Summary of Presentations Addressing the Nuclear Waste Technical Review Board's Comments in their November 25, 2003 Letter

Presented to:
Nuclear Waste Technical Review Board

Presented by:
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Washington D.C.

Outline

- Goals/Objectives
- Summary of Conclusions from Presentations on
  - Seepage, Thermal Seepage and Thermal Hydrology
  - Presence and Characteristics of Deliquescent Brines
  - Aqueous Chemistry Evolution and Evaporation
  - Corrosion Resistance of Alloy 22
- Summary of Answers to Board's Questions

Goals/Objectives of DOE Presentations

- Answer questions and concerns raised in the Board's November 25, 2003 letter and provide additional clarification on particular topics related to repository performance during the "thermal pulse"
- Provide conceptual basis and key data and analyses of
  - The thermal hydrologic and thermal seepage evolution
  - The composition and deliquescence of salts within the dust likely to be present on the waste packages
  - The thermal chemical evolution of pore fluids in the rock and, following seepage, the drift
  - The corrosion initiation and propagation processes for the Alloy 22 waste package

Placing the In-Drift Environment and Corrosion into a Systems Context

- **Our presentations today focused on the data used to develop and substantiate the models used to define the expected environment on the waste package and expected degradation characteristics of Alloy 22 in those environments**
- **Uncertainty in the models and parameters are included in the systems representation**
- **Low probability events and unlikely processes are included in the systems representation**
- **The combined effects of low probability events, unlikely processes and uncertainty in models and parameters are included in the risk assessment of repository performance**

Processes Potentially Affecting Corrosion During the Thermal Pulse

- Drift degradation processes affect the thermal hydrologic evolution and drip shield performance
- Thermal hydrologic processes (which control the in-drift temperature and relative humidity) affect the likely deliquescent conditions on the waste package surface
- Deliquescent salt chemistry affects the likely composition of brines on the waste package surface in the absence of seepage
- Thermal seepage processes affect the likelihood that aqueous solutions evolved in the rock can contact the drip shield and/or waste package

Processes Potentially Affecting Corrosion During the Thermal Pulse (continued)

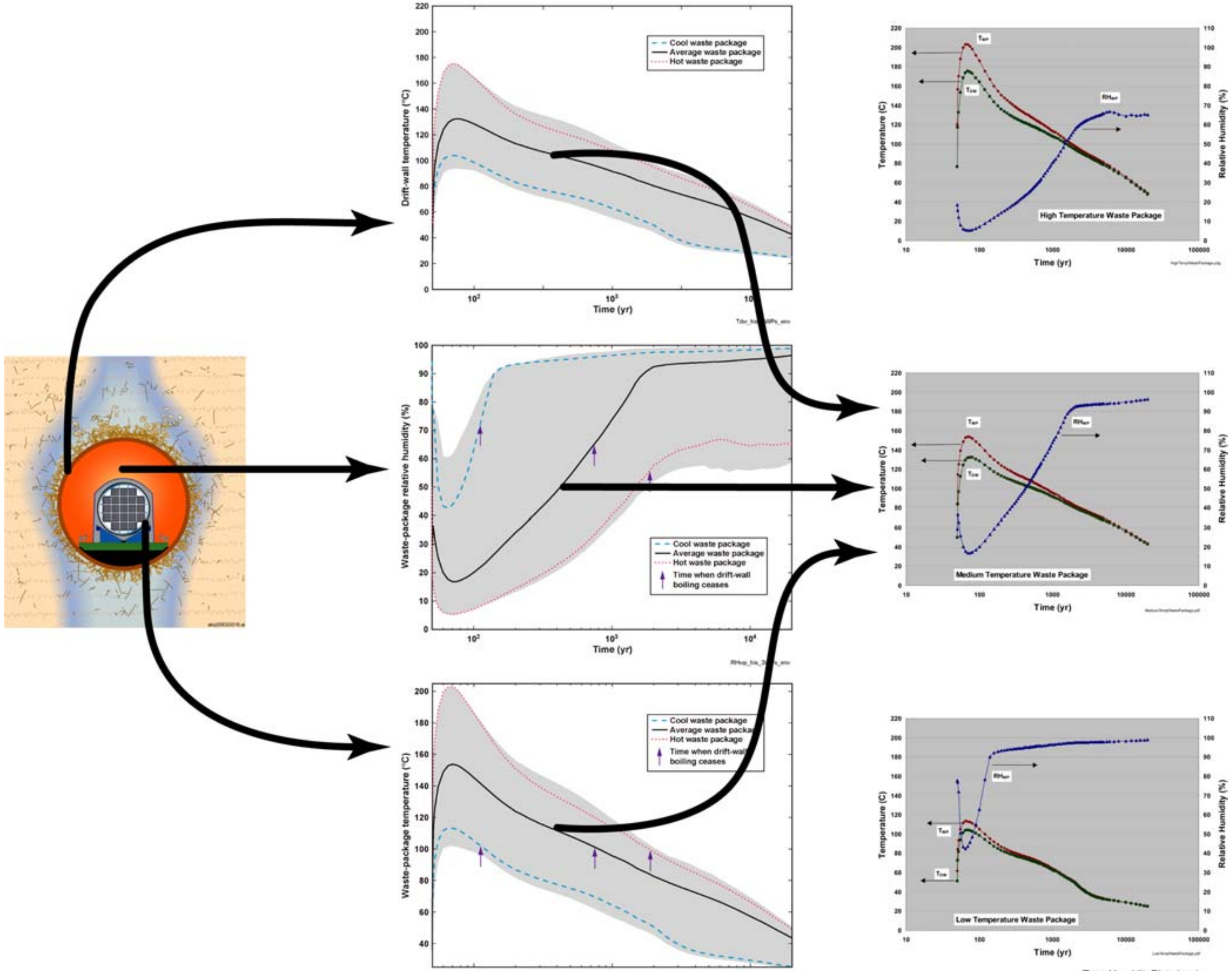
- Aqueous solution chemistry affects the likely brines that could contact the drip shield (or the waste package if the drip shield no longer provides protection)
- The repassivation and corrosion potentials for Alloy 22 are affected by the chemistry of the brines and salts as well as the temperature and crevice
- These potentials in turn affect the likelihood that localized crevice corrosion will be initiated
- The rate of crevice corrosion is affected by the chemistry and temperature

In-Drift Thermal Hydrologic Response - Temperature and Relative Humidity

- Rock mass thermal conductivity used in models are based on *in-situ* tests and include effects of variable lithophysal porosity
- Thermal hydrology models are based on comparison to *in-situ* tests, analogs and have been compared to alternative models
- Temperature and humidity calculations include variability and uncertainty in thermal conductivity
- The likelihood and extent of rockfall and drift degradation have been addressed in thermal responses
  - The insulating effects of rockfall are included in low probability seismic scenarios
- The effects of natural ventilation have been conservatively ignored in thermal hydrologic calculations but have been included in evaluating condensation effects

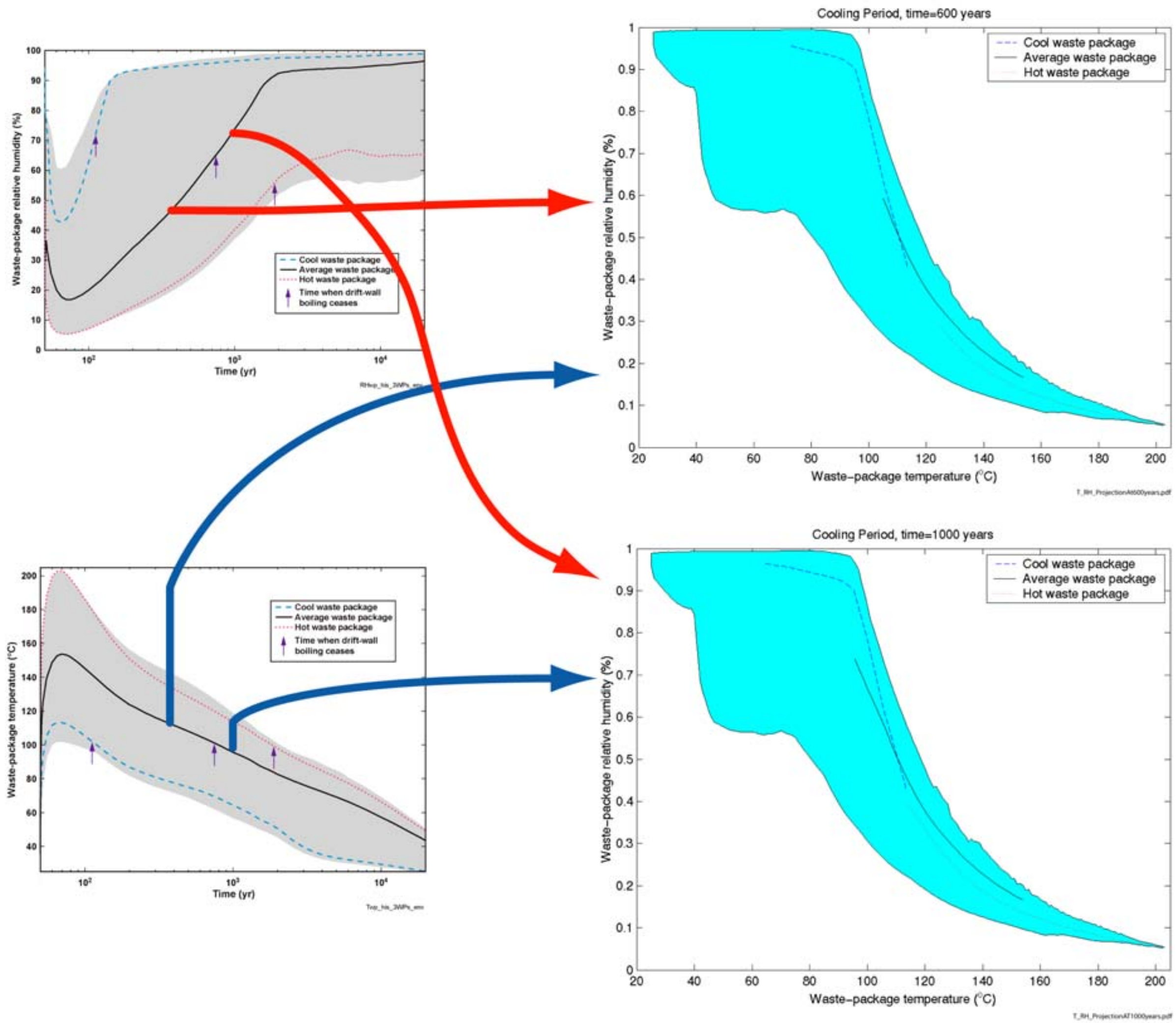
A reasonable range of thermal hydrologic conditions in the drift have been developed for use in the risk assessment

In-Drift Thermal Hydrologic Response - Temperature and Relative Humidity



TempHumidityPlots1a.ai

In-Drift Thermal Hydrologic Response - Temperature and Relative Humidity

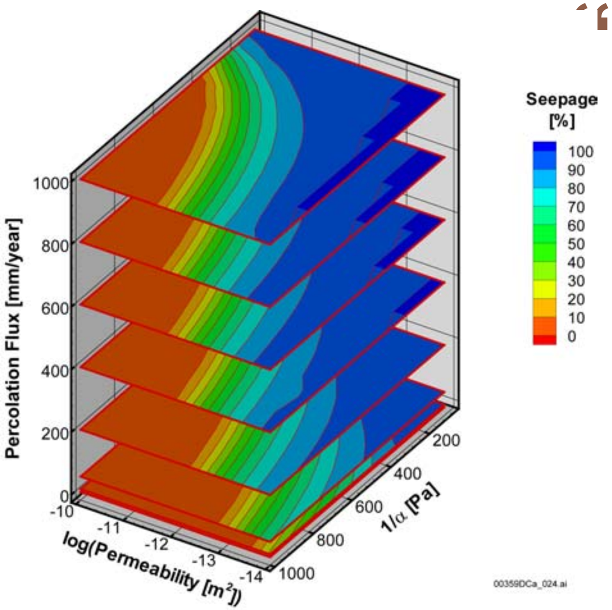


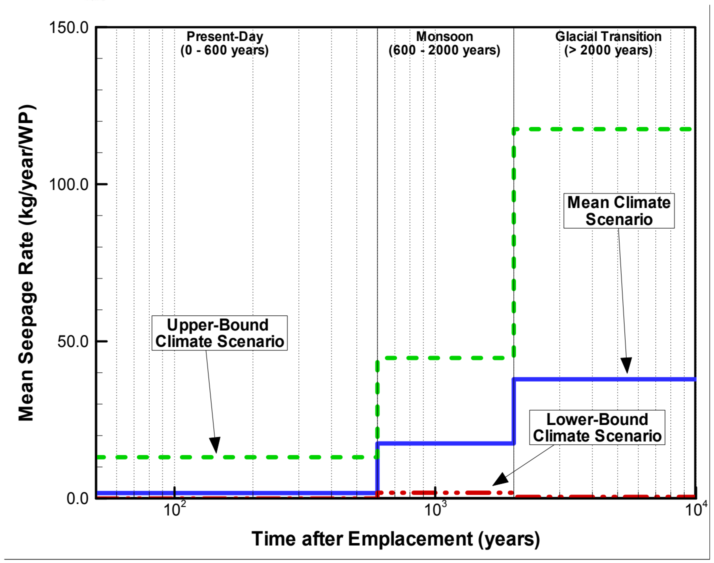
Seepage Into Drifts - During and After "Thermal Pulse"

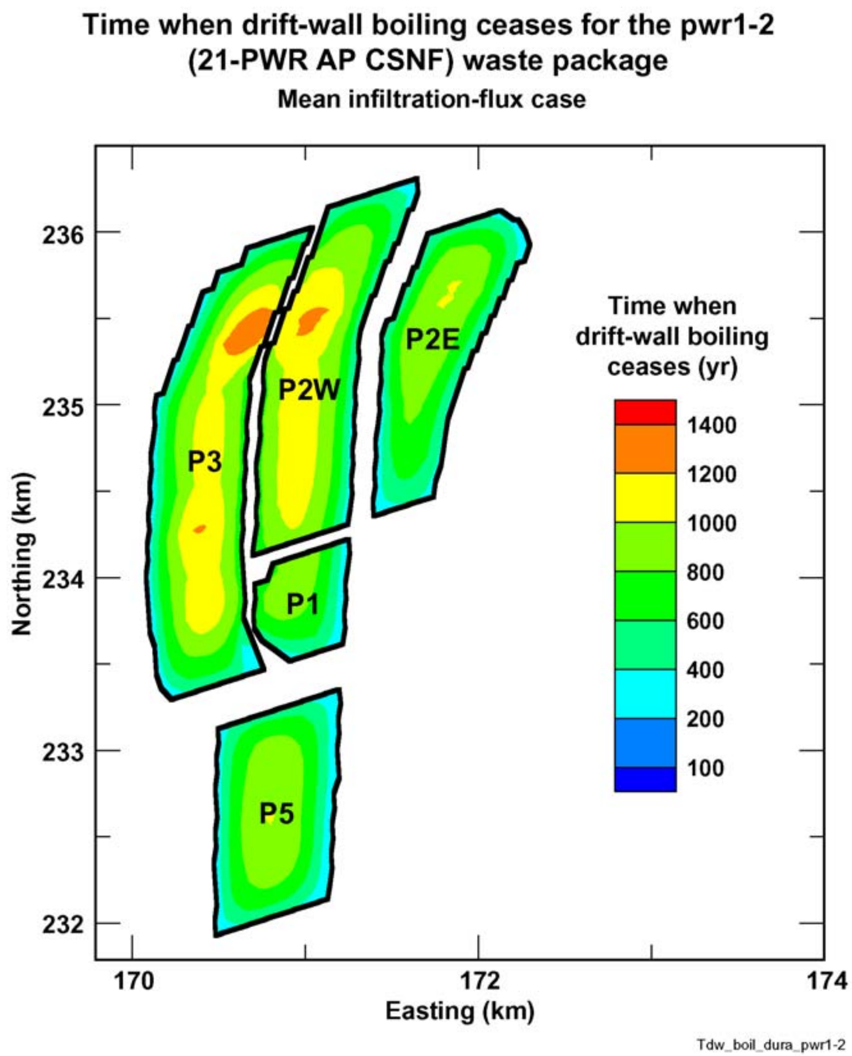
- Seepage and thermal seepage models are based on *in-situ* tests and have been compared to natural analogs and alternative models
- Seepage does not occur when the temperature at the drift wall is greater than boiling
- Seepage, when it occurs is limited to a small fraction of the percolation flux and about 10-30% of the drip shields
- The likelihood and extent of rockfall and drift degradation have been addressed in thermal seepage responses

A range of thermal hydrologic conditions yield a range of possible locations and amounts of seepage during and subsequent to the thermal pulse

Seepage Into Drifts - During and After "Thermal Pulse"





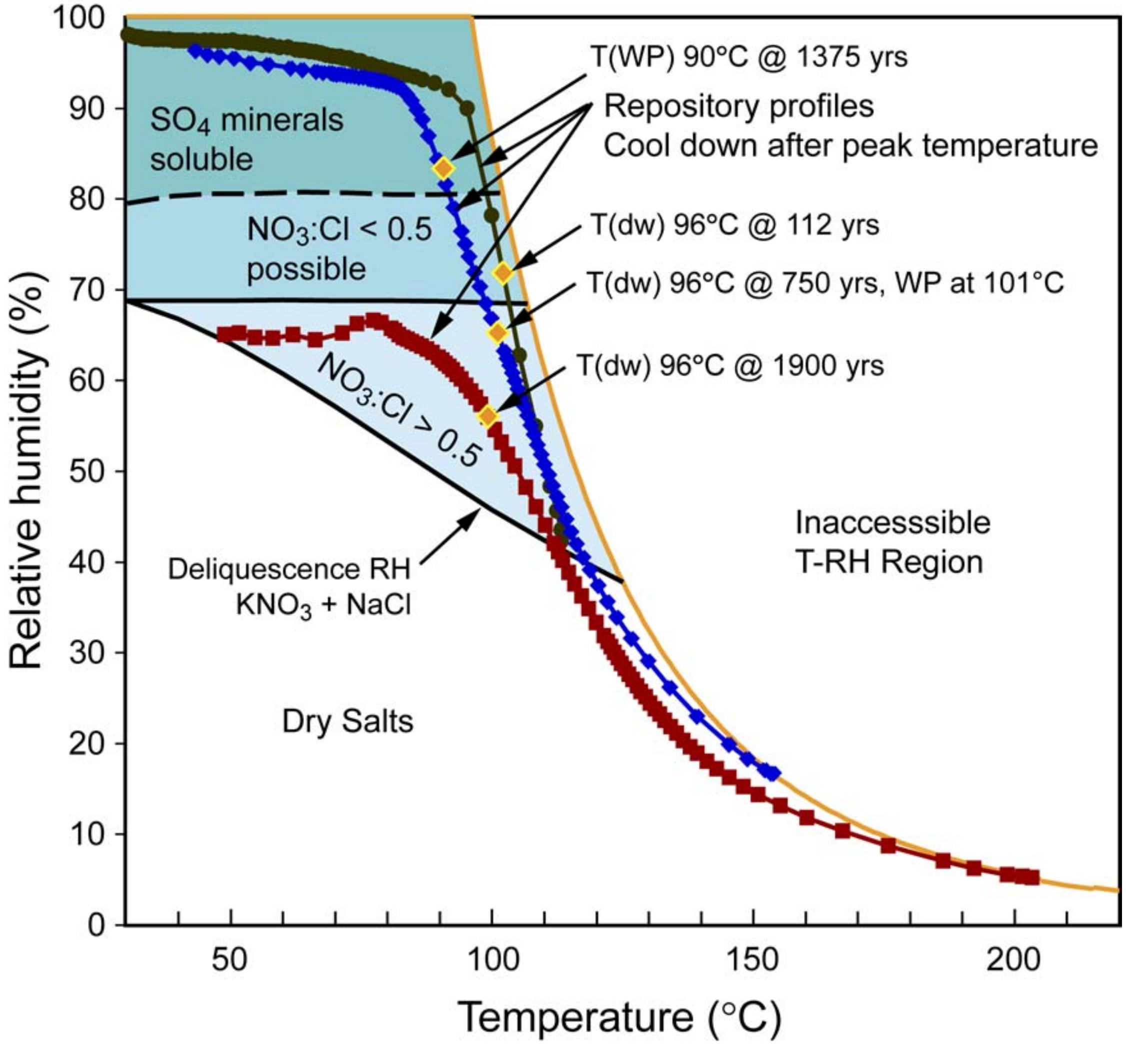


Chemical Evolution of Salts During the "Thermal Pulse"

- No calcium or magnesium chloride salts have been observed in Yucca Mountain salts
  - Surface occurrences are unstable and nearby sources are not known
- Ca and Mg chloride salts are unstable at the temperature and humidity conditions at Yucca Mountain and will react to more stable phases
- Tests indicate that even if such salts were present and stable, they would quickly volatilize
- The open system present at Yucca Mountain would allow any acid gas to disperse and dissolve
- Salts likely present in Yucca Mountain dusts are halite, gypsum, potassium nitrate, calcite, bassanite
  - These salts are not aggressive with respect to Alloy 22 corrosion

Salts likely to be present on the waste package during the thermal pulse do not cause widespread corrosion

Chemical Evolution of Salts During the "Thermal Pulse"

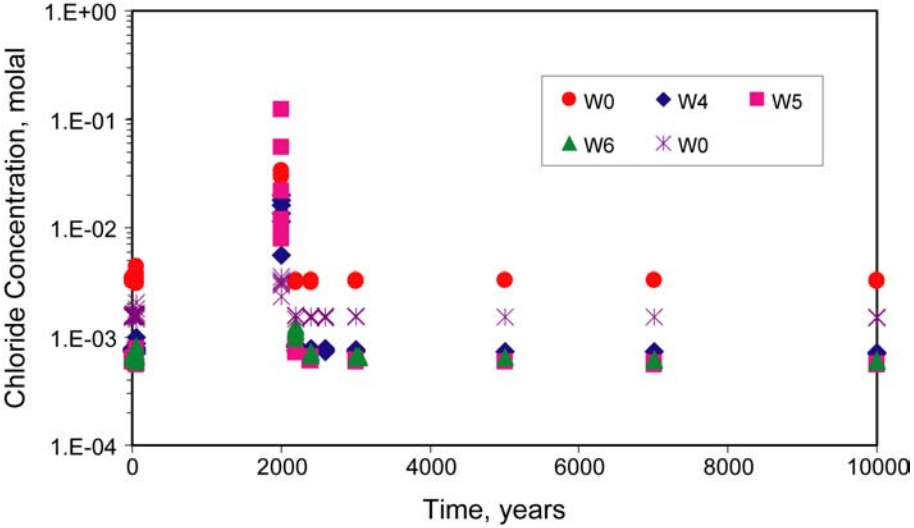


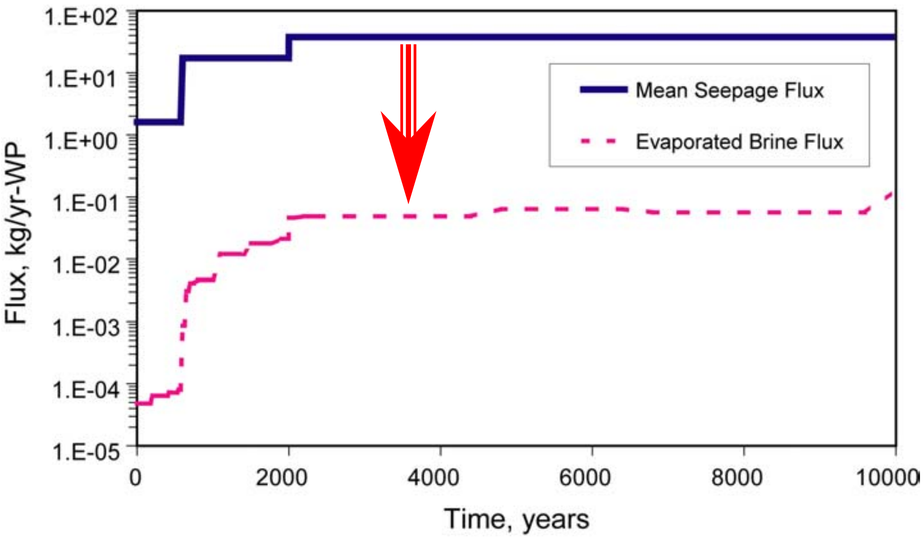
Aqueous Chemistry Evolution After the "Thermal Pulse"

- **The chemistry evolution is based on *in-situ* and laboratory data**
- **The evolution of pore water chemistry can be simply defined with respect to major chemistry types**
- **The initial aqueous chemistries in the unsaturated zone generally evolve into sulfate or bicarbonate brines**
  - **W0-type waters are only a chloride brine at early times when the temperatures at the drift wall are significantly above boiling, precluding seepage**
  - **Formation of $CaCl_2$ brines is unlikely due to precipitation of calcium in rock and drifts as calcite, fluorite or stellerite**
- **These brines do not contact the waste package unless and until the drip shield has degraded sufficiently to allow liquid flow through the degraded surface**
- **The probability of initiating localized corrosion for the sulfate and carbonate brines is a function of their NO_3 and Cl contents which are a function of relative humidity**

A range of aqueous chemical conditions are developed in the rock that are propagated in the drift dependent on the thermal hydrologic conditions in the drift

Aqueous Chemistry Evolution After the "Thermal Pulse"





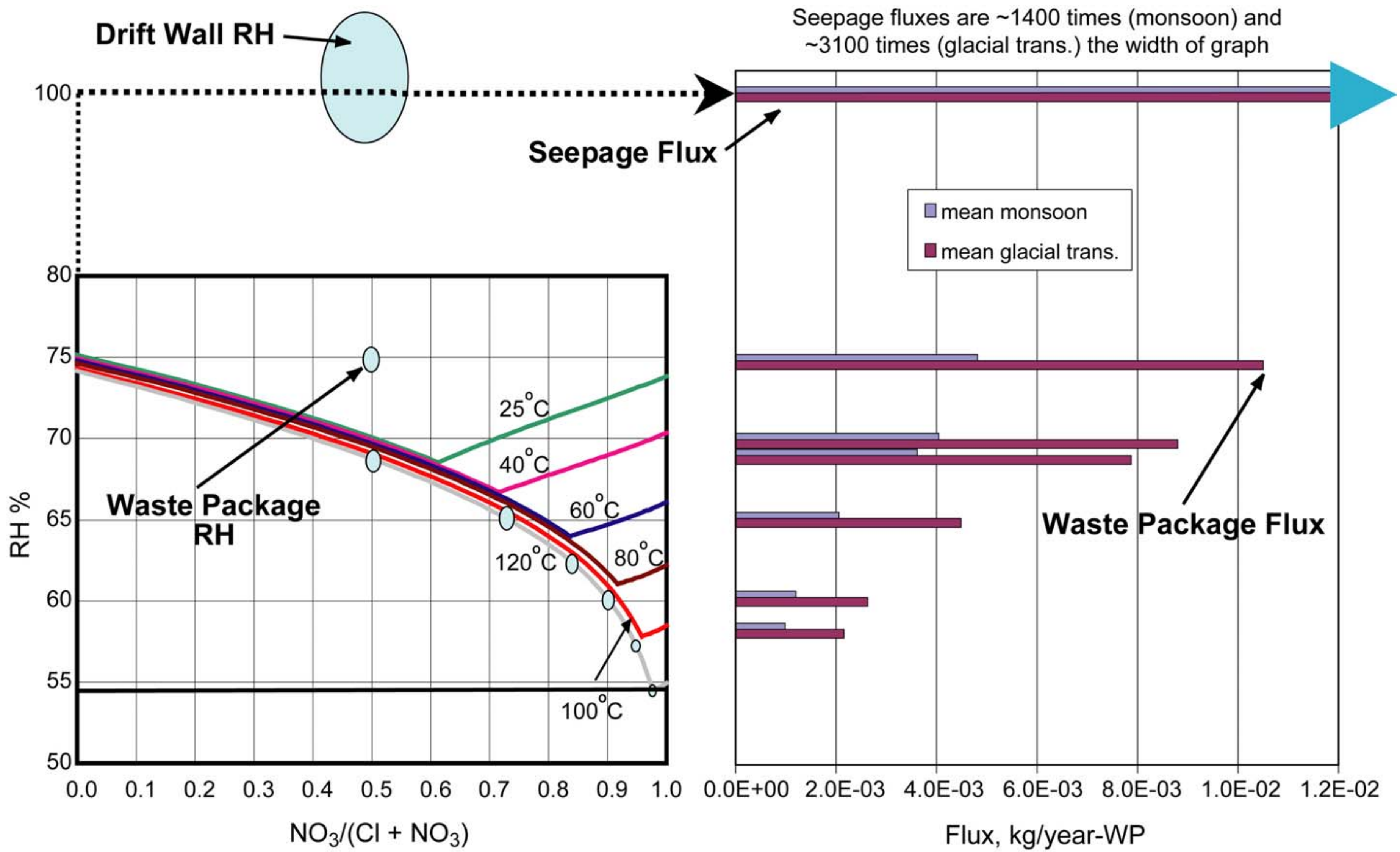
	Seepage Compositions			Brine Compositions		
Time	Cl	NO_3	NO_3/Cl	Cl	NO_3	NO_3/Cl
years	millimolal	millimolal	mole ratio	molal	molal	mole ratio
650	0.73 to 3.3	0.13 to 0.31	0.07 to 0.42	7.2	5.9	0.81
1500	0.73 to 1.3	0.13 to 0.31	0.10 to 0.42	7.0	4.1	0.59
5200	0.73 to 1.3	0.13 to 0.31	0.10 to 0.42	3.2	0.58	0.18
9200	0.60 to 3.3	0.04 to 0.10	0.03 to 0.09	2.7	0.15	0.06

Volume and Chemistry of Possible Brines Formed in the Drift

- **The thermal evolution of the aqueous phases is a very small volume of water**
  - **Potentially mobile portion is about 1 liter per waste package**
  - **Seepage amounts are ~20 - 40 l/year per waste package**
- **This volume must be concentrated by several thousand fold to have chloride concentrations of relevance to localized corrosion**
  - **Evaporated water volumes are ~ 1 - 100 ml/year per waste package**
- **As the aqueous fluid is concentrated at lower relative humidities, the nitrate concentration increases**

The range of volumes and concentration of chemical species is determined by the range of in-drift thermal hydrologic conditions

Volume and Chemistry of Possible Brines Formed in the Drift

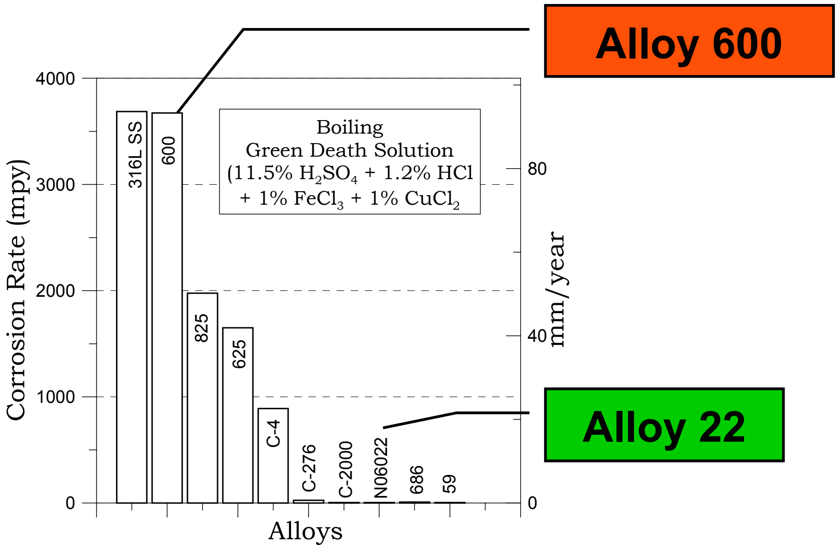


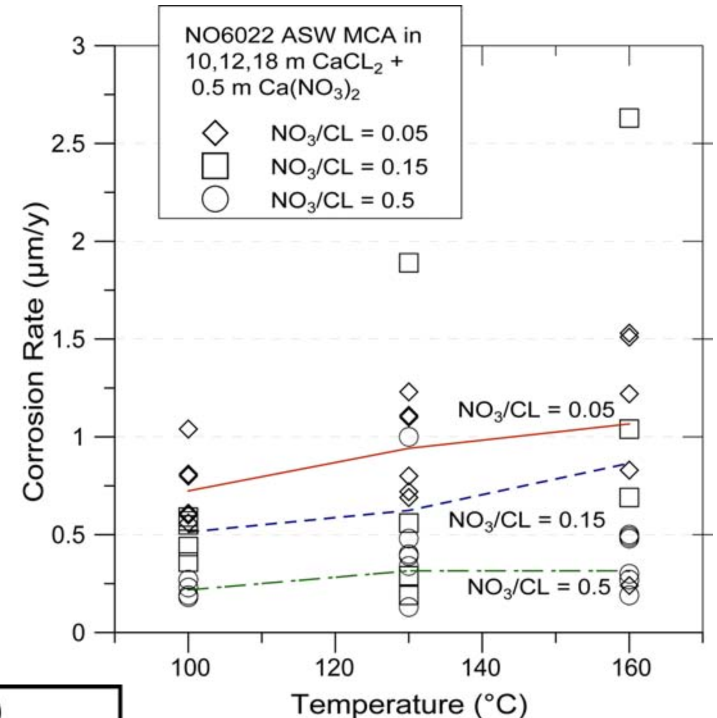
Corrosion Resistance of Alloy 22

- Alloy 22 is a highly corrosion resistant metal
  - Confirmed by laboratory evaluations in harsh environments
  - Verified by industrial experience
- Passive metals have extremely low corrosion rates
  - Alloy 22 is passive over a wide range of realistic repository conditions
  - Corrosion rates of passive Alloy 22 range from 1.0 - 0.01 microns per year
  - Corrosion rates determined from linear polarization tests and long term corrosion test facility

Reasonable range of corrosion rates used in general and local corrosion models

Corrosion Resistance of Alloy 22





Solution		Corrosion Rate (µm/yr.)			
		Temperature °C			
NO_3/Cl	Total Molality	120	140	160	220
0.05	8.4	-	<0.02#	-	-
0.31	21.2	<0.02*	<0.02*	<0.02*	0.02#
0.5	6.7	-	0.06#	-	-
6.7	9.6	<0.02*	0.13*	0.13*	-

* Exposure time: 157 days
\# Exposure time: 130 days

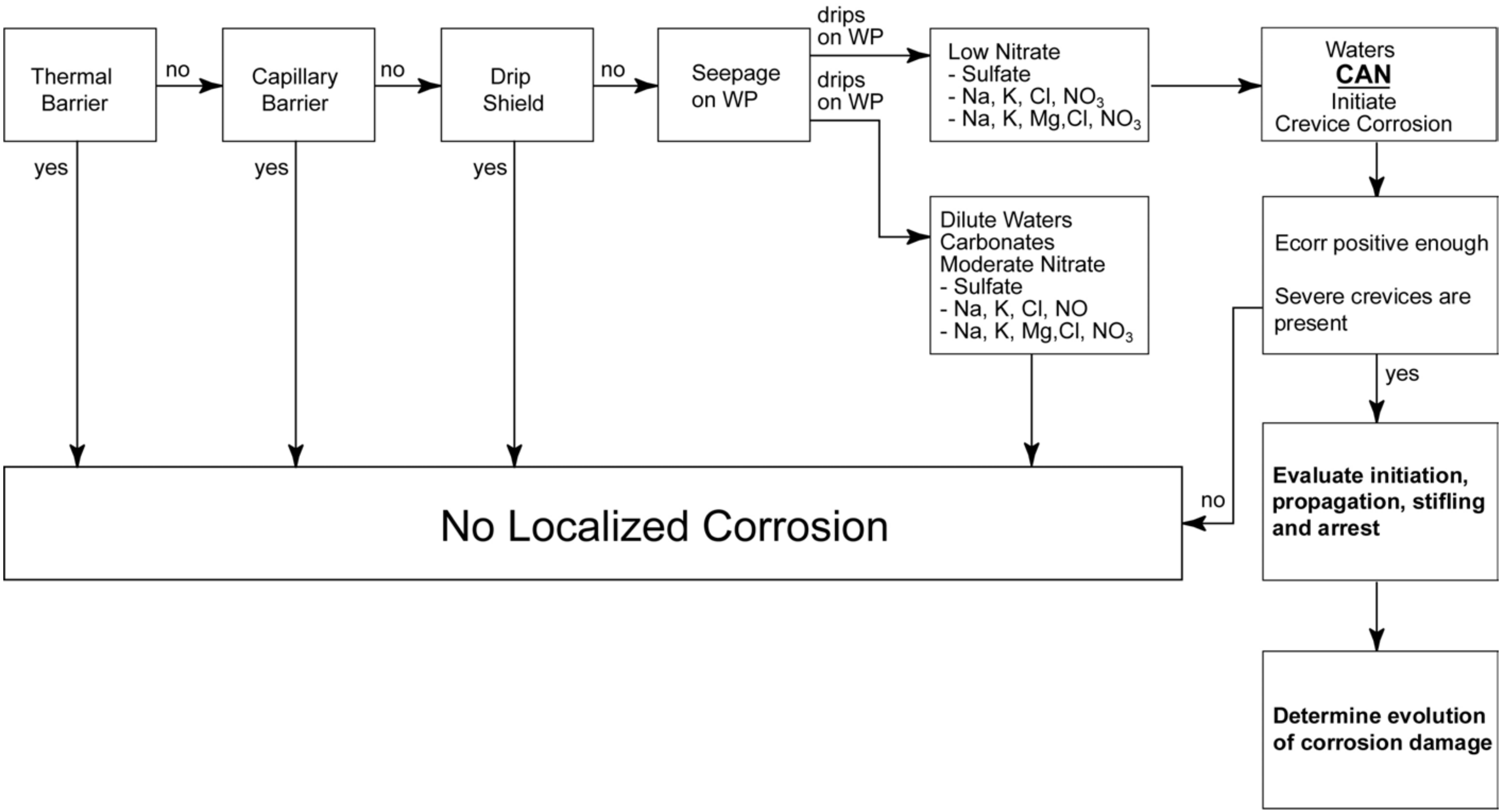
These Na and K base environments cannot exist under Yucca Mountain conditions

Localized Corrosion Conditions

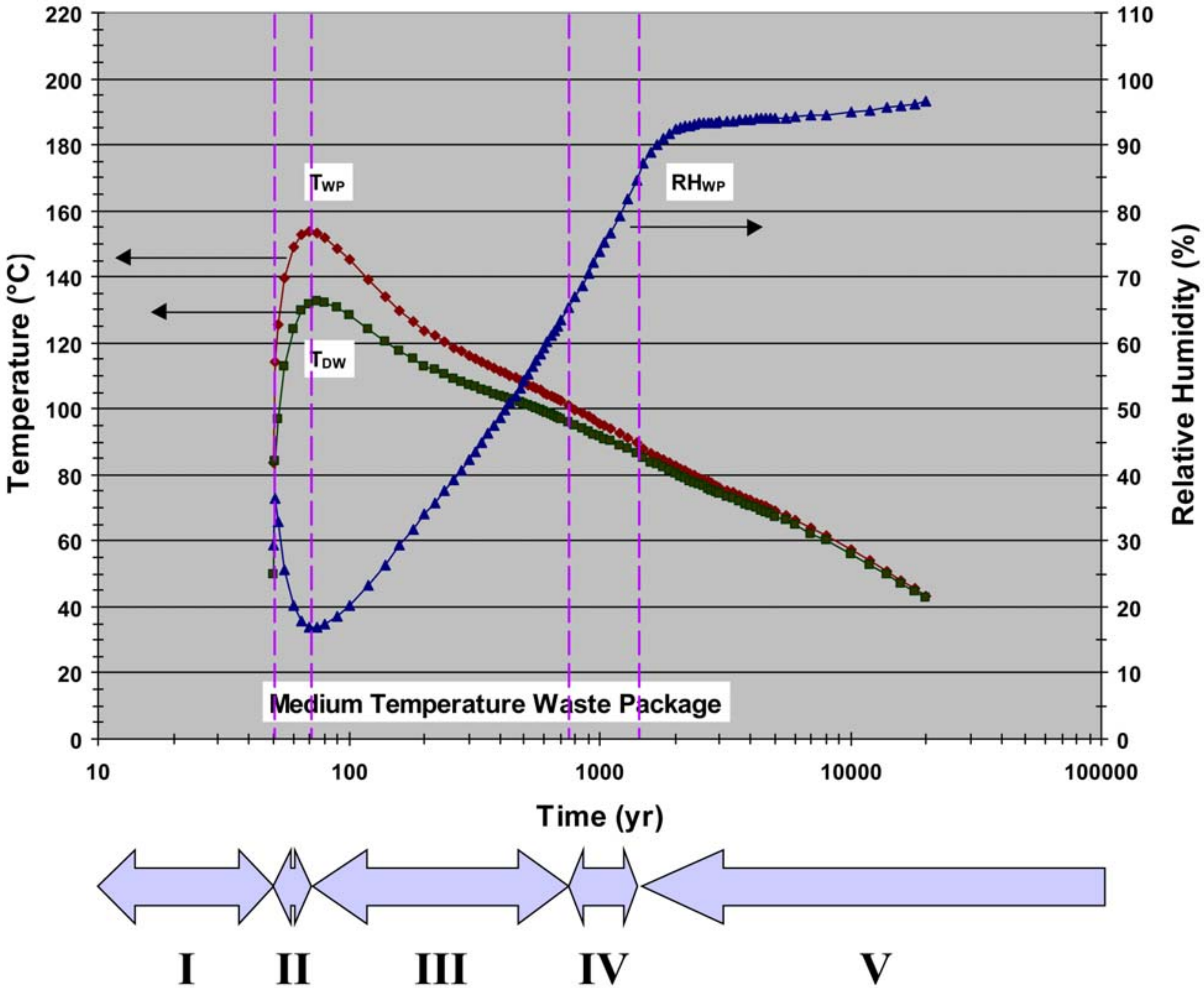
- Several processes and features prevent dripping onto waste packages
  - Thermal (vaporization) barrier, capillary barrier, and drip shield
- Where no drips fall on waste package no significant corrosion damage occurs
- Localized corrosion can be initiated if the brine contacting the waste package has a sufficiently low NO_3/Cl ratio and the temperature exceeds a minimum threshold
  - The likelihood of both conditions is determined by the thermal-hydrologic-chemical evolution in the rock and drift and the degradation of the drip shield

Conditions to support localized corrosion are possible during Period IV <u>if</u> the NO_3/Cl ratio is less than a critical value, <u>if</u> the temperature is greater than a critical value, <u>if</u> E_{corr} is positive enough, and <u>if</u> severe crevices are present

Localized Corrosion Logic Diagram



Relevant Time Periods for Localized Corrosion



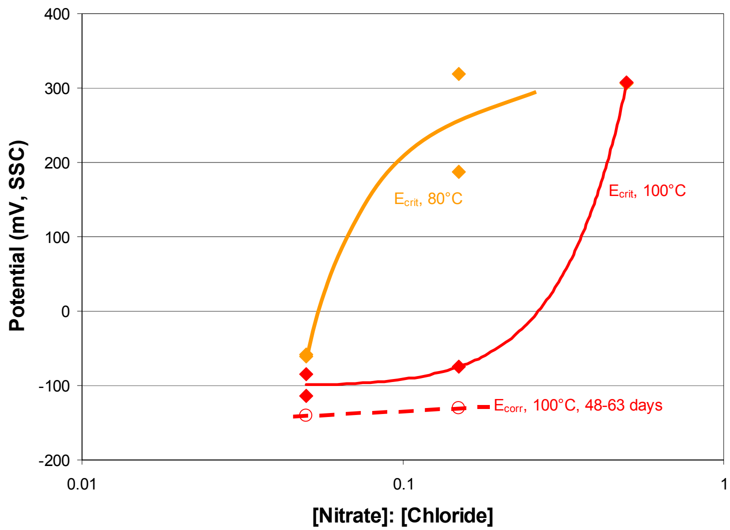
Corrosion Initiation and Propagation

- Additional testing has been performed to better characterize the degradation characteristics of Alloy 22 under a range of chemical and thermal conditions
- Measured threshold potential and time evolution of corrosion potential
  - Long term open circuit potential (> 200 tests)
  - Cyclic polarization tests (> 300 tests)
- Results indicate effect of NO_3 inhibition
  - NO_3 : Cl > 0.5 at 100 C
  - NO_3 : Cl > 0.15 at 80 C
- Stifling of localized corrosion observed in potentiostatic tests

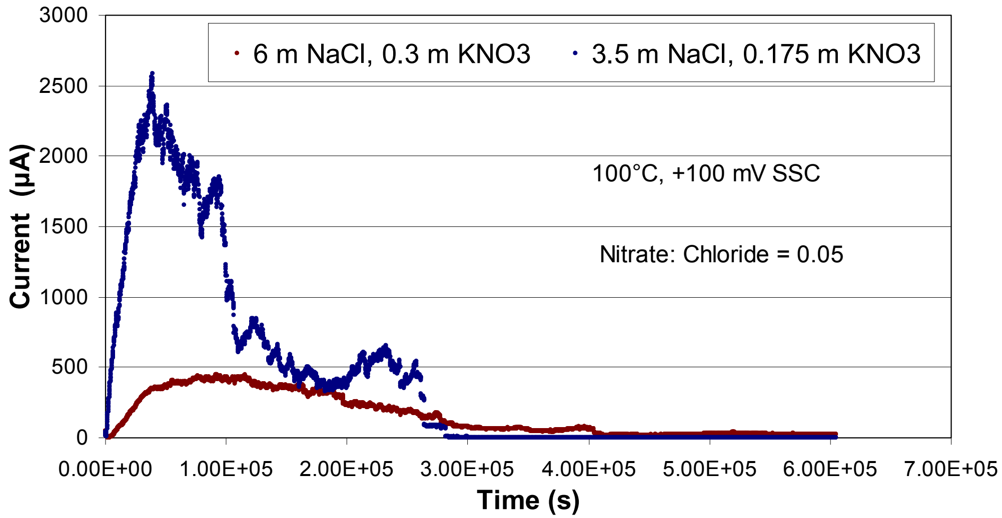
Reasonable ranges of threshold and corrosion potentials are used to evaluate probability of initiation of localized corrosion

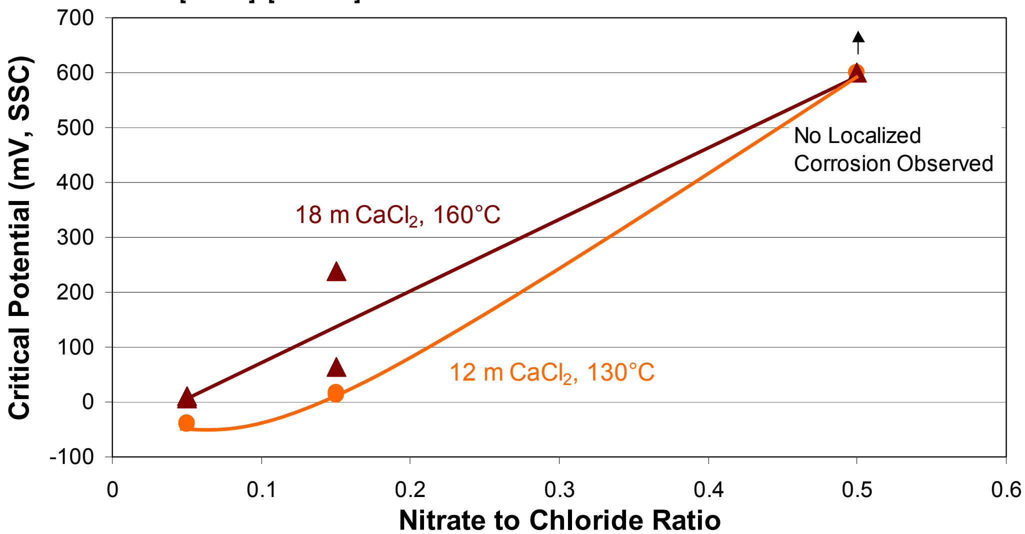
Corrosion Initiation and Propagation

At temperatures 80°C and 100°C the Critical Crevice Potential is Higher than the Corrosion Potential for Alloy 22 Welds in 6 m NaCl Solutions



Evidence of Crevice Corrosion Stifling in Alloy 22 Welds in NaCl Brines





Summary

- The Board's comments in the Nov 25 2003 letter reflected interpretations from information presented by DOE and others in the May 2003 meeting
- The information presented today answers the questions raised by the Board
- Additional data and analyses completed since last May have improved the conceptual understanding of the relevant processes during the thermal pulse
  - Additional thermal and seepage testing in the lower lithophysal rocks
  - Additional analyses using alternative models
  - Additional analyses of deliquescent salts
  - Additional linear and cyclic polarization tests over a range of chemical and thermal conditions

Conclusions

- **DOE has addressed the concerns raised by the Board using additional information**
- **DOE has used multiple lines of evidence to evaluate the likely in-drift conditions and degradation characteristics of Alloy 22 during the thermal pulse**
  - ***In-situ* and laboratory tests, validated models, comparison to alternative models, natural analogs**
- **DOE therefore concludes that the conditions necessary for widespread localized corrosion will not occur during the thermal pulse**

Conclusions

- **DOE is including the uncertainty in models and parameters (as well as “unlikely” events) in a reasonable representation of repository performance**