



# Analysis of NWTRB's Scenario Regarding Localized Corrosion by Formation of High-Temperature Deliquescent Brines

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**Additional authors:** Randy Arthur, Matt Kozak, Dave Shoemith

Presented to the US Nuclear Waste Technical Review Board, Washington DC, 18 May 2004



# Presentation Overview

- EPRI is concerned that the November 2003 NWTRB letter and report overstated both the likelihood and importance of localized corrosion during the thermal period
- EPRI commissioned an independent analysis of the TRB scenario
  - Evaluation of related work sponsored by the State of NV included
- EPRI Experts (Dr. John Kessler/ Coordinator)
  - Prof. Don Langmuir
  - Dr. Fraser King
  - Dr. Randy Arthur
  - Prof. Dave Shoesmith
  - Dr. Mick Apted



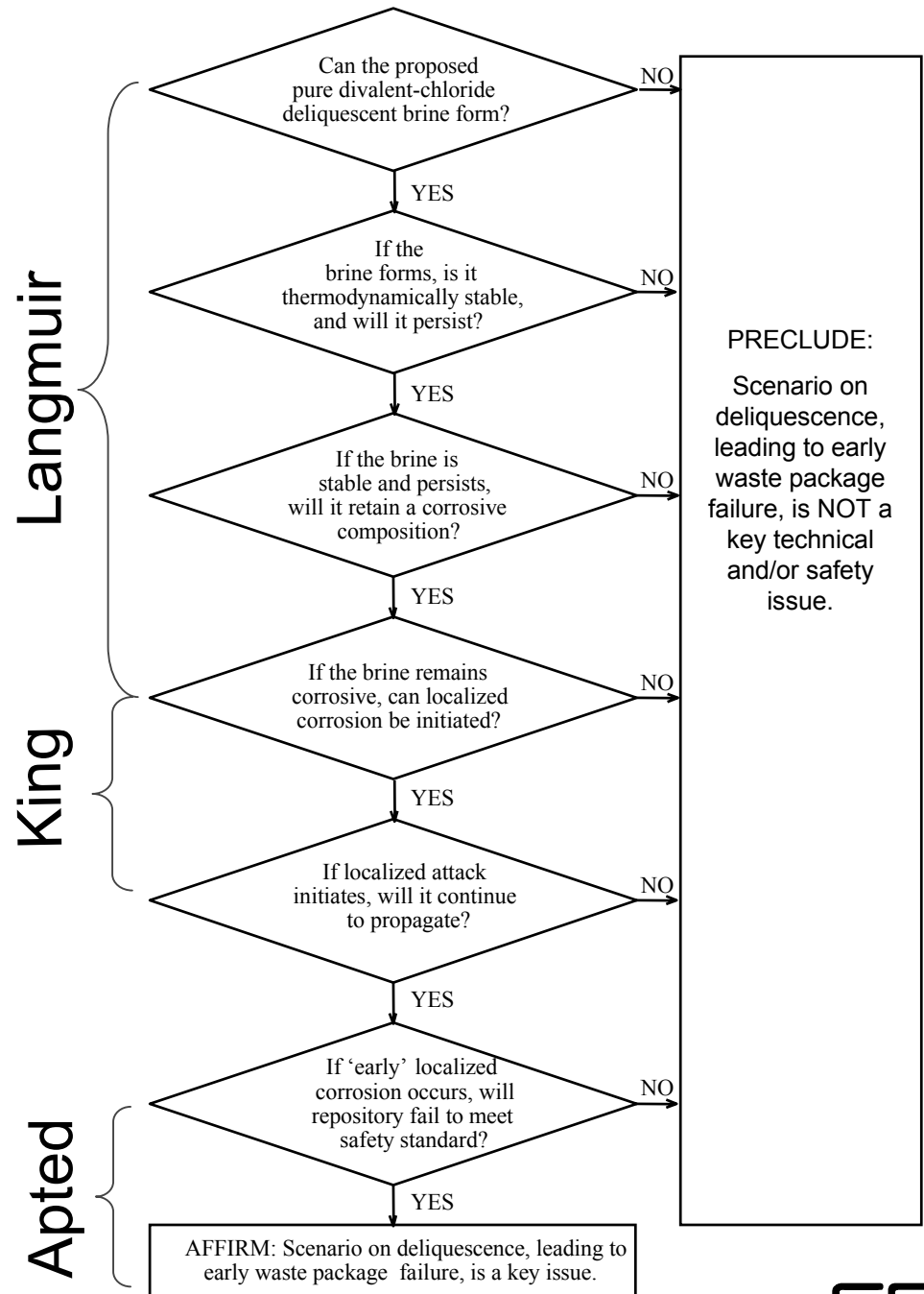
# Presentation Organization

- Decision-tree approach to evaluating NWTRB's scenario (Kessler)
- Geochemical analysis (Langmuir)
- Corrosion analysis (King)
- TSPA and regulatory compliance analysis (Apted)
- Conclusions (Apted)



# Decision Tree Approach for Systematic Scenario Evaluation

- All of the decision questions must be answered “yes” for the NWTRB’s deliquescence scenario to be of concern.



# Prerequisites (approximate) for Localized Corrosion of Alloy 22

- Environmental
  - Temperature  $>60-85^{\circ}\text{C}$
  - Nitrate:chloride ratio less than  $\sim 0.2$
- Mechanistic requirements
  - Local  $[\text{O}_2]$  depletion
  - Physical separation of anodic and cathodic processes
  - Localized acidification inside the occluded region



# EPRI Conclusion

- Multiple lines of evidence indicate there is no technical foundation nor safety-assessment basis to support concern about the NWTRB scenario.
  - EPRI analyses suggest the answer is likely to be “no” at *all* the decision points on the decision tree
  - Remainder of this presentation provides the bases for this conclusion
  - More detail in companion EPRI report (EPRI report number 1010941 (released at this meeting))



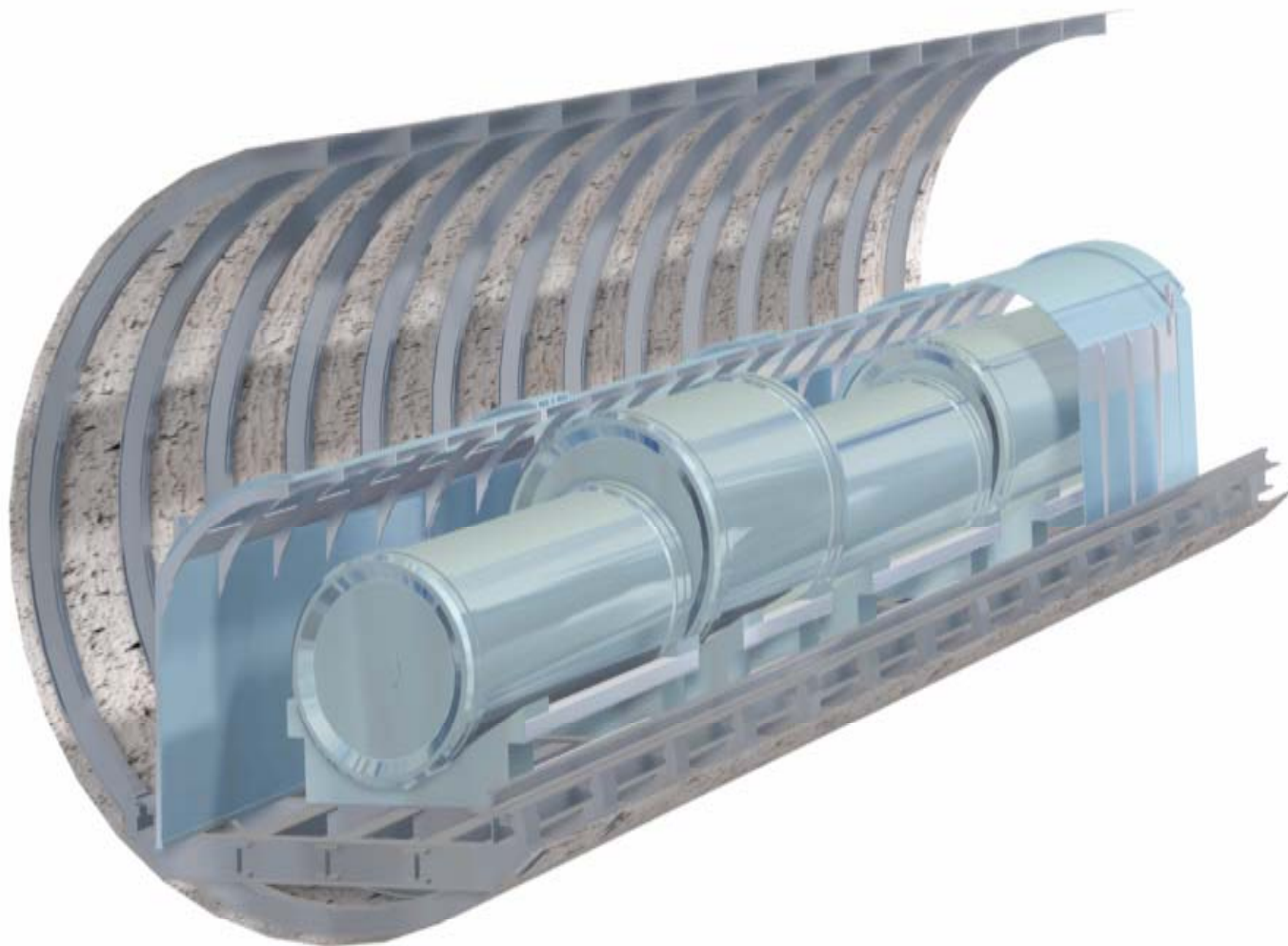
# EPRI's Geochemical Approach (Langmuir/Arthur)

- Any attempt to predict the reaction behavior of specific substances (e.g., the corrosivity of deliquescent salts and acid gases) must take into account potentially important reactions that could influence their concentrations and behavior in the ***Repository System***:
- Gas phase in the drift
- Waste and waste packages, invert, drip shield
- Other engineered materials (concrete, steel, backfill, etc.)
- Dust on waste packages that includes trace to minor amounts of soluble salts
- Geologic materials and pore waters in drift walls



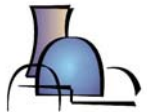
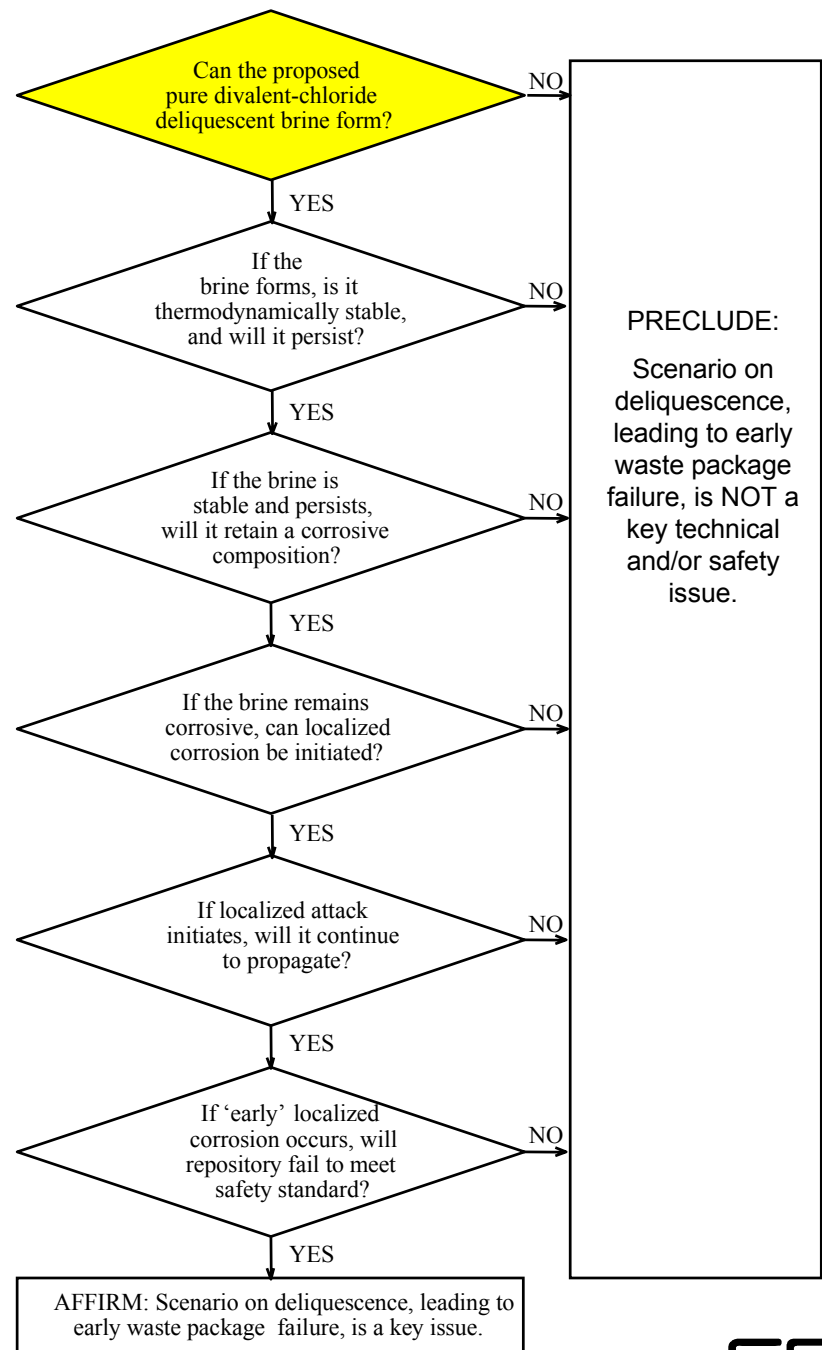


# Repository System





# Decision Tree Approach for Systematic Scenario Evaluation



# Will pure divalent-cation chloride deliquescent brines form?

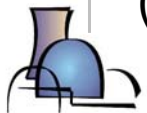
- Formation of possible deliquescent brine depends on salt-bearing dust adhering to container surface.
- EPRI's Approach: Evaluate dust as source material.
  - ESF dust data reported by Peterman et al. (2003).
  - EPRI has collected new data on wind-blown dust (EPRI 2004; Reheis and Izbicki, USGS, 2003). This is the likely dust to enter the repository after closure.
- Key data for both dusts
  - abundances of all soluble salts that may promote localized corrosion (chloride) and salts that inhibit localized corrosion (nitrate, sulfate, etc.).
  - abundances of minerals (feldspars, clays, carbonates, etc.) that will neutralize any acidity associated with deliquescent brine.



# Dust as the Source of Salts for Deliquescent Brine Formation

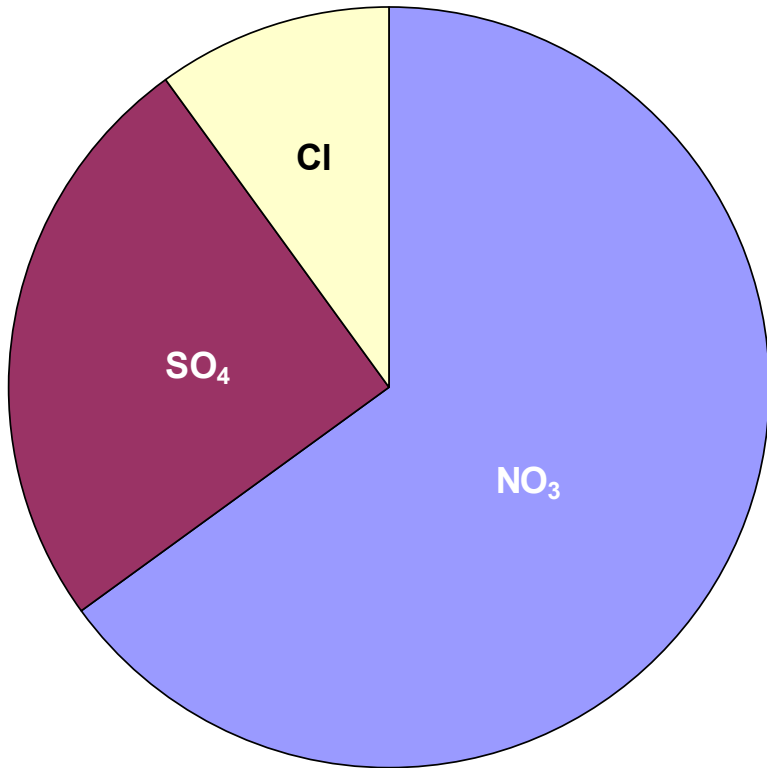
**Mole Percent of Ions in Soluble Salts in Wind-Blown Dust and ESF Dust and in Precipitation from Near Yucca Mountain.**

	Ca	Mg	Na	K	NO <sub>3</sub>	SO <sub>4</sub>	Cl
<b>Salts in wind-blown dust</b> (Reheis & Izbicki, 2003)	60	10	26	4	65	25	10
<b>Precip. chemistry maps,</b> (NADP, 1997, 2002)	60	10	25	5	66	23	11
<b>Red Rock Canyon precip,</b> (NADP 1997-2002)	68	12	18	3	69	20	11
<b>Death Valley precip,</b> (NADP, 2000-2002 )	54	7	37	3	63	19	18
<b>Salts in ESF dust</b> (Peterman et al., 2003)	40	4	42	14	33	42	25



# Soluble Salts in Wind-blown Dust

Anion Percent Values in Soluble Salts in Windblown Dust  
from Near Yucca Mountain



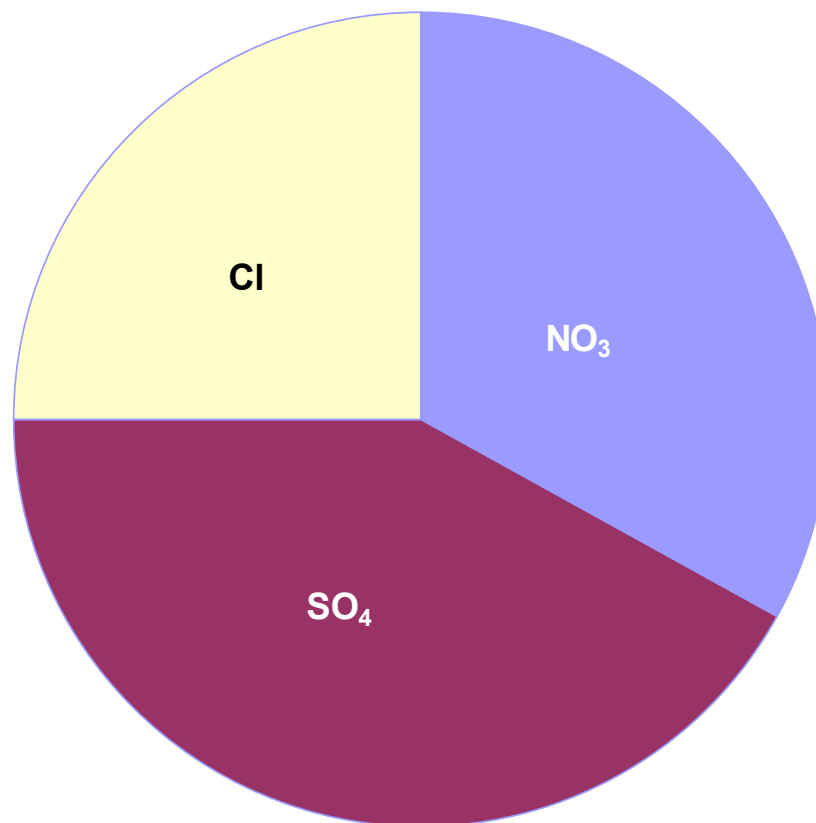
- Nitrate and sulfate inhibit initiation of localized corrosion.
- Chloride promotes initiation of localized corrosion.
- Nitrate + sulfate >> chloride (ratio = 9/1). (Corrosive ratio <0.2).



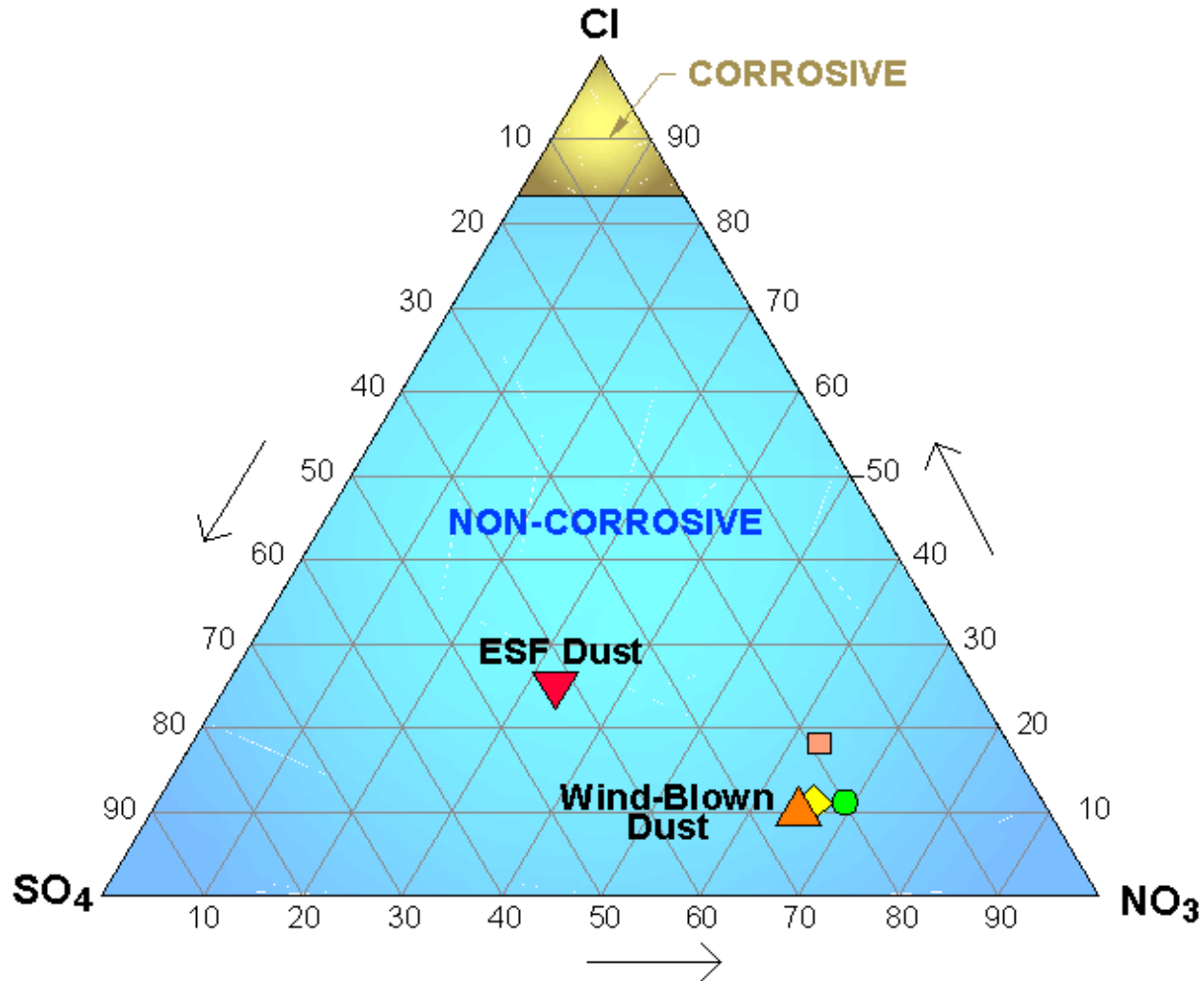
# Soluble Salts in ESF Dust

- Nitrate and sulfate inhibit initiation of localized corrosion.
- Chloride promotes initiation of localized corrosion.
- Nitrate + sulfate  $\gg$  chloride (ratio = 3/1). (Corrosive ratio  $<0.2$ ).

Anion Percent Values in Soluble Salts in ESF Dust

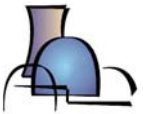


# Non-Corrosivity of Soluble Salts in ESF Dust and Wind-Blown Dust



# CaCl<sub>2</sub> Brine Behavior at Elevated Temperatures

- At elevated T's, a pure CaCl<sub>2</sub> brine will dissolve co-existing NO<sub>3</sub> and SO<sub>4</sub> salts in dust leading to a mixed-anion brine that will deliquesce at a lower RH than pure CaCl<sub>2</sub> brine.
- This brine will have a higher (NO<sub>3</sub>+SO<sub>4</sub>)/Cl ratio than pure CaCl<sub>2</sub> brine.



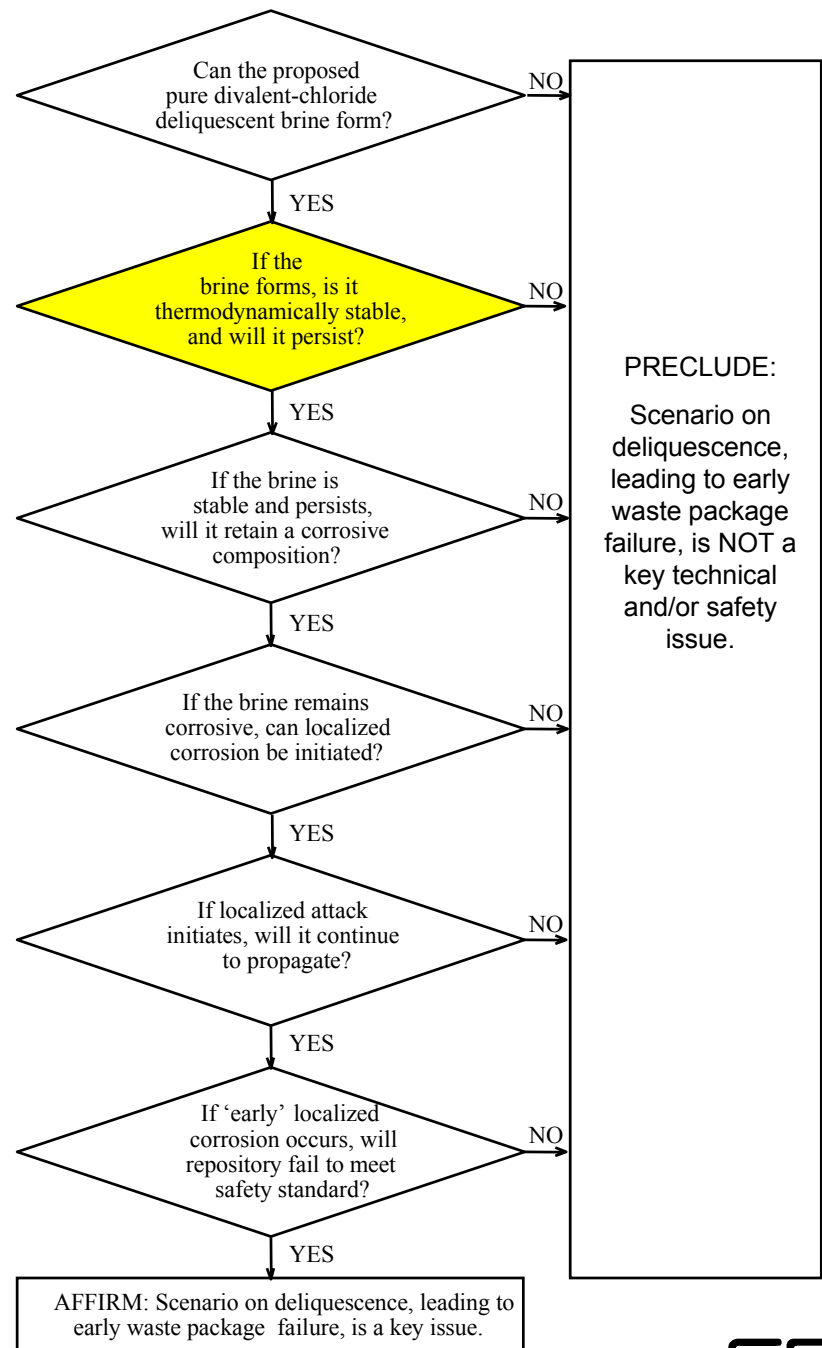


# Will Pure Divalent-Cation Chloride Deliquescent Brines Form?

- **Highly unlikely.**
- During the thermal pulse ( $T > 100^\circ\text{C}$ ) the only source of chloride salts is dust (e.g., ESF dust, especially wind-blown dust).
- The predominant solids in dusts ( $>90\%$ ) are alumino-silicates (feldspar and clay), silicates and carbonate minerals.
- Wind-blown dust has  $<10\%$  soluble salts and only  $0.4\%$  Cl, while ESF dust has  $<0.3\%$  soluble salts and only  $0.018\%$  Cl. The abundance of anions is in the order  $\text{NO}_3 \geq \text{SO}_4 > \text{Cl}$ .
- $\text{CaCl}_2$  brines will tend to re-dissolve  $\text{NO}_3$  and  $\text{SO}_4$  salts in dust creating a mixed-anion brine.
- Reaction of Mg in brines with silicates in the dust will remove Mg from the brines.

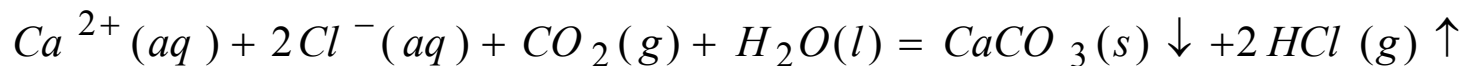
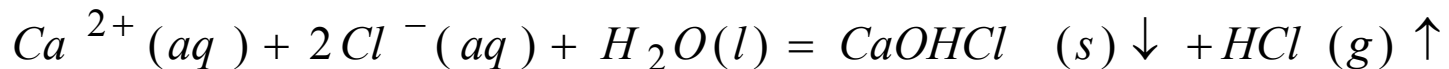
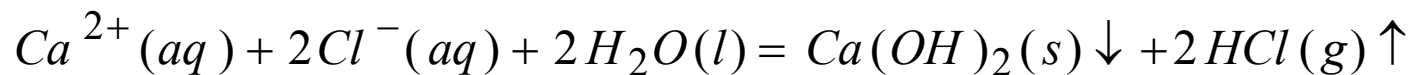


# Decision Tree Approach for Systematic Scenario Evaluation



# If Brine Forms, Will it be Stable and Persist?

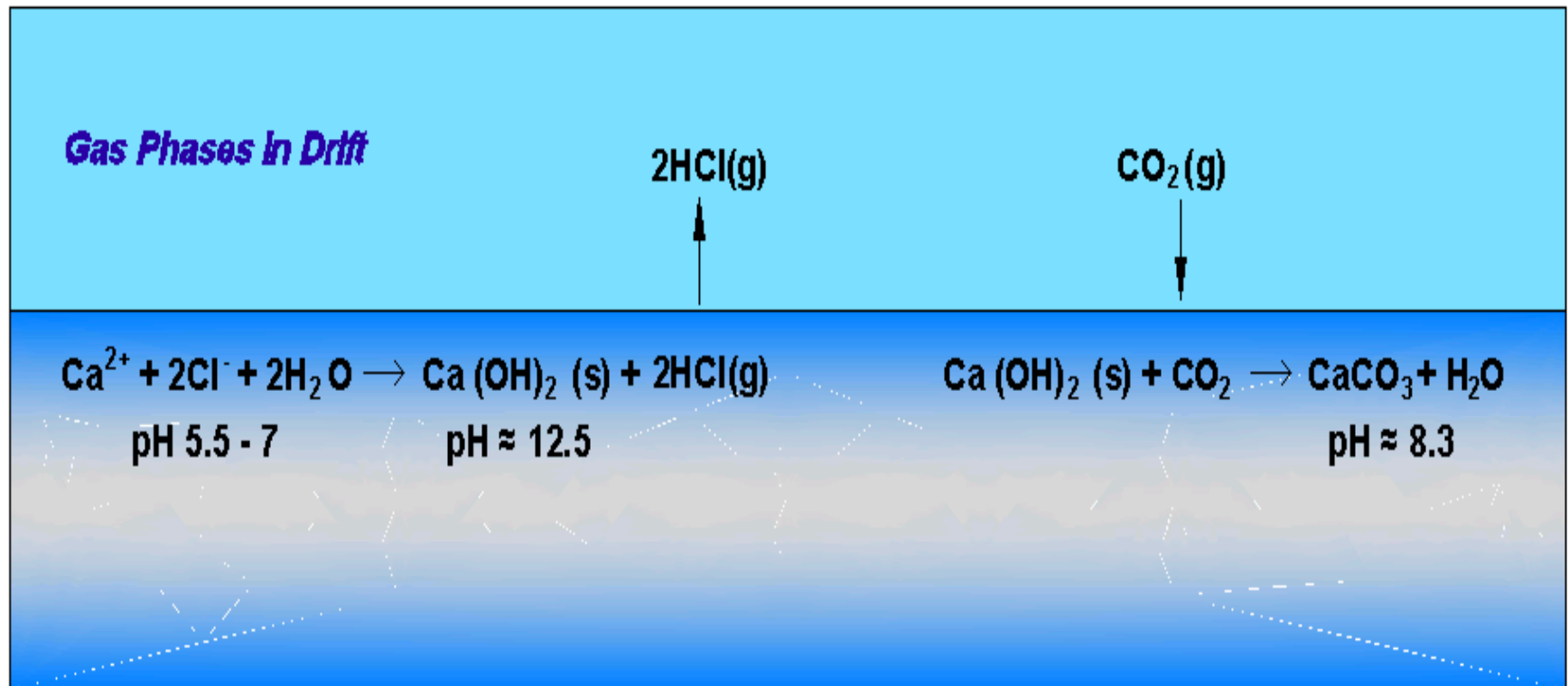
- EPRI's Approach: Model open-system reactions of repository
- Loss of volatile acid-gas species [HCl(g), HNO<sub>3</sub>(g)], will act to destabilize any brine.
- Possible reactions in the breakdown of deliquescent CaCl<sub>2</sub> salt:



- Continued transport of HCl away from waste package surface will drive above reactions to the right-hand side, leading to loss of brine and formation of an alkaline mineral residue on waste package surface.



# Possible Steps in the Breakdown of Deliquescent Calcium Chloride Salts on the Surface of a Waste Package



# Importance of the Relative Reactive Surface Areas of the Waste Package and Drift Wall

- Concentration gradient of acid gases will be from hotter waste packages toward the cooler drift wall.
- The tendency for reaction of acid gases will be proportional to reactive areas of solid surfaces that contact those gases.
- Based on the geometric surface areas of a WP and the drift wall, and expected roughness of the drift wall, the reactive surface area of a WP is <5% of the area of the drift wall.
- Based on size of tuff particles, assuming a 1 mm skin of drift wall, WP surface area is <1% of that of drift wall.



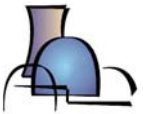
# Modeling Results: the Formation and Stability of CaCl<sub>2</sub> Deliquescent Brines

System	$p_{\text{HCl(g)}}$ (bar)	$p_{\text{H}_2\text{O(g)}}$ (bar)	Ca <sup>2+</sup> (molal)	Cl <sup>-</sup> (molal)	Deliquescent brine stable?	Stable Ca mineral
<i>Closed</i> WP (146°C)	10 <sup>-3.5</sup>	1	14.03	28.06	yes	CaCl <sub>2</sub> :2H <sub>2</sub> O
<i>Open</i> WP(146°C)	10 <sup>-11.5</sup>	4.2	0.11	0.21	no	CaCO <sub>3</sub>
<i>Open</i> Drift Wall (96°C)	10 <sup>-14.5</sup>	4.3	0.003	0.001	no	CaCO <sub>3</sub>



## EQ3/6 reaction of acid gases [HCl(g)] with minerals in drift wall (initial pH 8.3) at 96°C and 1 bar. Example of albite

- Added HCl(g) reacts with albite feldspar in drift wall, pH drops to 5.6 and Na-beidellite clay precipitates.
- As add more HCl(g), kaolinite clay and halite precipitate, and pH stabilizes indefinitely at 5.7.



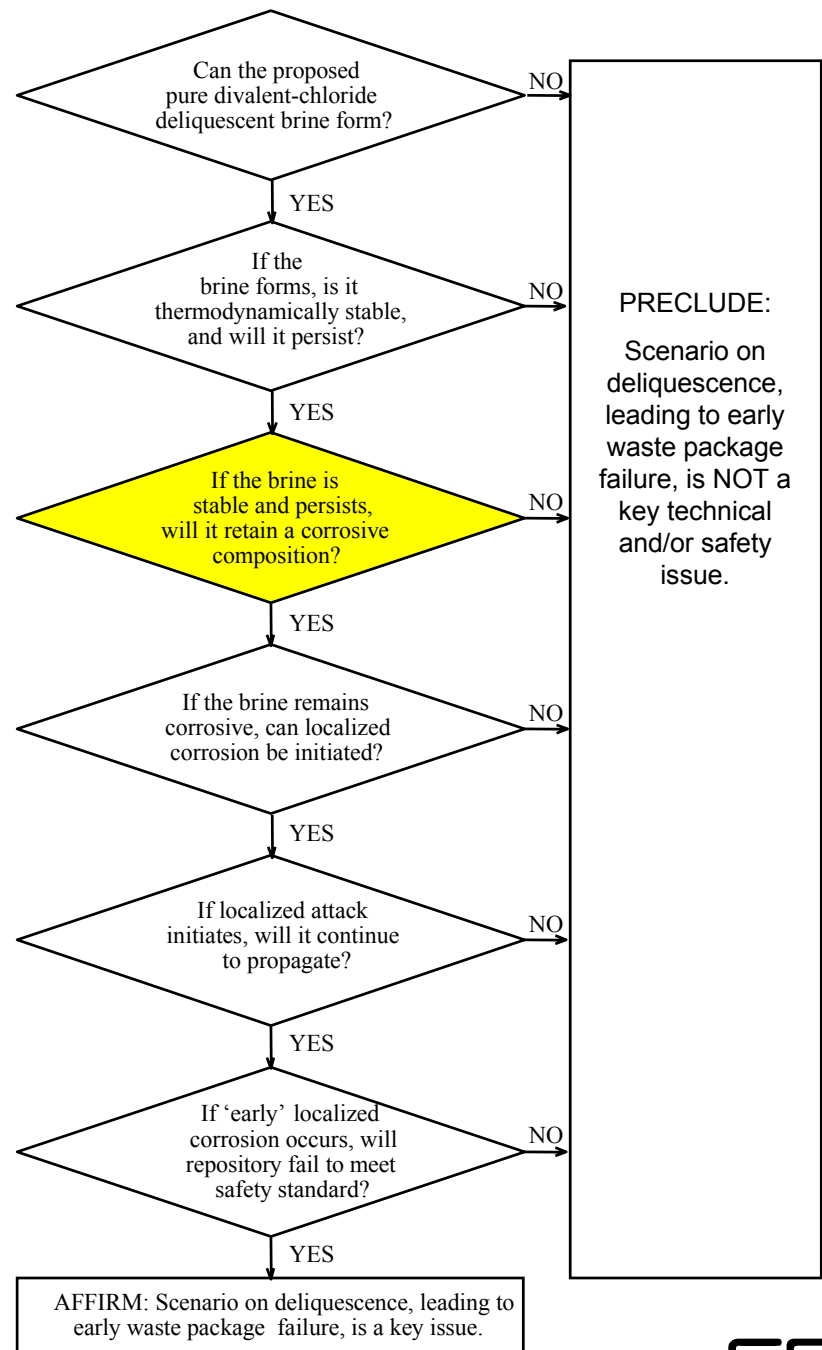


# If Brine Forms, Will it be Stable and Persist?

- **No.**
- Continued release of  $\text{HCl}(\text{g})$  from  $\text{CaCl}_2$  brine will eventually lead to loss of all the brine and formation of a non-deliquescent, alkaline solid residue (e.g.  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ ) on the WP surface.
- The concentration gradient of volatile  $\text{HCl}(\text{g})$  will drive its migration from the hot WP surface across the open drift to cooler drift walls, where it will dissolve in pore waters and be neutralized by reaction with basic tuff minerals.
- Surface area of cooler drift walls available for this reaction with acid gases  $\gg$  surface area of WP (area ratio  $\sim 20/1$  to  $>100/1$ ).



# Decision Tree Approach for Systematic Scenario Evaluation



# If the brine persists, will chemical conditions within the brine necessary for initiation of localized corrosion be maintained?

- EPRI's Approach: Model chemical processes that might create conditions necessary for initiation of localized corrosion.
- TRB has speculated that a brine may form under a "crust" or in an occluded location, so that closed-system conditions prevail.
- Under such assumed closed-system conditions, a deliquescent brine cannot lose volatile HCl, hence reactions will be limited to solid phases in the dust, Alloy 22 and the brine.



## Average Mineral Composition of ESF Dust and Wind-Blown Dust

The Strongly Basic Character of Wind-Blown Dust, and of ESF Dust and Drift Walls (Both Tuff)

	<u>Mineral</u>	<u>ESF Dust</u>	<u>Wind-Blown Dust</u>
		<u>Wt %</u>	<u>Wt%</u>
Basic Minerals	K-spar	31.7	10.5
	Albite	23.9	5.7
	Oligoclase		12.1
	Anorthite	0.8	
	Kaolinite		4.2
	Montmorillonite		6.6
	Smectites	2.1	
	Illite + muscovite	0.3	8.9
	Biotite		5.4
	Goethite		1.4
	Calcite		6.6
Dolomite		1.2	
	<b>Sum</b>	<b>58.9</b>	<b>62.5</b>
Inert Minerals	Tridymite	4.4	
	Cristobalite	23.7	
	Quartz	12.7	26.3
	Rutile		0.4
	Gypsum		1.1
	<b>Sum</b>	<b>40.9</b>	<b>27.7</b>
	<b>Soluble Salts</b>	<b>0.3</b>	<b>9.6</b>



# Equilibrium pH Values for Major Minerals in ESF Dust (= Topopah Spring Tuff) and/or in Wind-blown Dust at 25°C and Atmospheric CO<sub>2</sub> Pressure

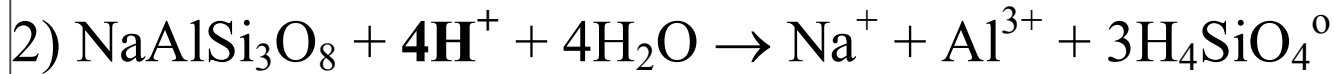
Mineral	Formula	Equilibrium pH
K-feldspar	KAlSi <sub>3</sub> O <sub>8</sub>	6.5
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	6.8
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	6.8
Calcite	CaCO <sub>3</sub>	8.3



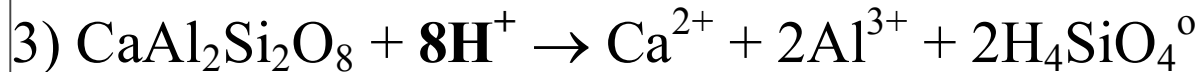
# Example Acid-Base Mineral Reactions That Will Neutralize Any Acid



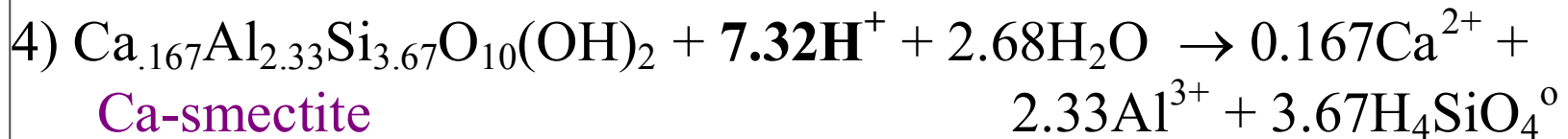
K-spar



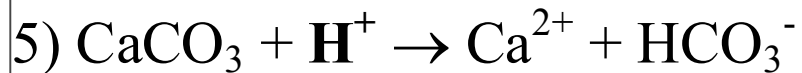
Albite



Anorthite



Ca-smectite



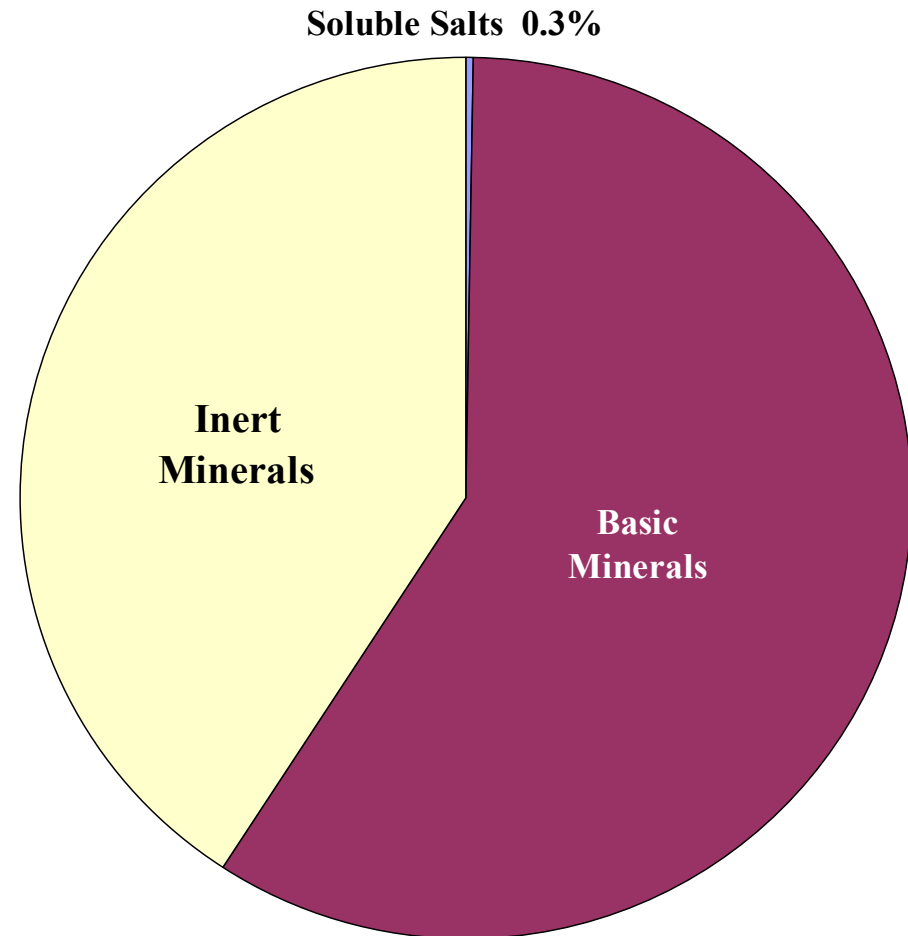
Calcite



# Neutralization of Acids by ESF Dust

- **Inert minerals:**  $\text{SiO}_2$  forms (41%)
- **Basic minerals:** feldspars, micas, smectite clay (59%)
- **Soluble salts** 0.3 %
- **0.13% of basic minerals can neutralize all possible HCl +  $\text{HNO}_3$  from soluble salts**

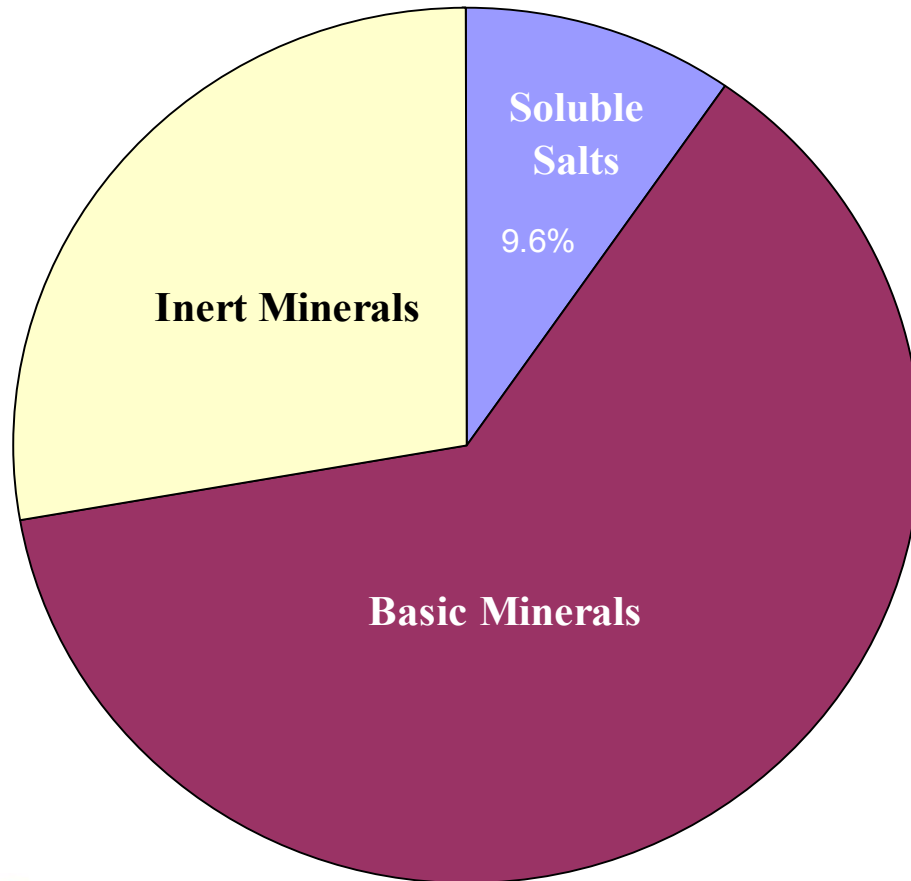
Weight % Minerals in ESF Dust





# Neutralization of Acids by Wind-blown Dust

## Weight % Minerals in Wind-Blown Dust

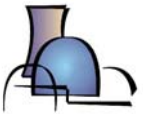


- **Inert minerals:**  $\text{SiO}_2$  forms, gypsum (27.7%)
- **Basic minerals:** feldspars, clays, micas, carbonates (62.5%)
- **Soluble salts** (9.6%)
- **7.3% of basic minerals can neutralize all possible  $\text{HCl} + \text{HNO}_3$  from soluble salts**



# Composition of a calcium-chloride saturated, deliquescent brine and its gas phase, isolated from the drift atmosphere at 146°C and 1 bar total pressure. EQ3/6 calculation.

$m\text{Ca}^{2+}$	14.03
$m\text{Cl}^-$	28.06
$m\text{H}^+$	$10^{-6.15}$ (neutral $m\text{H}^+ = 10^{-5.82}$ )
$p_{\text{H}_2\text{O}(\text{g})}$	1 bar
$p_{\text{HCl}(\text{g})}$	$10^{-3.5}$ bar



# Effect of dissolution of calcite or albite in dust on $mH^+$ of isolated deliquescent $CaCl_2$ brine at $146^\circ C$ and 1 bar. EQ3/6 calculation.

Initial brine  $mH^+ = 10^{-6.15}$

Add trace of calcite:  $mH^+$  drops to  $10^{-10.6}$

Add trace of albite feldspar:  $mH^+$  drops to  $10^{-8.35}$   
and Na-beidellite clay precipitates, then  
 $mH^+$  drops to  $10^{-8.8}$ .



## If the brine persists, will chemical conditions within the brine necessary for initiation of localized corrosion be maintained?

- **No.**
- Naturally occurring minerals in dust have a strong and rapid buffering capacity and will neutralize acidity.
- Abundance of basic mineral phases greatly exceeds that of soluble salts in dust.
- Corrosion-inhibiting soluble salts (nitrates, sulfates) greatly exceed concentration of chloride salts
- Ratio of [nitrate+sulfate/ chloride] is 3 to 1 in ESF dust and 9 to 1 in wind-blown dust.

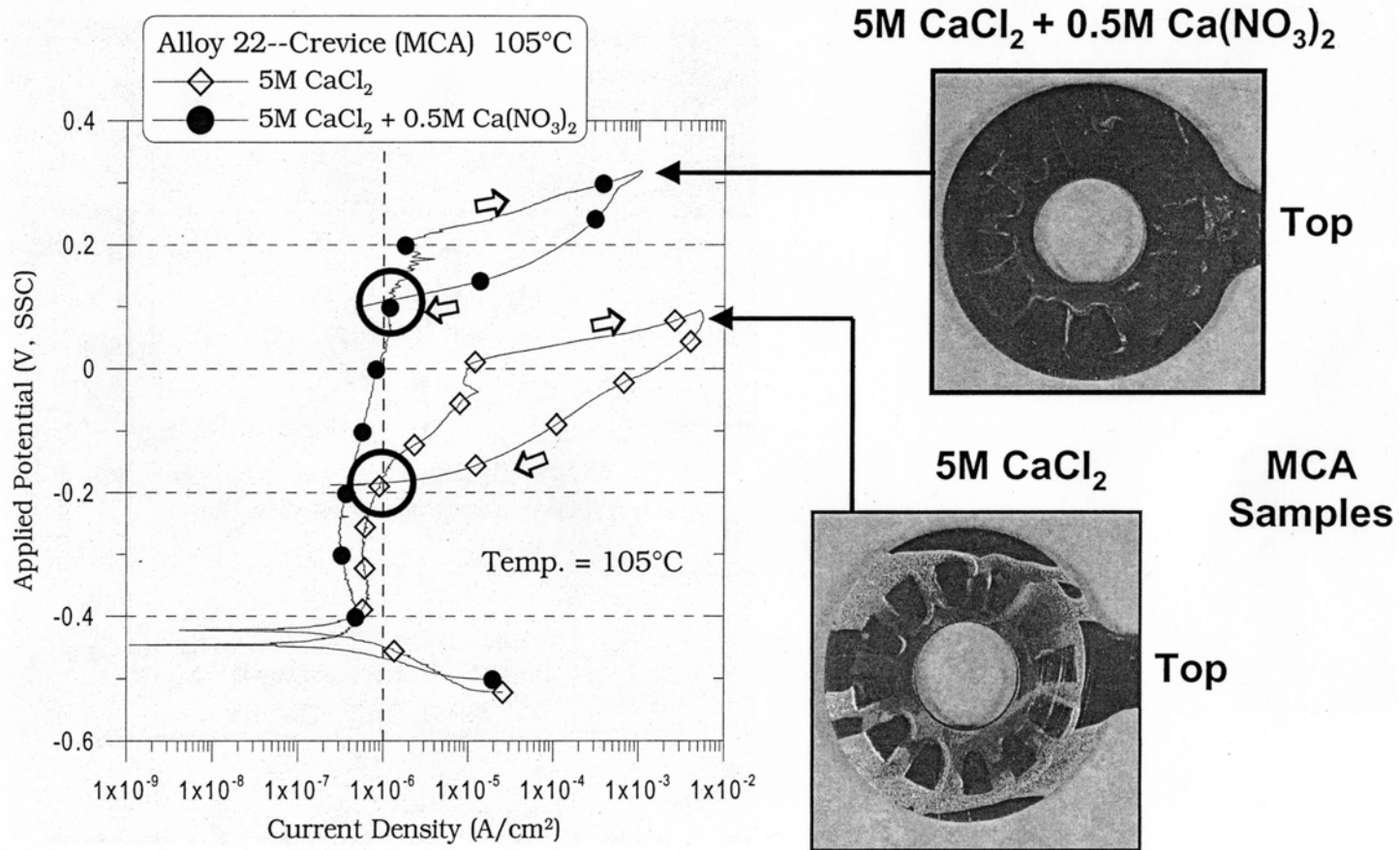


# EPRI's Approach to Corrosion Issues in Deliquescent Brines

- **Two questions:**
  - **If a corrosive brine forms and persists on the surface of the waste package, will localized corrosion initiate?**
    - $[\text{NO}_3^- + \text{SO}_4^{2-}]:[\text{Cl}^-]$  ratios and localized corrosion
    - Are dust deposits and salt crusts effective crevice formers?
      - Inadequate spatial separation of anodic and cathodic sites
      - No differential  $[\text{O}_2]$  cell
      - No local acidification
  - **If localized corrosion initiates, will it propagate to failure?**
    - Stifling mechanisms for localized corrosion
    - EPRI TSPA predictions of localized penetration



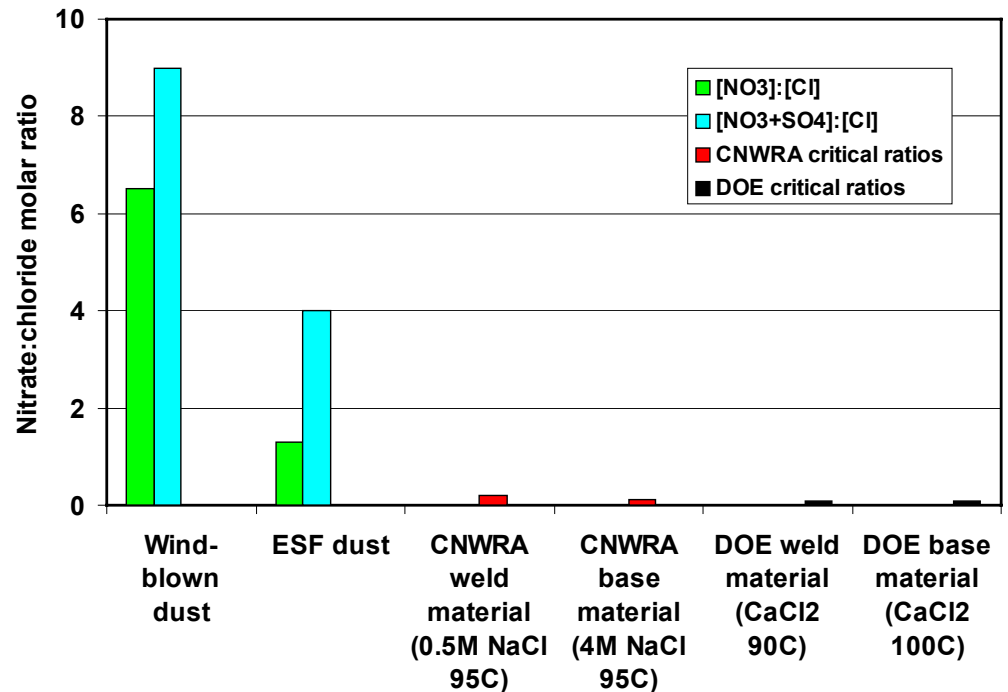
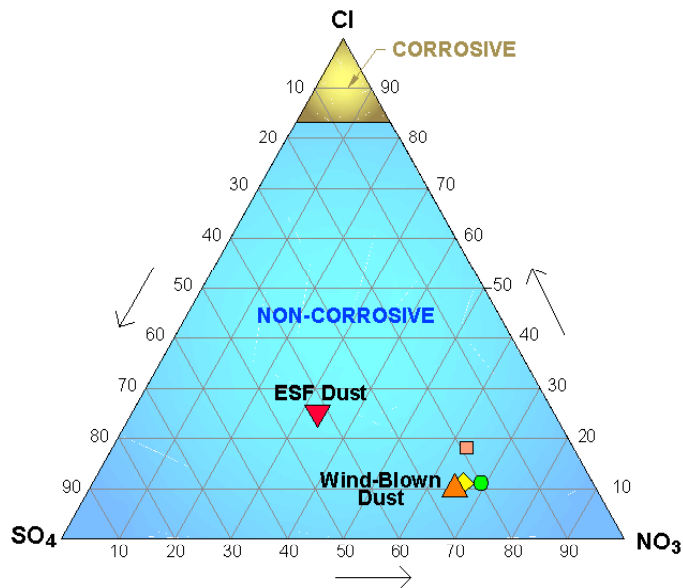
# Inhibitive Effects of Nitrate Ions



- Nitrate (and sulfate) ions clearly inhibit localized film breakdown, shifting  $E_B$ ,  $E_{RP}$  to potentials far more positive than  $E_{CORR}$  at sufficiently high  $[\text{NO}_3^- + \text{SO}_4^{2-}]:[\text{Cl}^-]$  ratio



# Comparison of Dust Composition to that Required for Localized Corrosion



- As shown earlier, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> dominate over Cl<sup>-</sup> in YM dusts
- Ratio of inhibitive:aggressive solutes in dust >> ratio required to prevent initiation of localized corrosion



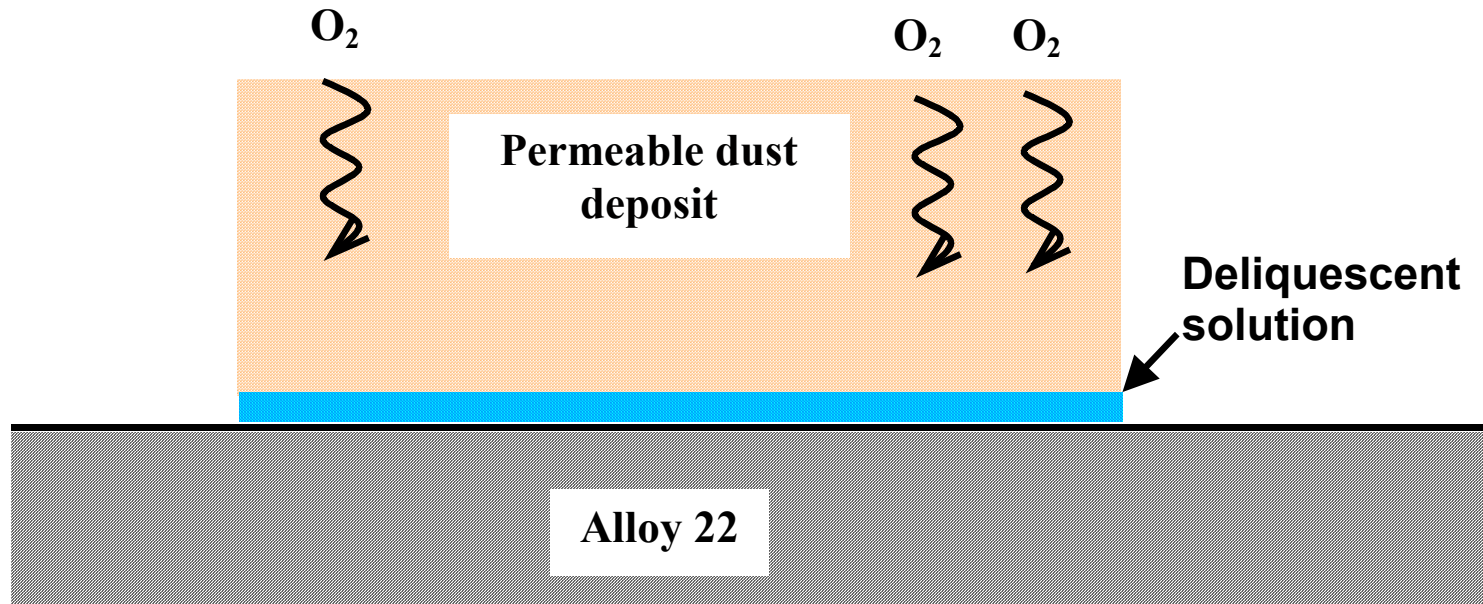
# Can a Permeable Crevice Former Support the Initiation of Localized Corrosion?

- Sequence of events in the initiation and propagation of localized corrosion:
  - Local depletion of  $O_2$  in the occluded region
  - Consequent spatial separation of anodic and cathodic reactions
  - Dissolution of metal within occluded region
  - Hydrolysis of metal ions and local acidification
  - Propagation inside crevice supported by cathodic reduction of  $O_2$  outside and  $H^+$  inside occluded region
  - Migration of charge-balancing anions into crevice
- Permeable dust deposits and salt crusts will not support localized corrosion because:
  - Permeable to  $O_2$ 
    - Preventing creation of differential  $[O_2]$  cell and separation of anodic and cathodic reactions
  - Buffering/neutralization of  $H^+$  produced by hydrolysis
    - Preventing local acidification within “occluded” region





# Conceptual Model of Permeable Dust Deposit



- Can permeable dust deposit create a differential [O<sub>2</sub>] cell?
  - Compare the rate of O<sub>2</sub> consumption on the WP surface with its rate of replenishment
- Note: the figure shows a simplified conceptual model for calculation purposes. In reality, the deliquescent solution is not expected to form a continuous water film on the waste package surface.



# Mass Transport Through Porous Media

- Well-studied, predictable phenomenon
  - Nuclear waste disposal in saturated repositories
    - **Clay-based barriers**
  - Agriculture and soil sciences
    - **Supply of O<sub>2</sub> to plant roots**
- Effects of porous deposits on corrosion processes
  - Restrict mass transport of reactants to, and corrosion products away from, the corroding interface
    - **Effective diffusion coefficient**

$$D_{\text{EFF}} = \varepsilon \tau_f D_0$$

- Block fraction of surface
  - **Effective surface area for corrosion given by**

$$A_{\text{PORE}}/A_{\text{GEOM}} = \varepsilon_{\text{bulk}}$$

**(randomly oriented, randomly sized pores)**

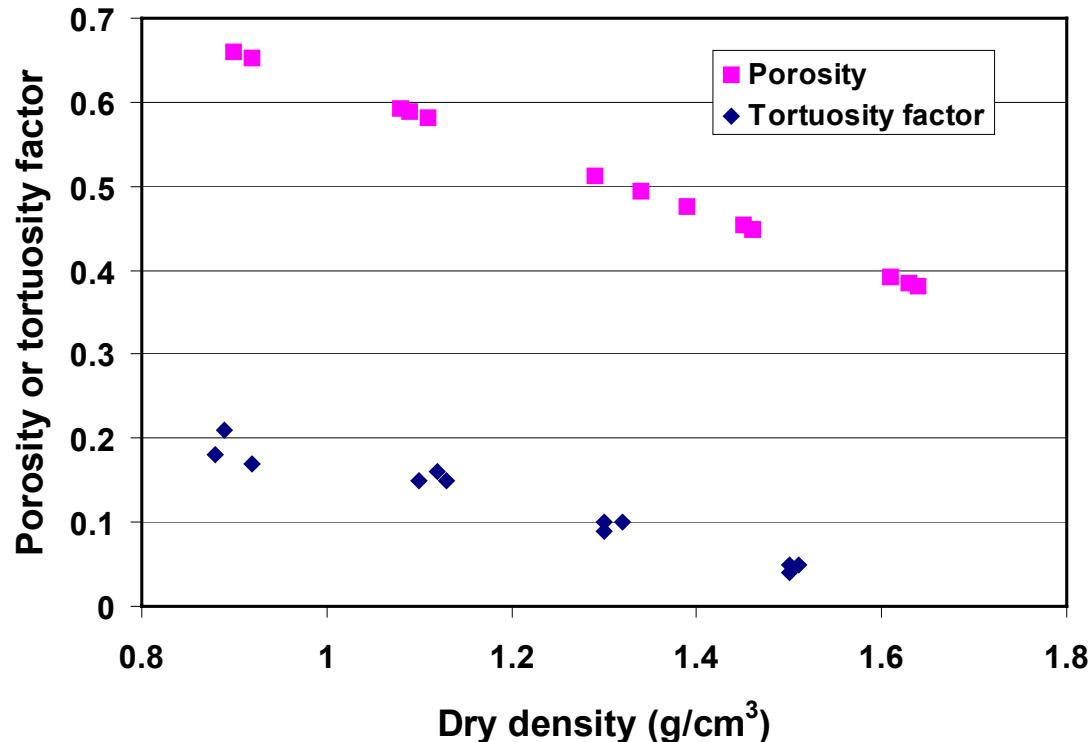


# Required Input Data

- Rate of replenishment of  $O_2$ 
  - Rate-determining step is diffusion through thin water film
    - $O_2$  diffusion in unsaturated dust deposit many orders of magnitude faster than diffusion in solution
  - Porosity and tortuosity factor of deposit
    - Compacted montmorillonite clay, model SG deposit
  - Concentration of  $O_2$ 
    - Function of T and salt concentration
  - Thickness of water film
- Rate of  $O_2$  consumption
  - Equal to passive current density



# Porosity and Tortuosity Factor



- Data for highly compacted montmorillonite clay (Oscarson et al. 1992)
- Hand-compacted magnetite powder (Millet and Fenton 1993)
  - Porosity 0.55-0.65, tortuosity factor 0.64-1.0
- Conservatively assume porosity 0.5, tortuosity factor 0.2



# Other Input Data

- Bulk O<sub>2</sub> concentration (Battino et al. 1983)
  - Salting-out effect – assume 5M CaCl<sub>2</sub> ( $c_{5M \text{ CaCl}_2}/c_{\text{H}_2\text{O}} = 0.127$ )
  - Effect of temperature on O<sub>2</sub> solubility
- Thickness of deliquescent water film
  - Based on TGA mass change reported by Farmer (2003)
    - 1.7 mg for 17 cm<sup>2</sup> coupon
    - Water layer thickness = 1 micron (10<sup>-4</sup> cm)
- Effect of temperature on diffusion coefficient
  - Activation energy 19 kJ/mol
- Rate of O<sub>2</sub> consumption
  - Based on passive current density from Cragnolino (2003)

$$i_{\text{pass}} = i_0 \exp[-\Delta E/RT]$$

$$\Delta E = 44.7 \text{ kJ/mol}$$



# Comparison of Rate of O<sub>2</sub> Consumption and Replenishment

- Rate of O<sub>2</sub> consumption

$$i_{\text{pass}} = i_0 \exp[-\Delta E/RT]$$

- Rate of O<sub>2</sub> replenishment
  - Steady-state flux given by

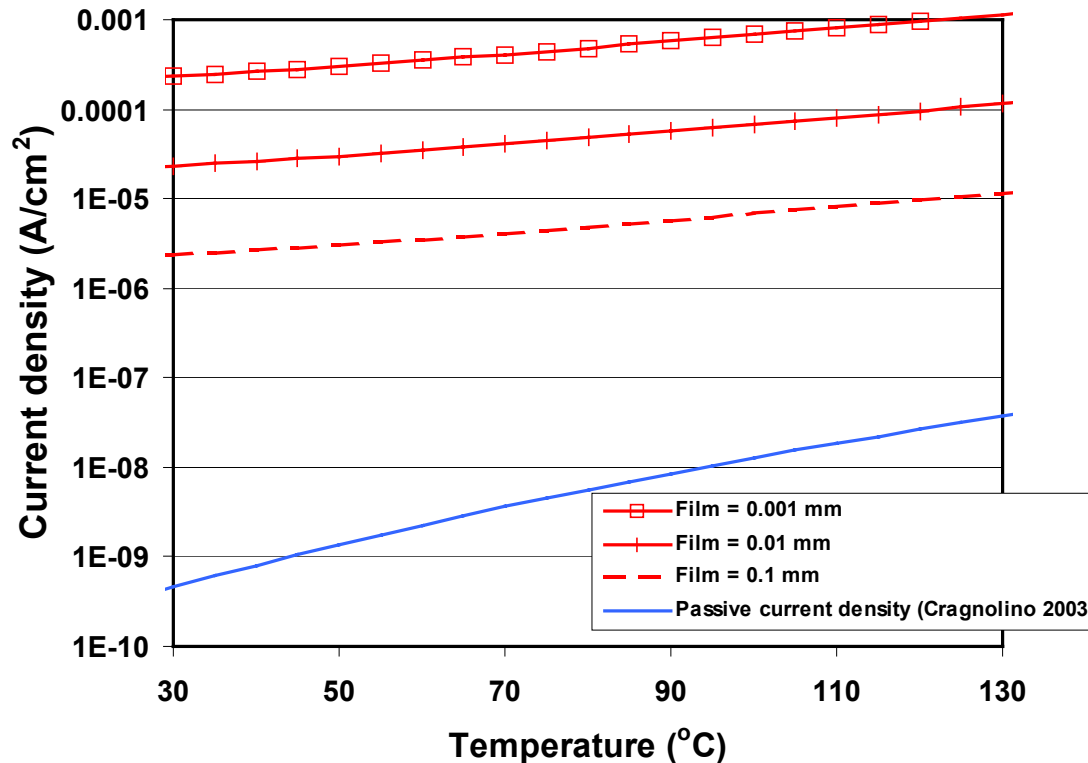
$$i_{\text{O}_2} = 4F\varepsilon\tau_f D_{\text{O}_2} c_{\text{O}_2}/x$$

Water film thickness  $x = 0.001$  mm (DOE TGA data)

$= 0.01, 0.1$  mm (sensitivity analysis)



# Comparison of Rate of O<sub>2</sub> Consumption and Replenishment (2)



- Rate of O<sub>2</sub> replenishment is 3-6 orders of magnitude faster than its rate of consumption
- Therefore, no O<sub>2</sub> depletion and no differential [O<sub>2</sub>] cell is created
  - Interfacial [O<sub>2</sub>] = 99.996% of bulk [O<sub>2</sub>] for 1 micron water film



# Time Dependence of Localized Penetration Rate

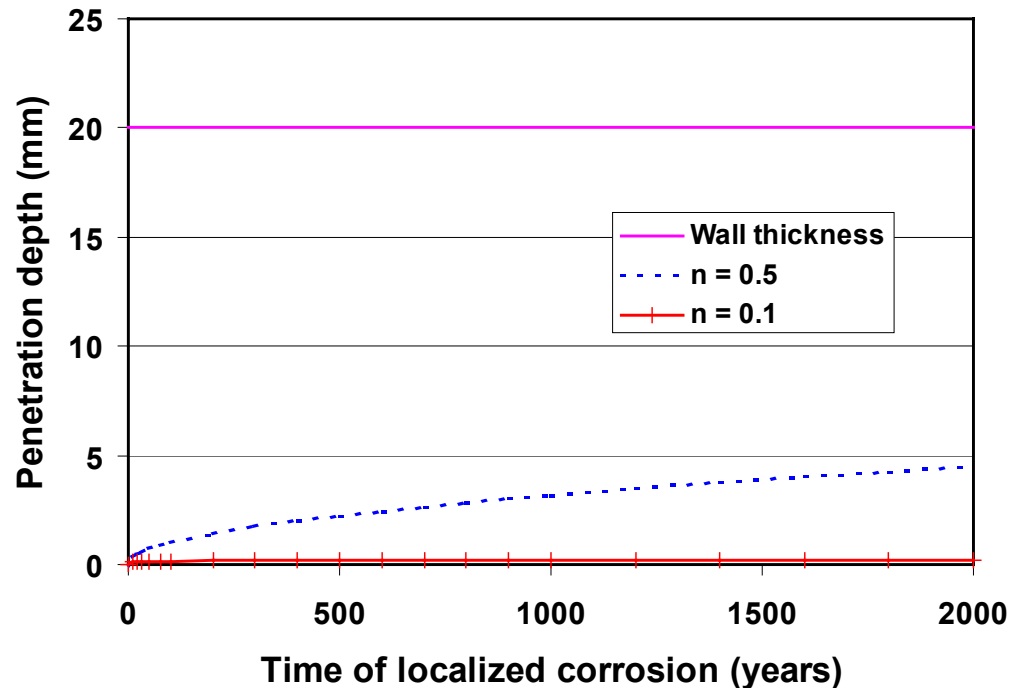
- Even in the unlikely event of the initiation of localized corrosion, there is strong evidence to suggest that corrosion will be stifled
- Stifling mechanisms:
  - Loss of critical crevice chemistry
    - Ion-exchange of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  for less-aggressive  $\text{Na}^{+}/\text{K}^{+}$
    - Neutralization/buffering of  $\text{H}^{+}$  generated by hydrolysis prevents crevice propagation supported by internal cathodic  $\text{H}^{+}$  reduction
      - Alumino-silicates, carbonate minerals
  - Loss of separated anodic and cathodic reactions
    - Permeable dust deposits permits  $\text{O}_2$  into occluded region
  - Mass transport limitations by precipitated corrosion products
    - Diffusion or  $iR$  control of propagation rate
- Net effect of stifling mechanisms is time-dependent propagation rate

$$\text{depth of penetration} = B t^n \quad \text{where } n < 1$$





# Time-Dependent Penetration Rate Included in EPRI TSPA Calculations



- Value of B based on data from 10% FeCl<sub>3</sub> for less-corrosion-resistant alloy
- Values of n (0.1-0.5) based on other alloy systems in literature
- IMARC predictions show corrosion stifling prior to wall penetration (EPRI 2000, 2002; Shoesmith and Massari 2001)

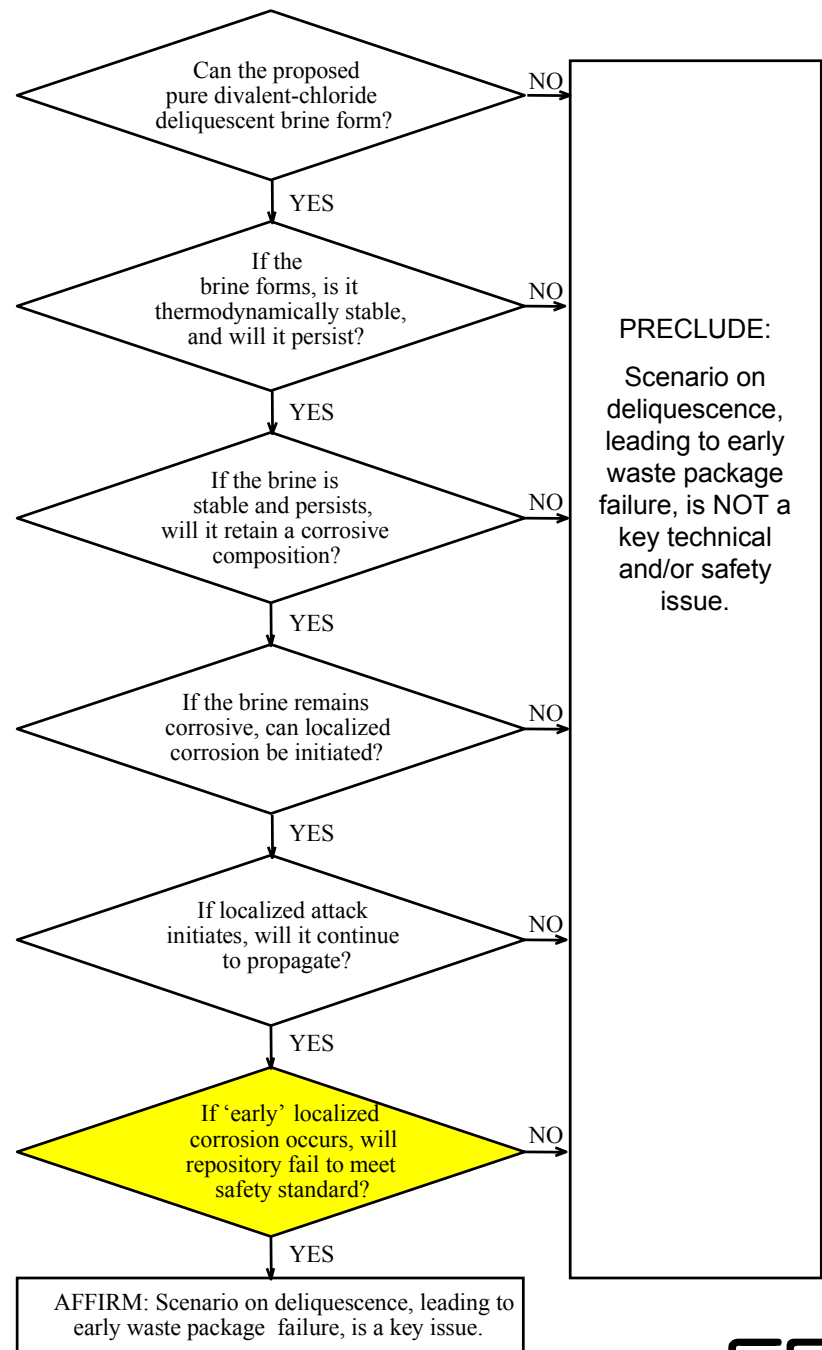


# Summary of EPRI Corrosion Analysis

- **If a corrosive brine forms and persists on the surface of the waste package, will localized corrosion initiate?**
  - **No.**
    - Concentration of inhibitors in deliquescent solutions exceeds that of aggressive  $\text{Cl}^-$  ions
    - Permeable dust and salt deposits will not support initiation because:
      - No spatial separation of anodic and cathodic reactions
      - No localized acidification because of buffering/ neutralization by basic minerals in dust
- **If localized corrosion initiates, will it propagate to failure?**
  - **No.**
    - Even if localized corrosion is assumed to somehow initiate, propagation will not result in through-wall penetration because of various stifling processes



# Decision Tree Approach for Systematic Scenario Evaluation



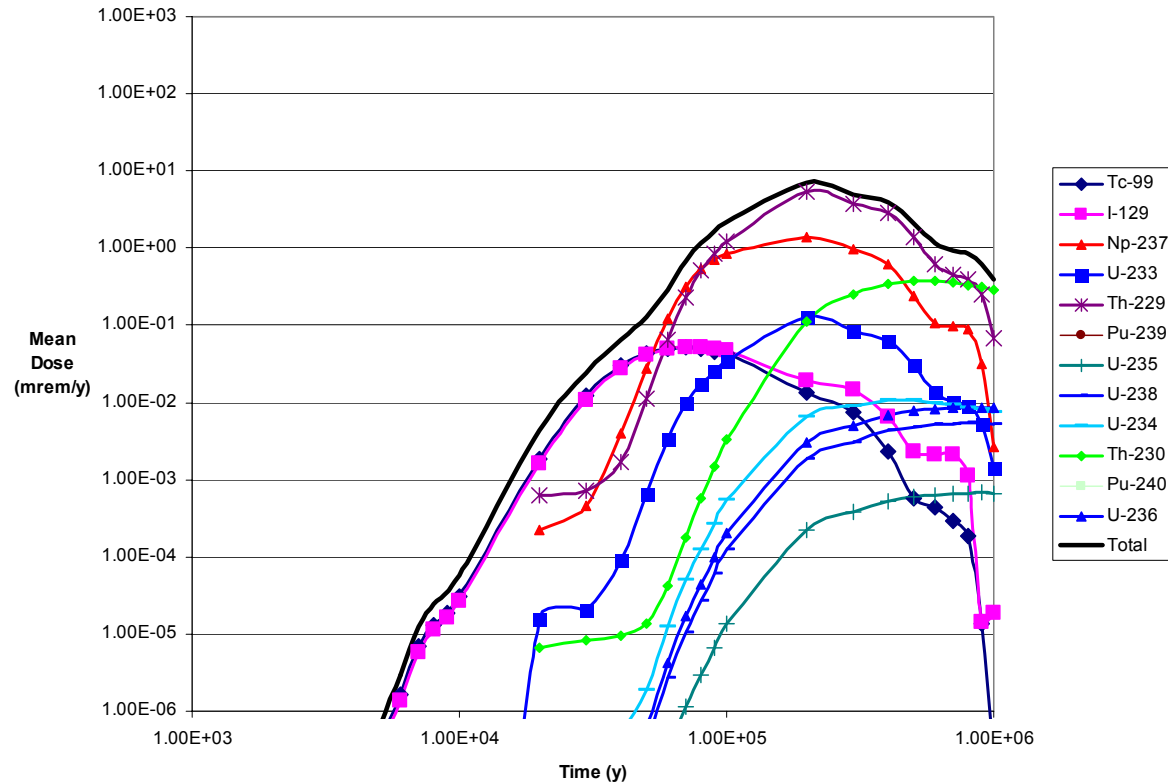
# If waste packages are locally penetrated, will releases exceed regulatory compliance criteria?

- EPRI Approach: Apply total system performance assessment (TSPA) to evaluate the sensitivity and relative importance of this postulated scenario with respect to regulatory compliance.
- USNRC (2003): TSPA is a viable and necessary approach to provide risk-based insights and guidance to any license application for a nuclear waste repository because “[m]ultiple barriers, as an element of a defense-in-depth approach, results in a robust repository system that is more tolerant of failures and external challenges.”

-  The US National Academy of Science (1995) also endorses TSPA as “the only way to evaluate

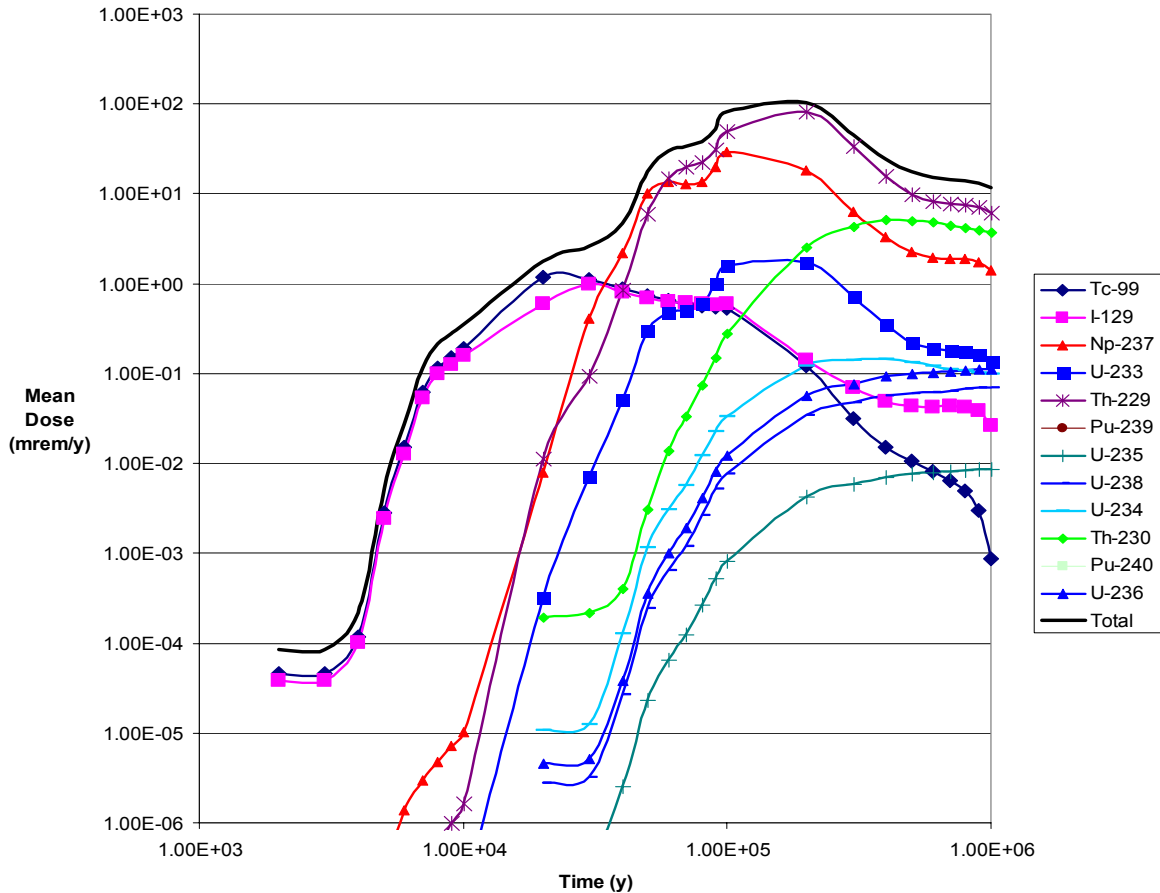
# Regulatory Compliance Analysis: 100% of Waste Packages Initially Failed

- Assume
  - All WPs fail by local penetration at  $t = 0$
  - Drip shield intact
- Result
  - Release dominated by I-129 and Tc-99 (*instant release fraction*)
  - Compliance with EPA and NRC regulatory criteria for 10,000 years (and beyond).



# Regulatory Compliance Analysis: Container and Drip Shield Initially Failed

- Assume
  - All containers fail by local penetration at  $t = 0$
  - All drip shields fail by local penetration at  $t = 0$
- Result
  - Release dominated by I-129 and Tc-99 (*instant release fraction*)
  - Compliance with EPA and NRC regulatory criteria for 10,000 years.
  - Maximum dose comparable to natural background



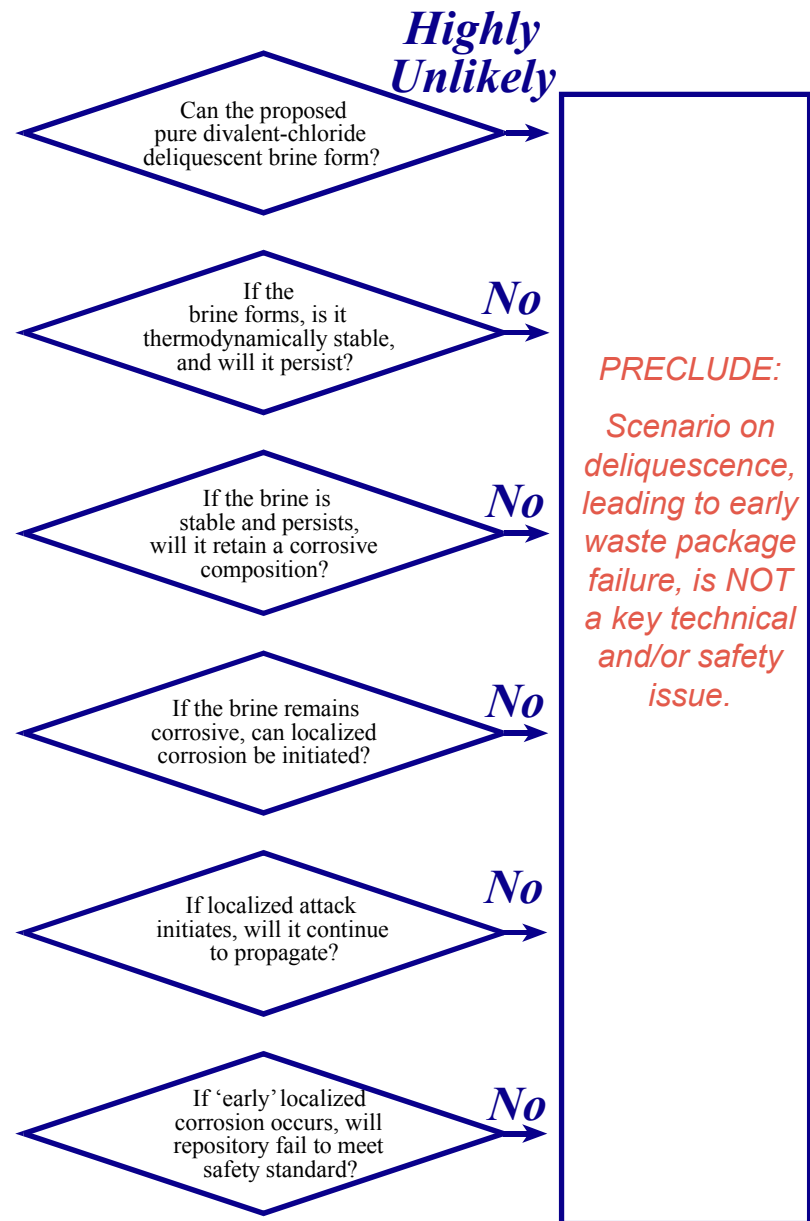
# If waste packages are locally penetrated, will releases exceed regulatory compliance criteria?

- **No.**
- Even assuming initial localized failure of *all* waste packages, the resulting release rate of radionuclides complies with all regulatory safety criteria for all times up to and beyond 10,000 years after repository closure.
- Even assuming initial localized failure of *all* waste packages, *and* loss of drip shield functionality, the resulting release rate of radionuclides complies with all regulatory safety criteria for 10,000 years after repository closure.
- Long-term safety for a nuclear waste repository at Yucca Mountain is robustly assured by multiple barriers and isolation processes.



# Conclusion

- According to EPRI's independent analyses, all of the questions are answered "no" or "highly unlikely".
- All decision-point questions must be answered "yes" for NWTRB's scenario to be of concern.
- Based on multiple lines of evidence, EPRI concludes **there is no technical foundation or safety-compliance basis for continued concern about deliquescent brines leading to early failure of waste packages by localized corrosion.**



AFFIRM: Scenario on deliquescence, leading to early waste package failure, is a key issue.





# Backups



**Weight percent minerals in wind-blown dust excluding organic matter.**  
**Quantitative mineralogy by Slaughter (2004)\*. USGS sample trap numbers**  
**(e.g. T2) and their dates of sampling (e.g. 89 = 1989) are also given.**

Sample Trap	T2- 89	T3- 87	T4- 86	T6- 89	T15- 89	Average	Std Dev
Quartz	22.49	24.39	25.85	25.62	33.32	26.33	3.69
Rutile	0.25	0.41	0.28	0.61	0.34	0.38	0.13
Mnt morillonite	7.78	11.45	9.76	3.12	1.04	6.63	3.95
Goethite	1.41	1.34	0.63	1.57	1.96	1.38	0.43
Biotite	4.85	6.42	3.75	5.81	5.94	5.35	0.95
Illite-muscovite	0.00	6.40	0.00	8.66	19.53	6.92	7.18
Illite	8.88	0.00	0.00	1.30	0.00	2.04	3.46
Albite	16.10	11.05	1.21	0.00	0.13	5.70	6.64
Sanidine	10.04	9.62	18.31	9.15	5.14	10.45	4.30
Oligoclase	0.00	4.03	19.49	21.20	16.02	12.15	8.54
Gypsum	0.12	1.97	3.16	0.07	0.00	1.06	1.28
Kaolinite	5.40	4.53	2.51	5.52	2.81	4.15	1.27
Calcite	11.20	12.68	1.34	8.02	0.00	6.65	5.13
Dolomite	0.00	0.00	0.00	2.78	2.99	1.15	1.41
Soluble Salts	11.47	5.71	13.69	6.58	10.70	9.63	3.02
	99.99	100.00	99.98	100.01	99.92	99.98	

\*Dr. Maynard Slaughter, Crystal Research Laboratories, Greeley, CO



# Relative Reactive Surface Areas of Waste Package, Drip Shield and Drift Walls Considering Roughness of Drift Walls\*

	Circumference (mm)	Percent of total if drift wall has zero roughness	Percent of total if drift wall has roughness of 2x	Percent of total if drift wall has roughness of 7x
Drift Walls	17290	47.2	64.1	86.2
Drip Shield	12720	34.7	23.7	9.1
Waste Package	6630	18.1	12.2	4.7
Total of Circumferences		36640 mm (100%)	53925 mm (100%)	140380 mm (100%)

\*A roughness of 7x is typical for geological materials (White & Peterson, 1990)

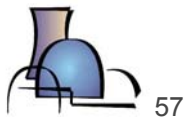


# Relative Reactive Surface Areas in the Repository Assuming a Reactive Skin of Rock 1 mm Thick on the Walls of the Drift\*

## Reactive Surface Areas (%)

Drift walls	97.9
Drip shield	1.4
Waste package	0.7

\*Also assumed: Individual tuff grains have a diameter of 60  $\mu\text{m}$  and an area of 394  $\text{cm}^2/\text{g}$  (Dobson et al., 2003).



# Neutralization Capacity of Wind-Blown Dust for Potential Acidity

Mineral	Average Wt.%in Dust	Moles Mineral per kg Dust	Moles Protons consumed per mole mineral	Moles Protons that can be neutralized by 1 kg dust
Albite	5.7	0.22	4.00	0.87
Sanidine	10.5	0.38	4.00	1.50
Oligoclase	12.1	0.46	4.80	2.20
Biotite	5.4	0.12	12.00	1.38
Illite-muscovite	6.9	0.17	12.00	2.08
Illite	2.0	0.05	8.00	0.42
Montmorillonite	6.6	0.19	6.60	1.29
Kaolinite	4.2	0.16	6.00	0.97
Goethite	1.4	0.16	3.00	0.47
Calcite	6.6	0.66	1.00	0.66
Dolomite	1.2	0.06	2.00	0.13
Quartz	26.3	4.38	0.00	0.00
Rutile	0.4	0.05	0.00	0.00
Gypsum	1.1	0.06	0.00	0.00
Soluble Salts	9.6			
<b>Neutralization Capacity/kg dust</b>				<b>11.97 moles</b>



# Neutralization Capacity of ESF Dust (Topopah Spring Tuff) for Potential Acidity

Mineral	Wt.% in dust	Moles Mineral per kg dust	Moles Protons consumed per mole mineral	Moles Protons that can be neutralized by 1 kg dust
K-spar	31.7	1.14	4.00	4.57
Albite	23.9	0.91	4.00	3.65
Anorthite	0.85	0.03	8.00	0.24
Smectite clays	2.12	0.06	7.32	0.42
Illite	0.29	0.01	8.00	0.06
SiO <sub>2</sub> forms	40.8	6.82	0.00	0.00
Soluble Salts	0.3			

**Neutralization Capacity/kg dust**

**8.95 moles**

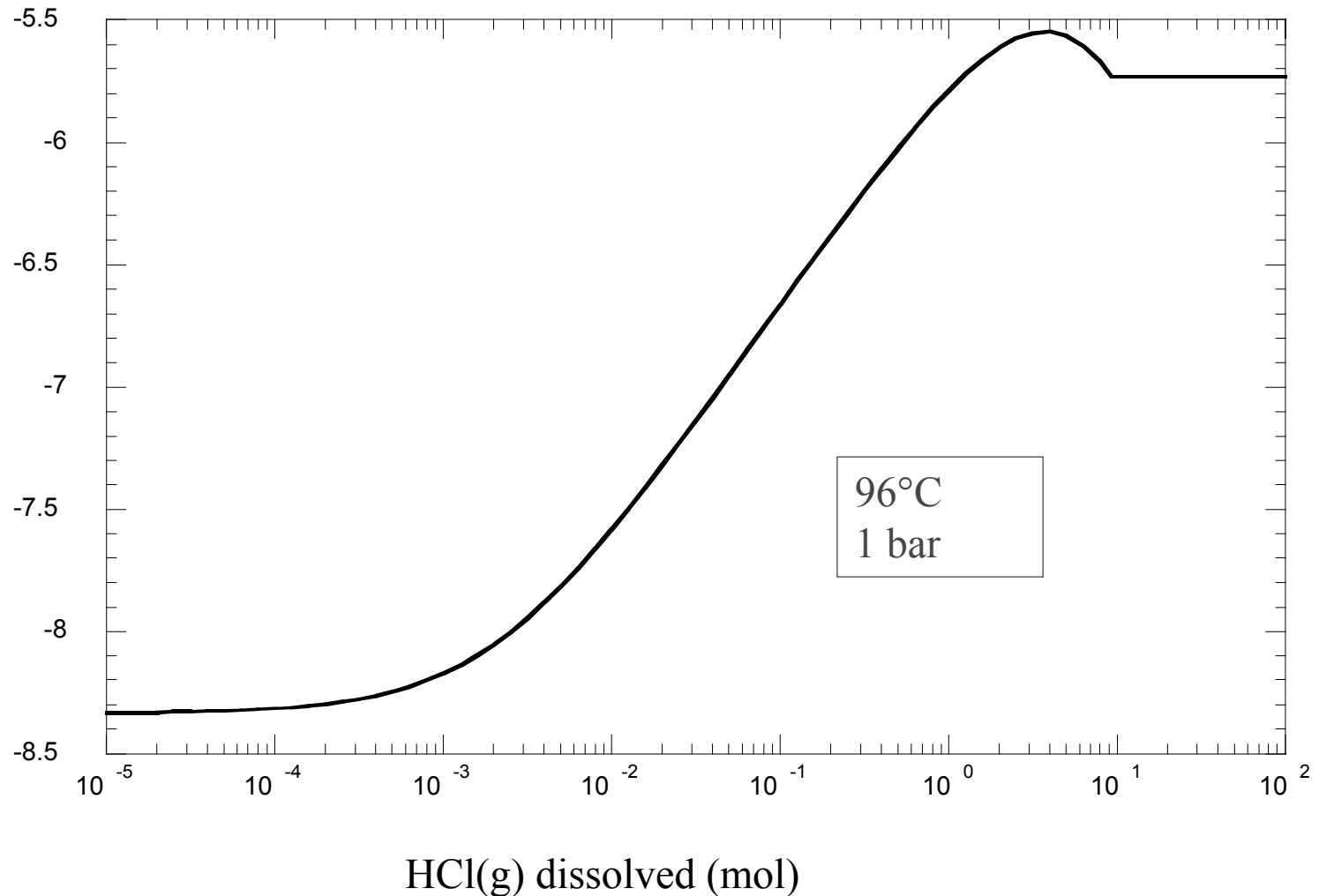
# The Acid-Neutralization Capacity of Dusts Compared to the Potential Acidity of Brines Derived from and in Contact with Dusts

			<b>H<sup>+</sup> Neutr. Capacity of Basic Minerals (mol/kg dust)</b>	<b>Acidity if all (NO<sub>3</sub> + Cl) Were in (HNO<sub>3</sub> + HCl) (mol/kg dust)</b>	<b>Mol% Basic Minerals Consumed to Neutralize this Acidity</b>
	<b>Soluble Salts Wt%</b>	<b>Basic Minerals Wt%</b>			
<b>Wind-Blown Dust</b>	<b>9.6</b>	<b>62.6</b>	<b>12.0</b>	<b>0.88</b>	<b>7.3</b>
<b>ESF Dust</b>	<b>0.3</b>	<b>58.9</b>	<b>9.0</b>	<b>0.012</b>	<b>0.13</b>



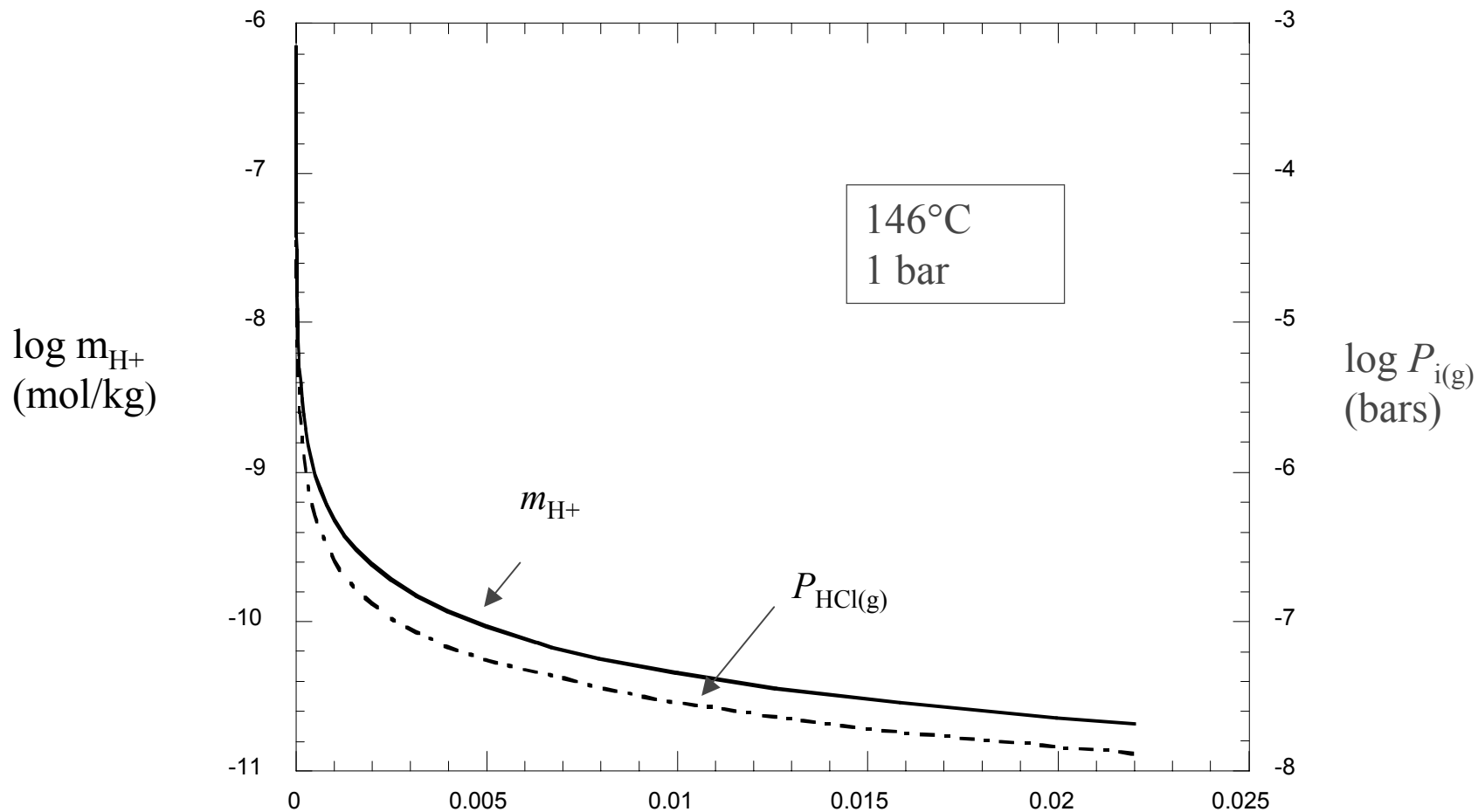
# Buffering of Near-Neutral Conditions by Albite + Na-beidellite + kaolinite ( $\pm$ halite)

$\log m_{\text{H}^+}$   
(mol/kg)

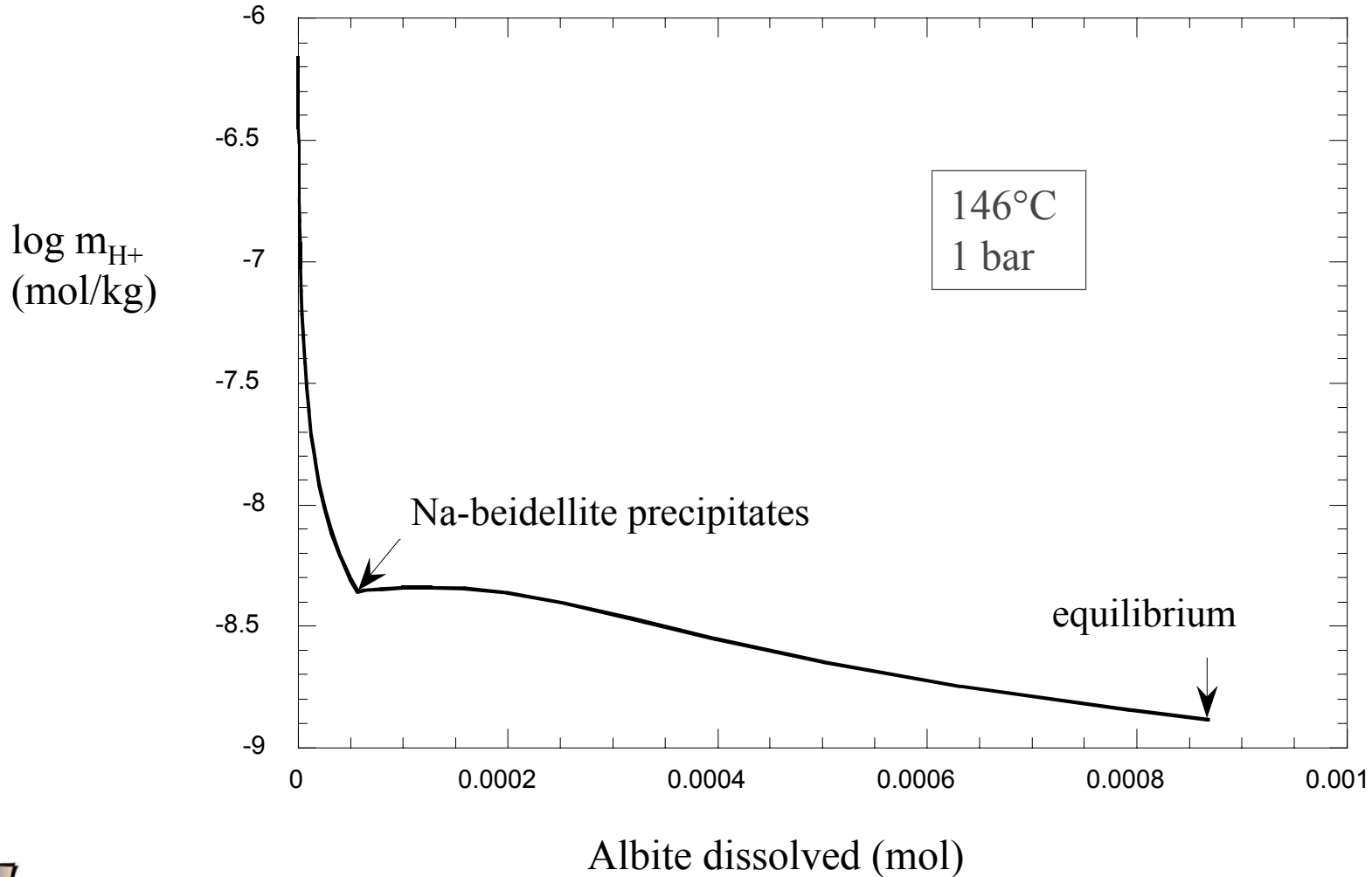




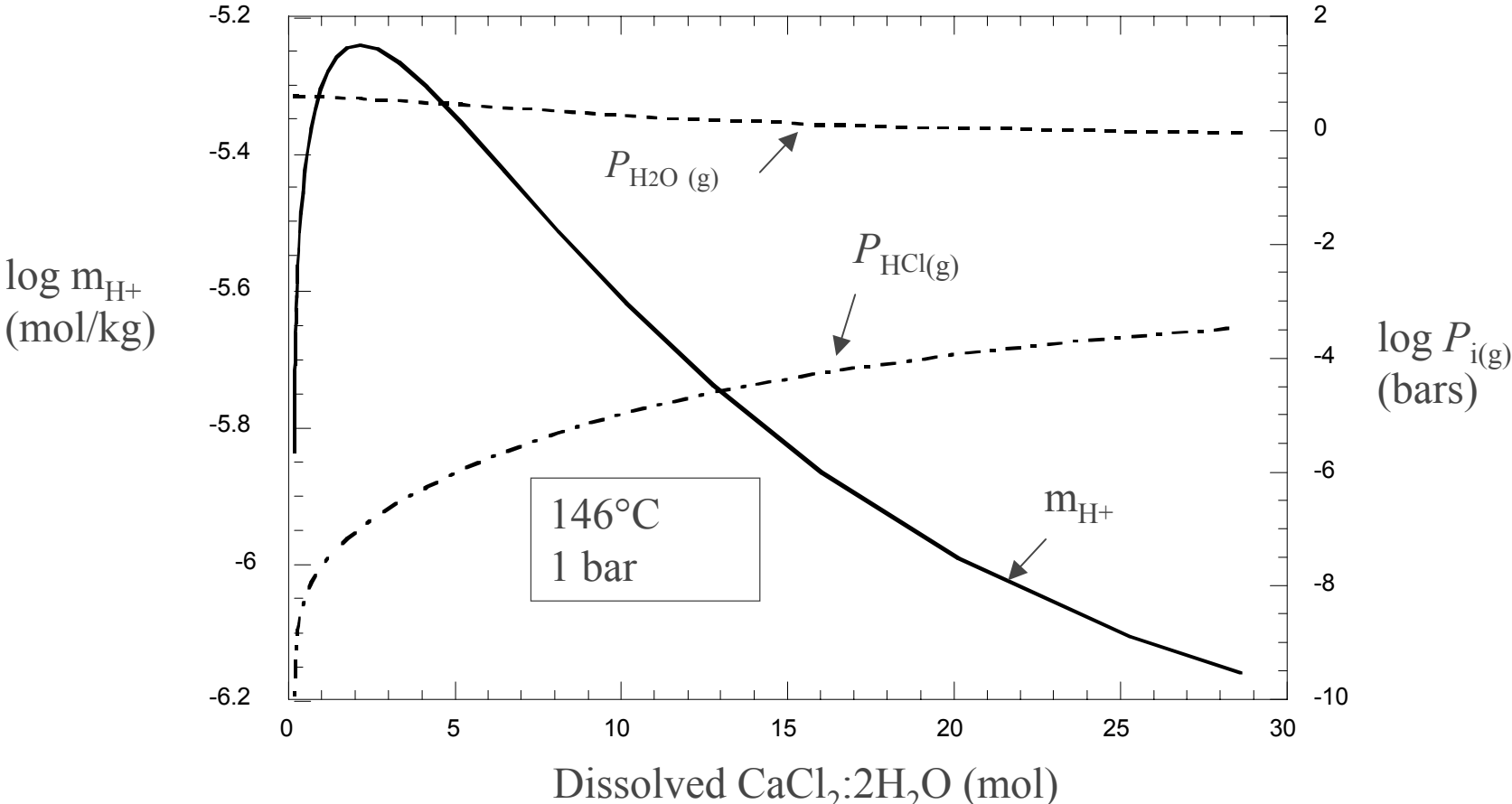
# Effect of Dissolution of Calcite in Dust on 'Acidity' in $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Deliquescent Brine



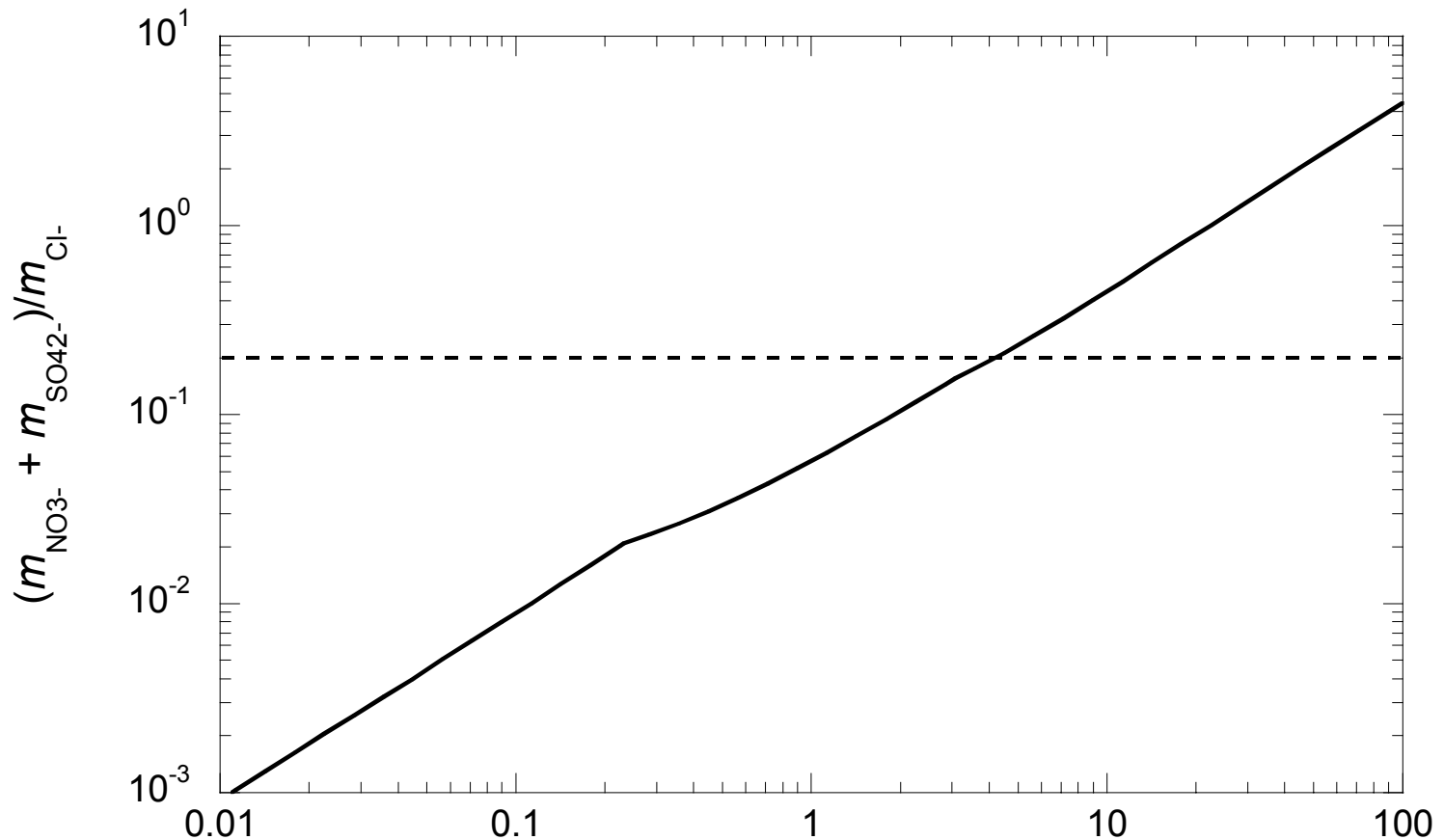
# Effect of Dissolution of Albite in Dust on 'Acidity' in $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Deliquescent Brine



# Chemical Evolution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Deliquescent Brine



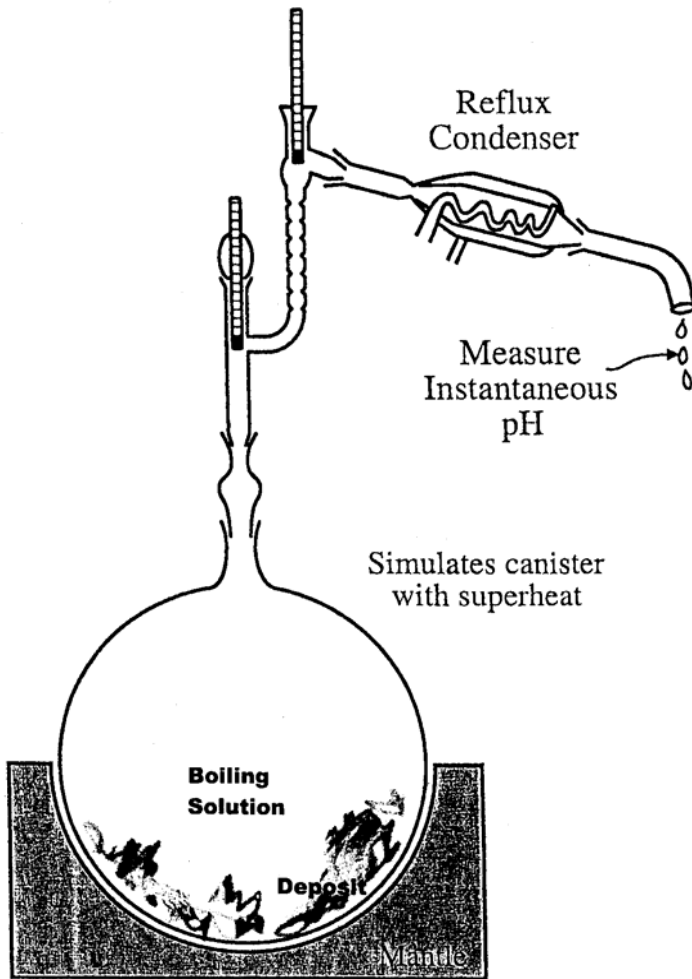
# Effects of adding equal amounts of $\text{NO}_3$ and $\text{SO}_4$ salts from dust on the potential corrosivity of an initially pure $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ deliquescent brine



NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> dissolved in brine (mol % relative to initial Cl<sup>-</sup>)



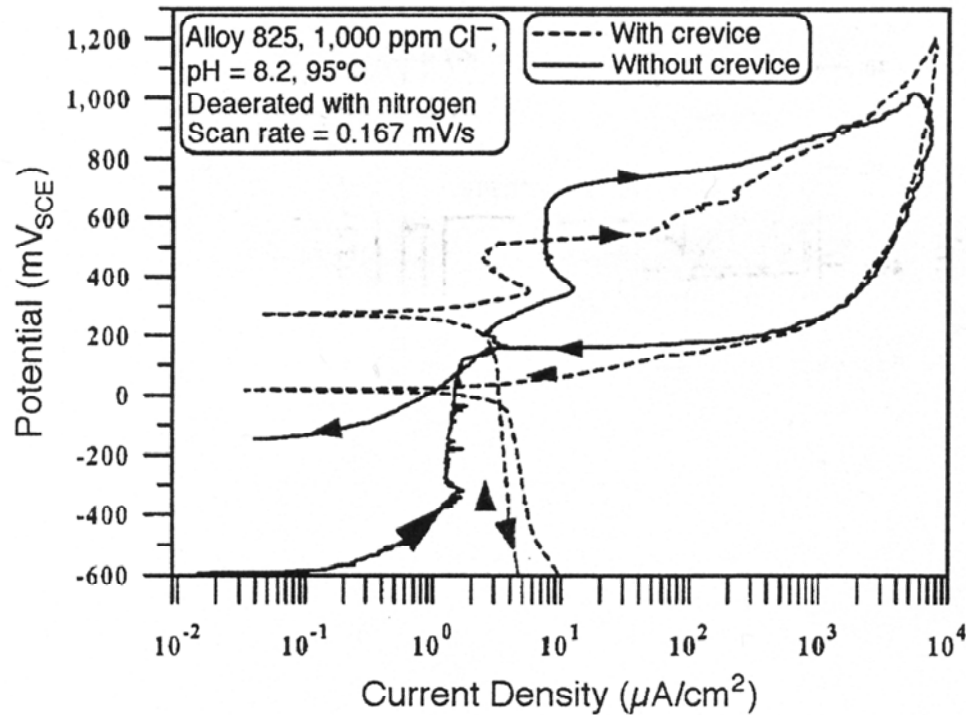
# Critique of State of Nevada Reflux Tests



- Distillation/condenser apparatus does not realistically simulate the actual emplacement drift/repository system.
- Tests omit volumetrically dominant basic minerals present in drift walls and in dust on waste packages.
- Condensation of acid gases most likely in cooler drift walls which have an area perhaps 20-100 times greater than that of waste package.
- Acid gases will be neutralized by reaction with tuff minerals in drift walls (no refluxing onto waste packages).
- Nevada proposed chemical reactions uncertain in part because of lack of identification of solid residue.



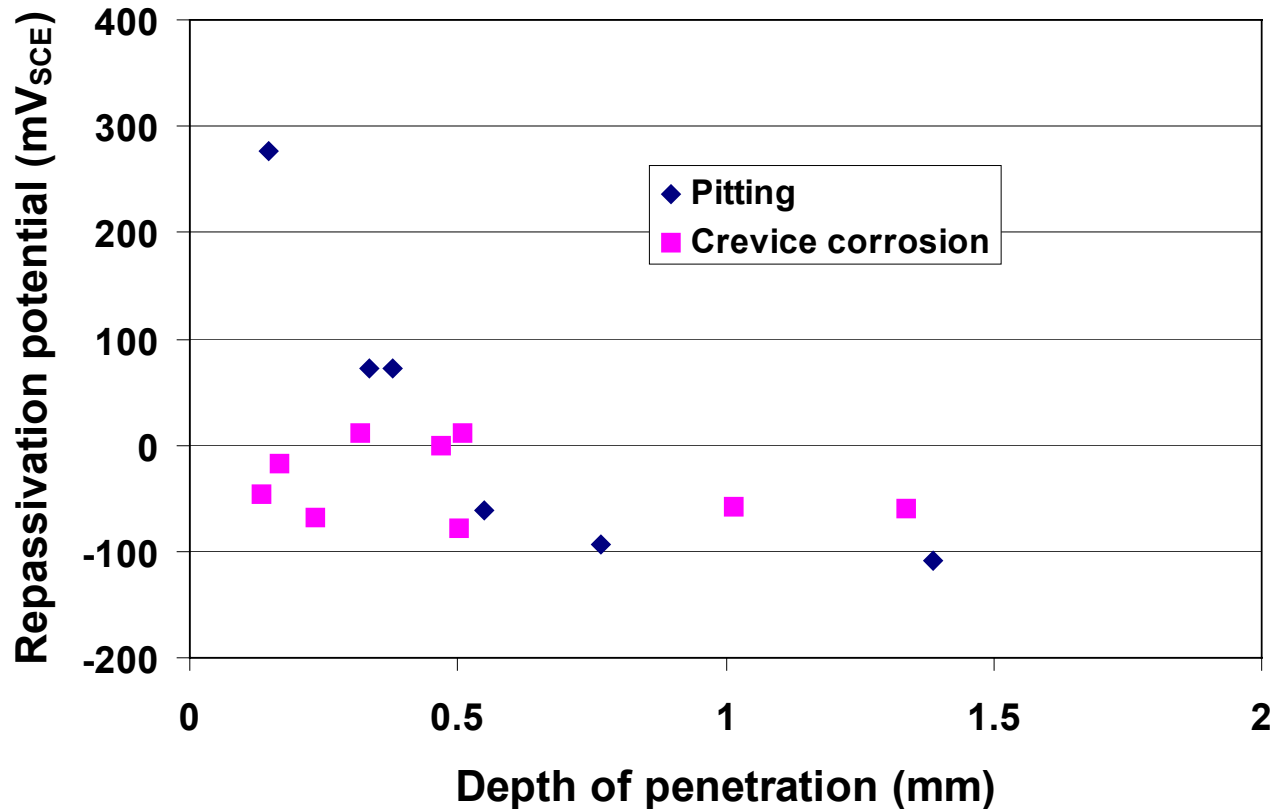
# Effect of crevice on breakdown and re-passivation potentials



- Crevice leads to easier film breakdown and more difficult re-passivation
- Note: effect of crevice on local acidification only (no differential [O<sub>2</sub>] cell)
- From Dunn et al., Corrosion 52, 1996, 115-124.,



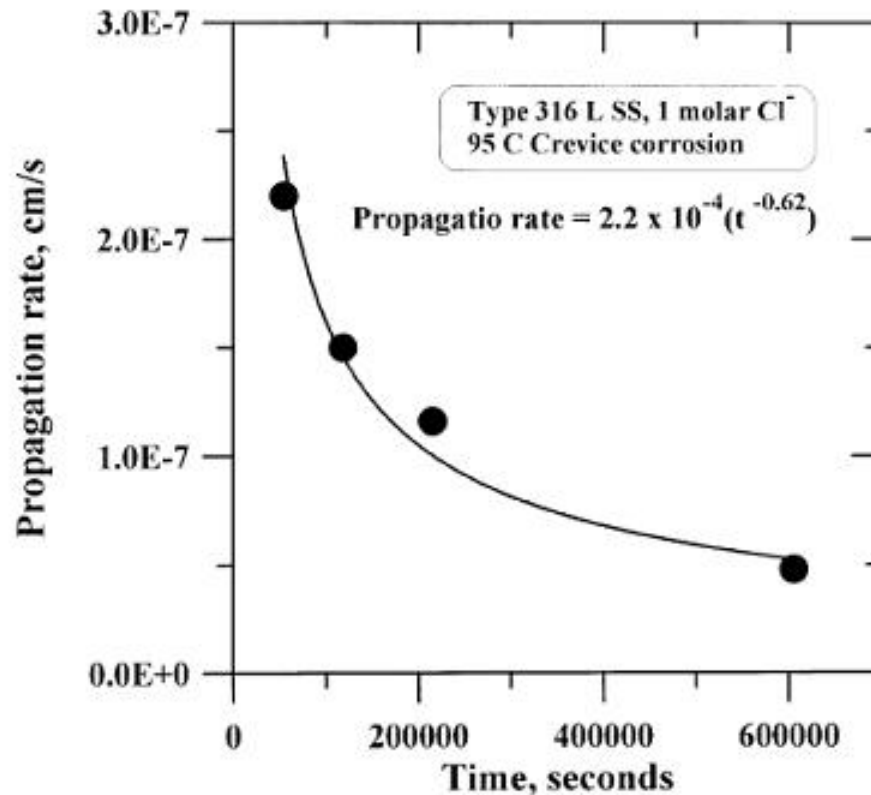
# Comparison of Repassivation Potentials for Pitting and Crevice Corrosion



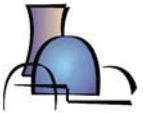
- Based on Dunn et al., Corrosion 52, 1996, 115-124



# Time Dependence of Crevice Corrosion Rate for 316L Stainless Steel

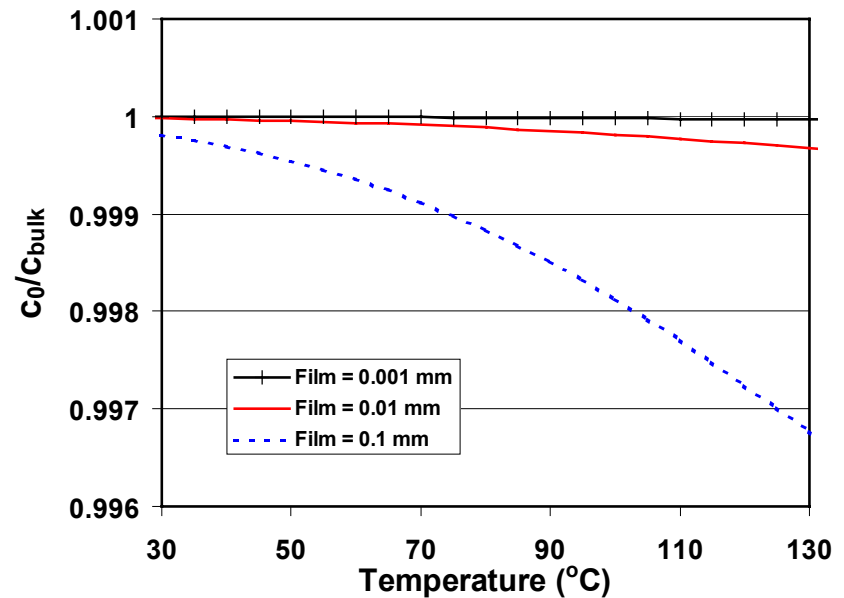
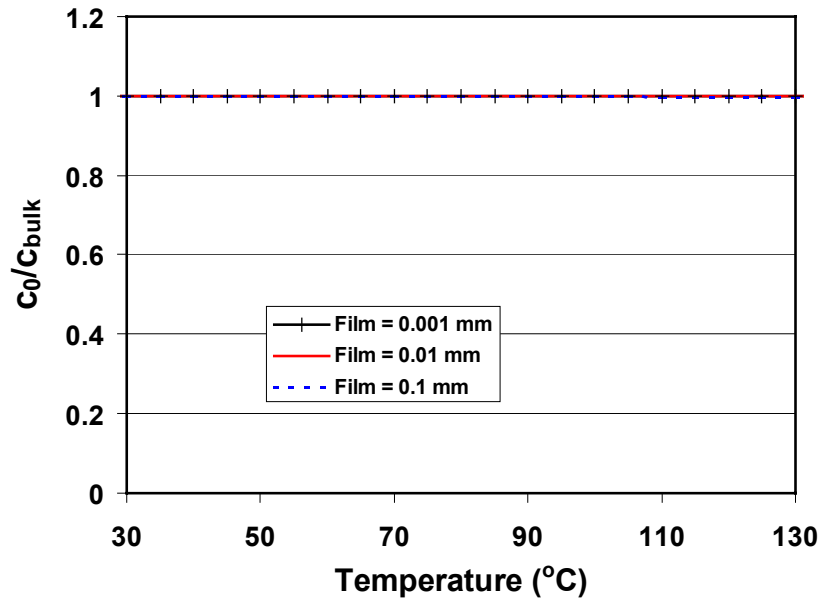


- Dunn et al., CORROSION/96, paper no. 97





# Ability of Dust Deposit to Create a Differential Aeration Cell



- Ratio of interfacial  $O_2$  concentration to that in the bulk solution
- Predicted ratio  $> 0.99996$  for expected water film thickness



# Inability of Permeable Deposit to Support Local Acidification, Hence, Initiation

- Without separation of anodic and cathodic reactions there will be no net  $H^+$  formation in “occluded” region



- Buffering/neutralization of  $H^+$  produced by hydrolysis
  - Alumino-silicate minerals will buffer ~pH 5
  - Carbonate minerals will neutralize  $H^+$

