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EPRI's Analysis of the Potential for Localized Corrosion of Alloy 22 Waste Packages in Multi-salt Deliquescent Brines

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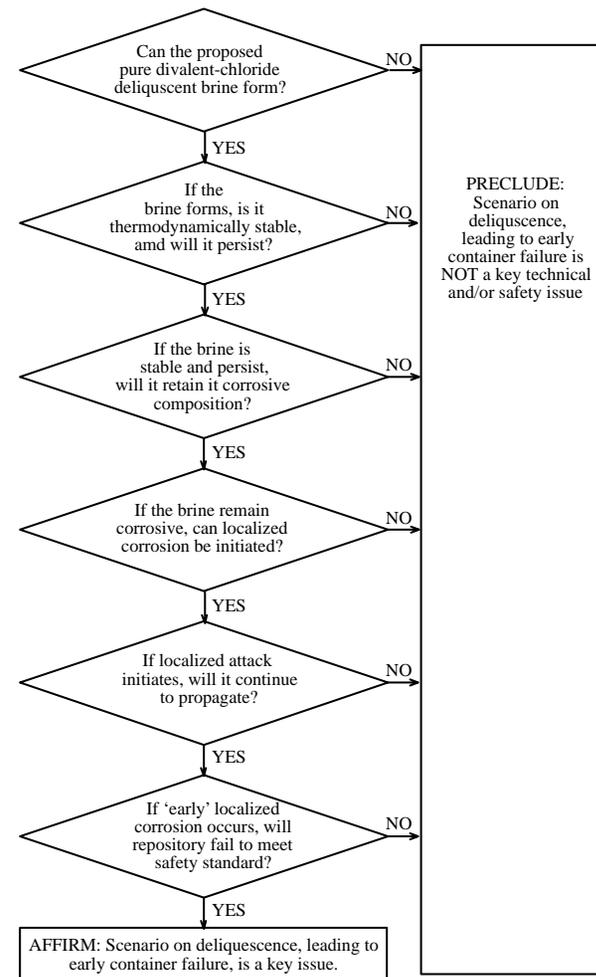
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EPRI's Analysis of Localized Corrosion in Multi-salt Deliquescent Systems

- EPRI's approach
 - Independent analysis based on DOE, CNWRA, and other available data
 - Best-estimate of waste package corrosion behavior
- Decision Tree approach
 - Extended 2004 treatment for divalent cation deliquescent brines to multi-salt systems
 - Brine formation and persistence
 - Localized corrosion consequences
 - Initiation
 - Propagation/stifling
 - Description of the expected evolution of corrosion behavior in repository
 - Various postulated multi-salt systems
 - Effects of degassing

EPRI's Decision Tree Approach

- Multiple lines of argument
 - Formation and stability of the environment
 - If environment forms and is stable, will LC result?
 - What are the consequences for WP lifetimes?
- Approach applied to single, divalent cation brines in 2004
- Extended here to possible multi-salt deliquescent brines



Will Multi-salt Deliquescent Brines Form?

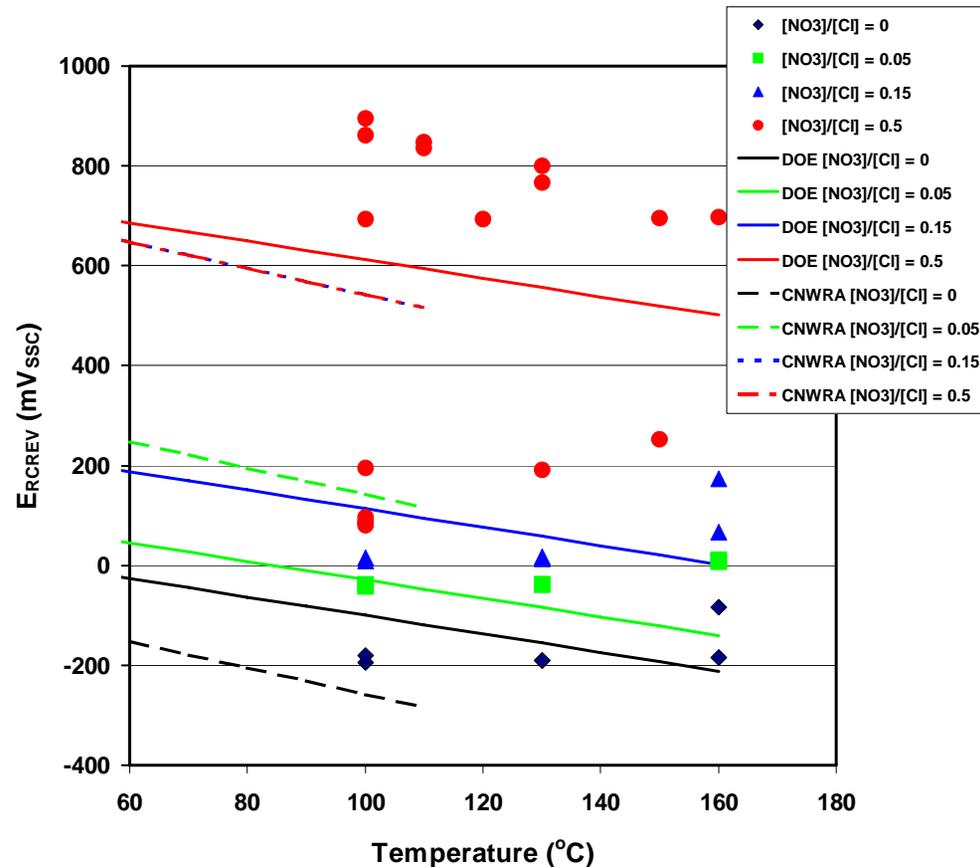
- Precursor salts inferred from EQ3/6 geochemical modelling
 - DOE identify three possible salt “assemblages”
 - A: $\text{NaCl} + \text{KNO}_3$
 - B: $\text{NaCl} + \text{KNO}_3 + \text{NaNO}_3$
 - C: $\text{NaCl} + \text{KNO}_3 + \text{NaNO}_3 + \text{Ca}(\text{NO}_3)_2$
 - EPRI modeling concurs with DOE modeling, only if brines are in equilibrium with only CO_2 in gas phase
 - If there is equilibrium with $\text{HCl}(\text{g})$ and $\text{HNO}_3(\text{g})$, in addition to CO_2 , then EPRI predict formation of carbonate-, sulfate-based assemblages
 - These nitrate- and chloride-free assemblages would deliquesce at much lower temperatures ($\sim 105^\circ\text{C}$) than the nitrate-based assemblages considered by DOE

If high-temperature deliquescent brines do form, are they stable?

- Acid degassing will lead to loss of HCl and HNO₃ from deliquescent brines if they are formed
- Volatile gaseous species will be removed from the surface by diffusion and advection and will be consumed by reaction with the overwhelming mass of minerals in the drift walls
- Acid degassing favoured by neutral-acidic pH
 - pH-buffering by calcite and mineral phases present in dust expected to promote continued acid degassing
- Acid degassing will tend to lower corrosivity of the deliquescent solution by:
 - Reducing the overall salinity of the brine
 - Preferential degassing of HCl over HNO₃
 - Resulting in dry-out of the brines as residual mineral assemblages will only deliquesce at lower temperature

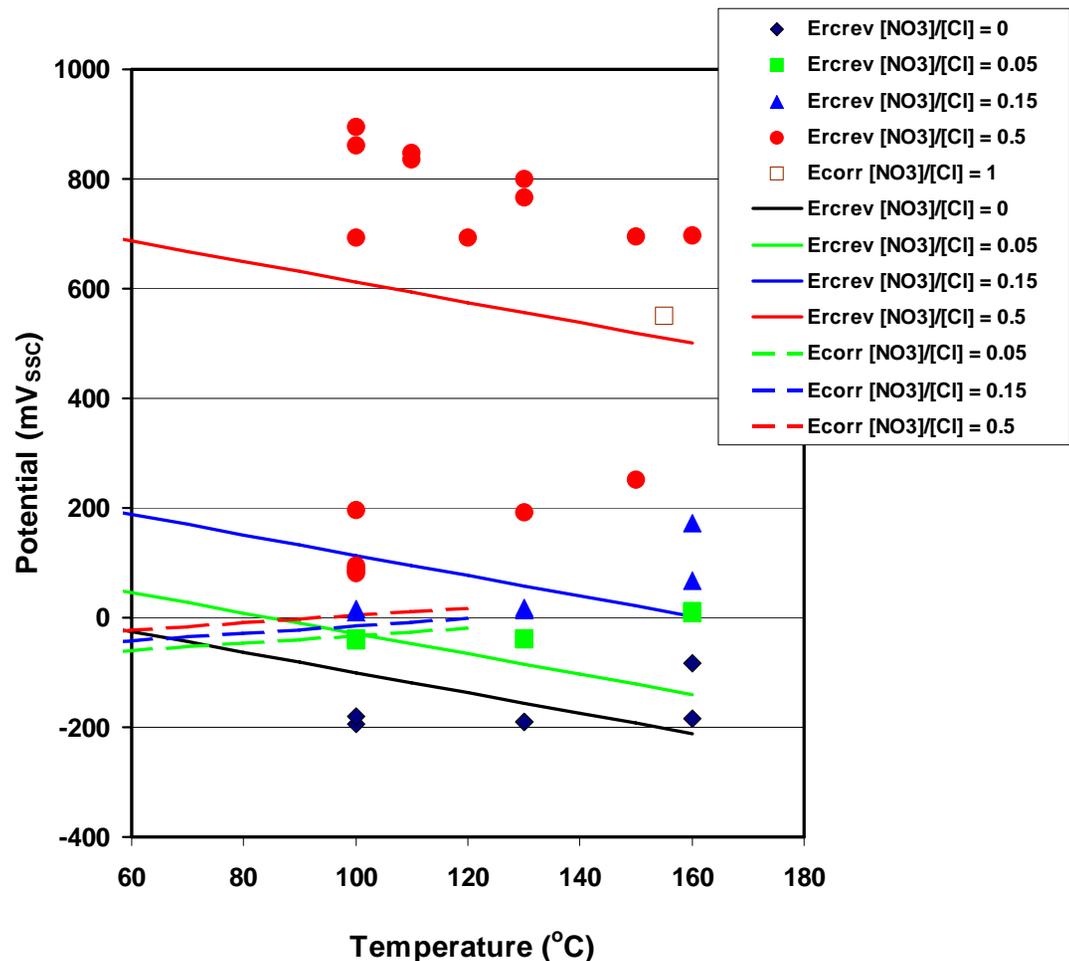
Would the proposed deliquescent brines be corrosive?

- Let us assume that nitrate-based, “high-temperature” deliquescent brines are formed
- Nitrate has been shown to inhibit initiation of LC over a wide range of temperatures
 - DOE experimental data in concentrated Cl:NO₃ brines up to 160°C (Ilevbare et al., PVP2006)
 - DOE E_{rcrev} model fitted to data up to 160°C (ANL-EBS-MD-000003, Oct 2004)
 - CNWRA E_{rcrev} model fitted to data up to 105°C (Dunn et al, 2005 MRS)
 - Model predictions for 20 m Cl, pH7
- All data sets give consistent results
 - CNWRA model slightly more conservative



Would the proposed deliquescent brines be corrosive?

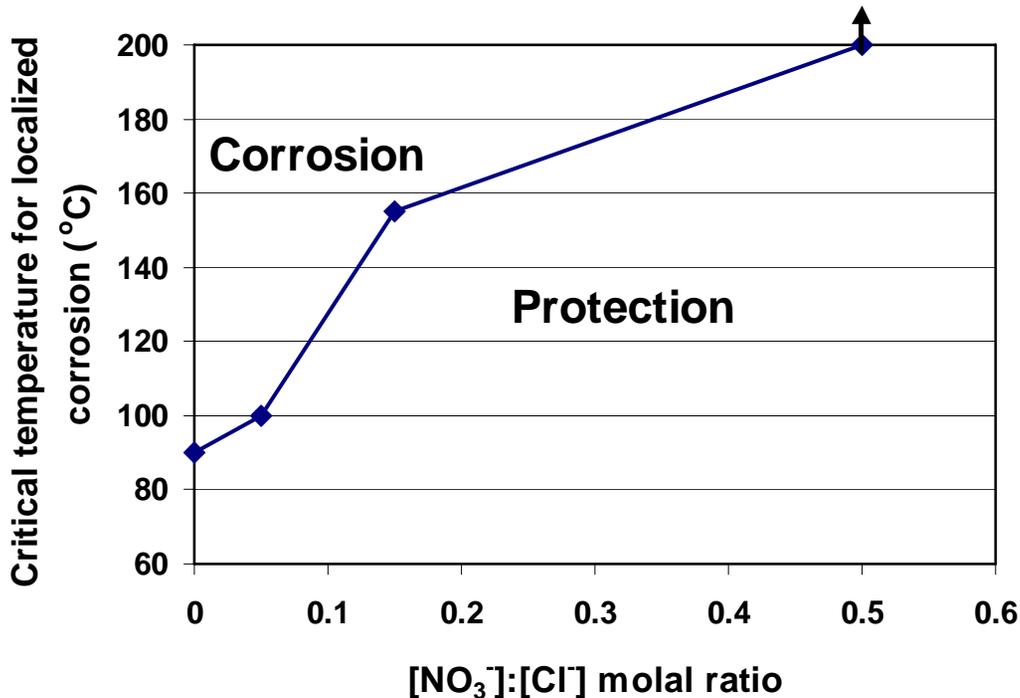
- Comparison of DOE E_{rcrev} and E_{corr} data
 - Includes recent experimental data in simulated proposed deliquescent brines at high temperature
- Comparison can be used to define a critical temperature for the initiation of LC based on electrochemical measurements
 - Defined as the temperature at which $E_{corr} > E_{rcrev}$
 - Function of $[NO_3^-]:[Cl^-]$



Would the proposed deliquescent brines be corrosive?

- Nitrate should be an effective inhibitor of LC at elevated temperature
 - Nitrate reduction results in increase in pH
$$\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$$
 - Nitrate reduction on surfaces external to crevice slower than inside occluded region because of higher pH
 - NO_3^- reduction inside crevice will lead to increase in pH, reducing rate of anodic dissolution
 - NO_3^- concentration will be maintained in crevice by electromigration (in contrast to diffusion only for uncharged species, such as O_2)
 - Crevice solution will likely enrich in NO_3^- as transference number (t) of NO_3^- exceeds that of Cl^-
 - Consequently, NO_3^- should continue to be an effective LC inhibitor at elevated temperature and existing LC model should be applicable at higher temperatures ($>160^\circ\text{C}$)

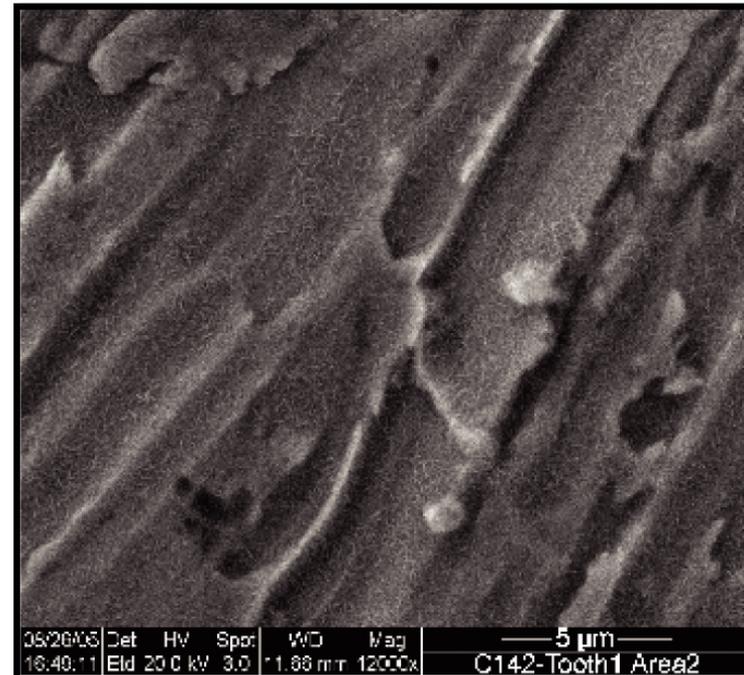
Would the proposed deliquescent brines be corrosive?



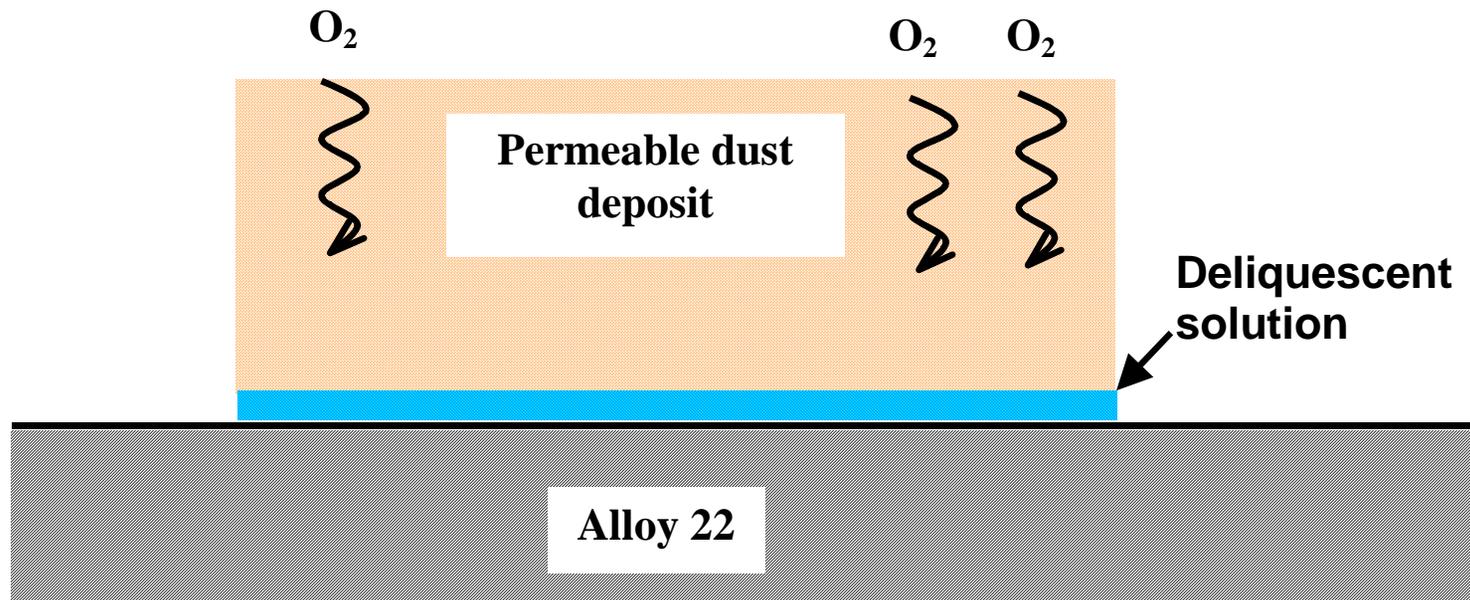
- Even if deliquescent brines form at high temperature, NO₃⁻ effective inhibitor, especially at [NO₃⁻]:[Cl⁻] > 0.5
- Will be used later to assess time-dependent corrosion behavior of WP

Would the proposed deliquescent brines be corrosive?

- Recent LLNL autoclave tests (Dixit et al, UCRL-TR-217393, 2006) report LC in high-temperature concentrated NO_3^- solutions
- However, evidence presented shows minor dissolution in crevice regions (a few microns at most)
- Closed system, meaning that vapor-phase samples subjected to unrealistic acidified condensate
- Creviced samples added to test after a prior period of general corrosion testing
 - Could environment have been unrealistically oxidizing due to presence of dissolved Cr(VI)/Mo(IV)?
- Minor apparent dissolution is consistent with an inhibiting effect of NO_3^-

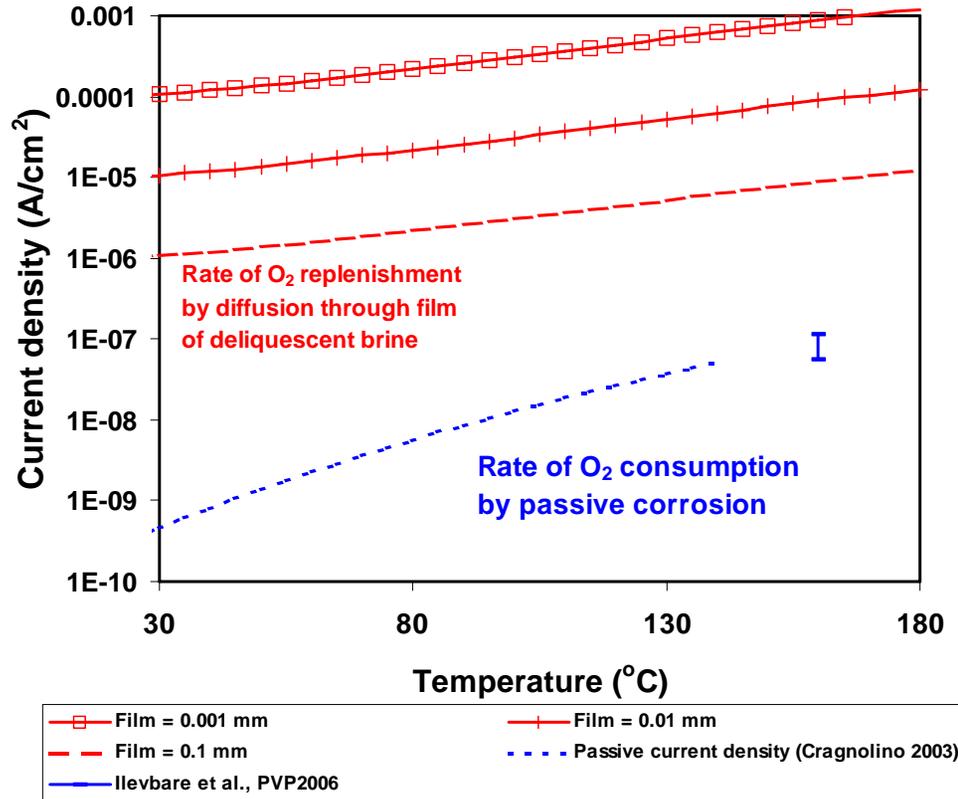


Will a dust deposit act as an effective crevice former?



- 2004 conceptual model of permeable dust deposit
- Can permeable dust deposit create a differential [O₂] cell?
 - Compare the rate of O₂ consumption on the WP surface with its rate of replenishment
 - Updated for proposed high-temperature deliquescent brines

Will a dust deposit act as an effective crevice former?



- Rate of O_2 replenishment is 2-3 orders of magnitude higher than rate of supply by diffusion through deliquescent film
- Differential $[O_2]$ cell necessary for LC initiation will not be created under a dust deposit

If LC does initiate, will it continue to propagate?

- Strong experimental evidence in support of stifling
 - Stifling has long been included in EPRI model based on analogy with behavior of other alloys

$$D = kt^n$$

Range of n values 0.1-0.5

- DOE data from anodically polarized specimens (Analysis of Dust Deliquescence FEP Screening, ANL-EBS-MD-000074, August 2005)

$$D = A + kt^n$$

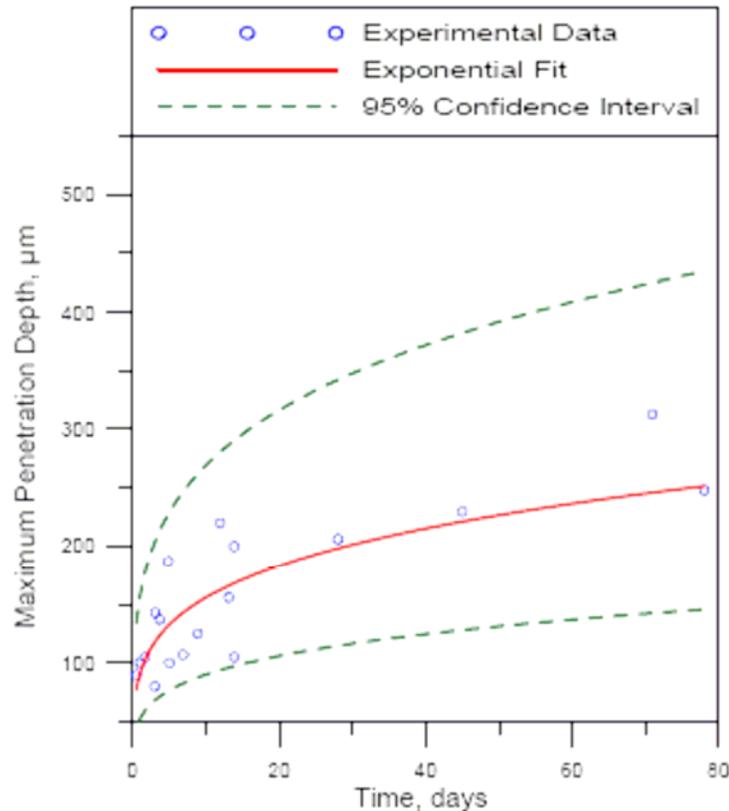
Average n = 0.44 (range 0.09-0.69)

- CNWRA data from MCA samples in 5 M NaCl + 2×10^{-4} M CuCl_2 at 95°C (Pan et al., IHLRWM 2006)

$$D = kt^n$$

Average n = 0.23

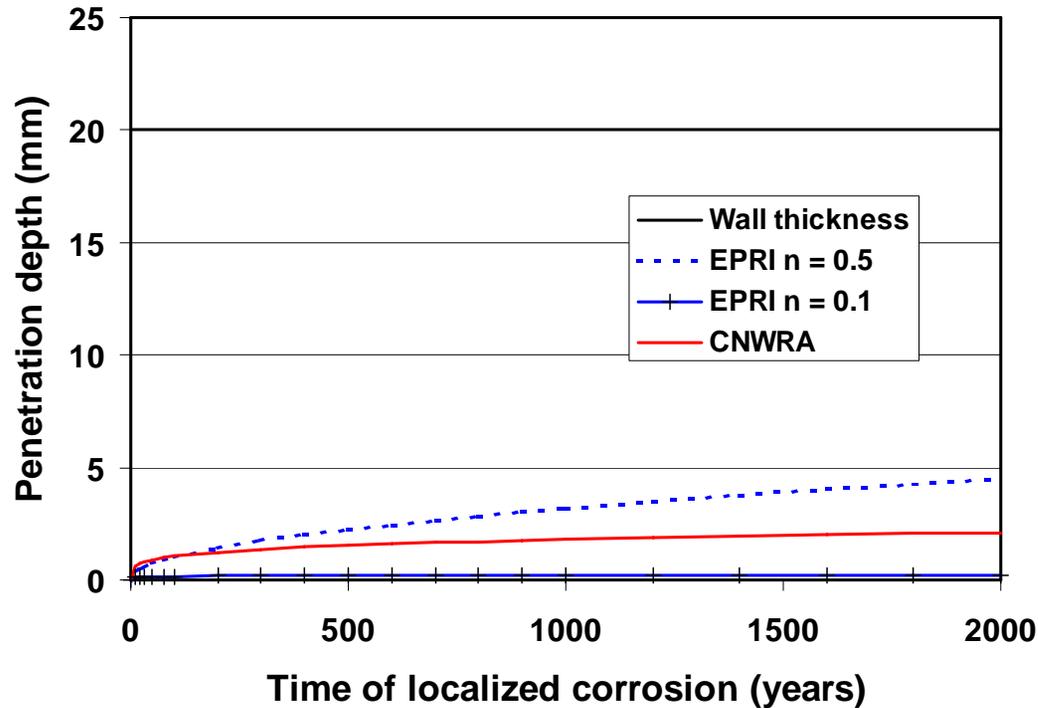
If LC does initiate, will it continue to propagate?



Y.-M. Pan et al, IHLRWM 2006

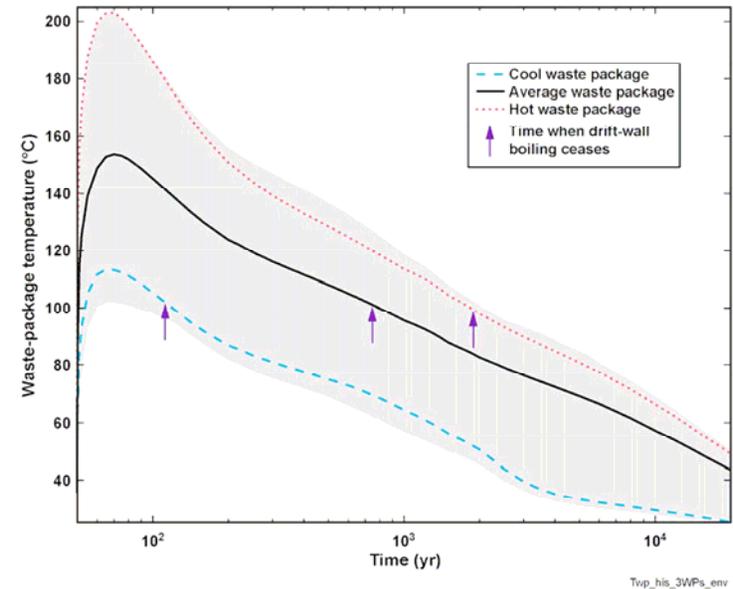
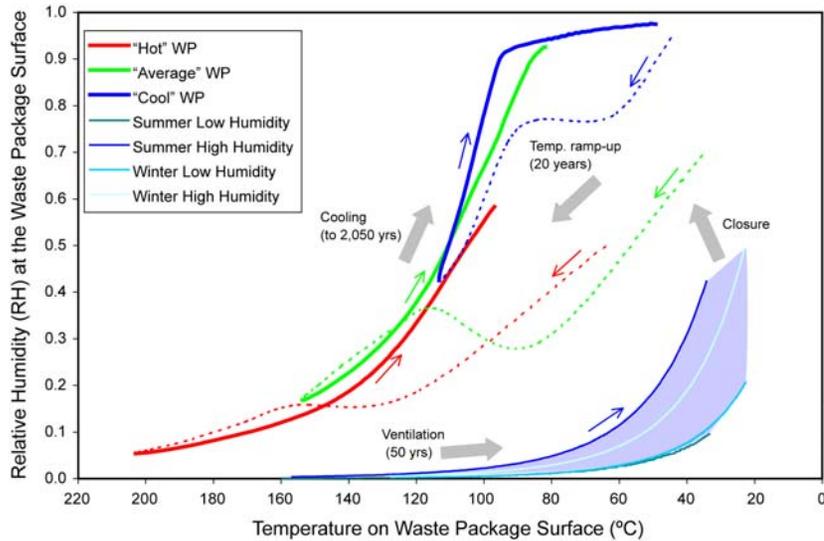
- Mechanism of stifling still unclear
 - iR drop
 - Mass-transport effects
 - Loss of critical crevice chemistry by catalysis of H^+ reduction
 - Negative shift in E_{CORR} upon initiation of LC
- Additional stifling mechanisms for WP
 - Time-dependent evolution of environment
 - pH buffering by minerals in dust
- Regardless, there is very strong evidence that stifling will limit the extent of LC penetration should it initiate

If LC does propagate, will WP failure result?



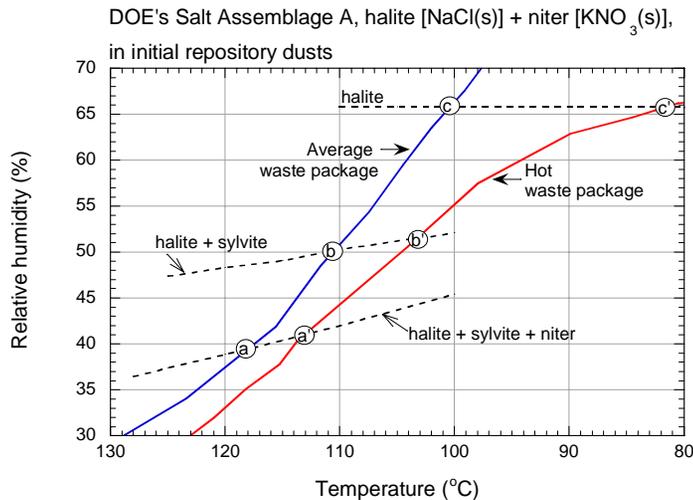
- LC stifling will limit propagation long before penetration of the WP occurs.

Expected evolution of corrosion behavior of WP surface under dust deposits



- Consider formation and consequences of deliquescent brines in t-T-composition space rather than in T-%RH space
- For illustrative purposes, assume that the DOE Assemblages A, B, and C exist

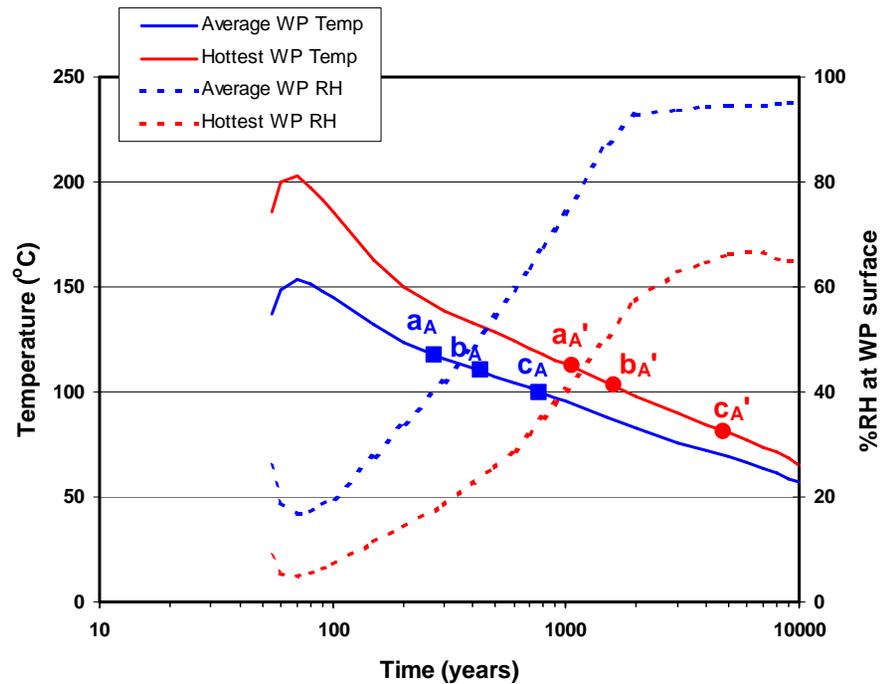
Evolution of conditions for Assemblage A (no acid degassing assumed)



| Brine ^a | <i>t</i> ^b (yrs) | <i>T</i> (°C) | <i>rh</i> (%) | pH | Na ⁺ | K ⁺ | Cl ⁻ | NO ₃ ⁻ | NO ₃ ⁻ /Cl ⁻ |
|------------------------------|-----------------------------|---------------|---------------|------|-----------------|----------------|-----------------|------------------------------|---|
| <i>Average waste package</i> | | | | | | | | | |
| <i>a</i> | 200-300 | 117.9 | 39.5 | 5.32 | 6.14 | 15.10 | 2.83 | 18.43 | 6.5 |
| <i>b</i> | 400-500 | 110.5 | 50.0 | 5.23 | 4.81 | 13.70 | 4.77 | 13.75 | 2.9 |
| <i>c</i> | 700-800 | 100.3 | 65.8 | 5.34 | 5.87 | 5.87 | 5.87 | 5.87 | 1.0 |
| <i>Hot waste package</i> | | | | | | | | | |
| <i>a'</i> | ≈ 1000 | 113.0 | 41.0 | 5.28 | 6.06 | 14.84 | 2.96 | 17.94 | 6.1 |
| <i>b'</i> | 1500-2000 | 103.5 | 51.3 | 5.18 | 4.88 | 13.26 | 4.81 | 13.33 | 2.8 |
| <i>c'</i> | 4000-5000 | 81.5 | 65.8 | 5.27 | 5.79 | 5.79 | 5.79 | 5.79 | 1.0 |

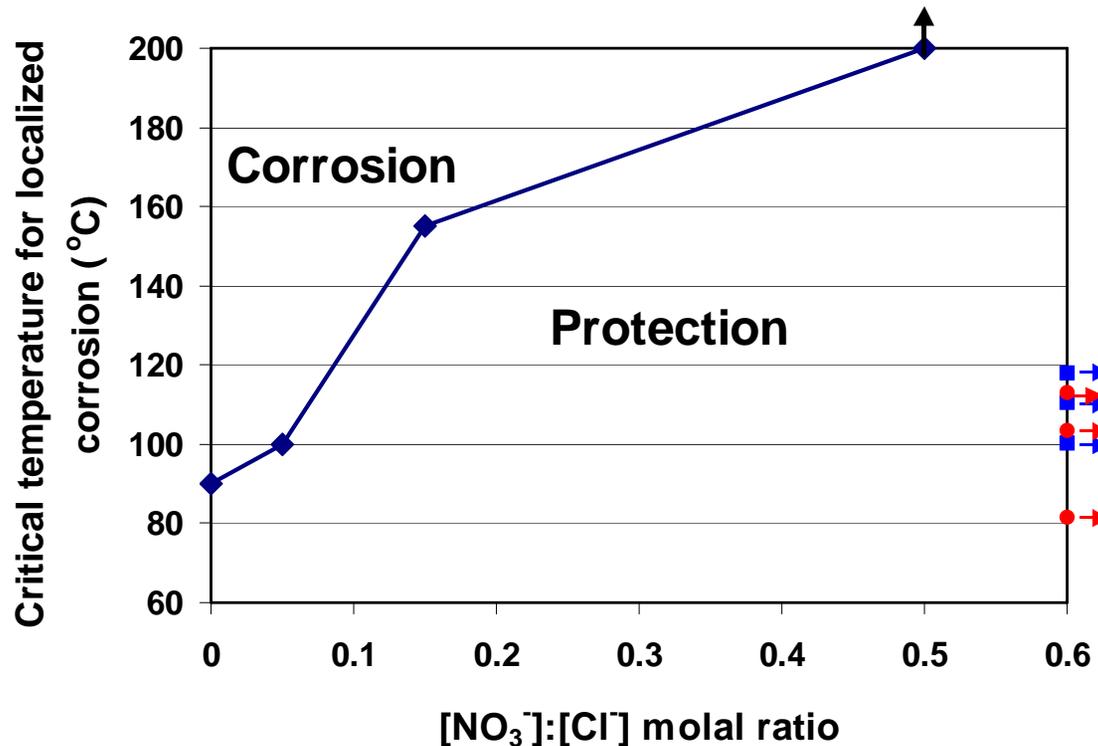
- For the 2-salt system
 - Deliquescence first predicted at temperatures of 113°C and 118°C for hot and average WP, respectively (points a and a')
 - If there is no degassing, surface remains wet, but brine solution becomes more dilute
 - Composition of brine and nature of solids continues to evolve as %RH increases (points b/b' and c/c')
- Assumes
 - An assemblage of NaCl and KNO₃ is present initially
 - No acid degassing

Evolution of conditions for Assemblage A (no acid degassing assumed)



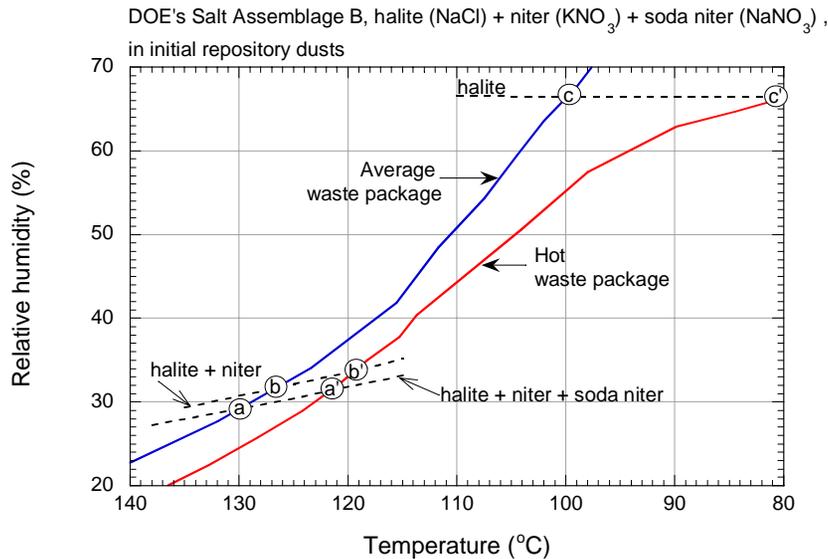
| Brine | t (yrs) | T (°C) | rh (%) | pH | Cl ⁻ | NO ₃ ⁻ | NO ₃ ⁻ /Cl ⁻ | E_{CORR} (mV _{SSC}) | E_{rcrev} (mV _{SSC}) |
|------------------------------|-----------|----------|----------|------|-----------------|------------------------------|---|------------------------------------|-------------------------------------|
| <i>Average waste package</i> | | | | | | | | | |
| <i>a</i> | 271 | 117.9 | 39.5 | 5.32 | 2.83 | 18.43 | 6.5 | 299 | >1000 |
| <i>b</i> | 429 | 110.5 | 50.0 | 5.23 | 4.77 | 13.75 | 2.9 | 272 | >1000 |
| <i>c</i> | 759 | 100.3 | 65.8 | 5.34 | 5.87 | 5.87 | 1.0 | 233 | 865 |
| <i>Hot waste package</i> | | | | | | | | | |
| <i>a'</i> | 1050 | 113.0 | 41.0 | 5.28 | 2.96 | 17.94 | 6.1 | 296 | >1000 |
| <i>b'</i> | 1600 | 103.5 | 51.3 | 5.18 | 4.81 | 13.33 | 2.8 | 270 | >1000 |
| <i>c'</i> | 4700 | 81.5 | 65.8 | 5.27 | 5.79 | 5.79 | 1.0 | 225 | 920 |

Evolution of conditions for Assemblage A (no acid degassing assumed)



- Assemblage A would not result in localized corrosion even in the event of no acid degassing

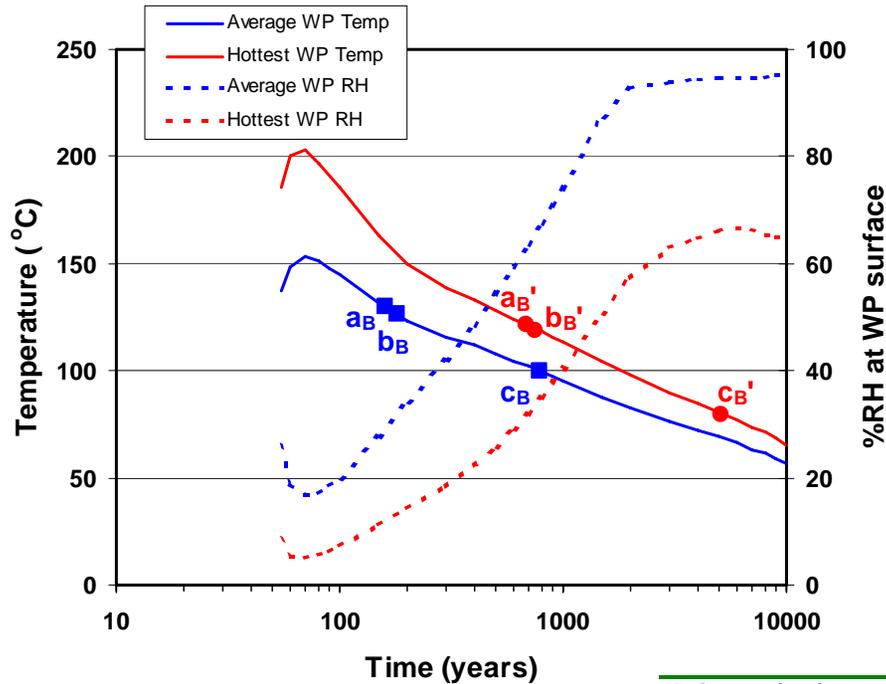
Evolution of conditions for Assemblage B (no acid degassing assumed)



| Brine | t (yrs) | T (°C) | rh (%) | pH | Na ⁺ | K ⁺ | Cl ⁻ | NO ₃ ⁻ | NO ₃ /Cl ⁻ |
|------------------------------|-----------|--------|--------|------|-----------------|----------------|-----------------|------------------------------|----------------------------------|
| <i>Average waste package</i> | | | | | | | | | |
| a | 150-200 | 130.0 | 29.2 | 5.42 | 15.55 | 12.21 | 0.52 | 27.23 | 52.4 |
| b | 150-200 | 126.8 | 30.1 | 5.39 | 15.50 | 12.06 | 0.53 | 27.03 | 51.0 |
| c | 700-800 | 99.8 | 66.5 | 5.36 | 7.95 | 3.97 | 3.97 | 7.95 | 2.0 |
| <i>Hot waste package</i> | | | | | | | | | |
| a' | 600-700 | 121.6 | 31.4 | 5.35 | 15.44 | 11.81 | 0.55 | 26.71 | 48.6 |
| b' | 700-800 | 119.3 | 33.8 | 5.34 | 13.12 | 12.36 | 0.76 | 24.73 | 32.5 |
| c' | 5000-6000 | 80.0 | 66.5 | 5.29 | 7.87 | 3.94 | 3.94 | 7.87 | 2.0 |

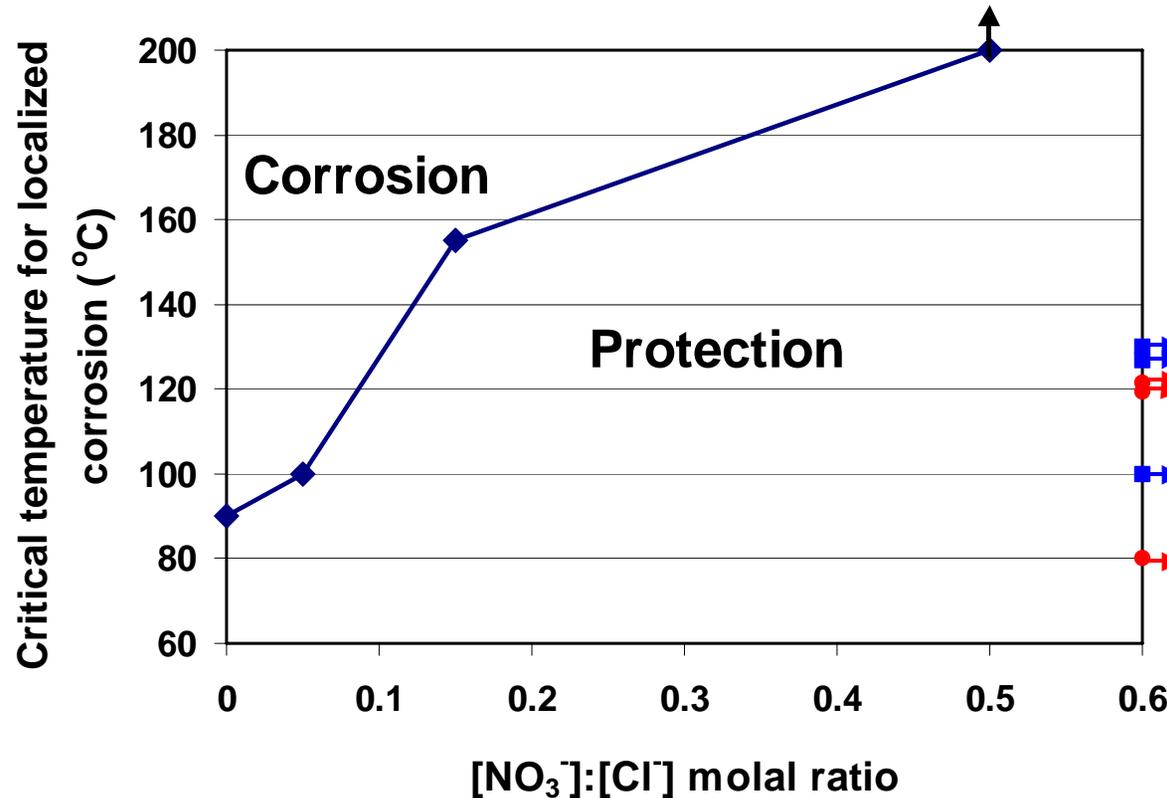
- For the 3-salt system
 - Deliquescence first predicted at temperatures of 122°C and 130°C for hot and average WP, respectively (points a and a')
 - If there is no degassing, surface remains wet, but brine solution becomes more dilute
 - Composition of brine and nature of solids continues to evolve as %RH increases (points b/b' and c/c')
- Assumes
 - An assemblage of NaCl, KNO₃, and NaNO₃ is present initially
 - No acid degassing

Evolution of conditions for Assemblage B (no acid degassing assumed)



| Brine | <i>t</i> (yrs) | <i>T</i> (°C) | <i>rh</i> (%) | pH | Cl ⁻ | NO ₃ ⁻ | NO ₃ ⁻ /Cl ⁻ | <i>E</i> _{CORR} (mV _{SSC}) | <i>E</i> _{rcrev} (mV _{SSC}) |
|------------------------------|----------------|---------------|---------------|------|-----------------|------------------------------|---|---|--|
| <i>Average waste package</i> | | | | | | | | | |
| <i>a</i> | 160 | 130.0 | 29.2 | 5.42 | 0.52 | 27.23 | 52.4 | 352 | >1000 |
| <i>b</i> | 180 | 126.8 | 30.1 | 5.39 | 0.53 | 27.03 | 51.0 | 351 | >1000 |
| <i>c</i> | 780 | 99.8 | 66.5 | 5.36 | 3.97 | 7.95 | 2.0 | 257 | >1000 |
| <i>Hot waste package</i> | | | | | | | | | |
| <i>a'</i> | 680 | 121.6 | 31.4 | 5.35 | 0.55 | 26.71 | 48.6 | 349 | >1000 |
| <i>b'</i> | 750 | 119.3 | 33.8 | 5.34 | 0.76 | 24.73 | 32.5 | 340 | >1000 |
| <i>c'</i> | 5100 | 80.0 | 66.5 | 5.29 | 3.94 | 7.87 | 2.0 | 248 | >1000 |

Evolution of conditions for Assemblage B (no acid degassing assumed)

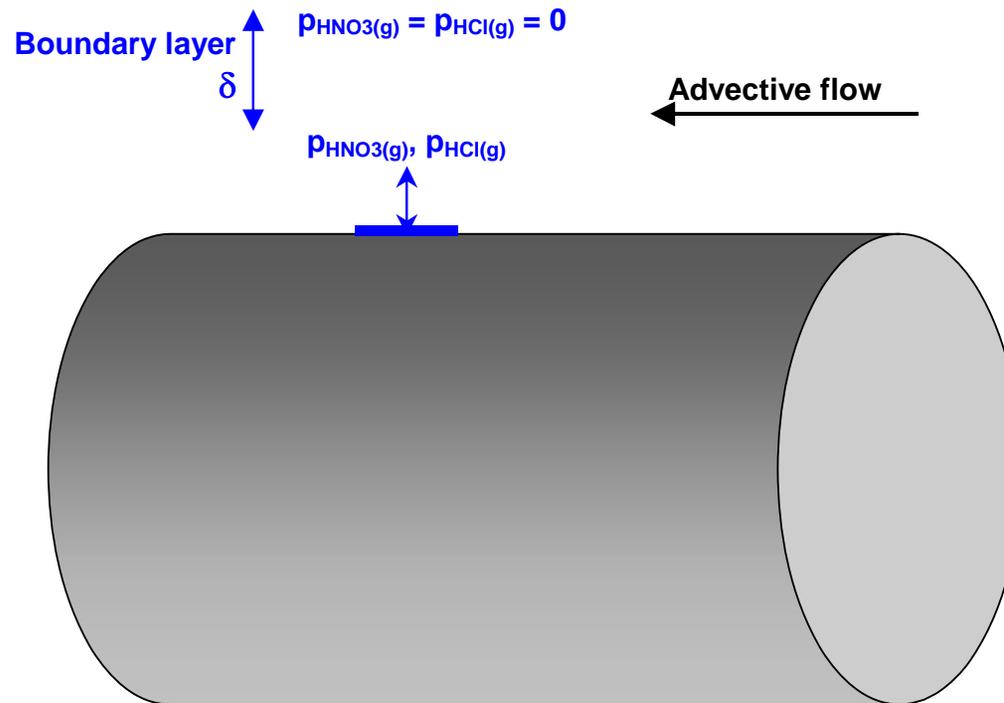


- Assemblage B would not result in localized corrosion even in the event of no acid degassing

Effects of acid degassing on Assemblage B

- Simple degassing model
 - Assume:
 - Gas phase HCl and HNO₃ above deliquescent brine is in equilibrium with dissolved species
 - Acid gas removed from surface by transport across a stagnant boundary layer
 - Rate-determining step is gas-phase diffusion across boundary layer
 - Thickness of boundary layer depends on rate of advective flow in drift
 - Low flow, thick boundary layer
 - High flow, thin boundary layer
 - Acid gas removed rapidly by reaction with minerals in drift walls or by dilution in drift atmosphere
 - $c = 0$ boundary condition

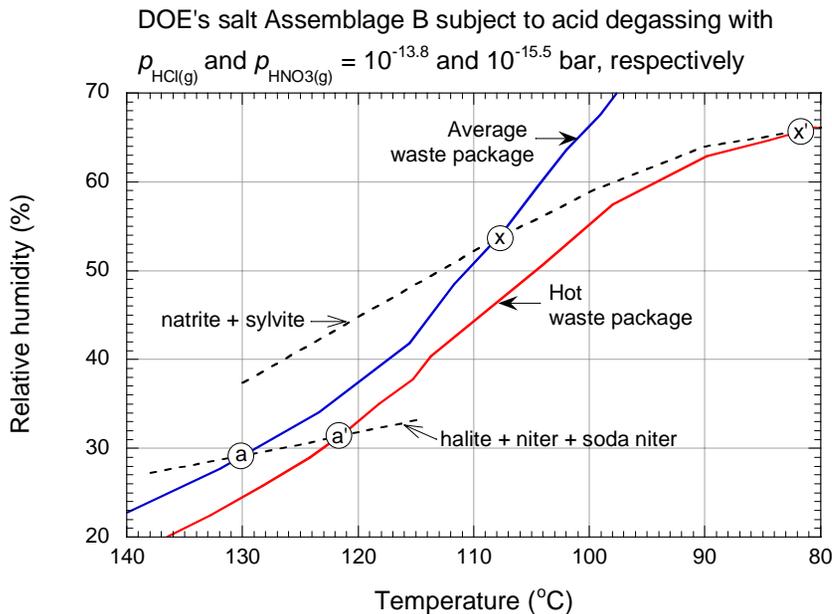
Simple conceptual acid degassing model



Estimated degassing period

- Flux of acid gas $\sim 5 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$
 - $p_{\text{HCl}}, p_{\text{HNO}_3} \sim 10^{-8} \text{ bar}$ at 160-220°C (Dixit et al., UCRL-TR-217393, 2006)
 - $D_{\text{HCl}, \text{HNO}_3} \sim 0.2 \text{ cm}^2 \text{ s}^{-1}$ (CRC Handbook)
 - $\delta \sim 1 \text{ mm}$ for high flow conditions
- Quantity of acid in brine solution $\sim 10^{-6} \text{ mol cm}^{-2}$
 - 1 μm -thick brine solution
 - 10 $\text{mol dm}^{-3} \text{ Cl}^-/\text{NO}_3^-$
- Time for complete degassing ~ 24 days
- Most important parameters
 - Rate of advective flow/boundary layer thickness
 - $p_{\text{HCl}}, p_{\text{HNO}_3}$
 - Assume brine pH is maintained near neutral by buffering by calcite and mineral phases in dust
- Based on this simple model, brine solutions could be de-stabilized by acid degassing relatively quickly

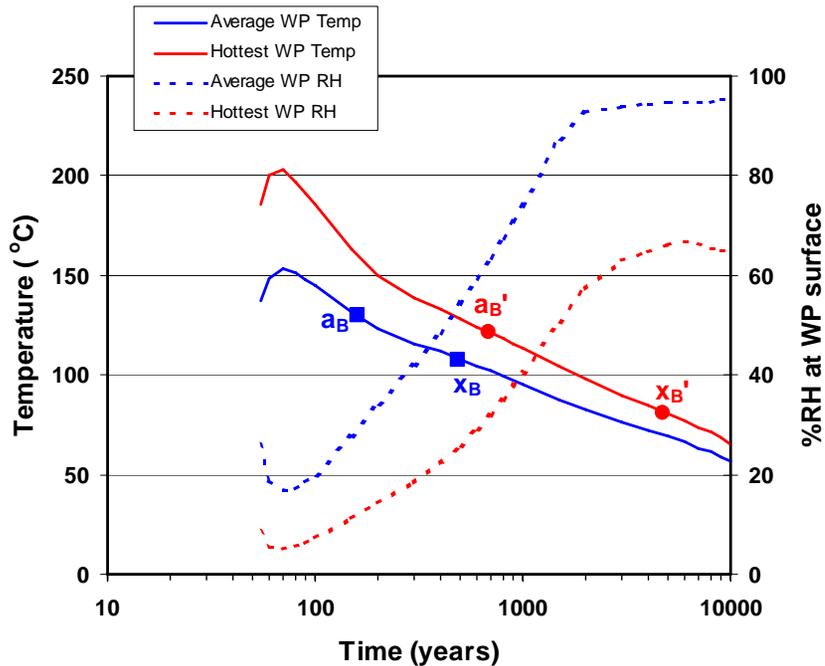
Evolution of conditions for Assemblage B (with acid degassing)



| Brine | <i>t</i> (yrs) | <i>T</i> (°C) | <i>rh</i> (%) | pH | Na ⁺ | K ⁺ | Cl ⁻ | NO ₃ ⁻ | CO ₃ ²⁻ | NO ₃ ⁻ /Cl ⁻ |
|------------------------------|----------------|---------------|---------------|------|-----------------|----------------|-----------------|------------------------------|-------------------------------|---|
| <i>Average waste package</i> | | | | | | | | | | |
| a | 150-200 | 130.0 | 29.2 | 5.42 | 15.55 | 12.21 | 0.52 | 27.23 | - | 52.4 |
| x | 400-500 | 108.1 | 53.6 | 10.8 | 2.3 | 14.1 | 2.5 | 2.3 | 5.5 | 0.9 |
| <i>Hot waste package</i> | | | | | | | | | | |
| a' | 600-700 | 121.6 | 31.4 | 5.35 | 15.44 | 11.81 | 0.55 | 26.71 | - | 48.6 |
| x' | 4000-5000 | 81.5 | 66.1 | 10.3 | 4.1 | 7.3 | 5.6 | 1.5 | 2.1 | 0.3 |

- For the 3-salt system
 - Deliquescence first predicted at temperatures of 122°C and 130°C for hot and average WP, respectively (points a and a')
 - Upon degassing, brine solution loses Cl⁻ and NO₃⁻ and dries out leaving a residual carbonate solid (Na₂CO₃)
 - No aqueous phase on surface between points a/a' and x/x'
 - As %RH increases, deliquescence occurs for a second time at x/x' with the formation of a CO₃²⁻-rich solution
- Assumes
 - An assemblage of NaCl, KNO₃, and NaNO₃ is present initially

Evolution of conditions for Assemblage B (with acid degassing)

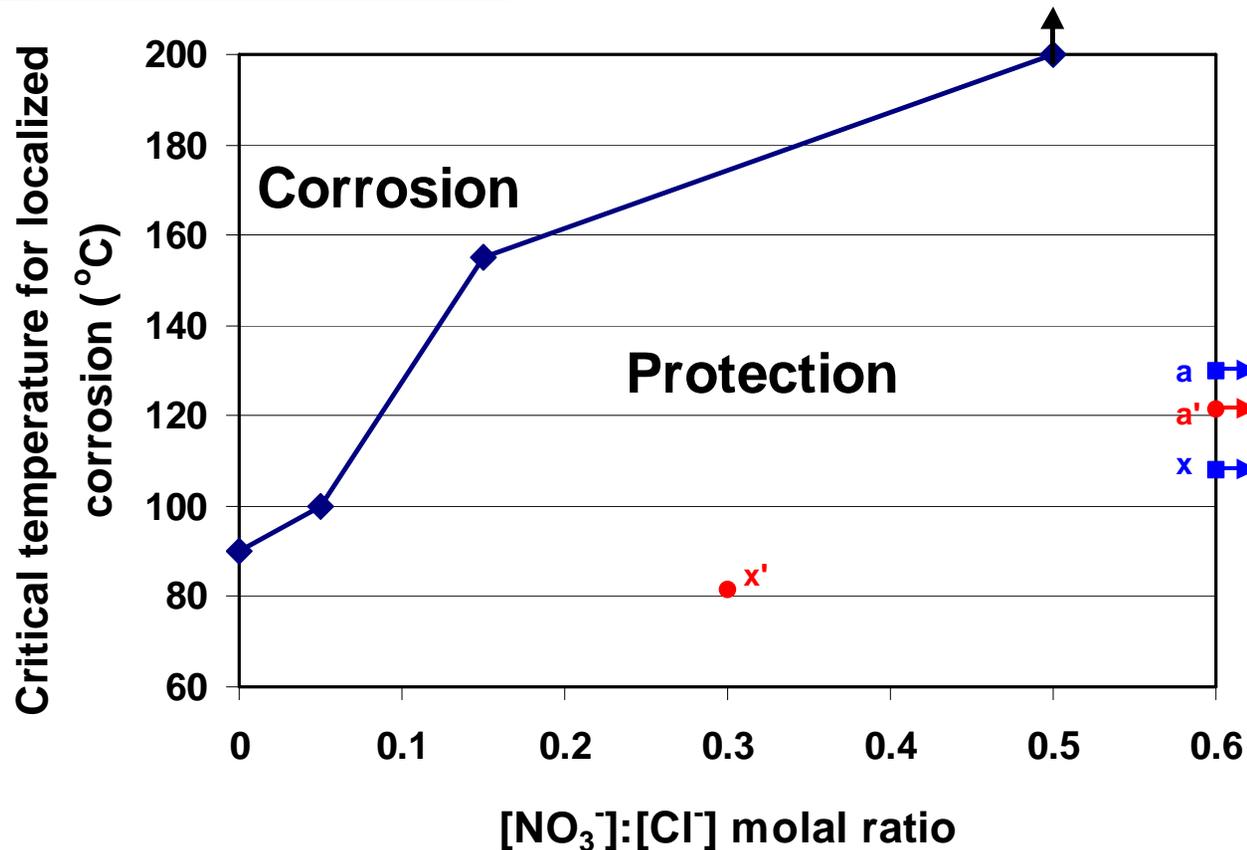


- WP surface is dry between a_B/a_B' and x_B/x_B'

| Brine | t (yrs) | T (°C) | rh (%) | pH | Cl^- | NO_3^- | CO_3^{2-} | NO_3^-/Cl^- | E_{CORR} (mV _{SSC}) | E_{rcrev} (mV _{SSC}) |
|------------------------------|-----------|----------|----------|------|--------|----------|-------------|---------------|---------------------------------|----------------------------------|
| <i>Average waste package</i> | | | | | | | | | | |
| a | 150-200 | 130.0 | 29.2 | 5.42 | 0.52 | 27.23 | - | 52.4 | 352 | >1000 |
| x | 400-500 | 108.1 | 53.6 | 10.8 | 2.5 | 2.3 | 5.5 | 0.9 | -95 | 648* |
| <i>Hot waste package</i> | | | | | | | | | | |
| a' | 600-700 | 121.6 | 31.4 | 5.35 | 0.55 | 26.71 | - | 48.6 | 349 | >1000 |
| x' | 4000-5000 | 81.5 | 66.1 | 10.3 | 5.6 | 1.5 | 2.1 | 0.3 | -122 | 728* |

* CNWRA E_{rcrev} model used to account for inhibiting effect of CO_3^{2-}

Evolution of conditions for Assemblage B (with acid degassing)



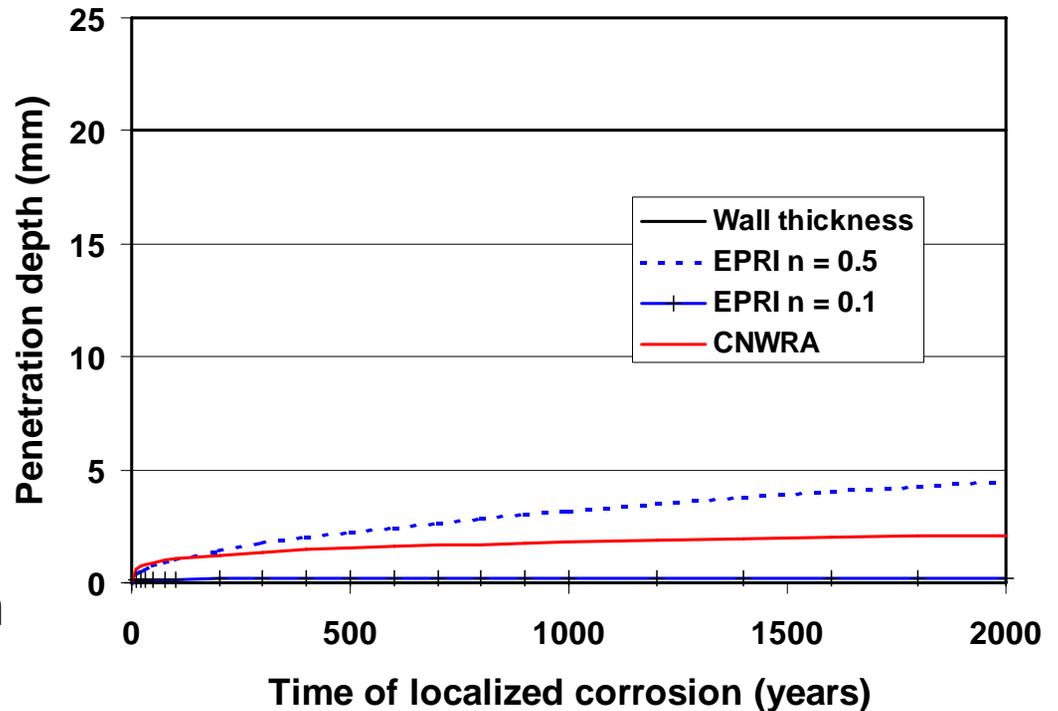
- Assemblage B would not result in localized corrosion in the event of acid degassing

Evolution of conditions for Assemblage C

- Assemblage C
 - NaCl-KNO₃-NaNO₃-Ca(NO₃)₂
- Because of high solubility of nitrates, Assemblage C would deliquesce at temperature exceeding range of EQ3/6 validation
 - Code fails to converge
- Qualitatively
 - Would expect initial brine (if such a salt assemblage is feasible) to transform into carbonate-rich system upon acid degassing
 - pH of brine maintained near neutral by CaCO₃ precipitation
 - Would expect WP surface to dry out after initial wetting
 - Initial brine composition unknown
 - High [NO₃⁻] likely to inhibit LC
 - Subsequent deliquescence of carbonate salts will not initiate LC due to inhibiting effect of CO₃²⁻ and relatively low temperature

Evolution of conditions for Assemblage C

- Even if LC is initiated in initial Assemblage C brine, extent of propagation prior to dry-out will be minimal



Summary

- Based on the EPRI decision tree, the proposed formation of high-temperature deliquescent brines is not considered to be an issue
 - Question of whether mineral assemblages required for the formation of high-temperature brines will be present in dust deposits
 - Deliquescent mineral assemblages that have been proposed will not lead to LC initiation, with or without acid degassing
 - Even in the unlikely circumstance that LC did initiate, there is now strong experimental evidence to indicate that Alloy 22 crevices will stifle and re-passivate
- Therefore, multiple lines of evidence indicate that no adverse effects will result from the deliquescence of dust minerals
- Robustness of argument demonstrated through the use of data from independent studies

EPRI's Decision Tree Approach

- Multiple lines of argument
 - Formation and stability of the environment
 - If environment forms and is stable, will LC result?
 - What are the consequences for WP lifetimes?
- No evidence to suggest that high-temperature deliquescent brines will impact safety of YM repository

