

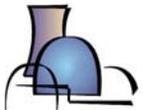


# EPRI-sponsored studies on the evolution of environments at Yucca Mountain

**Presenter: Randy Arthur**

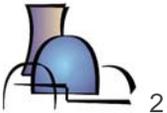
**Additional authors: Michael Stenhouse, Donald Langmuir, Fraser King, Mick Apted, John Kessler**

Presented to the Workshop on Localized Corrosion of Alloy 22 in Yucca Mountain Environments, Las Vegas, Nevada, 25-26 September 2006



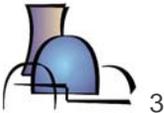
# Presentation focus

- Question 1 for panel discussion:
  - “ Are data, understanding and models sufficient to bound potential environments on waste packages in a repository in Yucca Mountain with reasonable confidence from a corrosion standpoint?”
- Possible deliquescence scenario
  - Soluble salts initially present in repository dusts

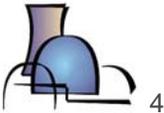


# Presentation topics

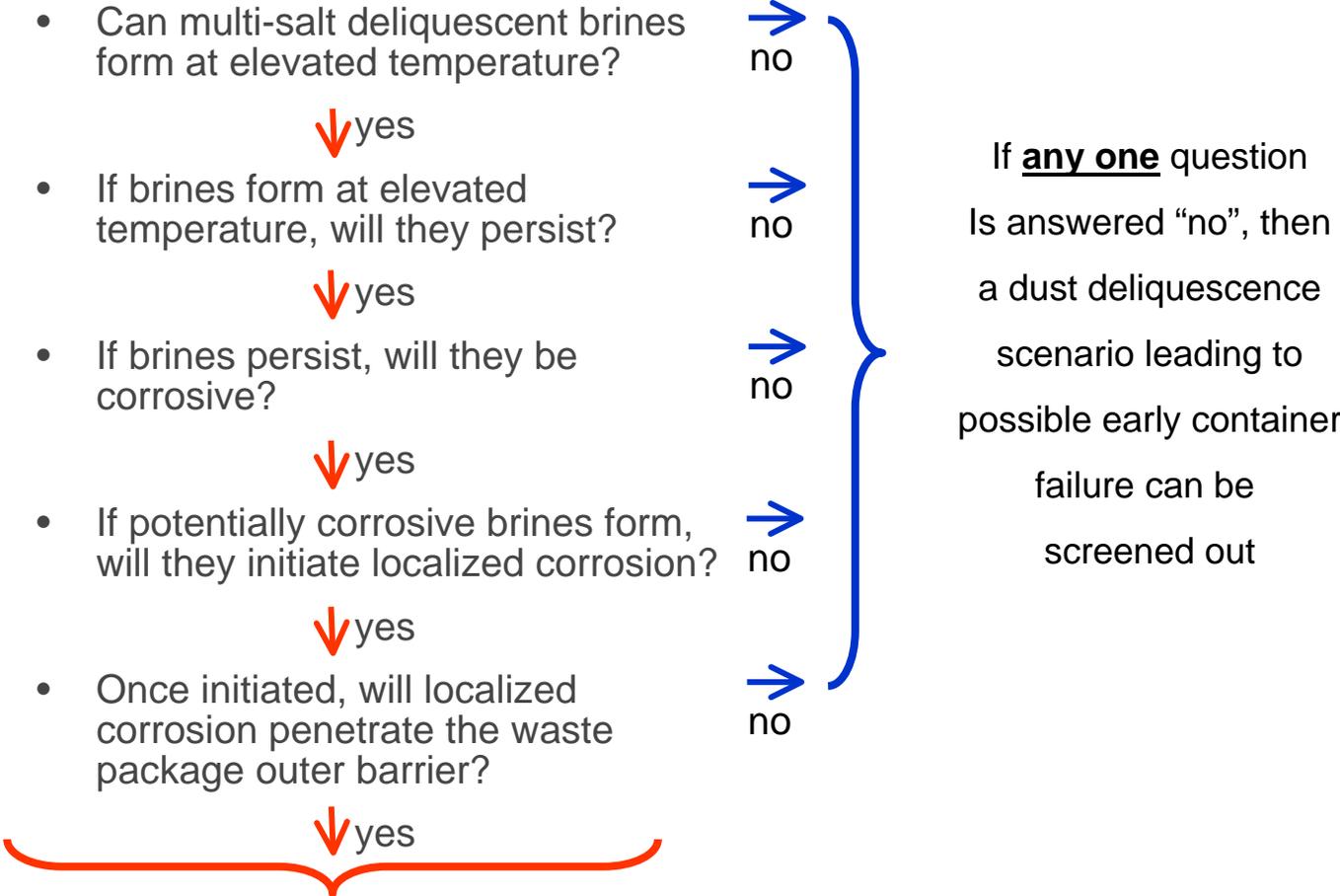
- Importance of dust mineralogy
- Summary of DOE's geochemical modeling approach for bounding dust mineralogy
- EPRI's alternative model
- Test of model predictions
- Concluding remarks



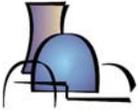
# Why is dust mineralogy important?



# DOE's decision tree for FEP screening of a dust deliquescence scenario

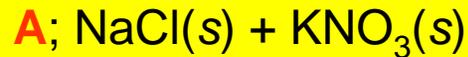


**All** questions must be answered “yes” for a dust-deliquescence scenario to be screened in



# Importance of dust mineralogy

DOE's screening starts with the assumption that 3 possible salt assemblages could exist in repository dusts:

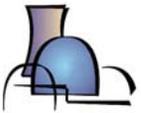


- Can multi-salt deliquescent brines form at elevated temperature?  
↓ yes
- If brines form at elevated temperature, will they persist?  
↓ yes
- If brines persist, will they be corrosive?  
↓ yes
- If potentially corrosive brines form, will they initiate localized corrosion?  
↓ yes
- Once initiated, will localized corrosion penetrate the waste package outer barrier?  
↓ yes

no  
no  
no  
no  
no  
no

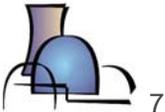
If any one question is answered "no", then a dust deliquescence scenario leading to possible early container failure can be screened out

All questions must be answered "yes" for a dust-deliquescence scenario to be screened in

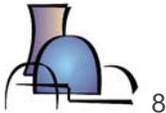


# Are initial salt assemblages A, B and C reasonably bounding?

- EPRI believes that the answer to this question is “**NO**”
  - lack of analytical data characterizing the soluble-salt mineralogy of plausible repository dusts
  - these assemblages are inferred by DOE using a geochemical modeling approach
  - the model appears to be unrealistic with respect to mass transfer of all relevant acid gases
  - more realistic assemblages would be less deliquescent



# DOE's evaporation model

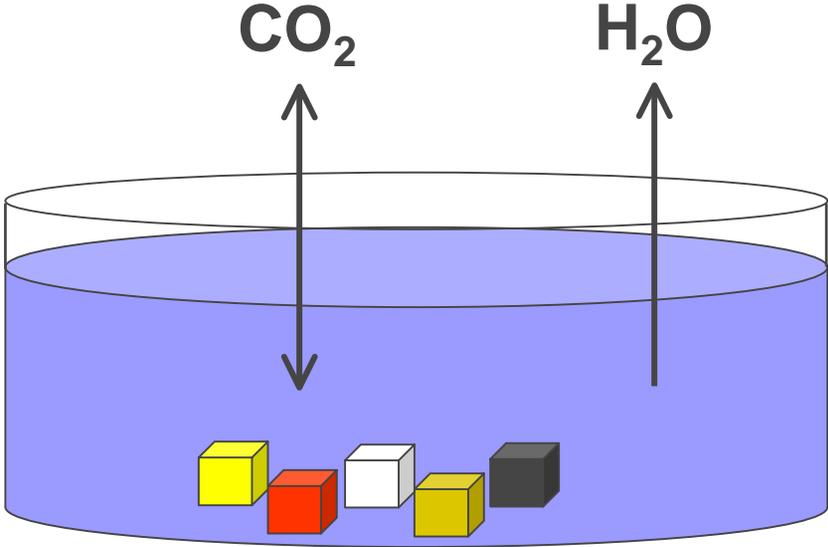


# Overview

- 54 leachates from dust samples collected at various locations in the ESF
- Leachate evaporation was simulated at 25°C, 1 bar total pressure and atmospheric  $p_{\text{CO}_2(\text{g})}$  ( $10^{-3.5}$  bar)
- Simulations were carried out using DOE's IDPS model
- The model was evaluated using EQ3/6 (ver. 8.0) and a high-temperature Pitzer thermodynamic database (*data0.ypf.R0*)

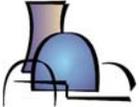


# Conceptual model



↑ Evaporation

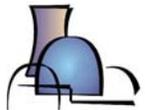
↕ Equilibrium constraint: Fixed partial pressure



# Approximations

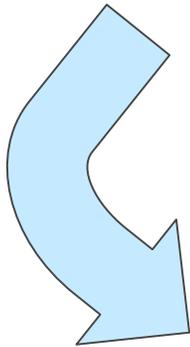
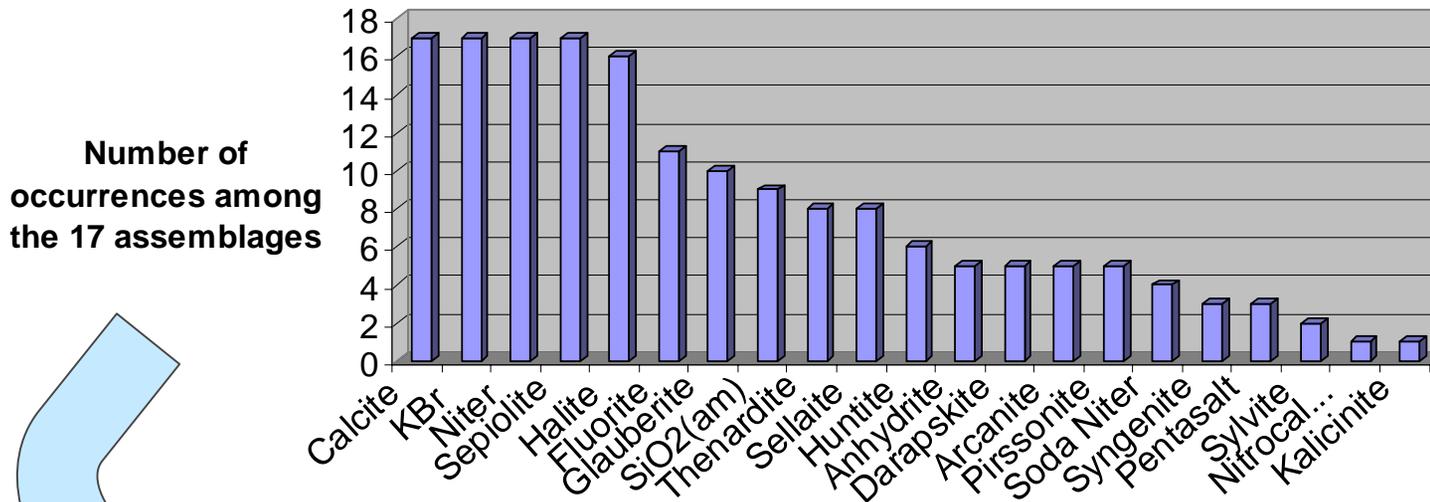
- ESF dusts may not be representative of dusts that will exist on waste package surfaces
  - ESF dusts are mostly crushed tuff with about 0.5 wt% soluble salts
  - wind-blown dusts have a higher soluble-salt content (10-15 wt%) and different composition
- Recent data\* suggest that most of the  $\text{NO}_3^-$  in tunnel-dust leachates is produced by dissolution of ammonium salts
- $\text{NH}_4\text{NO}_3(\text{s})$  [and  $\text{NH}_4\text{Cl}(\text{s})$ ] will decompose (sublimate) rapidly with increasing temperature
- Equilibrium mineralogy considered an “end-member” case of probable mechanical mixtures making up actual dusts  
-----

\* *Analysis of dust deliquescence for FEP screening* [ANL-EBS-MD-000074 REV 01]

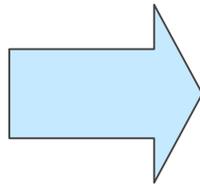


# Results

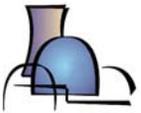
Distribution of salt and non-salt minerals produced by the evaporation of tunnel-dust leachates: 17 unique assemblages containing 10 minerals apiece



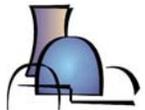
Abstraction based on groupings among the most deliquescent salts



- A: Halite + Niter
- B: Halite + Niter + Soda Niter
- C: Halite + Niter + Soda Niter + Nitrocalcite

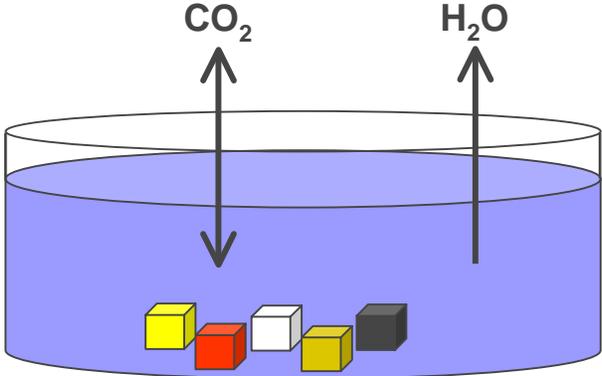


# EPRI's alternative model

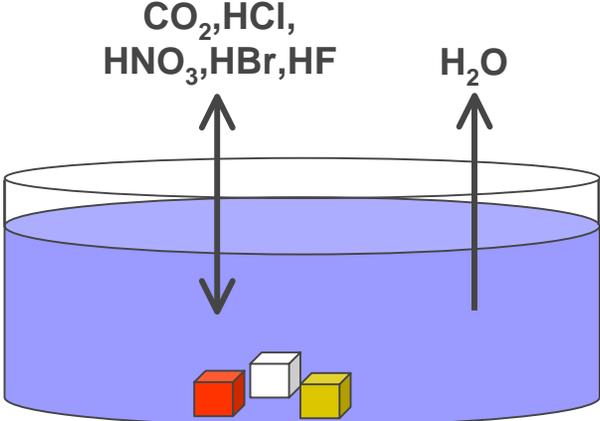


# Conceptual model variants

## DOE/EPRI-1

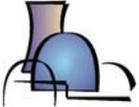


## EPRI-2



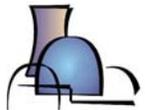
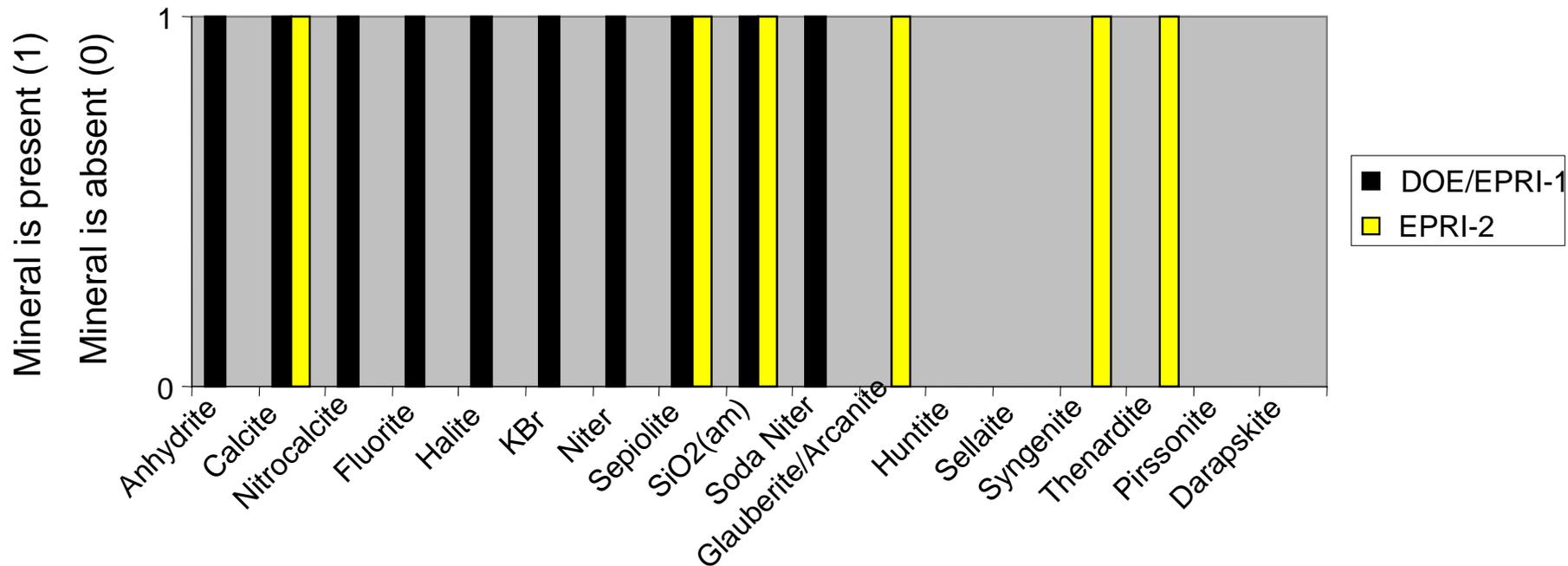
↑ Evaporation

↕ Equilibrium constraint: Partial pressures are fixed at atmospheric values



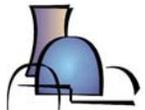
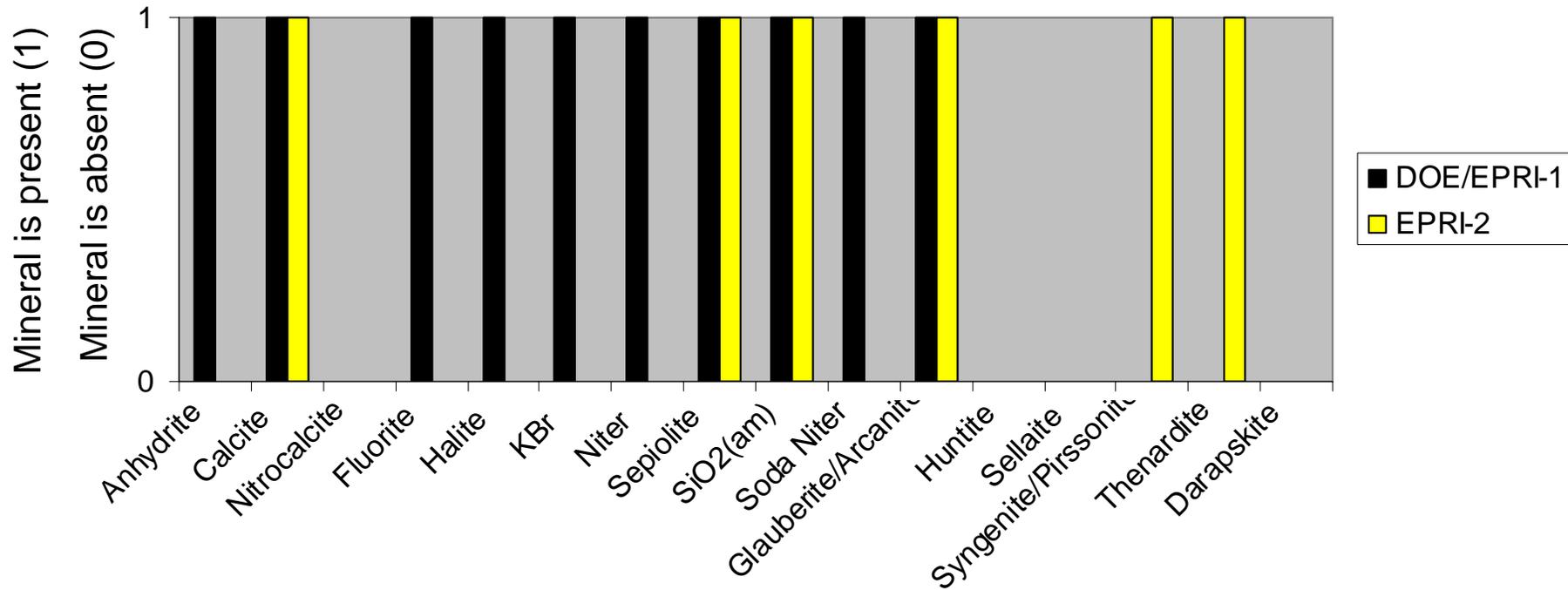
# Comparison of predicted eutectic mineral assemblages: Example 1 (nitrate salts not predicted in the EPRI-2 model)

P07 leachates (produce Assemblage C in the DOE/EPRI-1 models)



# Comparison of predicted eutectic mineral assemblages: Example 2 (nitrate salts not predicted in the EPRI-2 model)

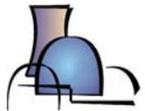
P14 leachates (produce Assemblage B in the DOE/EPRI-1 models)



# Comparison of model predictions: relative humidity at the eutectic

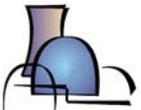
Model	Leachate categories <sup>a</sup>			
	P07	P14	P22	S82c
DOE/EPRI-1	38.9	54.8	54.8	54.8
EPRI-2	84.0 – 84.9	82.2 – 84.9	82.2 – 84.0	82.1

<sup>a</sup> - P07 leachates produce Assemblage C salts (halite + niter + soda niter + nitrocalcite) at dryout in the DOE/EPRI-1 models. P14, P22 and S82c leachates produce Assemblage B salts (halite + niter + soda niter) at dryout in the DOE/EPRI-1 models

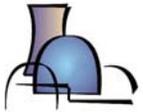


# Summary of model comparisons

- Equilibrium constraints on gas partial pressures strongly affect the predicted mineralogy of evaporated dust leachates
- Significant mineralogical differences are predicted using the DOE/EPRI-1 and EPRI-2 model variants:
  - nitrate salts precipitate in the DOE/EPRI-1 model
  - nitrate salts do not precipitate in the EPRI-2 model
- EPRI-2 salts are much less deliquescent than their DOE/EPRI-1-model counterparts
- EPRI believes that the EPRI-2 model is more realistic



# Test of model predictions

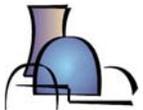


# USGS study\* on evaporation of tunnel-dust leachates

- Provides a basis for evaluation of evaporation-model predictions – does NOT constitute a direct determination of soluble salts in dust
- 5 dust samples obtained by vacuum sampling at various locations in the ESF
- Dust samples were immersed in deionized water for about 1 hour
- Leachates were separated from the remaining solids, and samples were analyzed for major cations and anions
- The leachates were then evaporated to dryness at room temperature
- Minerals precipitating as a result of evaporation were identified by x-ray diffraction

-----  
\* Described in Appendix E of “*Analysis of dust deliquescence for FEP screening*”

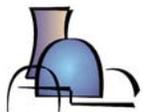
•[ANL-EBS-MD-000074 REV 01]



# XRD results from the USGS study (no nitrate salts detected)

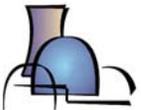
Salt	Composition	Dust Sample				
		1	2	3	4	5
Halite	NaCl	x	xx	xx	xx	xx
Sal Ammoniac	NH <sub>4</sub> Cl	x	x	x		
Calcite	CaCO <sub>3</sub>		xx			
Gypsum	CaSO <sub>4</sub> :2H <sub>2</sub> O	xx	x		x	
Hemihydrate	CaSO <sub>4</sub> :0.5H <sub>2</sub> O			xx	x	
Mascagnite	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	x				
Biphosphammite	(NH <sub>4</sub> ,K)H <sub>2</sub> PO <sub>4</sub>	x				
Weddelite	CaC <sub>2</sub> O <sub>4</sub> :2H <sub>2</sub> O		x	x		

xx – major constituent; x – minor constituent



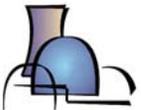
# Neither the DOE/EPRI-1 nor EPRI-2 models compare exactly with USGS results

- Leachate analyses from the USGS study are not available:
  - can only compare XRD results with model results using ESF tunnel-dust leachates originally reported by DOE
- Ammonium salts not present in DOE/EPRI-1 and EPRI-2 eutectic assemblages
  - $\text{NH}_4^+$  ( as well as total carbonate & pH) not included in original dust-leachate analyses
- Calcite present in DOE/EPRI-1 and EPRI-2 assemblages - detected in only one of the XRD analyses
- Nitrate salts predicted in DOE/EPRI-1 assemblages (but not in EPRI-2 assemblages) - not detected by XRD
- Halite not predicted in EPRI-2 assemblages (but is predicted in DOE/EPRI-1 assemblages) – detected in all of the XRD analyses
- Anhydrite predicted in DOE/EPRI-1 assemblages (but not in EPRI-2 assemblages) – only hydrated forms of  $\text{CaSO}_4$  detected by XRD



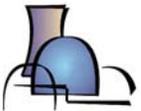
# Comments on the apparent absence of nitrate salts in the USGS assemblages

- Nitrate salts could be present in relative abundances that are below the detection limit of XRD ( $\approx 1\text{--}5\text{ vol}\%$ )
  - results of the DOE/EPRI-1 model suggest, however, that niter, and in some cases soda niter, would be at least as abundant as halite, and should therefore have been detected by XRD if they were present
- Consideration of dehydration equilibria involving gypsum and anhydrite suggests that the relative humidity at the eutectic was too high ( $> 79\%$ ) to stabilize assemblages containing the nitrate salts
  - the possibility cannot be ruled out, however, that gypsum (and hemihydrate) persist metastably



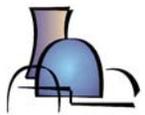
# Summary of comparisons between model predictions and experimental results

- Relevant experimental data are limited – conclusions are provisional
- Important discrepancies exist between experimental observations and results of the evaporation models (both DOE/EPRI-1 and EPRI-2)
- Some of the discrepancies likely result because the models do not presently consider certain leachate constituents ( $\text{NH}_4^+$ ), and approximate others (DIC, pH)
- Other discrepancies are more difficult to explain
  - apparent absence of nitrate salts in USGS experimental assemblages is inconsistent with DOE's key salt assemblages A, B and C

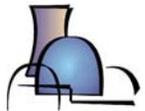


# Summary and concluding remarks

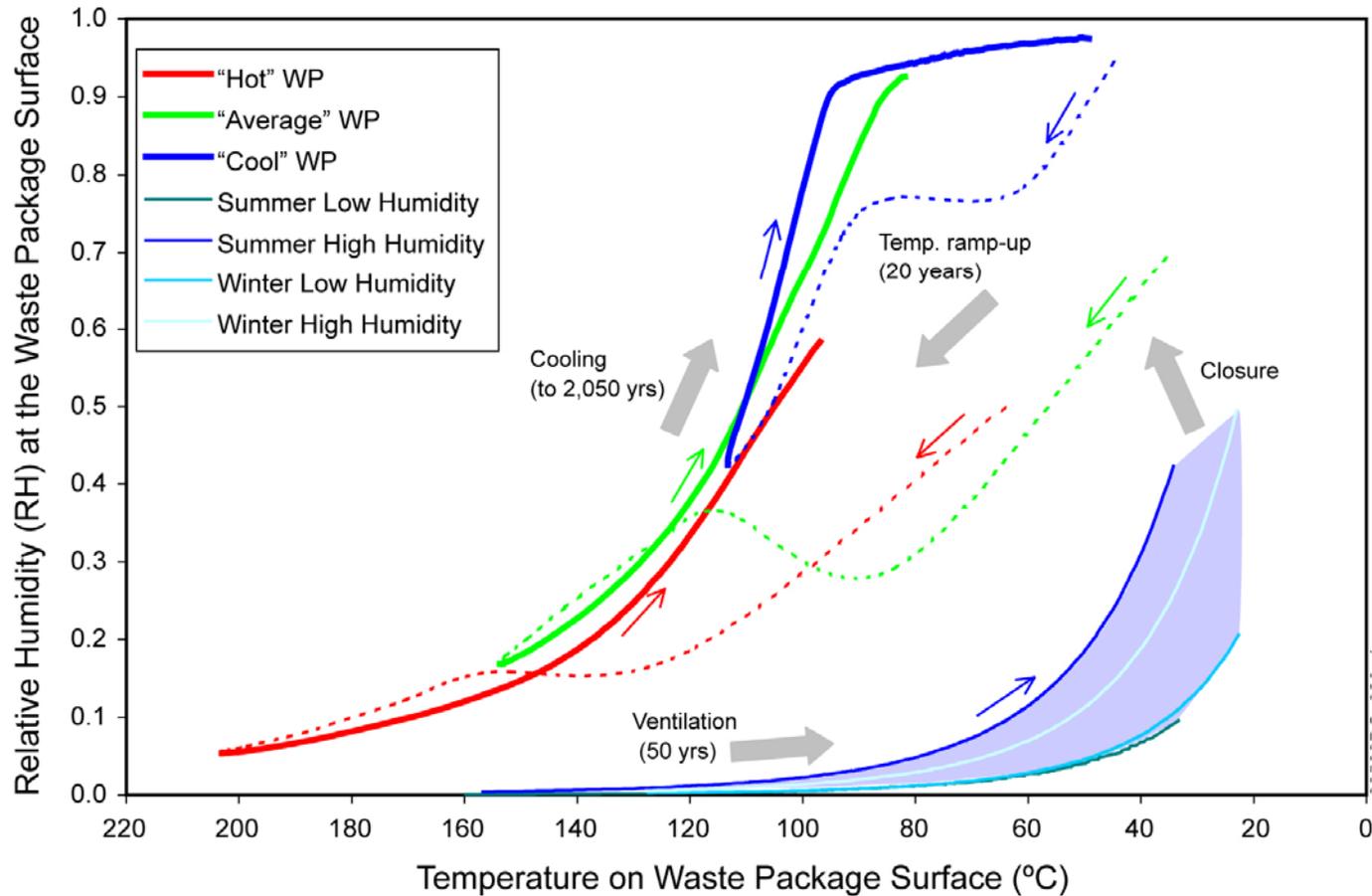
- DOE uses a geochemical modeling approach to infer the existence of nitrate-bearing salt assemblages for consideration in a possible dust-deliquescence scenario
- These assemblages are used by DOE to conservatively overestimate the maximum temperature at which a deliquescent brine could possibly form on waste package surfaces
- It is EPRI's position that consideration of these assemblages may be unnecessarily conservative because the evaporation model used to define them appears to be overly simplified with respect to acid-gas mass transfer
- In addition,
  - nitrate salts have not been detected in experimentally evaporated ESF dust leachates, which appears to contradict DOE's inference that such salts could be present initially in repository dusts
  - direct determination of the mineralogy of soluble salts in plausible repository dusts has not been reported
- EPRI concurs with DOE that other factors, not addressed here, would mitigate the persistence and corrosivity of any deliquescent brines that might be assumed to form in the in-drift environment



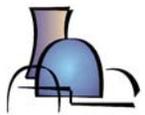
# Backups



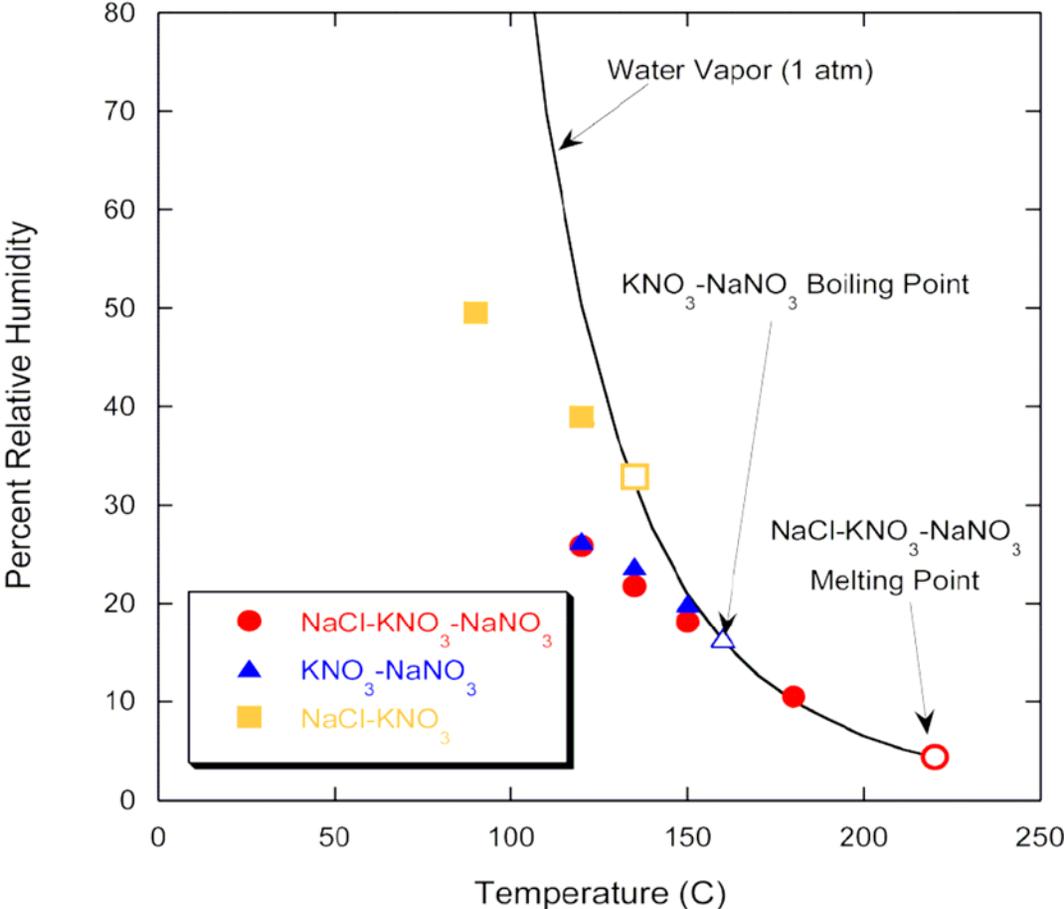
# Constraints on time, temperature and relative humidity at waste package surfaces



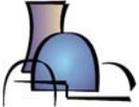
Source: Analysis of dust deliquescence for FEP screening [ANL-EBS-MD-000074 REV 01]



# Experimental deliquescence temperatures and relative humidities for several salt assemblages



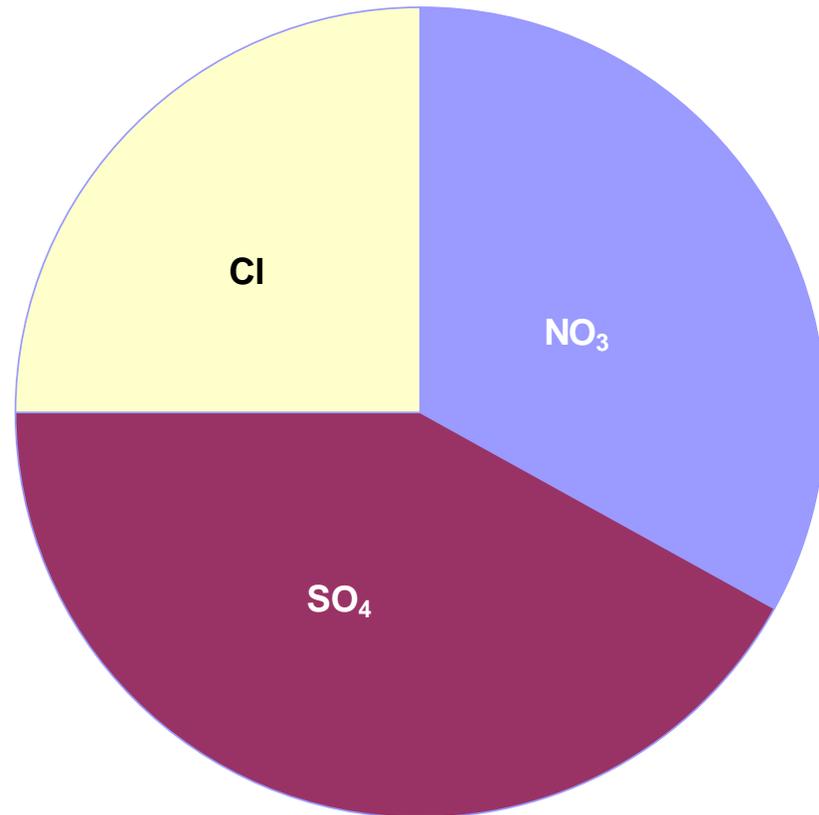
See "Analysis of dust deliquescence for FEP screening" [ANL-EBS-MD-000074 REV 01]



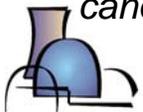
# Soluble salts in ESF dust

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

Anion Percent Values in Soluble Salts in ESF Dust

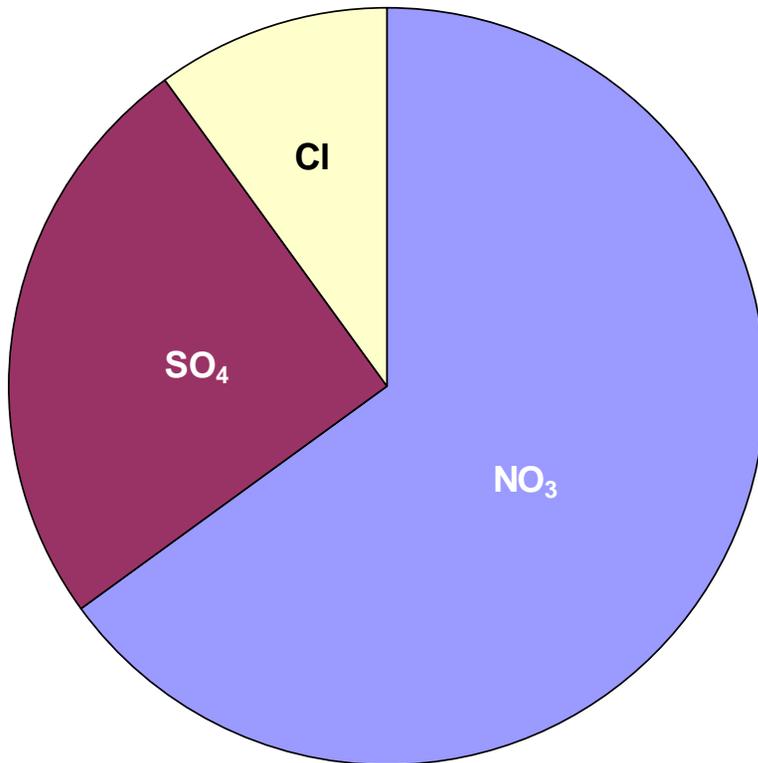


-----  
Source: *Comments regarding in-drift chemistry related to corrosion of containment barriers at the candidate spent fuel and HLW repository at Yucca Mountain, Nevada.* [EPRI, Palo Alto, CA, 2004. 1010941]



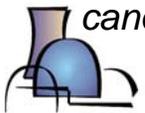
# Soluble salts in wind-blown dust

## 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  $\gg$  chloride (ratio = 9/1). (Corrosive ratio  $<0.2$ ).

-----  
Source: *Comments regarding in-drift chemistry related to corrosion of containment barriers at the candidate spent fuel and HLW repository at Yucca Mountain, Nevada.* [EPRI, Palo Alto, CA, 2004. 1010941]



# Mineral names and formulas

Anhydrite	$\text{CaSO}_4$
Calcite	$\text{CaCO}_3$
Nitrocalcite	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Fluorite	$\text{CaF}_2$
Halite	$\text{NaCl}$
KBr	$\text{KBr}$
Niter	$\text{KNO}_3$
Sepiolite	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$
$\text{SiO}_2(am)$	$\text{SiO}_2$
Soda Niter	$\text{NaNO}_3$
Glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$
Syngenite	$\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$
Thenardite	$\text{Na}_2\text{SO}_4$
Darapskite	$\text{Na}_3\text{NO}_3\text{SO}_4 \cdot \text{H}_2\text{O}$
Arcanite	$\text{K}_2\text{SO}_4$
Pirssonite	$\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$
Huntite	$\text{CaMg}_3(\text{CO}_3)_2$
Sellaite	$\text{MgF}_2$
Kalicipite	$\text{KHCO}_3$
Sylvite	$\text{KCl}$
Pentasalt	$\text{K}_2\text{Ca}_5(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$

