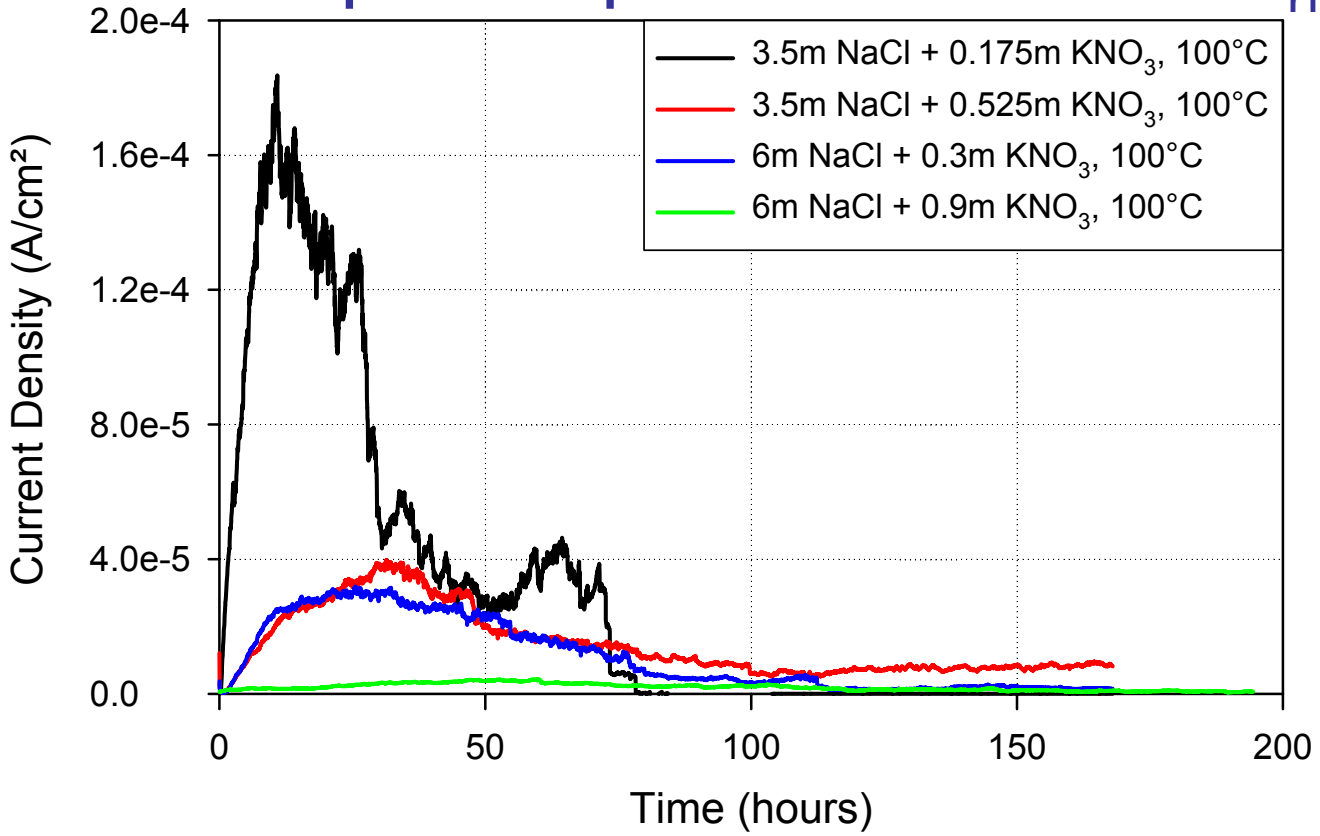
No localized corrosion observed on boldly exposed foils specimens

Stifling of Localized Corrosion in Alloy 22

There is Preliminary Evidence that Suggests Localized Corrosion will Stifle if it Occurs on Alloy 22

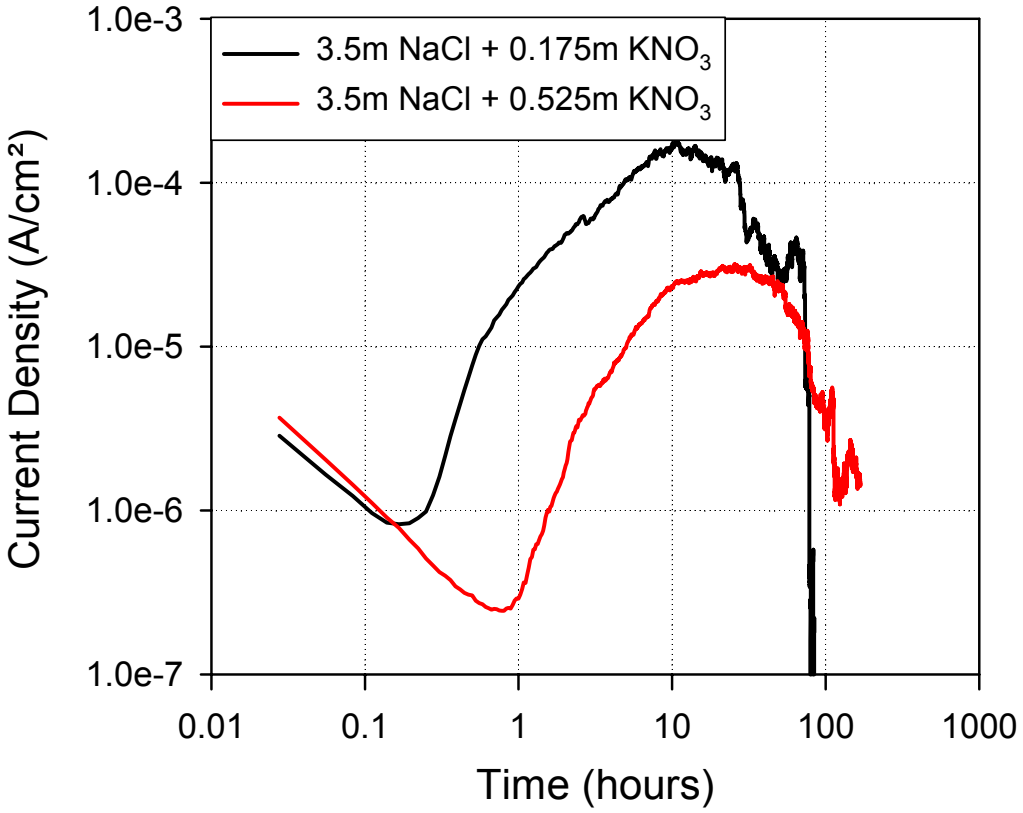
Current density as a function of time

Creviced specimens polarized ~100 mV above E_{r1}



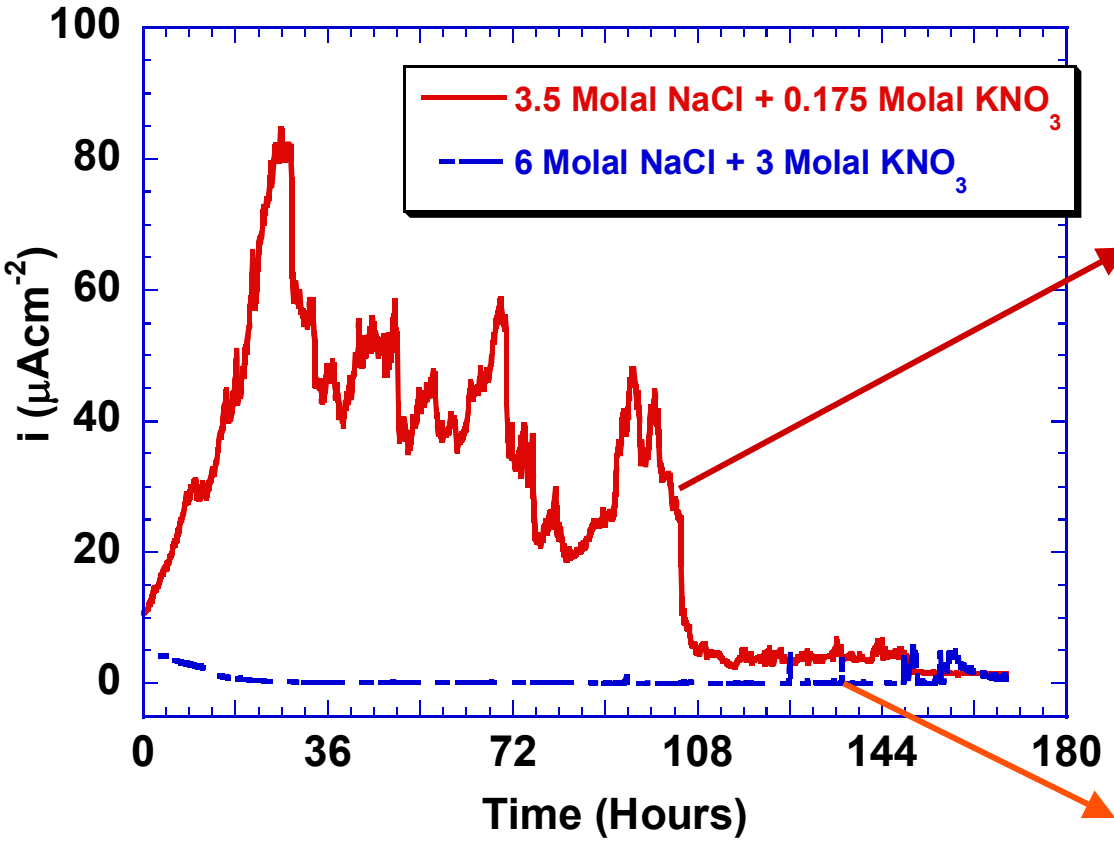
- **Even with no cathodic or reactant limitation, crevice corrosion initiated, propagated, then stifled in short-term tests**

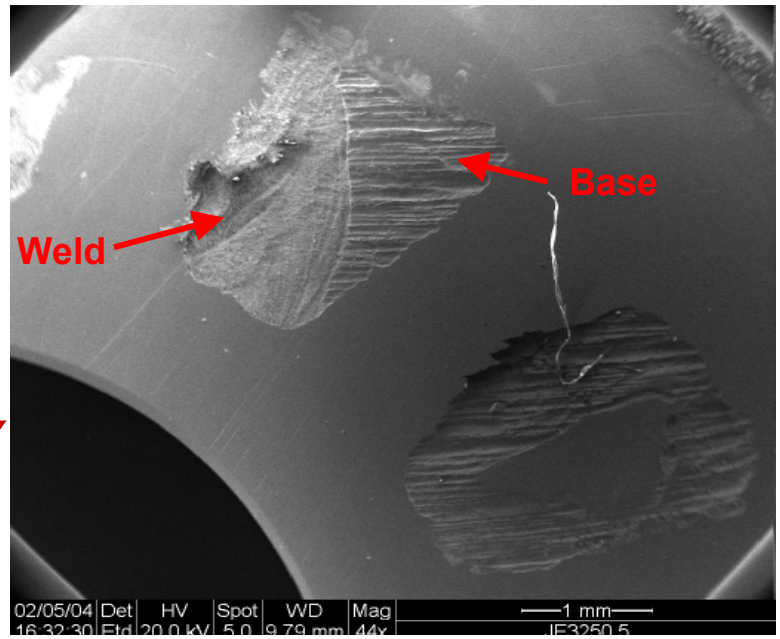
Nitrate Enhances Stifling of Localized Corrosion

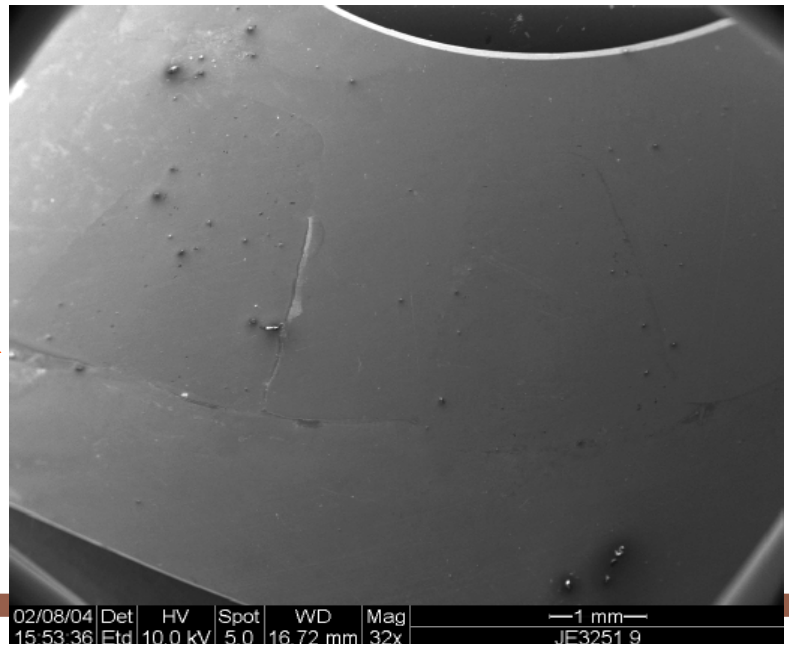


- **3.5 m NaCl at 100°C**
- **NO_3^-/Cl^- = 0.05 and 0.15**
- **+100 mV SSC**
- **Increased NO_3^-/Cl^- ratio delays initiation and decreases current density of localized corrosion**

Enhancement of Stifling by Nitrate is Apparent in the Amount of Dissolution Observed







Summary

- Deliquescent brines are nitrate rich and chloride poor
- Nitrate solubility increases and chloride solubility decreases as temperature increases in Na^+/K^+ based deliquescent brines
- Nitrate-rich brines do not support localized corrosion
- There is evidence that stifling will occur if localized corrosion initiates on Alloy 22