SAND2010-3349P

Advanced Conceptual and Numerical Methods for Modeling Subsurface Processes Regarding Nuclear Waste Repository Systems

Environmental Dependencies of Corrosion Modeling

DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

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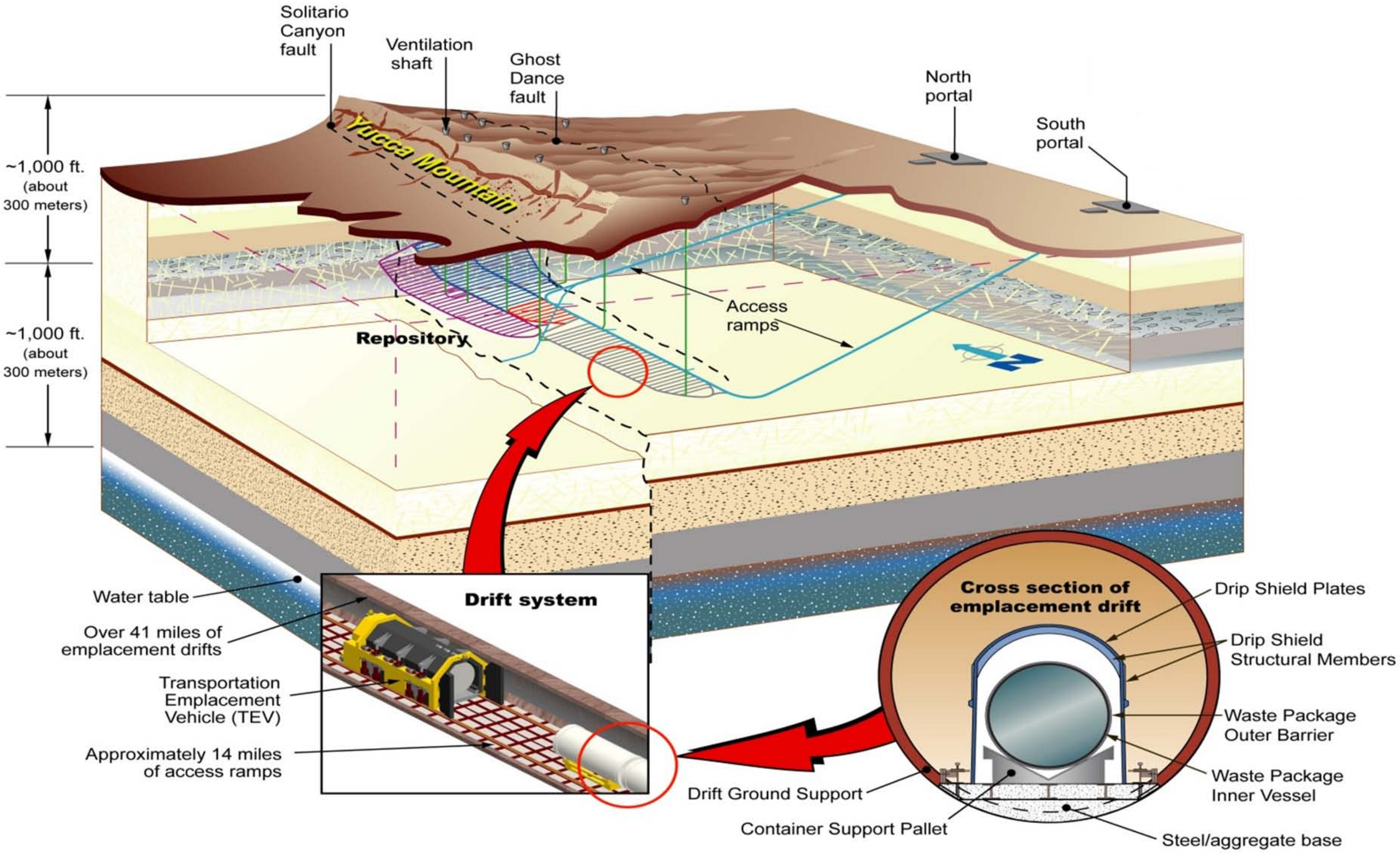
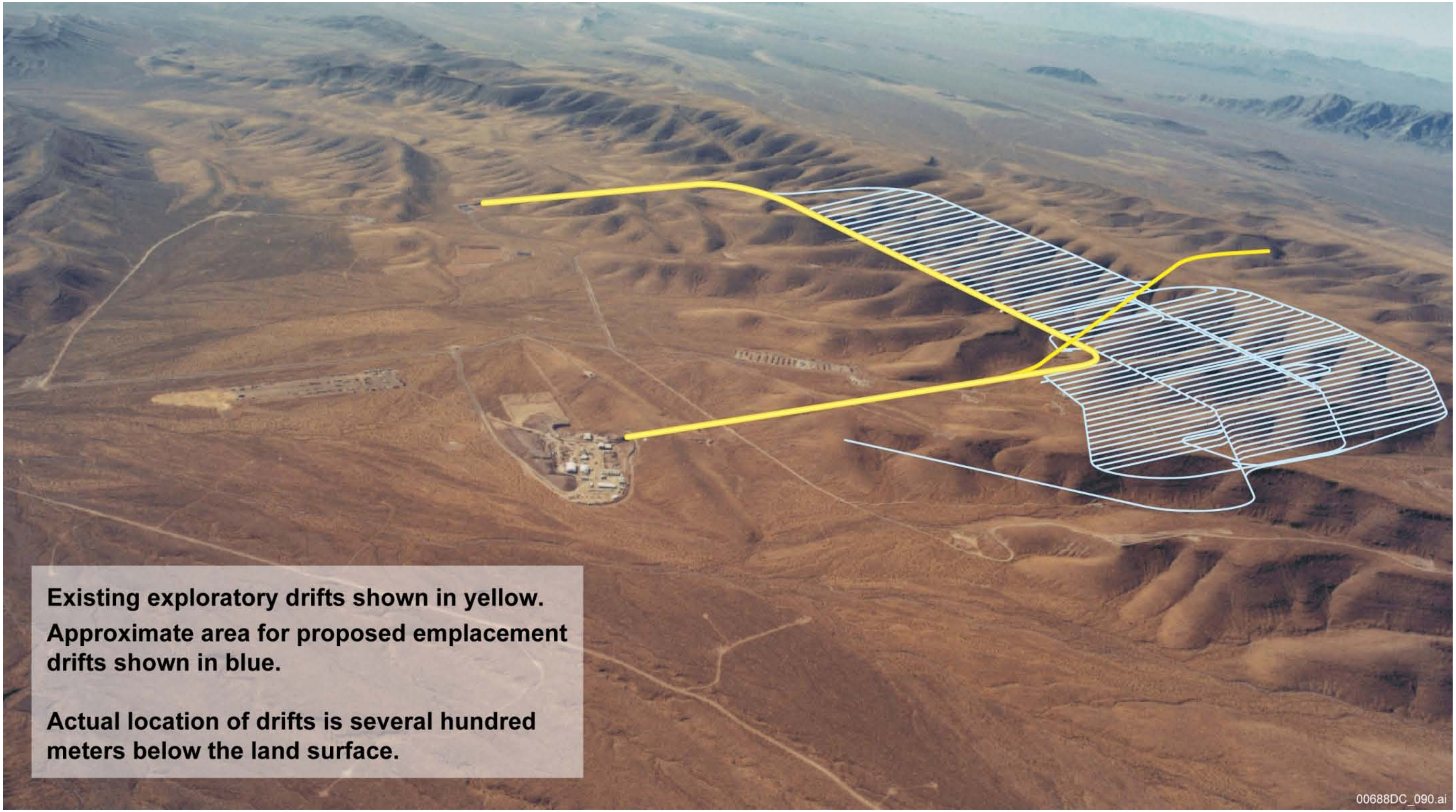
Outline

- Understanding the in-drift environment – Neil Brown
- Modeling the corrosion performance of engineered barrier materials – David Enos

The Natural and Engineered Barrier System



Locations of Exploratory and Emplacement Drifts

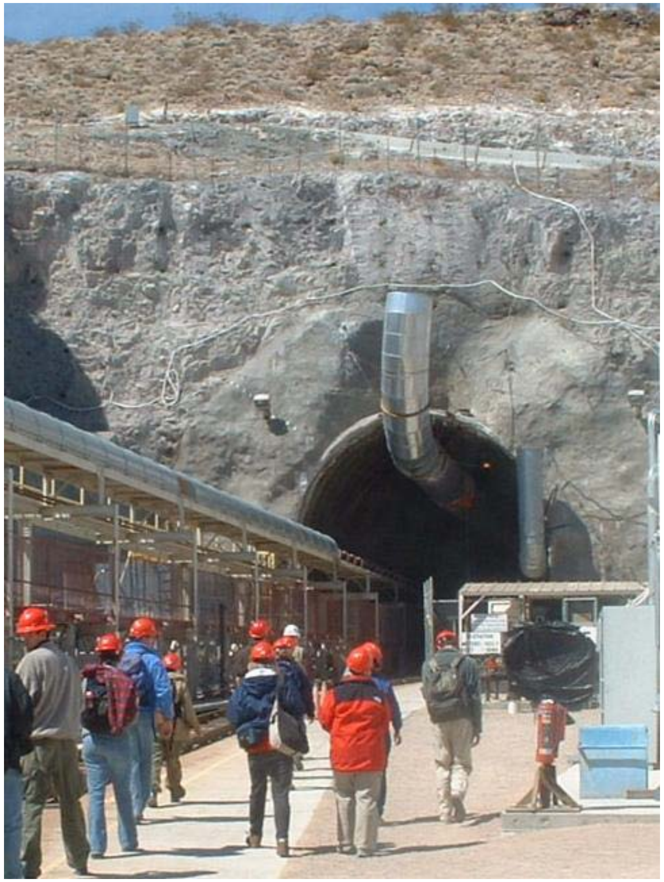


Existing exploratory drifts shown in yellow.

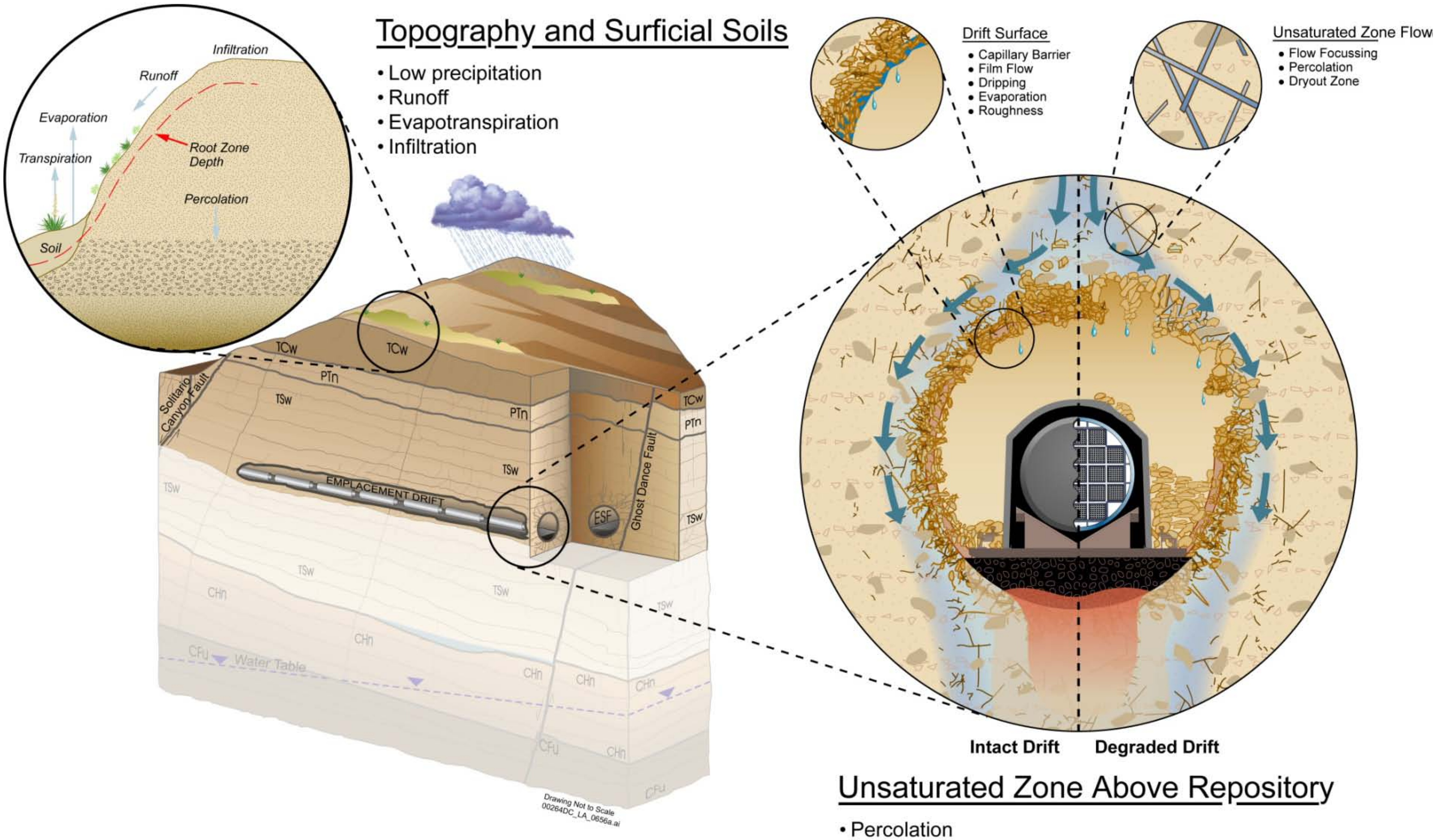
Approximate area for proposed emplacement drifts shown in blue.

Actual location of drifts is several hundred meters below the land surface.

Yucca Mountain Exploratory Tunnel



Upper Natural Barrier



Topography and Surficial Soils

- Low precipitation
- Runoff
- Evapotranspiration
- Infiltration

Drift Surface

- Capillary Barrier
- Film Flow
- Dripping
- Evaporation
- Roughness

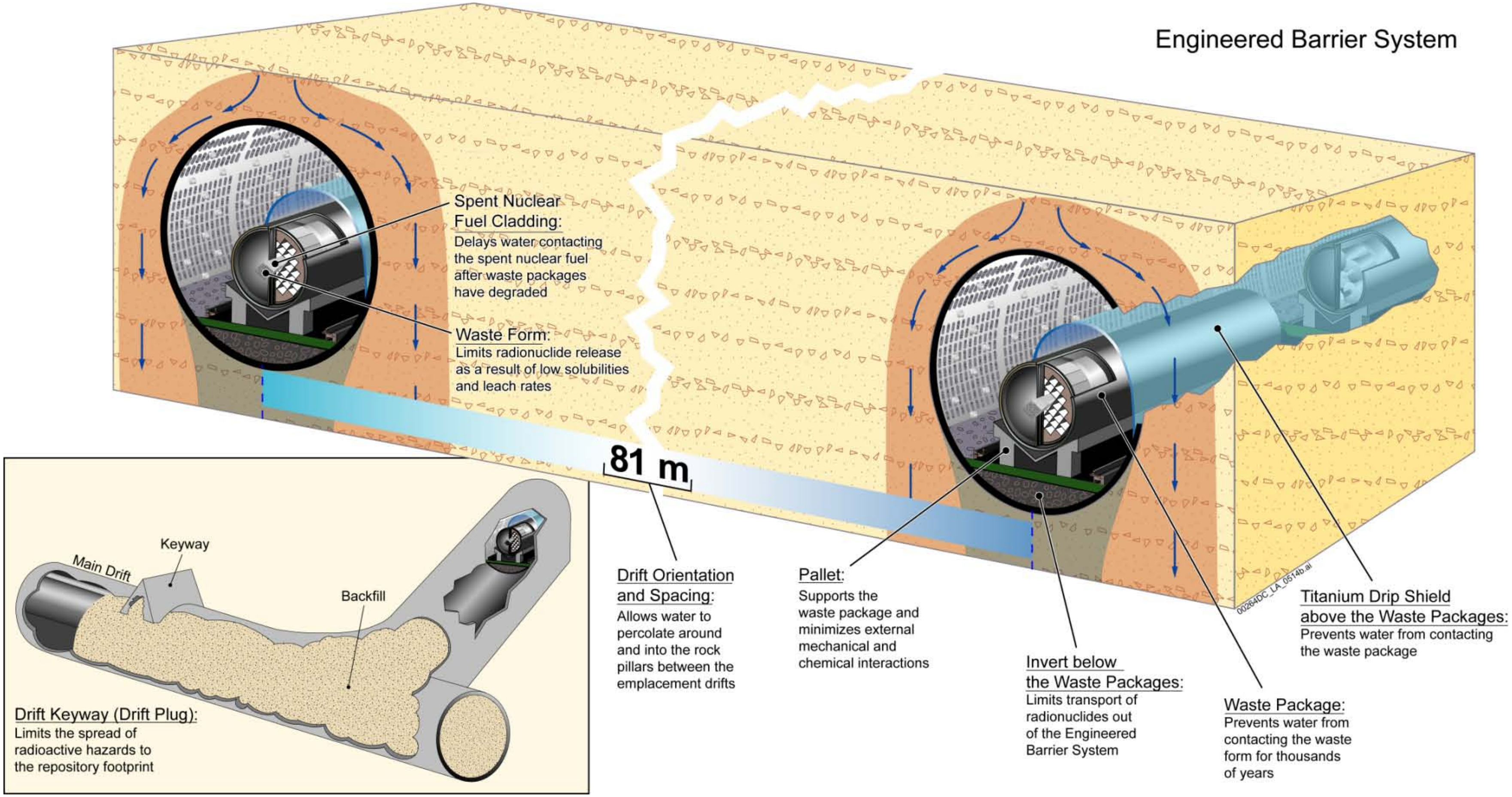
Unsaturated Zone Flow

- Flow Focussing
- Percolation
- Dryout Zone

Unsaturated Zone Above Repository

- Percolation
- Capillarity
- Lateral diversion

Engineered Barrier System



Spent Nuclear Fuel Cladding:
Delays water contacting the spent nuclear fuel after waste packages have degraded

Waste Form:
Limits radionuclide release as a result of low solubilities and leach rates

Drift Orientation and Spacing:
Allows water to percolate around and into the rock pillars between the emplacement drifts

Pallet:
Supports the waste package and minimizes external mechanical and chemical interactions

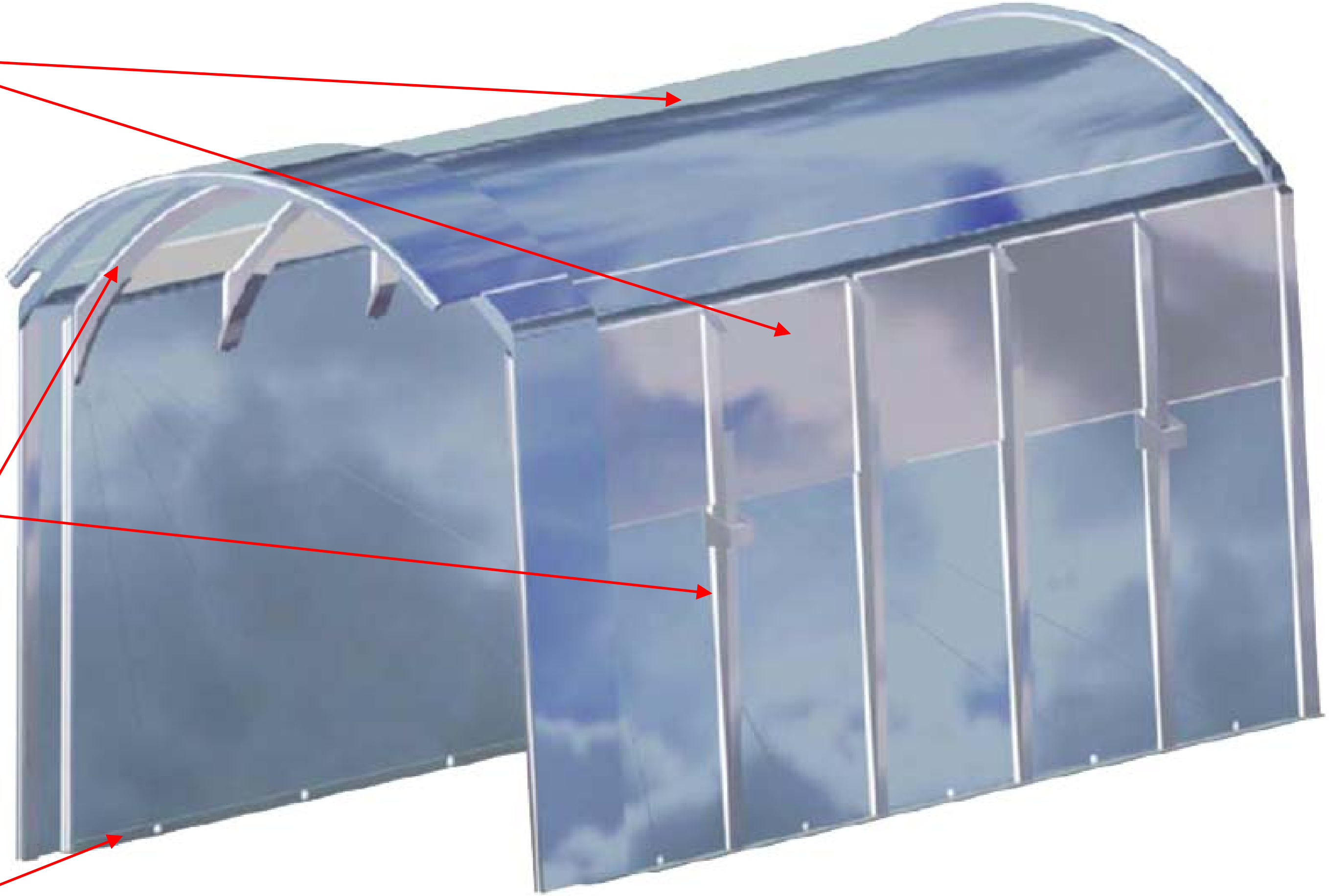
Invert below the Waste Packages:
Limits transport of radionuclides out of the Engineered Barrier System

Waste Package:
Prevents water from contacting the waste form for thousands of years

Titanium Drip Shield above the Waste Packages:
Prevents water from contacting the waste package

Drift Keyway (Drift Plug):
Limits the spread of radioactive hazards to the repository footprint

Engineered Barrier Components – The Drip Shield

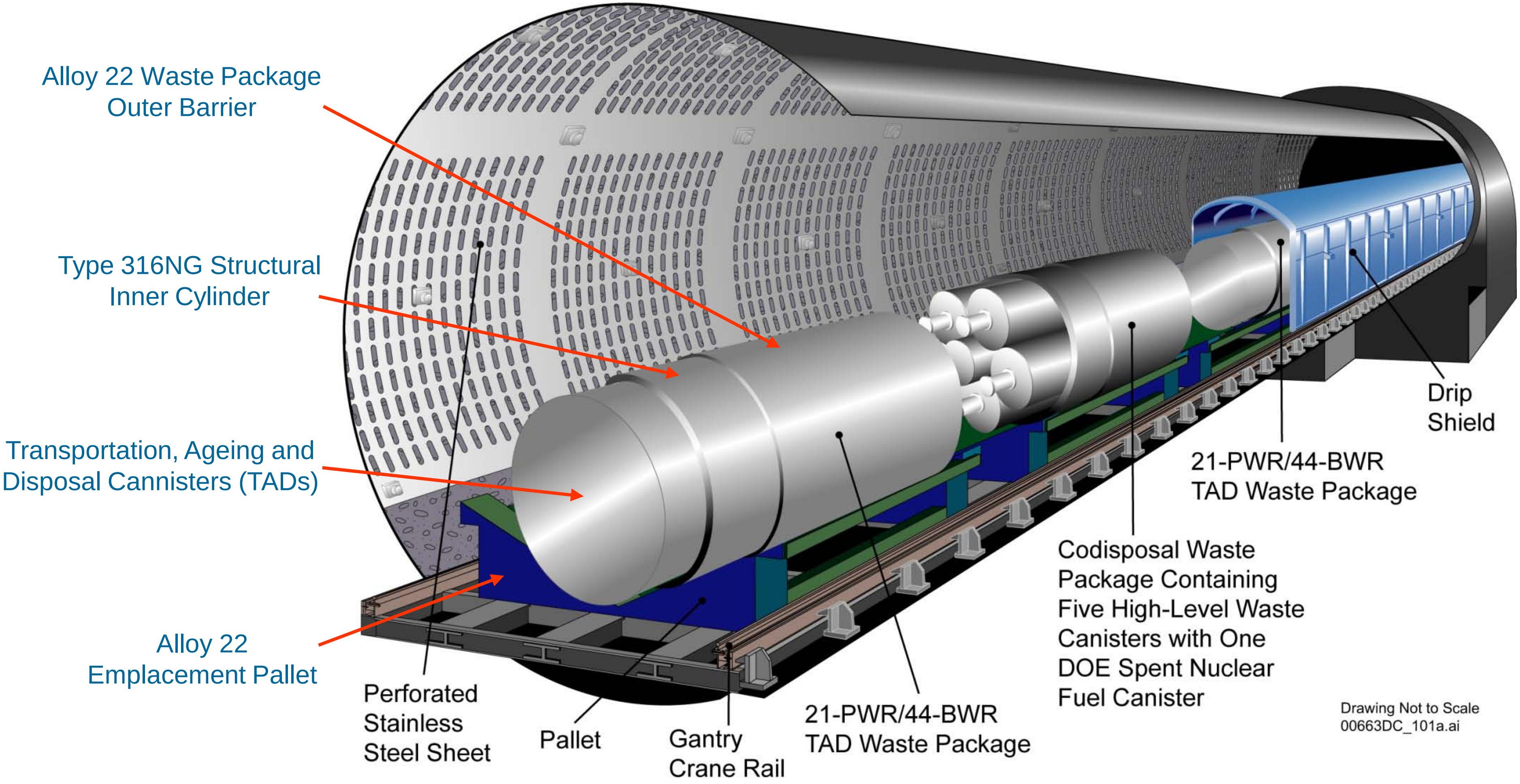


Ti-7 Shell
(~Ti Gr 2 + 0.12-0.15% Pd)

Ti-29 Struts and Bulkheads
(Ti Gr 5 + 0.08-0.14% Ru)

Alloy 22 Feet

Waste Packages in a Disposal Drift



Utilities load fuel into TADs which are shipped to Yucca Mountain

TADs loaded into waste packages, minimizing handling of bare fuel

The Primary Purpose of the Engineered Barrier is to Prevent or Reduce the Rate of Seepage Water Contacting the Waste

Engineered System Materials

- Drip Shield
  - Grade 7 Titanium plates
  - Grade 29 Titanium supports
  - Grade 7 / Grade 28 / Grade 29 welds

	Al	Pd	Ru	Ti	V
Grade 7	-	0.12-0.25	-	Bal.	-
Grade 28	2.5-3.5	-	0.08-0.14	Bal.	2-3
Grade 29	5.5-6.5	-	0.08-0.14	Bal.	3.5-4.5

- Waste Package
  - Annealed Alloy 22
  - Annealed Alloy 22 welds (longitudinal weld)
  - Stress relieved Alloy 22 welds (circumferential closure weld)

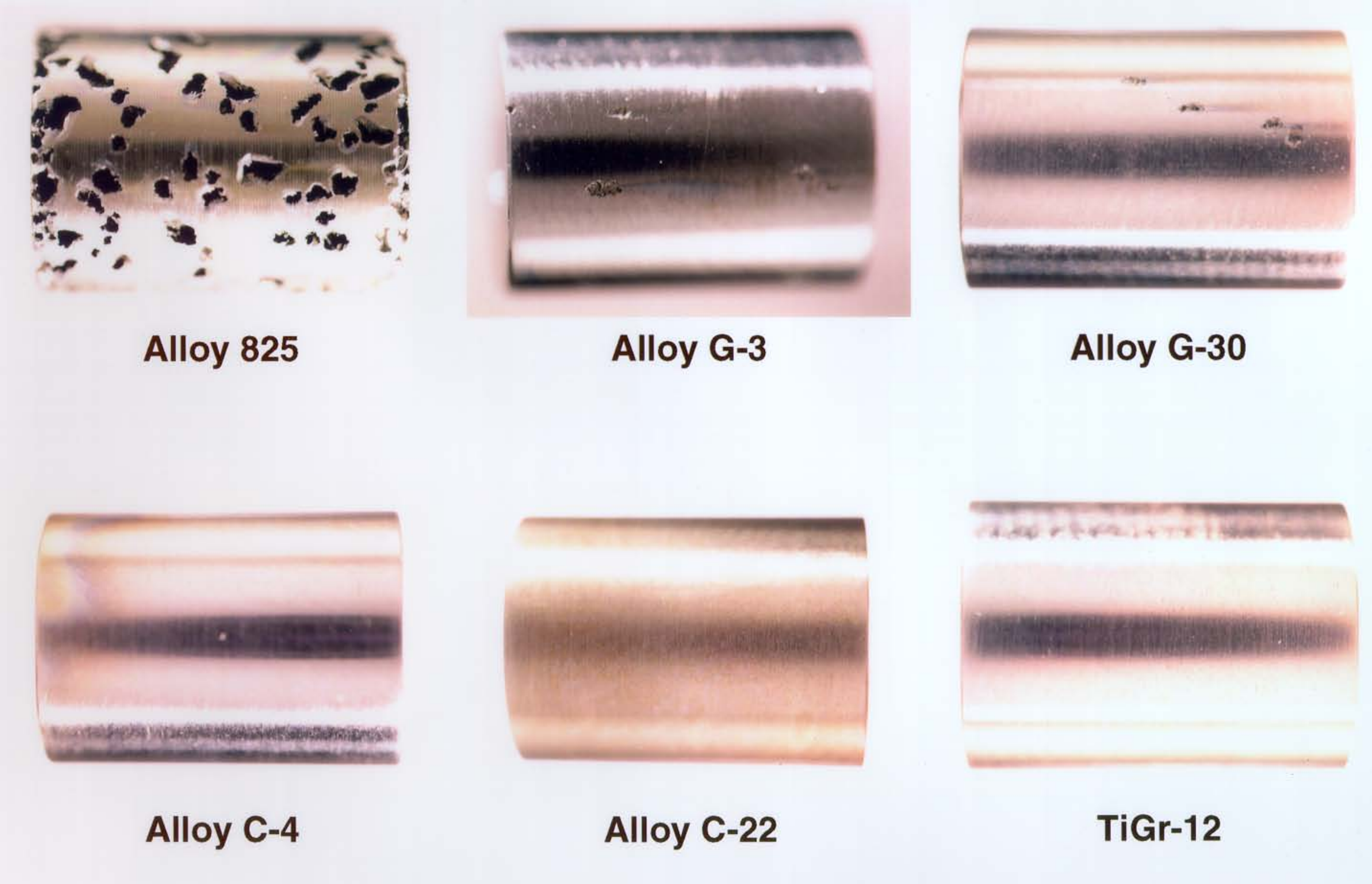
Alloy 22 Composition (N06022)							
Co	Cr	Fe	Mn	Mo	Ni	V	W
2.5 max	20-22.5	2.0-6.0	0.5 max	12.5-14.5	Bal.	0.35 max	2.5-3.5

Alloy 22 has an impressive analog - Hastelloy C

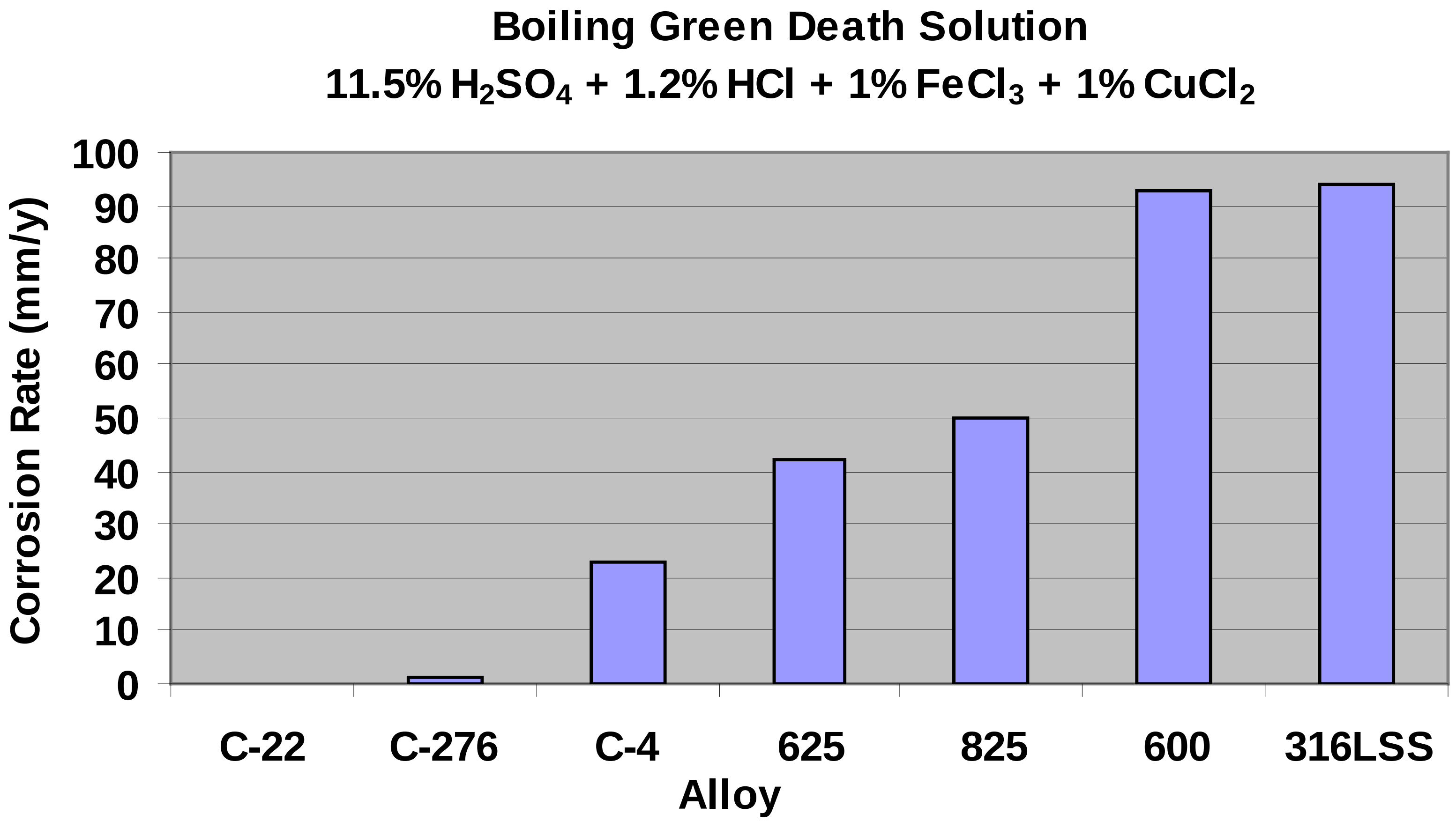
Exposed at Kure Beach, North Carolina since 1941 - 250 meters from ocean

Original mirror finish still intact after salt and debris washed from surface

Outstanding Pitting Resistance of Alloy 22: Superior to Other Candidate Materials



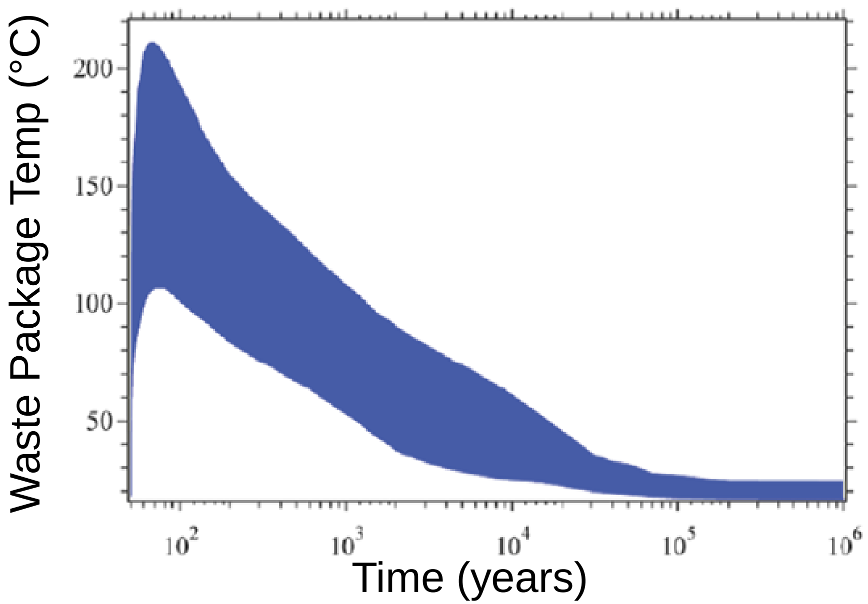
Localized Corrosion of Engineering Alloys

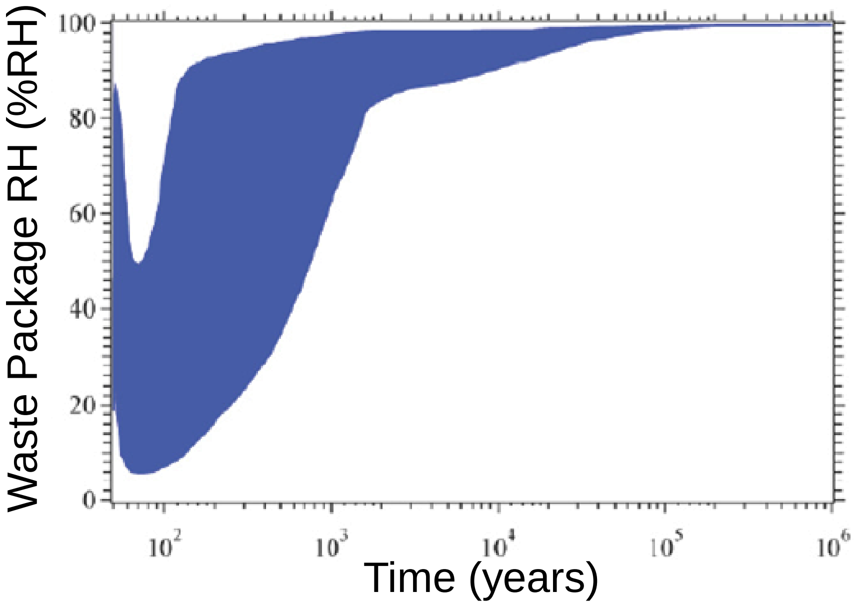


Green Death Solution: Solution Removed From Scrubbers Used to Wash Acidic Gases with Sea Water.

Environments That May Potentially Contact the Barrier Materials

- **Seepage environments**
  - Electrolyte chemistry defined by ambient water composition
  - Unlimited contaminant supply
  - Electrolyte may be continuous
- **Deliquescent environments**
  - Electrolyte chemistry defined by salt-bearing dusts deposited during repository ventilation
  - Limited contaminants
  - Electrolyte bound in the dust layer as droplets





Two Types of Chemical Environments

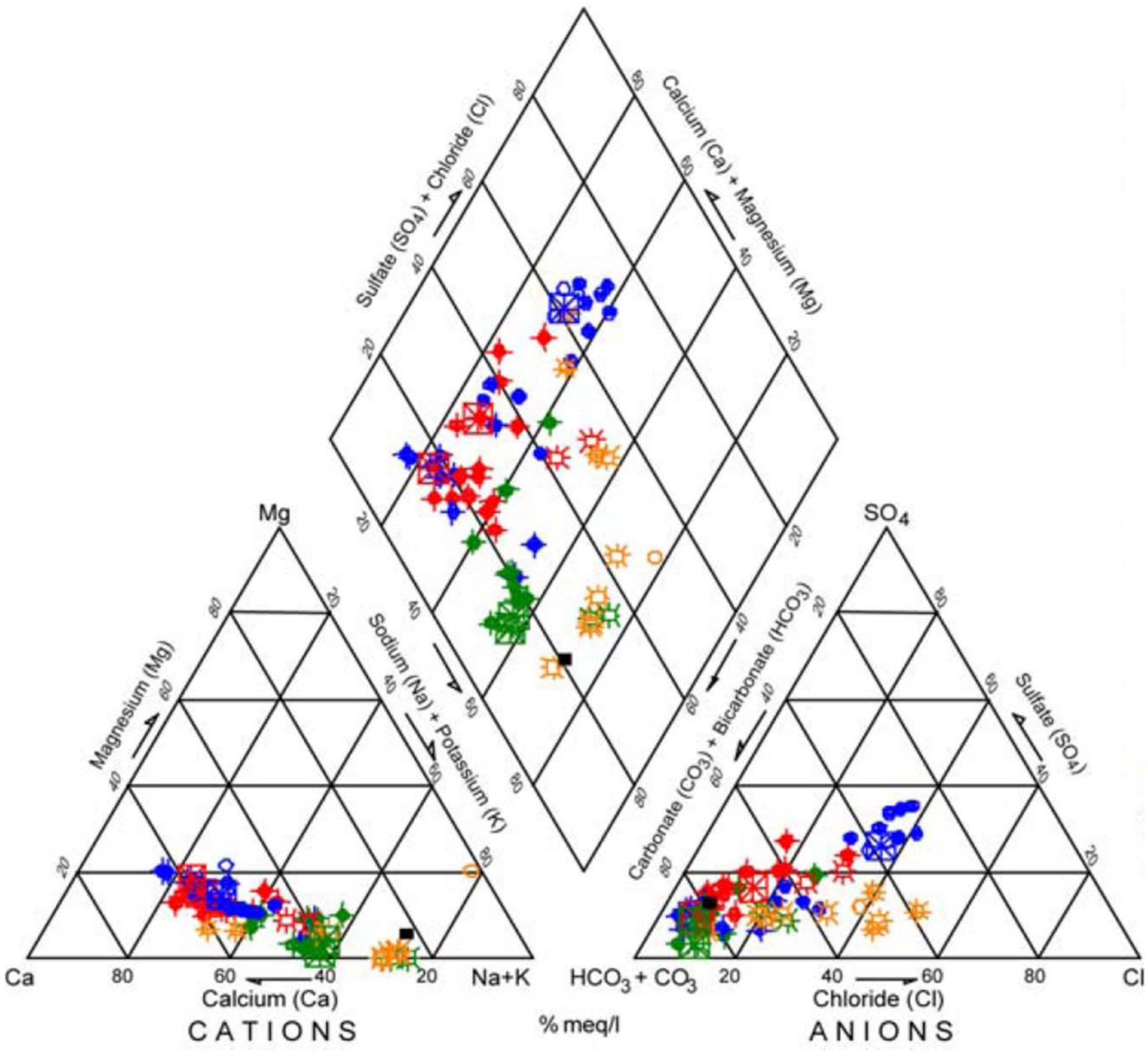
Deliquescence

- Dust containing soluble salts deposited on the WP during preclosure
- Multi-salt assemblages control deliquescence at higher temperatures
- NO_3^- is needed at high T
- Brine compositions become dilute as T decreases and RH increases
- Amount of brine is limited:
  - 1.8 µL/cm^2 (18 µm thick layer) at 120°C – decreasing with increasing temperature
- Chemistry is moderated by contact with rock-forming minerals in dust
- Brines can change with time due to degassing, deliquescence

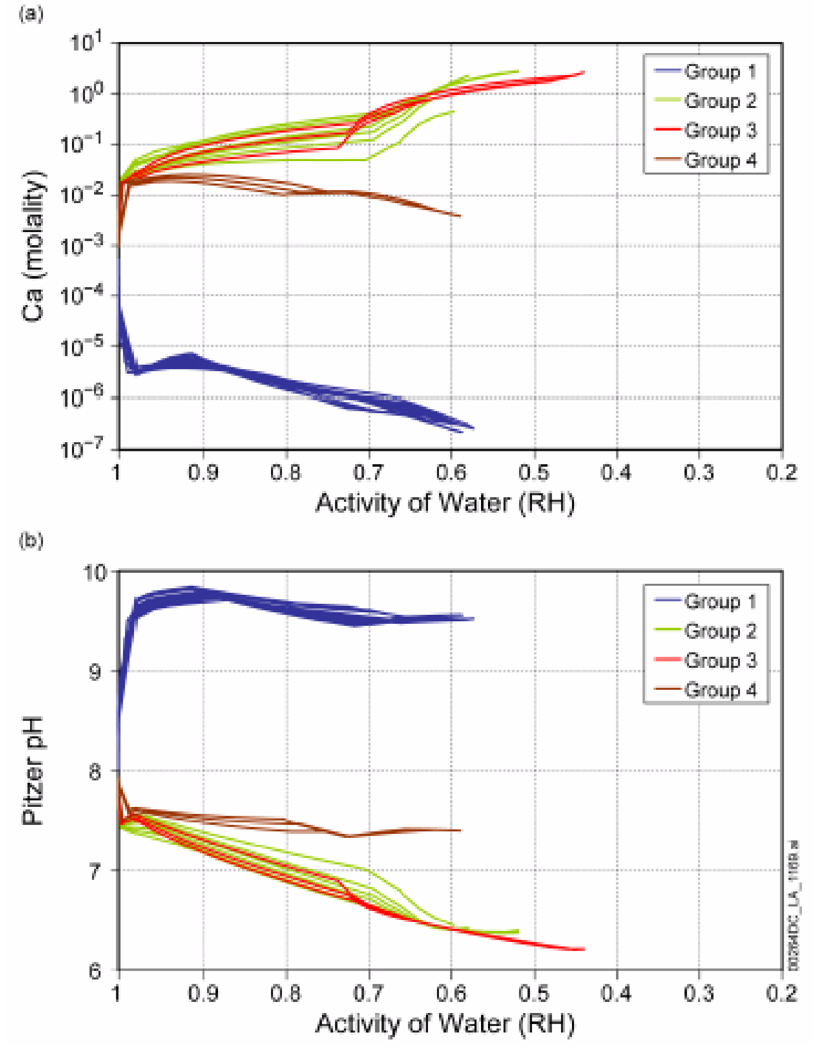
Seepage

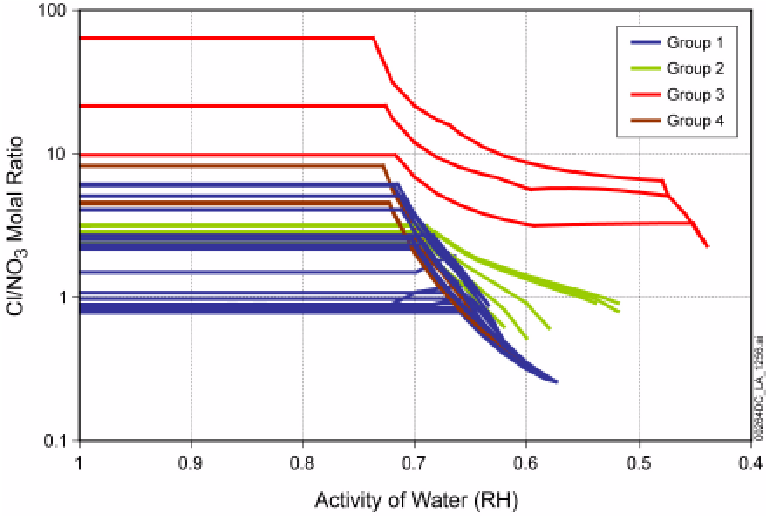
- Seepage may occur after cooldown ($T_{WP} < 105°C$)
- WP outer barrier is protected by the drip shields
- Residence time (equilibrium with T, RH at WP surface) controls the corrosion environment
- Chemical conditions (pH, Cl^-, NO_3^-, NO_3^-/Cl^-) are potentially corrosive during the early stages of cooldown
- Chemical fractionation may occur during transport

Water Chemistry is Controlled by Chemical Divides



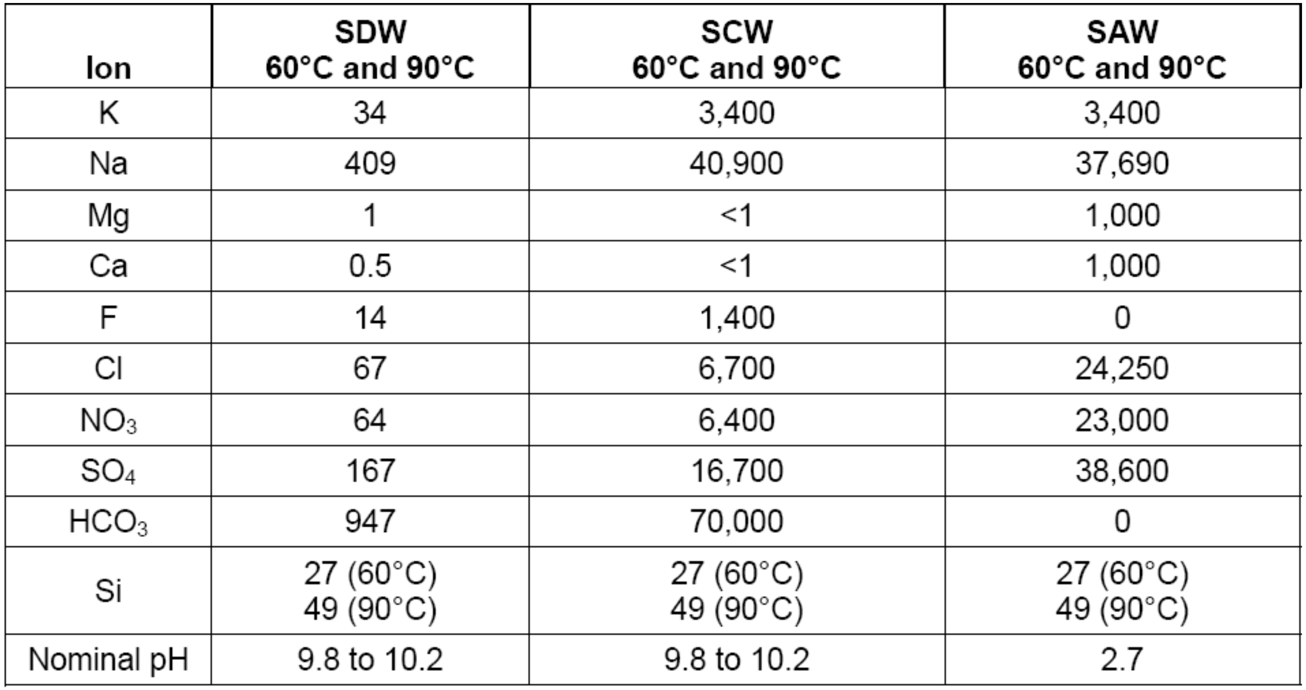
Chemical Divides Influence Chemistry of Concentrated Waters





Long-Term Exposure Testing Conditions

- Electrolytes: Simulated dilute water (SDW), Simulated acidified water (SAW) and Simulated concentrated water (SCW)
- Temperatures: 60ºC and 90ºC
- Specimen configurations: welded and non-welded, creviced and non-creviced
- Specimen locations: inundated, atmospheric and waterline



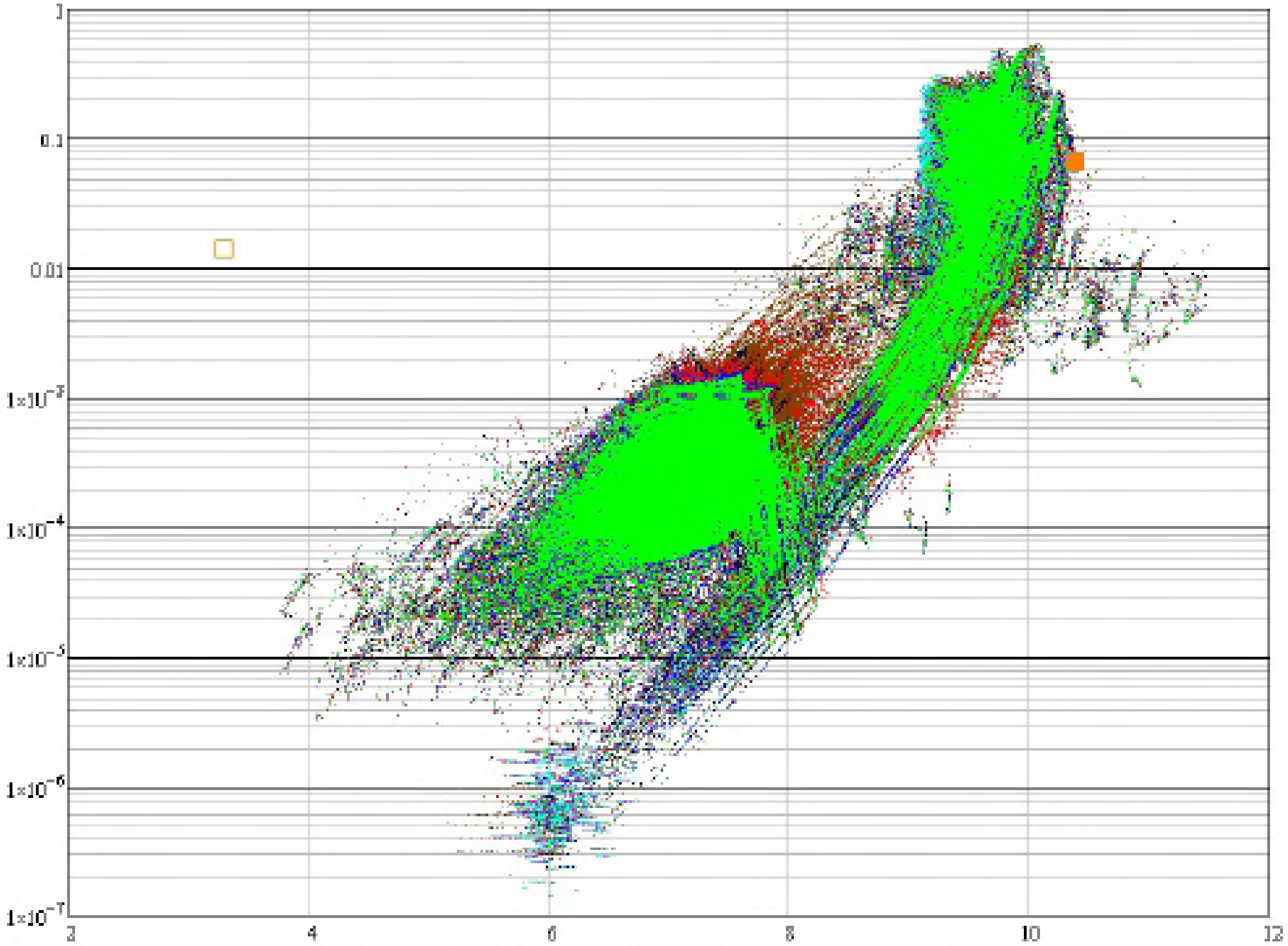
Ion	**SDW 60°C and 90°C**	**SCW 60°C and 90°C**	**SAW 60°C and 90°C**
K	34	3,400	3,400
Na	409	40,900	37,690
Mg	1	<1	1,000
Ca	0.5	<1	1,000
F	14	1,400	0
Cl	67	6,700	24,250
NO_3	64	6,400	23,000
SO_4	167	16,700	38,600
HCO_3	947	70,000	0
Si	27 (60°C) 49 (90°C)	27 (60°C) 49 (90°C)	27 (60°C) 49 (90°C)
Nominal pH	9.8 to 10.2	9.8 to 10.2	2.7

(concentrations are in parts per million)

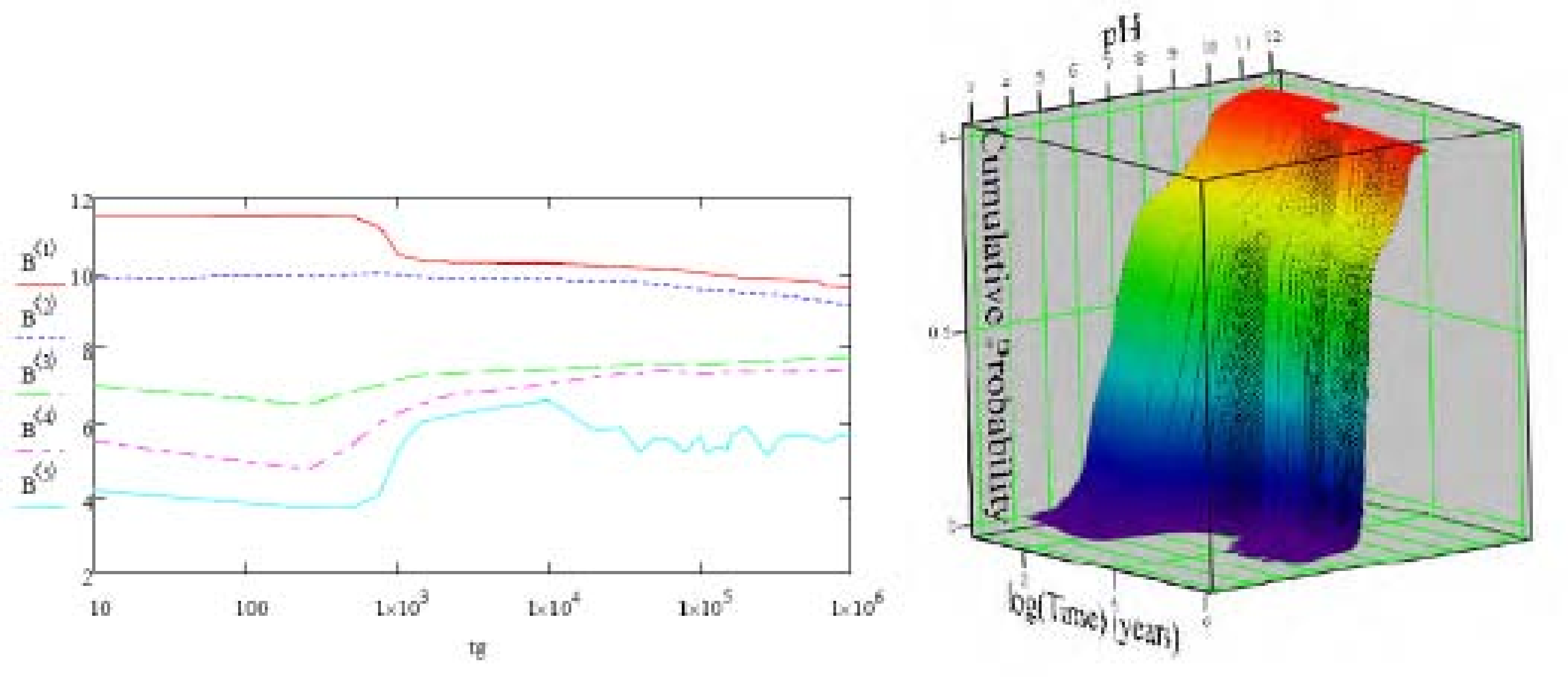
Min and Max Predicted Constituent Values that Could Affect Corrosion Performance

	Closure to 10,000 Years After Closure		10,000 Years to 10^6 Years After Closure	
Species or Parameter	**Minimum Value**	**Maximum Value**	**Minimum Value**	**Maximum Value**
pH	3.76	11.51	5.16	10.24
Cl (molal)	3.98×10^{-6}	26.69	3.98×10^{-6}	2.87
NO_3 (molal)	5.75×10^{-7}	51.77	5.57×10^{-7}	0.84
NO_3/Cl	0.016	9.28	0.016	1.28
F (molal)	1.44×10^{-7}	0.53	1.44×10^{-7}	0.27
Total C (molal)	7.91×10^{-6}	3.07	3.81×10^{-5}	1.44
Total S (molal)	1.67×10^{-6}	3.04	1.67×10^{-6}	0.80
Ca (molal)	6.76×10^{-7}	13.30	6.76×10^{-7}	0.13
Mg (molal)	7.20×10^{-8}	3.07	7.20×10^{-8}	0.22
Ionic Strength	4.16×10^{-5}	25.85	4.16×10^{-5}	5.24
pCO_2	1.09×10^{-4}	0.0208	1.98×10^{-4}	0.00429

Comparison of Corrosion Test Solutions to Predicted Chemistries pH and F



Predicted pH as Function of Time

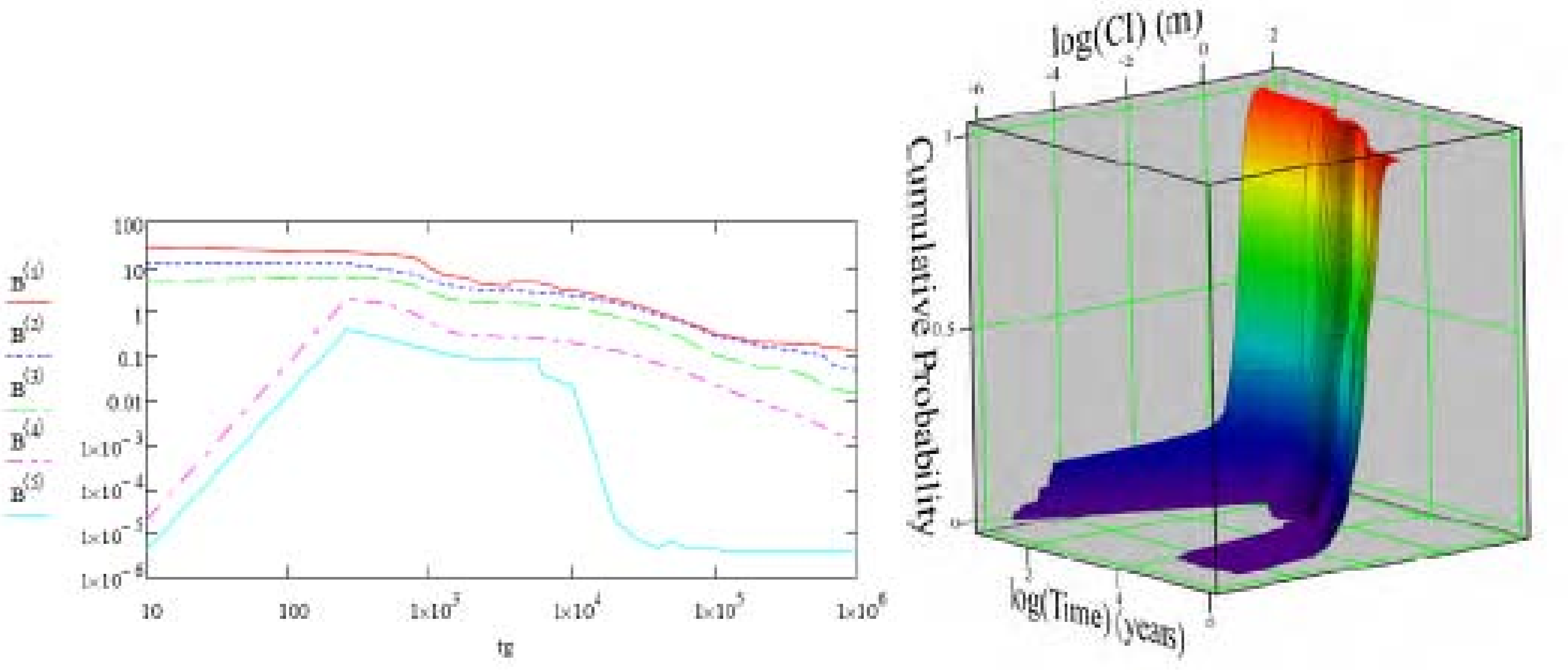


(a)

(b)

Upper, 95%, Median, Mean,
5%, Lower pH values

Predicted Cl$^-$ Concentration as Function of Time



(a) (b)

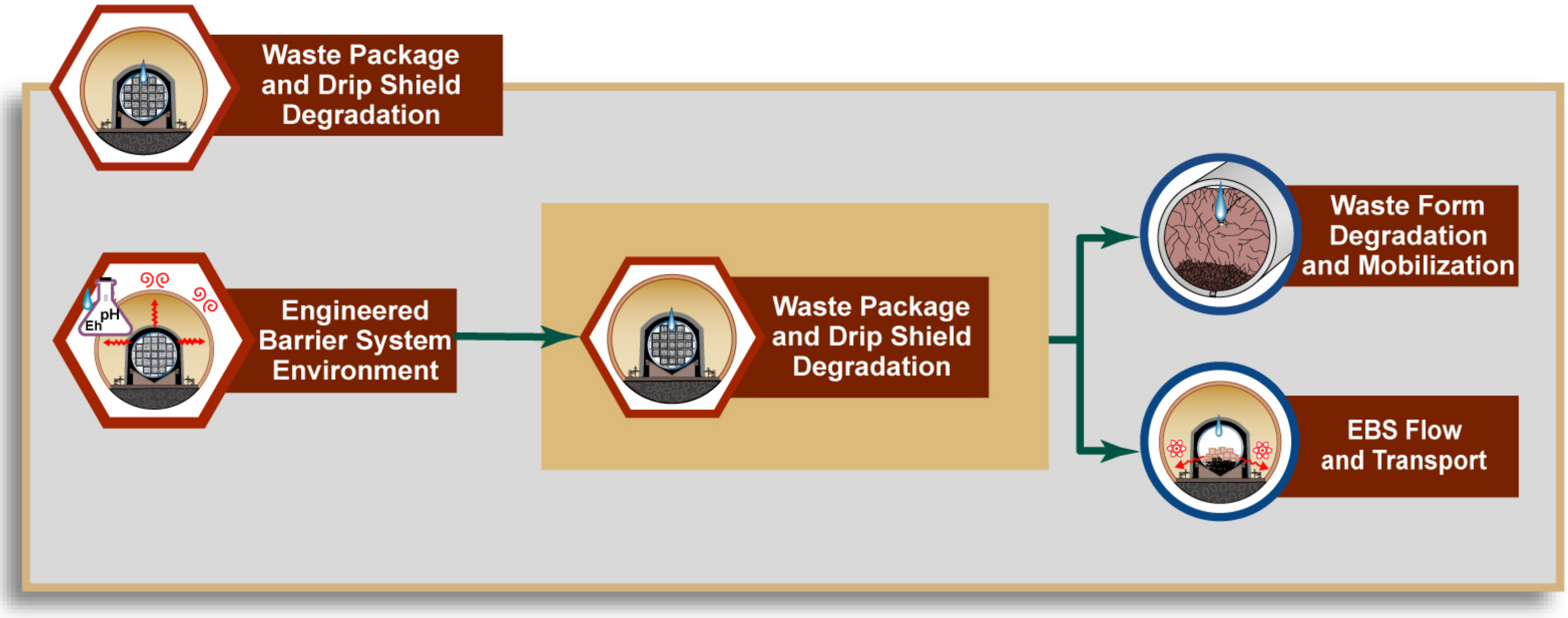
Upper, 95%, Median, Mean, 5%,
Lower Cl concentrations

Corrosion Environment Summary

- Water Chemistry and chemical divides result in a range of possible corrosion conditions, but not an unlimited combination
- Prior to initiation of corrosion experiments it is important to get good information regarding possible environments to minimize rework and support adequate model development
- Plan for a feedback loop between chemistry and corrosion experiments. If necessary corrosion experts need to have the chemistry better defined

Understanding and Effectively Modeling Corrosion of the Engineered Barrier

Identification and Linkages of Abstractions



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EBS = Engineered Barrier System

What to consider

- For each component of the engineered barrier system, need to consider the impact which known corrosion mechanisms will have on performance
    - General corrosion (GC)
    - Localized corrosion (LC)
    - Stress corrosion cracking (SCC)
    - Hydrogen embrittlement (HE)
    - Microbiologically influenced corrosion (MIC)

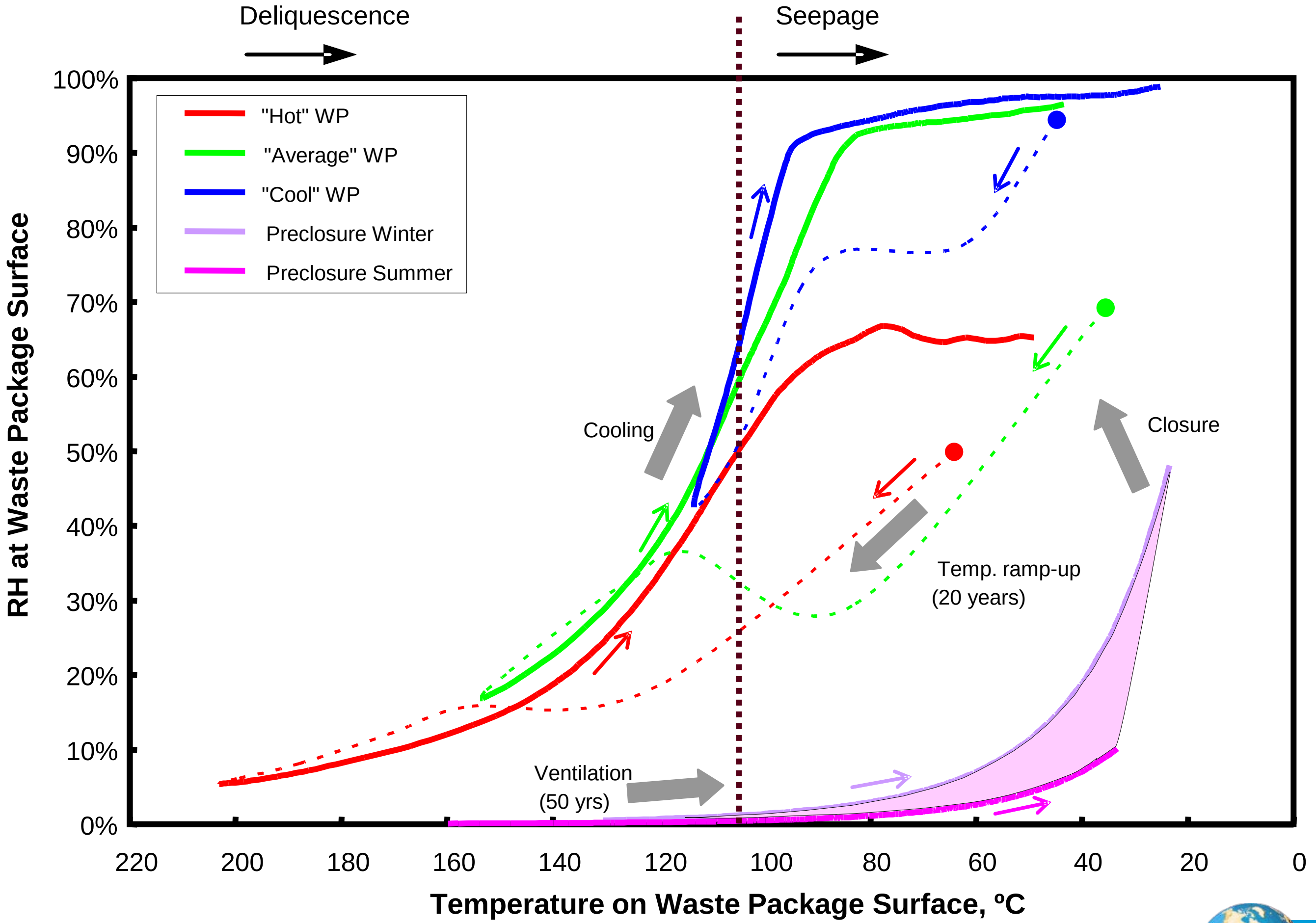
Controlling Variables

- The environment to which the material is subjected will determine which corrosion modes must be considered
  - Exposure temperature
  - Gaseous environment (oxygen, moisture, etc.)
  - Seepage chemistry

Evolution of Temperature/RH on the Waste Package Surface

Consider the anticipated in-drift conditions for Yucca Mountain as an example

- Different environments as a function of time



Two Types of Chemical Environments

Deliquescence

- Soluble salts deposited on the WP during pre-closure
- Drip shields control post-closure dust accumulation
- Multi-salt assemblages control deliquescence at higher temperatures
- Brine compositions become dilute as T decreases RH increases
- Amount of brine contacting metal surfaces is limited
- Chemistry is moderated by contact with rock-forming minerals in dust
- Brines change with time due to degassing, deliquescence

Seepage

- Seepage may occur after cooldown (T_{WP} < 105°C)
- WP outer barrier is protected by the drip shields
- Residence time (equilibrium with T, RH at WP surface) controls the corrosion environment
- Chemical conditions (pH, Cl^-, NO_3^-, NO_3^-/Cl^-) are potentially corrosive early during cooldown
- Chemical fractionation may occur during transport

Example – considerations for YMP

- Error in waste emplacement
- *General corrosion of the waste package*
- *General corrosion of the drip shields*
- *SCC of waste packages*
- SCC of drip shields
- *Localized corrosion (LC) of waste packages*
- LC of drip shields
- Hydride cracking of waste packages
- Hydride cracking of drip shields
- *Microbiologically Influenced Corrosion (MIC) of the waste packages*
- MIC of drip shields
- Internal corrosion of waste packages prior to breach
- Mechanical impact on waste package
- Mechanical impact on drip shields
- *Early failure of waste packages*
- Early failure of drip shields
- Copper corrosion in EBS
- LC on the waste package outer barrier (WPOB) due to dust deliquescence
- *Physical form of waste package and drip shield*
- Oxygen embrittlement of the drip shields
- Mechanical effects at EBS component interfaces
- Rockfall
- Creep of metallic materials in the waste package
- Creep of metallic materials in the drip shield
- Volume increase of corrosion products impacts waste package
- Electrochemical effects in EBS
- Thermal sensitization of waste packages
- Thermal sensitization of drip shields
- Thermal expansion/Stress of in-drift EBS components
- Gas generation (H_2) from waste package corrosion
- Radiolysis
- Radiation damage in EBS

From ANL-EBS-PA-000002, Rev. 5

Assembling a Corrosion Model

- What do you model, and what do you screen out?

- Numerous mechanisms – need to consider what is really important
  - Probability of a mechanism taking place
  - Impact of a mechanism if it takes place

- Model needs to be flexible enough to cover the things that matter, but if you consider everything, there may be unintended consequences

Experimental Program – Where do you start?

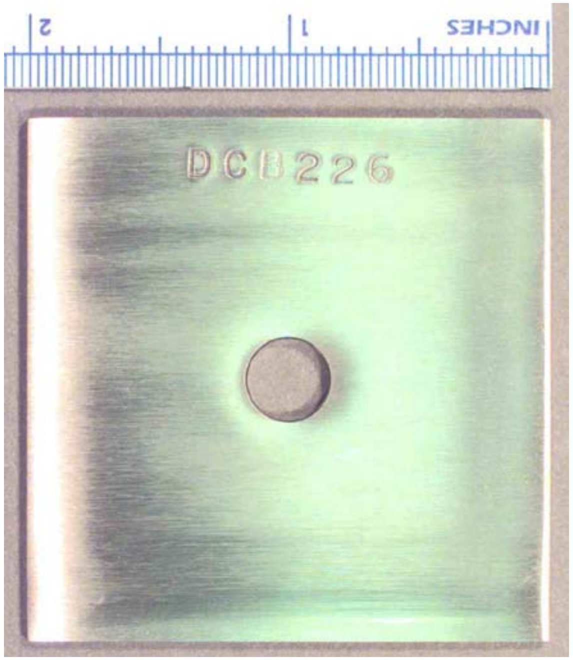
- You can’t test everything, so what do you evaluate and what do you exclude at the beginning?
  - Environments poorly defined
  - Material selections may be incomplete
  - Regulatory changes can happen

YMP – The Long Term Corrosion Test Facility

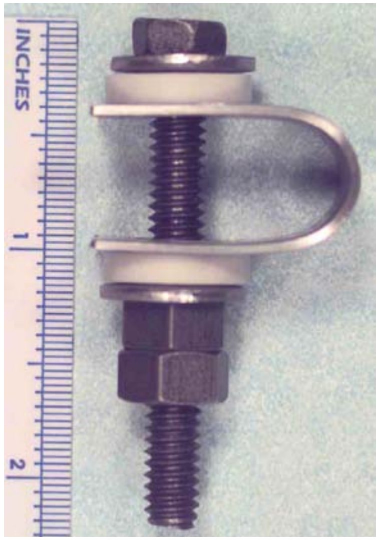
Test facility tanks

Test specimen rack

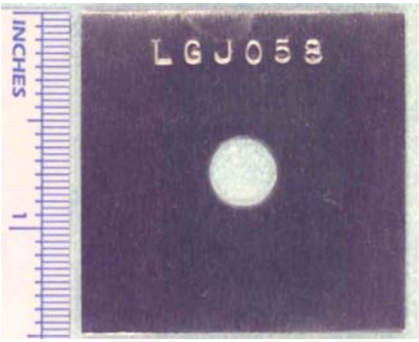
YMP – The Long Term Corrosion Test Facility



Crevice Coupon



U-Bend Specimen



Galvanic Coupon

Weight Loss Coupon

Summary: Seepage Environment

- Waste package temperature <105ºC
- RH varies from approx. 40% to 99+%
- Salt separation effect implemented for RH < 77%
- NO3-/Cl-controlled by ambient water composition
- Ca-Cl brines predicted during peak thermal period
- Wide range of pH (4.5 to 10.5 plus uncertainty)
  - Higher pH after cooldown (T_{dw}< 100ºC)
  - Increasing pH as repository cools
- Greatest potential for corrosive seepage chemistry occurs early during cooldown
- Open system with respect to gases (background acid gas concentrations low)

Example - Things to Include

- Example – Localized corrosion of Alloy 22

Experimentally demonstrated that while pitting is unlikely, crevice corrosion could be initiated in repository relevant seepage chemistries at sufficiently large applied potentials.

Monitoring of the open circuit potential in similar solutions revealed that it could increase to values more positive than the repassivation potential, suggesting that crevice corrosion initiation could take place

While there are theoretical reasons why stable propagation is unlikely, initiation is possible, and thus it is included in the corrosion model.

Exclude - probability

- Microbiologically influence corrosion of the WPOB

- Is Alloy 22 susceptible to MIC?

  Under the right set of conditions, MIC can take place

- Will conditions exist within a drift which promote bacterial activity (i.e., right combination of temperature, moisture content, and carbon source)?

- Since bacterial activity is not likely on the surface of a waste package, MIC can be excluded as it is improbable that conditions will exist under which it's possible.

Exclude - impact

- Stress corrosion cracking of the drip shield
- The drip shields may be subject to stress corrosion cracking under repository conditions.
  - (1) weld-induced residual stress,
  - (2) plasticity-induced residual stress caused by seismic events, and
  - (3) residual stress produced by rockfalls
- The tightness of stress corrosion cracks in passive alloys such as Titanium Grade 7 (i.e., small crack-opening displacement) and their tortuosity will limit the advection of liquids and solids through these cracks

- since the primary role of the drip shield is to keep water from contacting the waste package, stress corrosion cracking of the drip shield does not compromise the design purpose of the drip shield.

- stress corrosion cracking of drip shields is excluded for the drip shield due to low consequence to radiological exposures

Summary: Deliquescence Environment

- Brines can form only in small amounts at elevated T
- Physical environment
  - Unsaturated
    - Open system with respect to gases
  - Capillary and adsorptive retention in the dust layer further decreases available brine volume
- Chemical environment
  - $NaCl$ – KNO_3 (–$NaNO_3$) (–$Ca(NO_3)_2$) salt systems
    - Deliquescence at higher temp. requires multiple-salt assemblages
  - Nitrate-rich; NO3-/Cl-increases with higher temperature
  - Acid degassing
    - May occur initially; less as pH increases; unlikely to dry out
    - Background acid-gas pressures are very low
    - NO_3^-/Cl^- minimum ratio is controlled by temperature
  - Reaction with silicates buffers pH, removes divalent cations

Exclude – probability

- General corrosion of the waste package outer barrier requires the presence of an aqueous electrolyte on the metal surface
- Seepage can not take place when the drift wall temperature is greater than the boiling point of water.
- As there is no source for a liquid electrolyte on the metal surface, the probability of general corrosion taking place is effectively zero.

Exclude - impact

- Dry oxidation of Alloy 22

  Thermal oxidation of Alloy 22 as a function of time, resulting in the formation of an adherent, protective oxide layer of uniform thickness

  Rate constant and oxide thickness data obtained from literature

  Assuming a constant temperature of 350°C and ignoring the parabolic dependence of oxide thickness on time given, the total penetration depth in the WPOB by dry oxidation in10,000 years after permanent closure is only 93 μm

  So – will it take place? Almost certainly, but does it matter?

  Rate is negligible (i.e., 93 μm << 25 mm)

Exclude – Impact

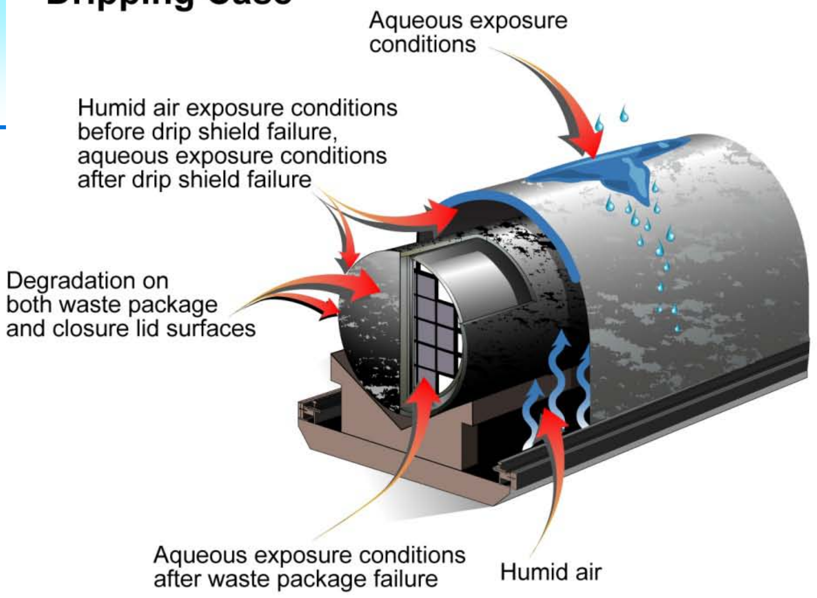
- Dust deliquescence - Small amounts of dust can be deposited on the waste package outer barrier surface during emplacement and preclosure operation. This dust can form highly concentrated brines under high temperature, high moisture content conditions
- If brine exists at elevated temperatures (>120°C), it will be benign, rather than corrosive, so initiation of localized corrosion and subsequent penetration of the waste package outer barrier is unlikely.
- The quantity of brine at elevated temperatures is small, which hinders corrosion initiation and extent.
- Even if localized corrosion were to initiate, it would not result in penetration of the waste package outer barrier. Thus, the overall consequence of dust deliquescence on the localized corrosion of the waste package outer barrier will be insignificant.
- Therefore, localized corrosion of Alloy 22 due to dust deliquescence is excluded based on low consequence.

WP and DS Degradation Conceptual Model

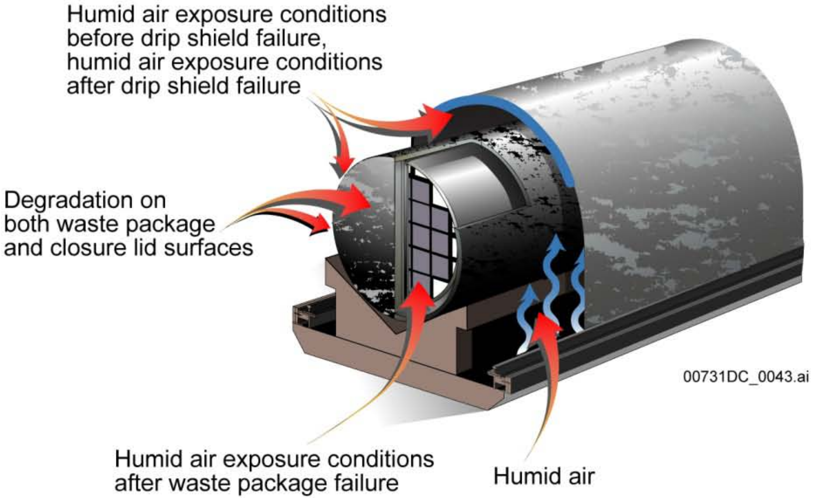
- **DS degradation (GC) not dependent on seepage contact**
- **WP GC and SCC not dependent on seepage water contact**
- **WP LC can initiate only if seepage contacts the WP surface**

After DS failure

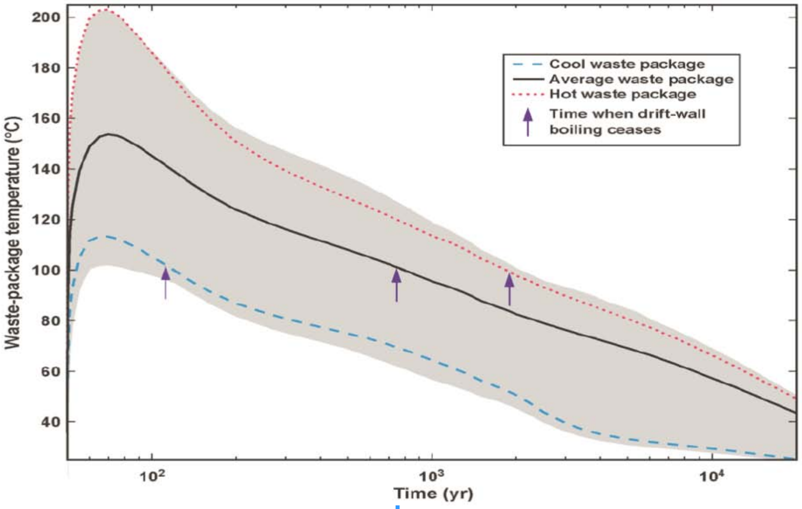
Dripping Case



Non-Dripping Case



Implementation—WP GC



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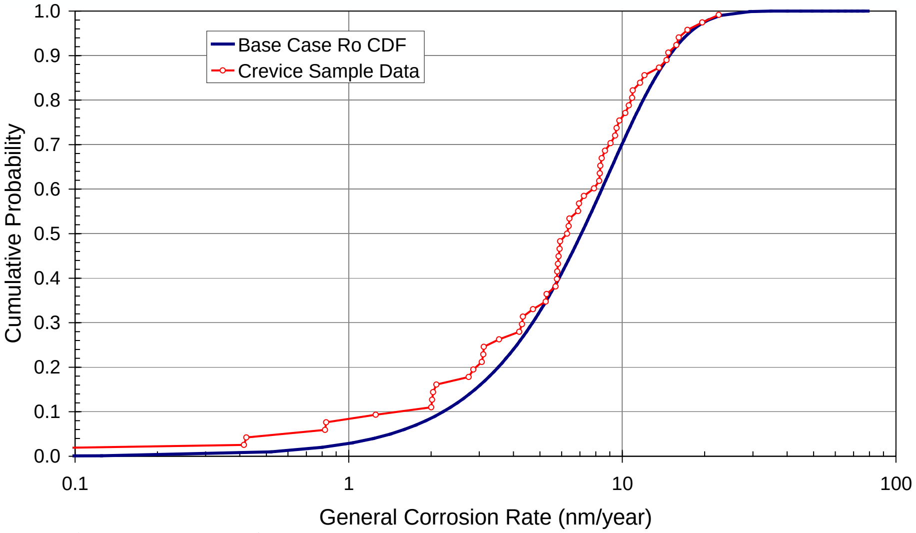
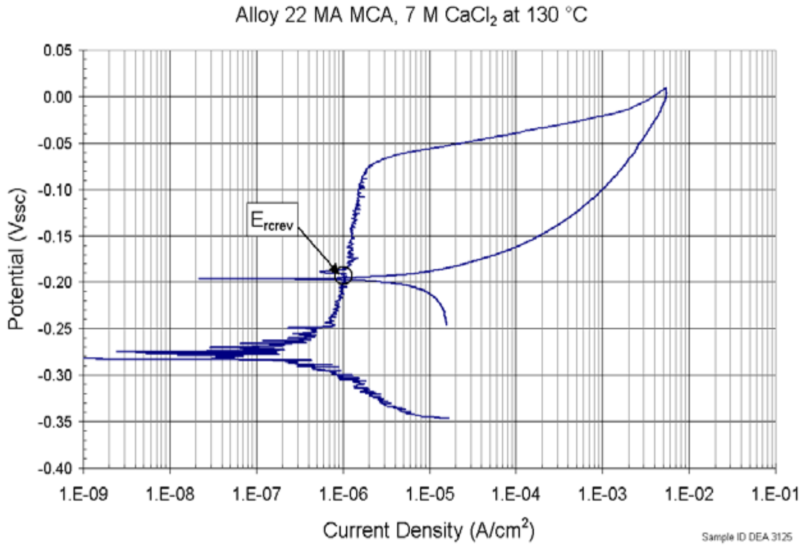


ANL-EBS-MD-000003

$$\text{Rate} = f_{MIC} \exp\left(C_o - \frac{C_1}{T} \right)$$

- **Temperature profiles**
  - **Spatial variability (WP-to-WP)**
- **C_o, pre-exponent, based on Weibull distribution fit to weight-loss data**
  - **Spatial variability (patch-to-patch)**
- **C_1, temperature dependence, based on normal distribution from polarization data**
  - **Epistemic uncertainty**
- **f_{MIC}, MIC multiplier**
  - **Epistemic uncertainty**

Implementation—WP LC

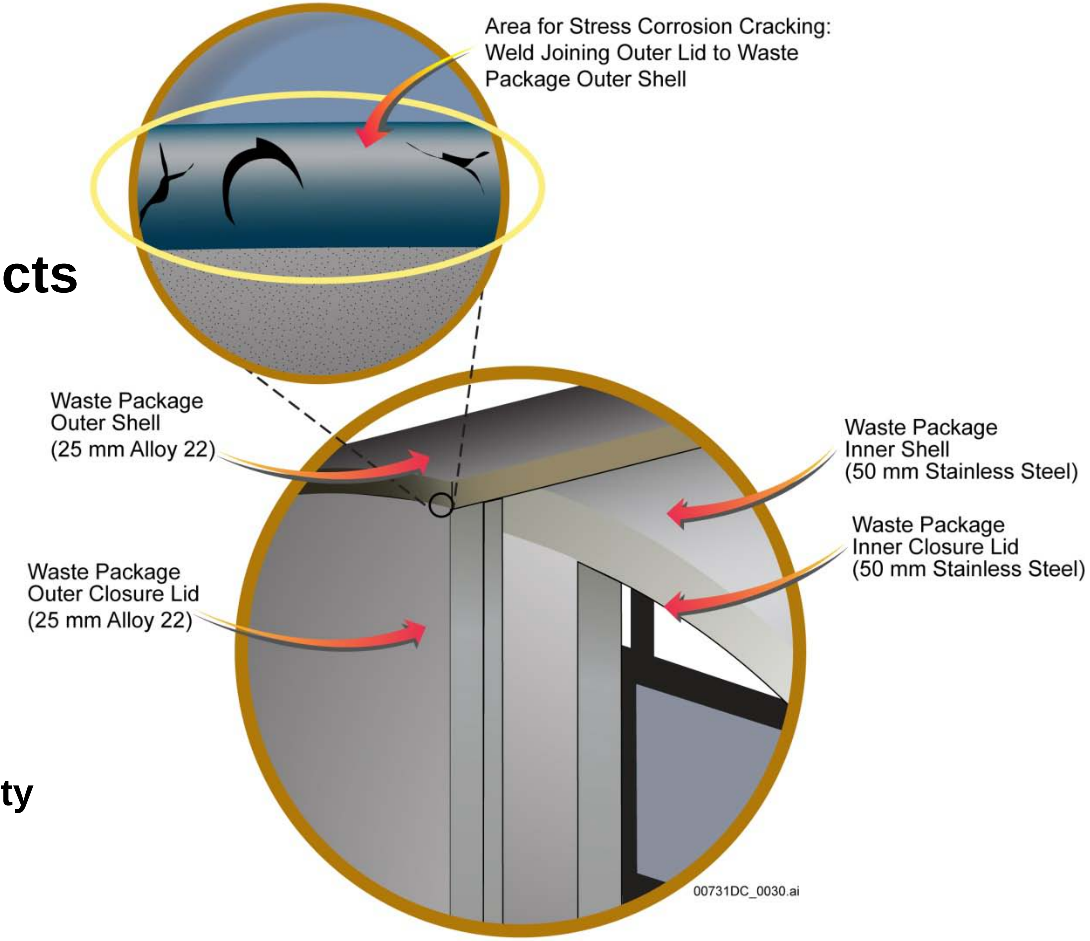


ANL-EBS-MD-000003

- Waste package areas contacted by seepage may be subject to LC
- If seepage occurs at RH < ~70% then model initiates LC
  - Potential for salt separation
- If seepage occurs at RH > ~70%
  - Compare
    - E_{corr}, long-term corrosion potential, to
    - E_{rcrev}, crevice repassivation potential
  - If E_{corr} ³ E_{rcrev} model initiates LC
    - E_{corr} and E_{rcrev} are functions of T, pH, [Cl $^-$], and [NO_3^-]
      - Epistemic uncertainty in fitting parameters
      - Spatial variability from thermal and chemical variations

Implementation—WP SCC

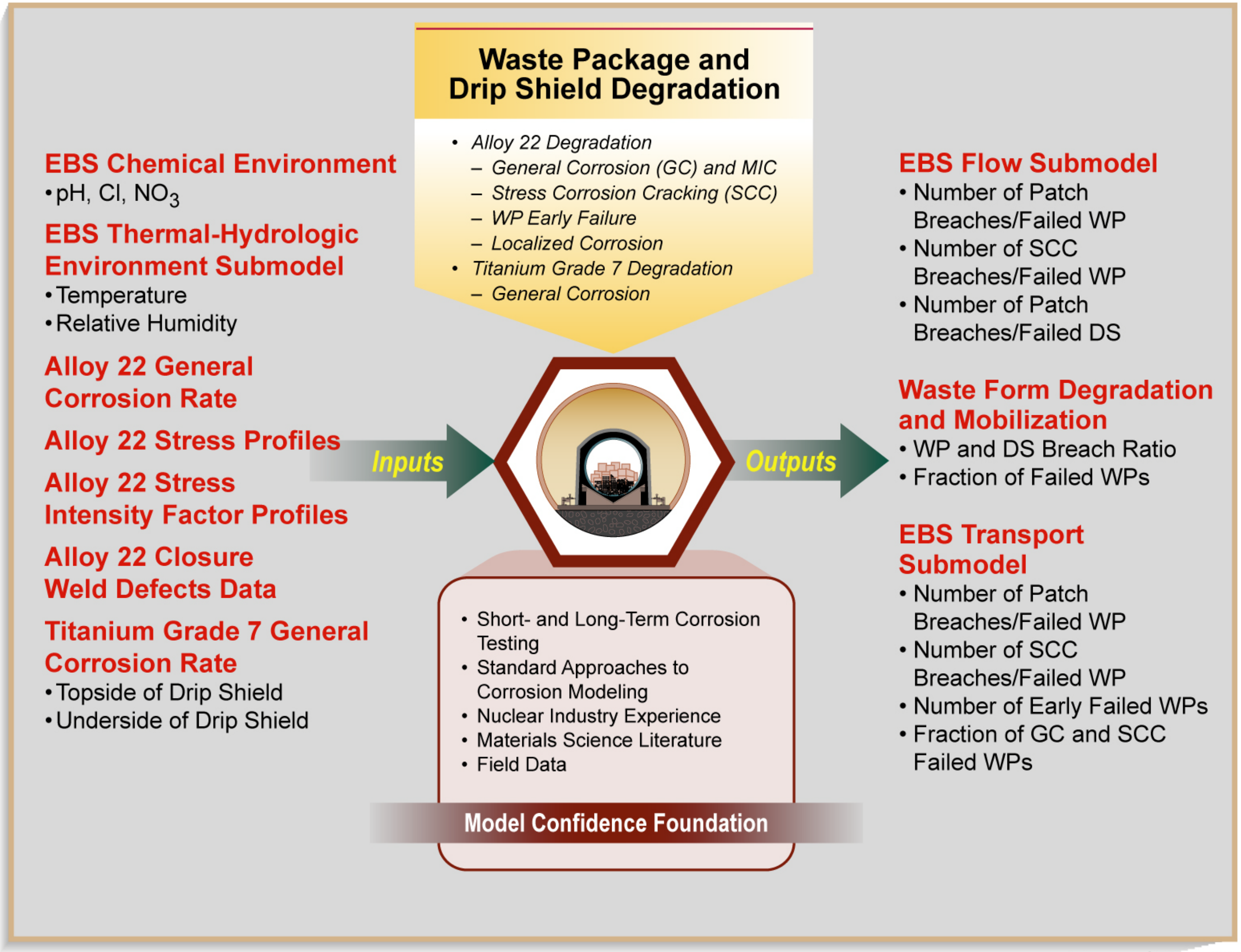
- Only in closure weld regions (in absence of seismicity)
  - Weld region plasticity burnished
  - Initiates at incipient defects or weld flaws
- Growth by Slip Dissolution Model
  - Rate of crack growth a function of
    - Stress intensity factor
      - Mainly epistemic uncertainty
    - Repassivation rate
      - Epistemic uncertainty



Treatment of Uncertainty and Variability

- **Treatment of uncertainty**
  - **WP GC temperature dependence**
  - **WP LC initiation model parameters**
  - **WP SCC stress and stress intensity factor profiles**
  - **WP SCC growth model parameters**
  - **WP MIC GC rate multiplier**
  - **DS GC rate**
- **Treatment of variability**
  - **WP GC/LC temperature/chemical inputs**
  - **WP GC pre-exponent term**
  - **WP SCC stress and stress intensity factor profiles**
  - **WP SCC closure weld flaw size/number**

Inputs, Outputs, Basis for Model Confidence



Waste Package and Drip Shield Degradation

- *Alloy 22 Degradation*
  - *General Corrosion (GC) and MIC*
  - *Stress Corrosion Cracking (SCC)*
  - *WP Early Failure*
  - *Localized Corrosion*
- *Titanium Grade 7 Degradation*
  - *General Corrosion*

Inputs

EBS Chemical Environment
- pH, Cl, NO_3

EBS Thermal-Hydrologic Environment Submodel
- Temperature
- Relative Humidity

Alloy 22 General Corrosion Rate

Alloy 22 Stress Profiles

Alloy 22 Stress Intensity Factor Profiles

Alloy 22 Closure Weld Defects Data

Titanium Grade 7 General Corrosion Rate
- Topside of Drip Shield
- Underside of Drip Shield

Outputs

EBS Flow Submodel
- Number of Patch Breaches/Failed WP
- Number of SCC Breaches/Failed WP
- Number of Patch Breaches/Failed DS

Waste Form Degradation and Mobilization
- WP and DS Breach Ratio
- Fraction of Failed WPs

EBS Transport Submodel
- Number of Patch Breaches/Failed WP
- Number of SCC Breaches/Failed WP
- Number of Early Failed WPs
- Fraction of GC and SCC Failed WPs

- Short- and Long-Term Corrosion Testing
- Standard Approaches to Corrosion Modeling
- Nuclear Industry Experience
- Materials Science Literature
- Field Data

Model Confidence Foundation

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Summary/Conclusions

- Identify potential mechanisms
- Evaluate probabilities and impact of each mechanism
- Develop model which is only as complex as it needs to be
  - Include what matters, exclude what doesn’t