

Near-Field Chemical Environment

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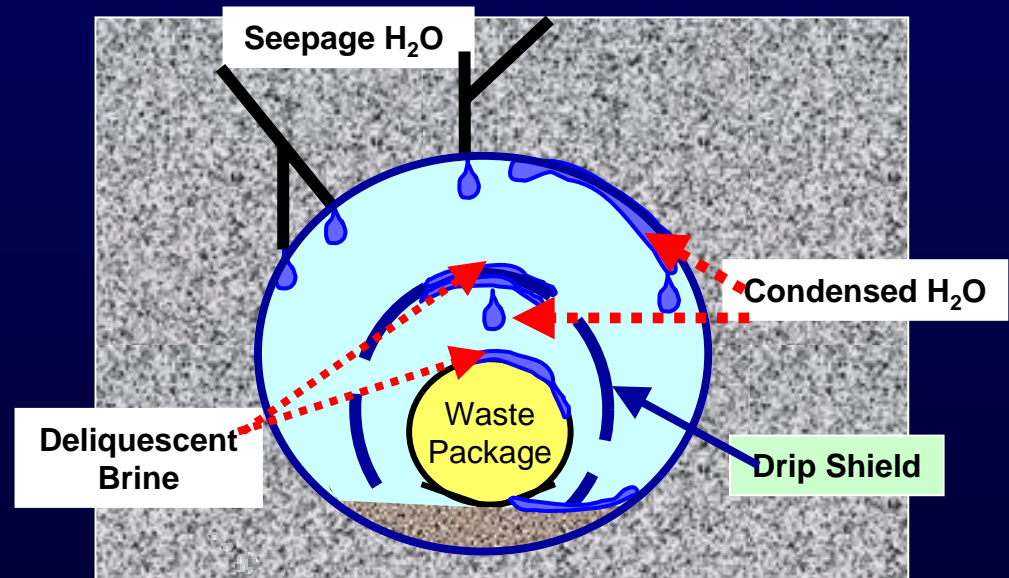


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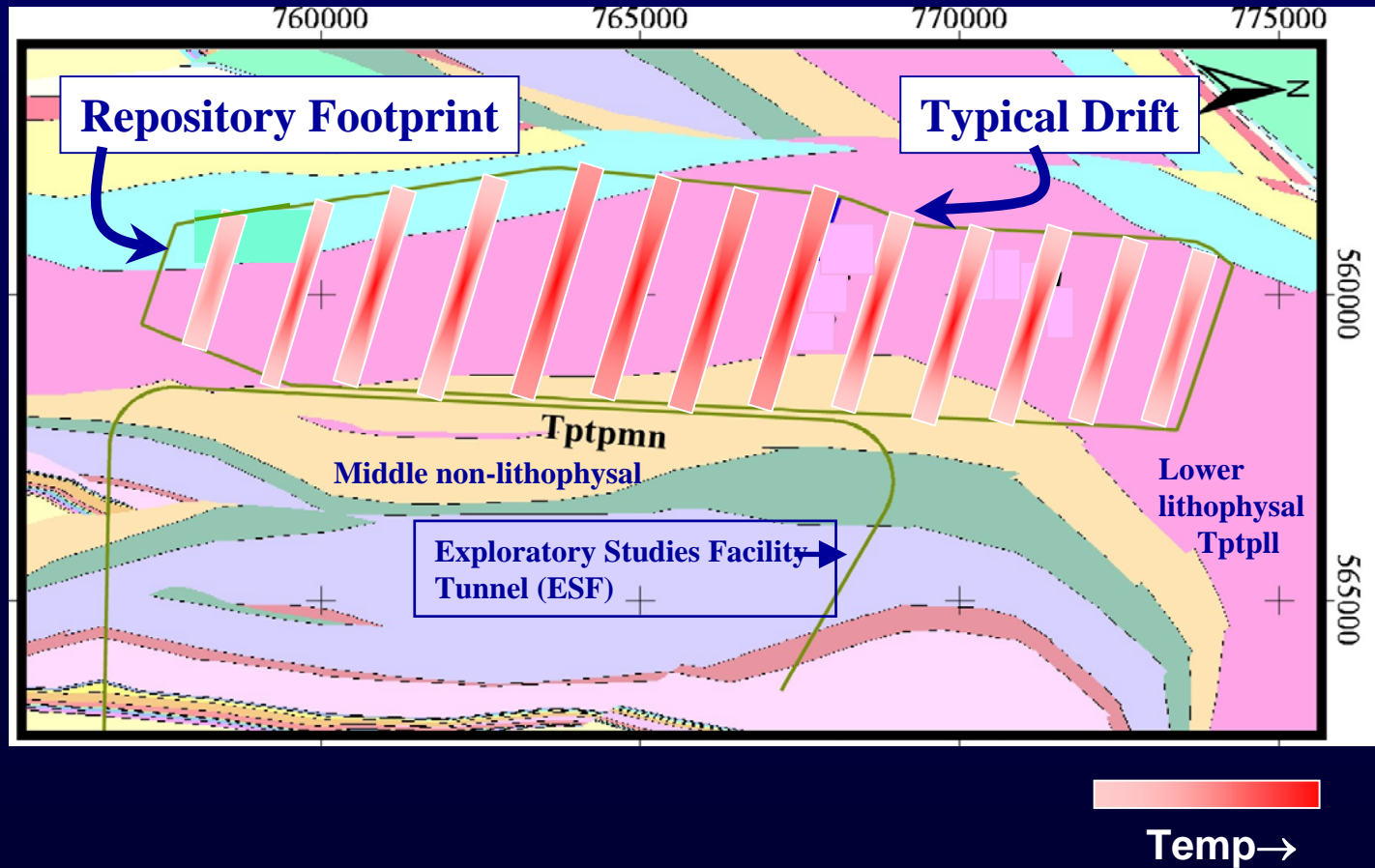


Introduction

- Potential sources of in-drift water
 - Seepage water
 - Deliquescent brines
 - Condensed water
- Chemistry of in-drift water will be altered by coupled thermal-hydrological-chemical processes



Schematic of Temperature and Relative Humidity Variations Within the Repository Footprint



Conceptual Model of In-Drift Thermal-Hydrological Environments Important to Aqueous Corrosion

In-Drift Environment	Thermal-Hydrologic Conditions	Estimated Duration (yr) [§]
1: Dry	$T_{DW} > 105\text{ }^{\circ}\text{C}$ (seepage threshold)	Center: ~900 Intermediate: ~500 Edge: 0
2: Seepage + Evaporation	$105\text{ }^{\circ}\text{C} \geq T_{DW} \geq 96\text{ }^{\circ}\text{C}$	Center: ~500 Intermediate: ~300 Edge: <50
3: Seepage + Evaporation + Condensation	$T_{DW} < 96\text{ }^{\circ}\text{C}$ $RH_{WP} < 90\text{ }%$	Center: ~200 Intermediate: ~200 Edge: ~100
4: Seepage + Condensation	$T_{DW} < 96\text{ }^{\circ}\text{C}$ $RH_{WP} > 90\text{ }%$	Center: ~8,400 Intermediate: ~9,000 Edge: ~9,900
DW—drift wall; DS—drip shield; WP—waste package; RH—relative humidity Reference: Browning et al. (2004) [§] Assuming no drift degradation		

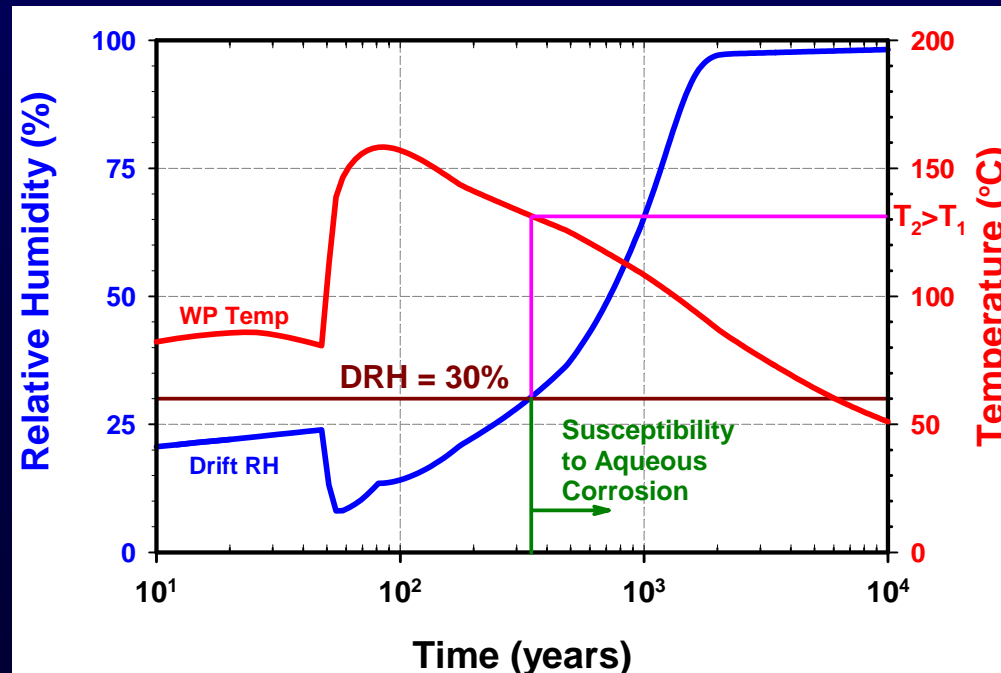
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Potential Corrosion Environments

- *Environment 1 (Dry Period, ~ 900 yr):*
Brines formed by deliquescence of salts on waste package surface could initiate localized corrosion
- *Environment 2 (Seepage + Evaporation, ~500 yr):*
Evaporation of seepage water could result in brines with high concentrations of corrosive species (Cl^- , F^-) on drip shield and on waste package surface (after drip shield failure); brines formed by salt deliquescence
- *Environment 3 (Seepage + Evap + Condensation, ~ 200 yr):*
Same as in Environment 2, but condensation could modify the quantity and chemistry of in-drift water
- *Environment 4 (Seepage + Condensation, ~ 8,400 yr):*
Water is relatively dilute; potential for localized corrosion likely is reduced

Deliquescence of Salt Mixtures

- Potential process for Environment 1 (~ 900 yr)
- Deliquescence relative humidity (DRH) determines time and temperature of rewetting of drip shield/waste package



Calculated In-Drift Relative Humidity and Waste Package Surface Temperature versus Time

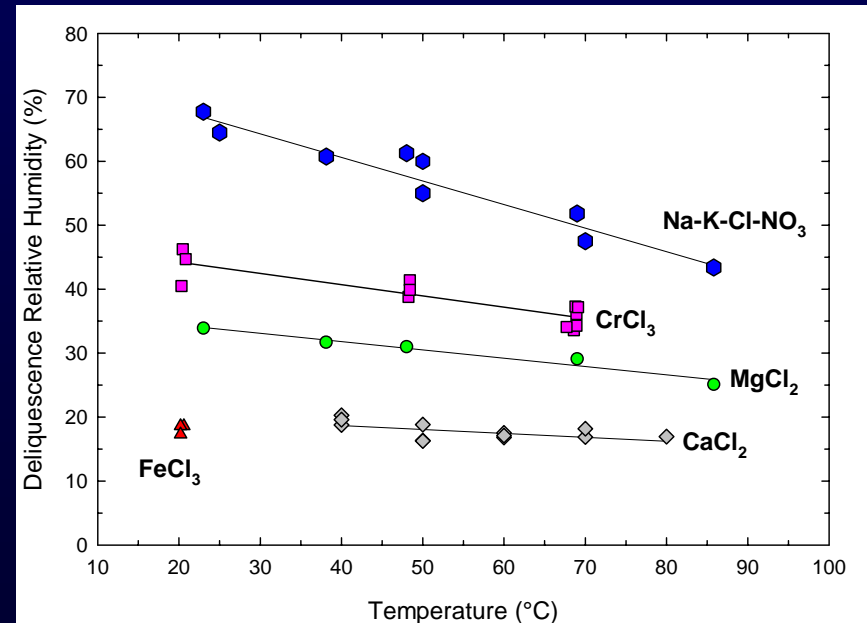
Deliquescence of Salt Mixtures (Cont'd)

- **CNWRA Experiments**

- Aqueous mixtures of cations Ca^{2+} , Mg^{2+} , Na^+ , K^+ and anions Cl^- , CO_3^{2-} , HCO_3^- , NO_3^- , SO_4^{2-} ; also CrCl_3 , FeCl_3
- Deliquescence relative humidity (DRH) measured using two methods: (a) hygrometer and (b) conductivity cell

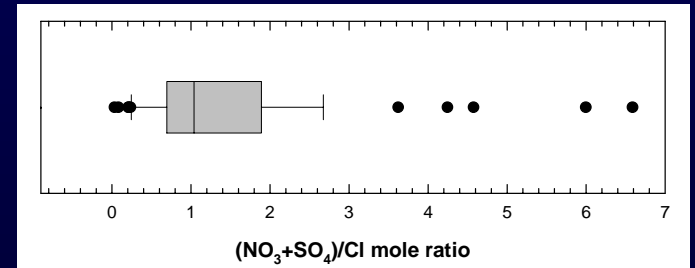
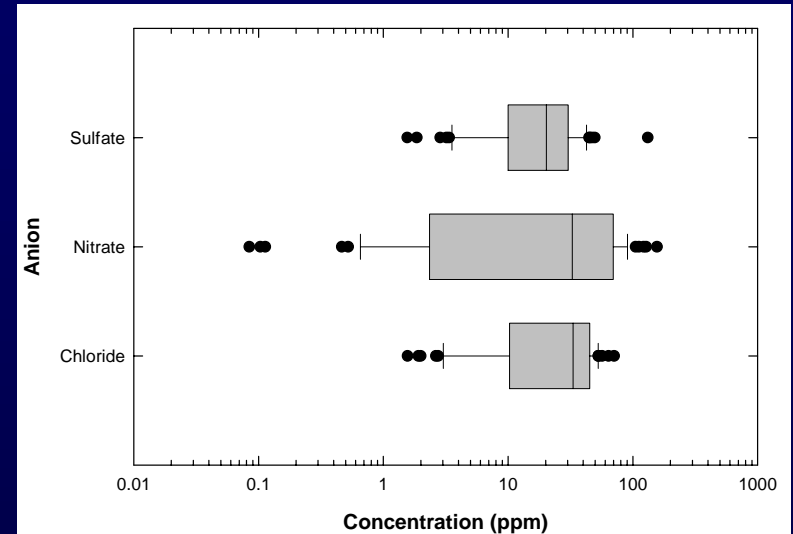
- **Results**

- Low DRH for salts with Ca^{2+} and Mg^{2+}
- Corrosion products contribute to low DRH
- Na-K-Cl-NO_3 mixture shows significant decreasing trend with temperature



Deliquescence of Salt Mixtures (Cont'd)

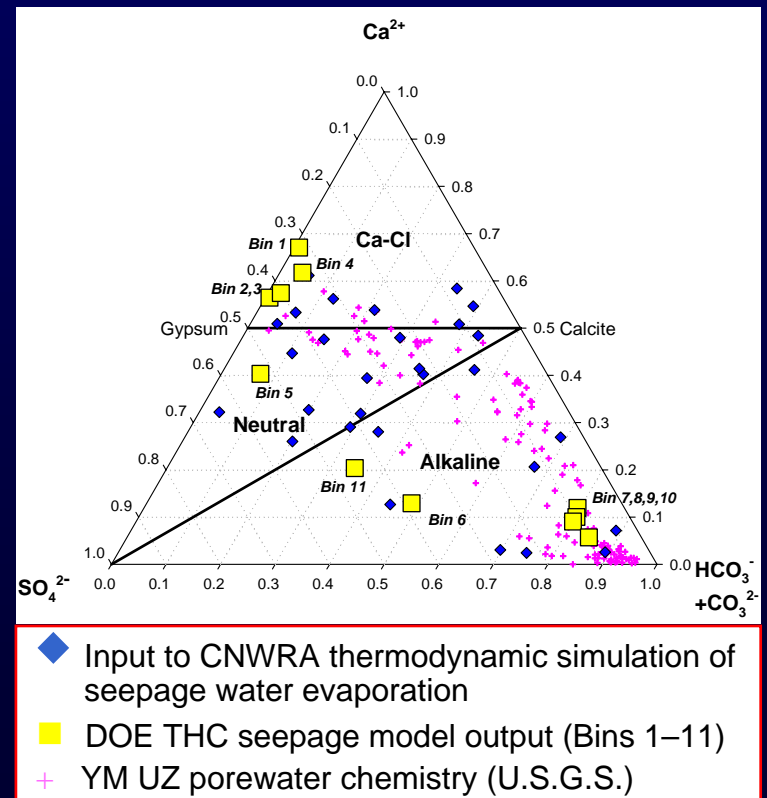
- Deliquescence of salts present in dusts affects performance only if corrosive brines are formed
- Data on composition of dust from Yucca Mountain and vicinity indicate the presence of significant concentrations of oxyanions (NO_3^- , SO_4^{2-}) that potentially can mitigate localized corrosion of Alloy 22



Concentrations of chloride, nitrate, and sulfate and $(\text{NO}_3 + \text{SO}_4)/\text{Cl}$ mole ratio of dusts collected at Yucca Mountain vicinity (Reheis, M.C., 2003, 2nd Inter. Workshop on Mineral Dust, 10-12 September 2003, Paris, France)

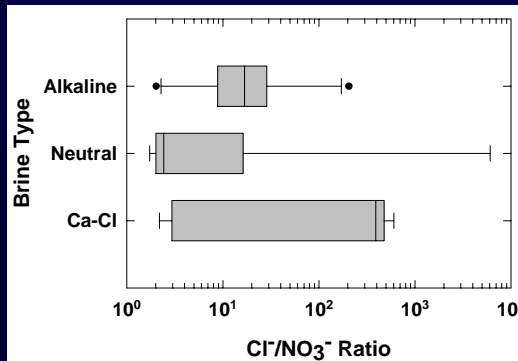
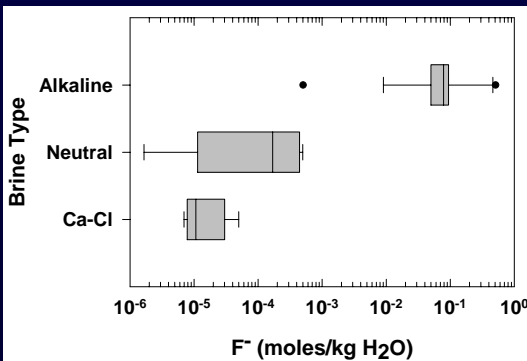
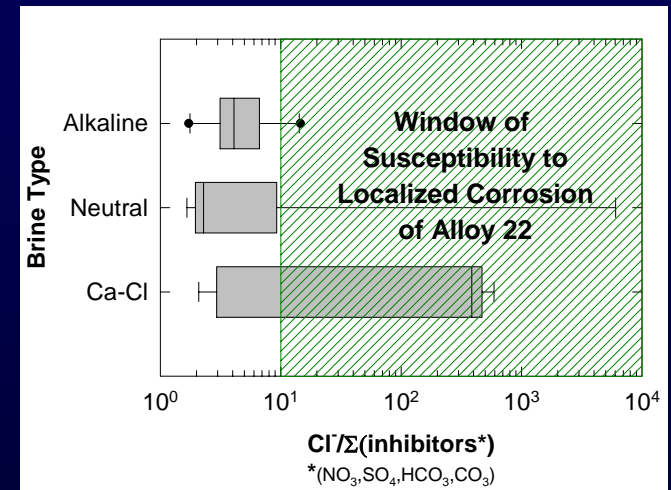
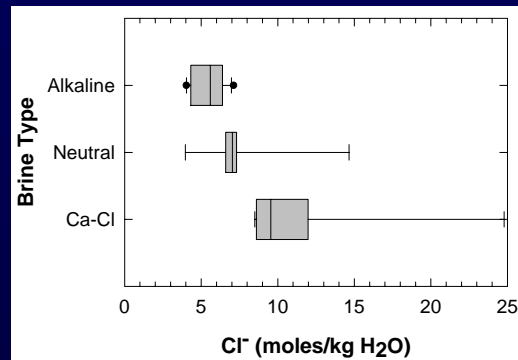
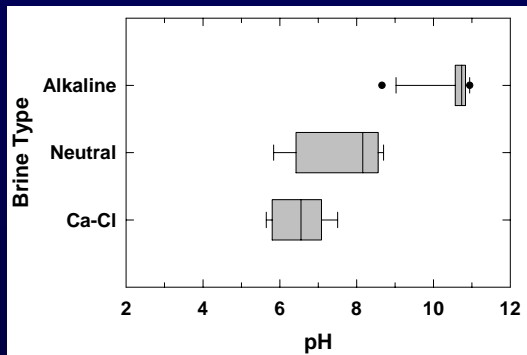
Evaporation of Seepage Water

- Potential process for Environments 2 & 3 (~500 & ~200 yr)
- Chemistry of brines formed by evaporation is dependent on initial composition of seepage water
- Thermodynamic simulations of evaporation, supplemented by chemical divide analyses, were used to evaluate the range in chemistry of water on the DS and on the WP surface (after DS failure), particularly concentrations of corrosive species (Cl^- , F^-) and inhibitors (e.g., NO_3^- , SO_4^{2-} , HCO_3^-)



Evaporation of Seepage Water (Cont'd)

- Some brines with high Cl^- and F^- concentration can result from evaporation of YM UZ porewaters, but most have high ratio of inhibitors (NO_3^- , SO_4^{2-} , HCO_3^- , CO_3^{2-}) to corrosive species (Cl^-)

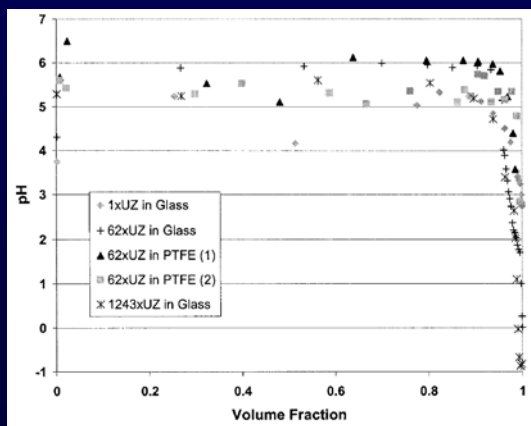


Note:

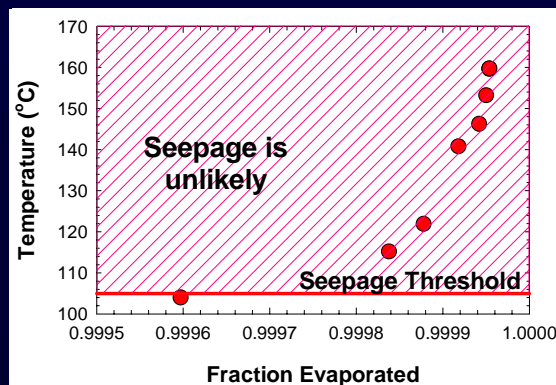
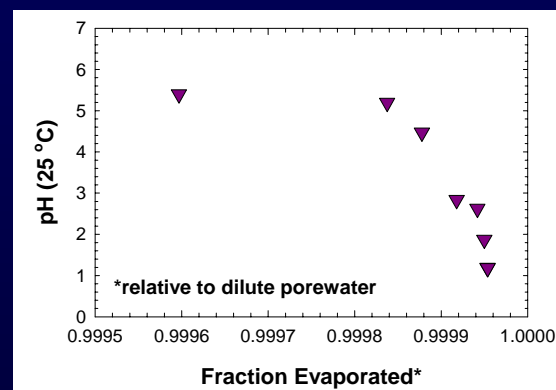
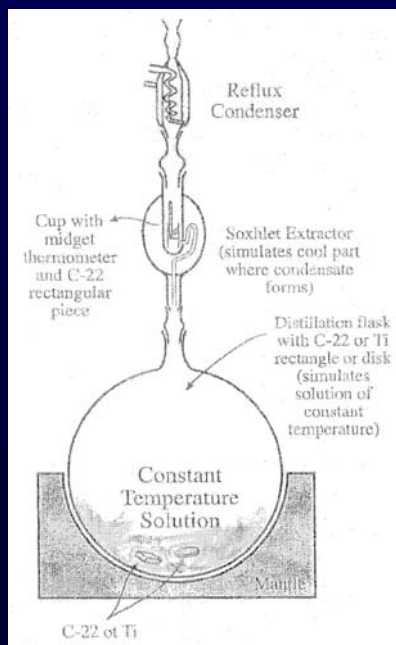
- Results shown are for $T = 110^\circ\text{C}$
- High $\text{Cl}^-/\text{NO}_3^-$ ratio is due to formation of CaNO_3^+ and NaNO_3 aqueous complexes, which have uncertain thermodynamic data

Acid Gas Volatilization

- Potential process for Environments 2 & 3 (~500 & ~200 yr)
 - Catholic University of America laboratory study showed acidic condensates with HCl and HNO₃ are formed by evaporation of Ca-Cl type porewater
 - CNWRA thermodynamic modeling of evaporation of Ca-Cl type porewater showed low pH condensates are formed

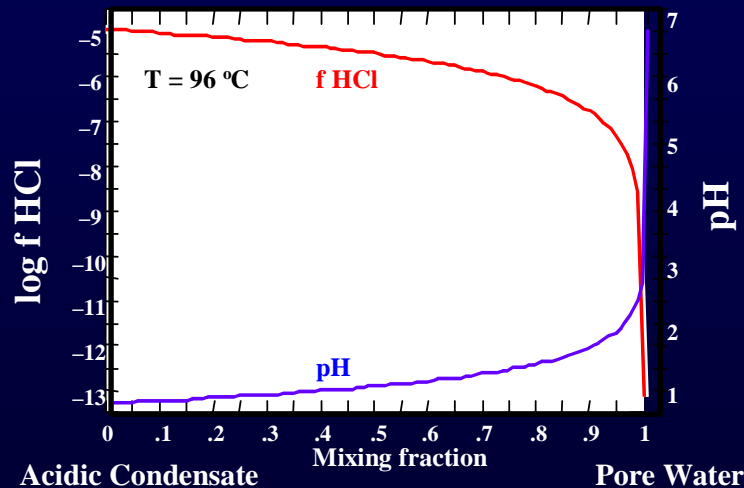


Experimental system used in CUA experiments (Pulvirenti et al., 2004)

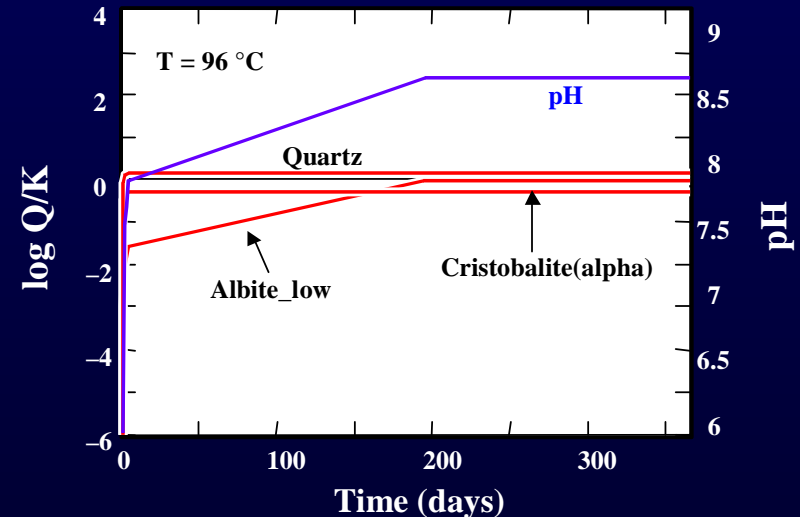


Acid Gas Volatilization (Cont'd)

- Acid generation possible for some seepage water compositions, but is likely not significant to performance
 - requires extreme degree of evaporation (factor of ~20,000 times)
 - requires high temperature ($T \gg$ seepage threshold)
 - acid gas will mix with other in-drift gases (natural convection)
 - buffered by interaction with wall-rock and in-drift materials



Compositional response to mixing fractions of pore water with acidic condensate (Browning et al., 2004)



Simulated kinetic reactions between Topopah Spring Tuff and condensate at $T = 96 \text{ } ^\circ\text{C}$ (Browning et al., 2004)

Summary

- In support of NRC regulatory activities, experiments and thermodynamic modeling were conducted to define the range in chemistry of waters that potentially can contact the drip shields and waste packages
- Of the four thermal-hydrologic environments considered, Environment 2 (estim. duration ~ 500 yr) has the greatest potential for accelerated corrosion of the drip shields and of the waste packages (after drip shield failure), but the concentration of corrosion inhibitors may be high enough to mitigate localized corrosion of Alloy 22
- Environment 4 (estim. duration > 8,000 yr) has limited potential for enhanced corrosion of the drip shields and waste packages

Acknowledgment

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