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CASE WESTERN RESERVE UNIVERSITY

The Proposed Yucca Mountain Repository from a Corrosion Perspective

Presented to:
MRS 2005-29th International Symposium on the Scientific Basis for Nuclear Waste Management

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Thrust Lead-OST&I Materials Performance
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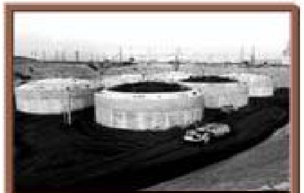
Introduction

- Corrosion is a primary determinant of waste package performance at the proposed Yucca Mountain Repository
  - The most likely degradation process
  - Controls the delay time for radionuclide transport from the waste package
  - Determines when packages will be penetrated and the shape size and distribution of those penetrations

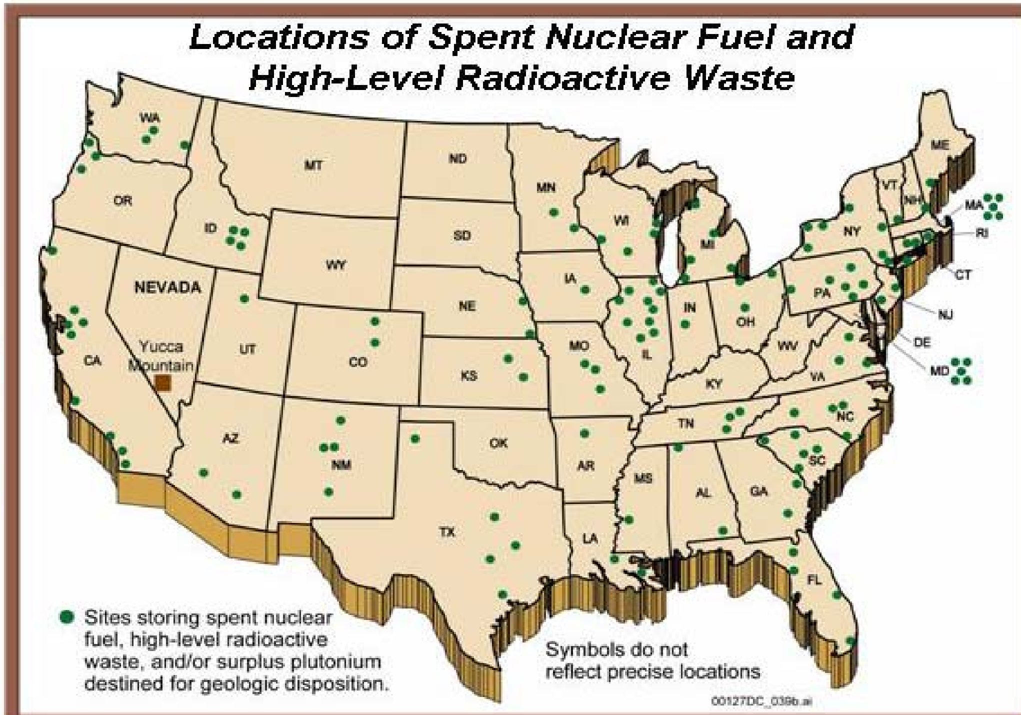
- In this presentation, the proposed Yucca Mountain Repository is viewed from a corrosion perspective

Locations of Spent Nuclear Fuel and High-Level Radioactive Waste



Defense Complex Clean-Up

Support of Nonproliferation Initiatives, e.g. Disposal of DOE Foreign Research Reactor Spent Fuel

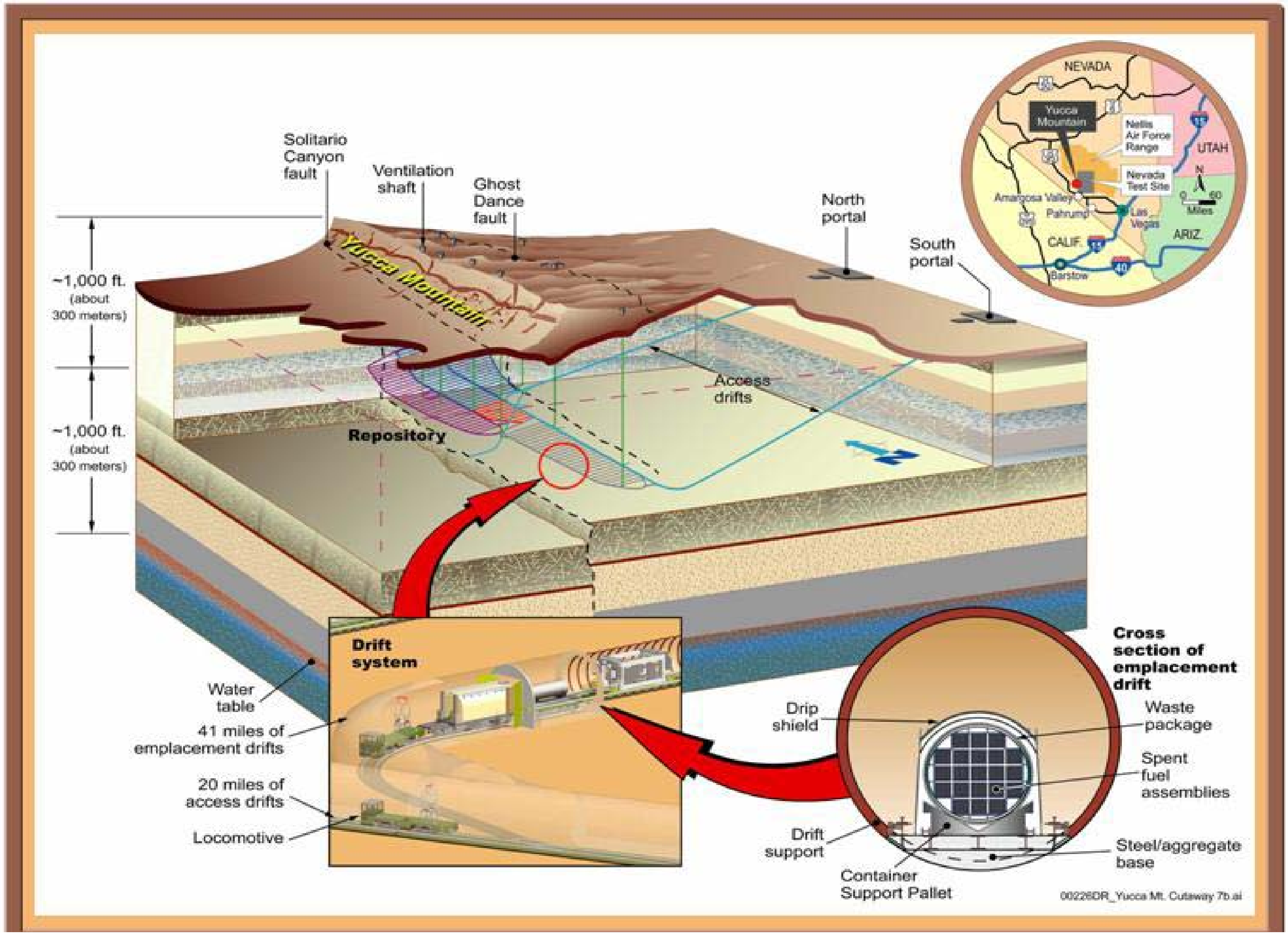


Commercial Spent Nuclear Fuel

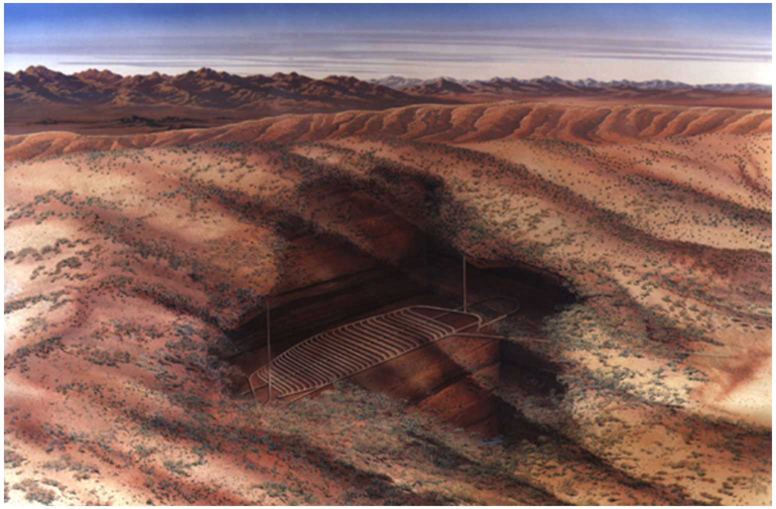
Disposition of Naval Reactor Spent Nuclear Fuel

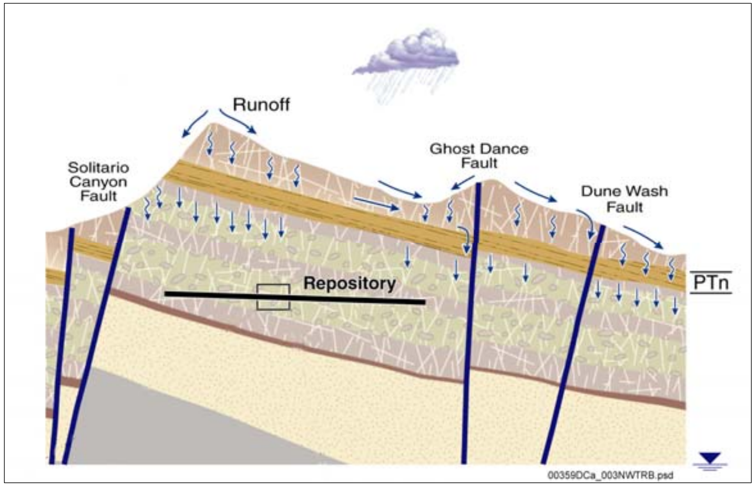
The Proposed Yucca Mountain Repository

Repository Reference Design Concept



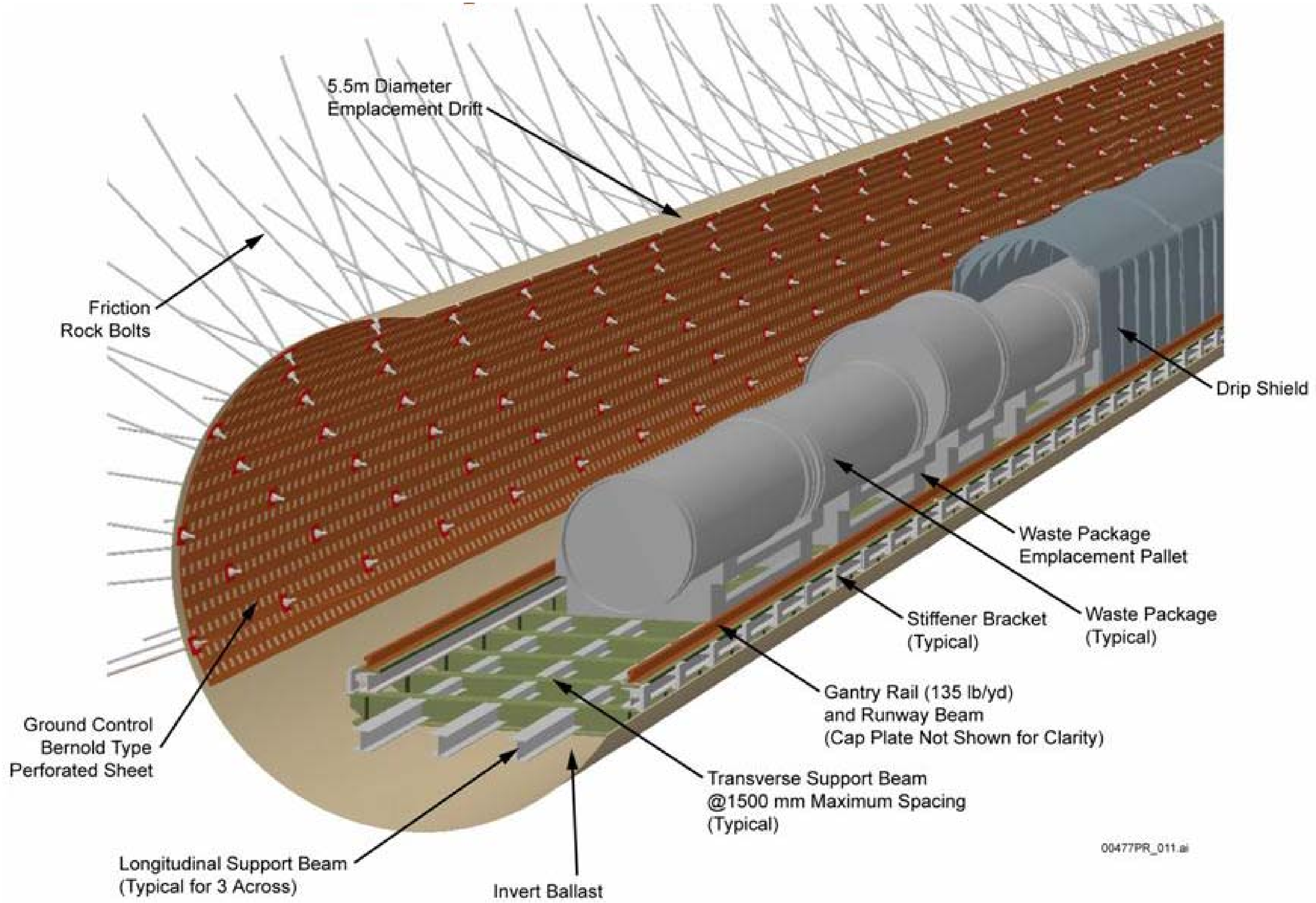
The Proposed Yucca Mountain Repository



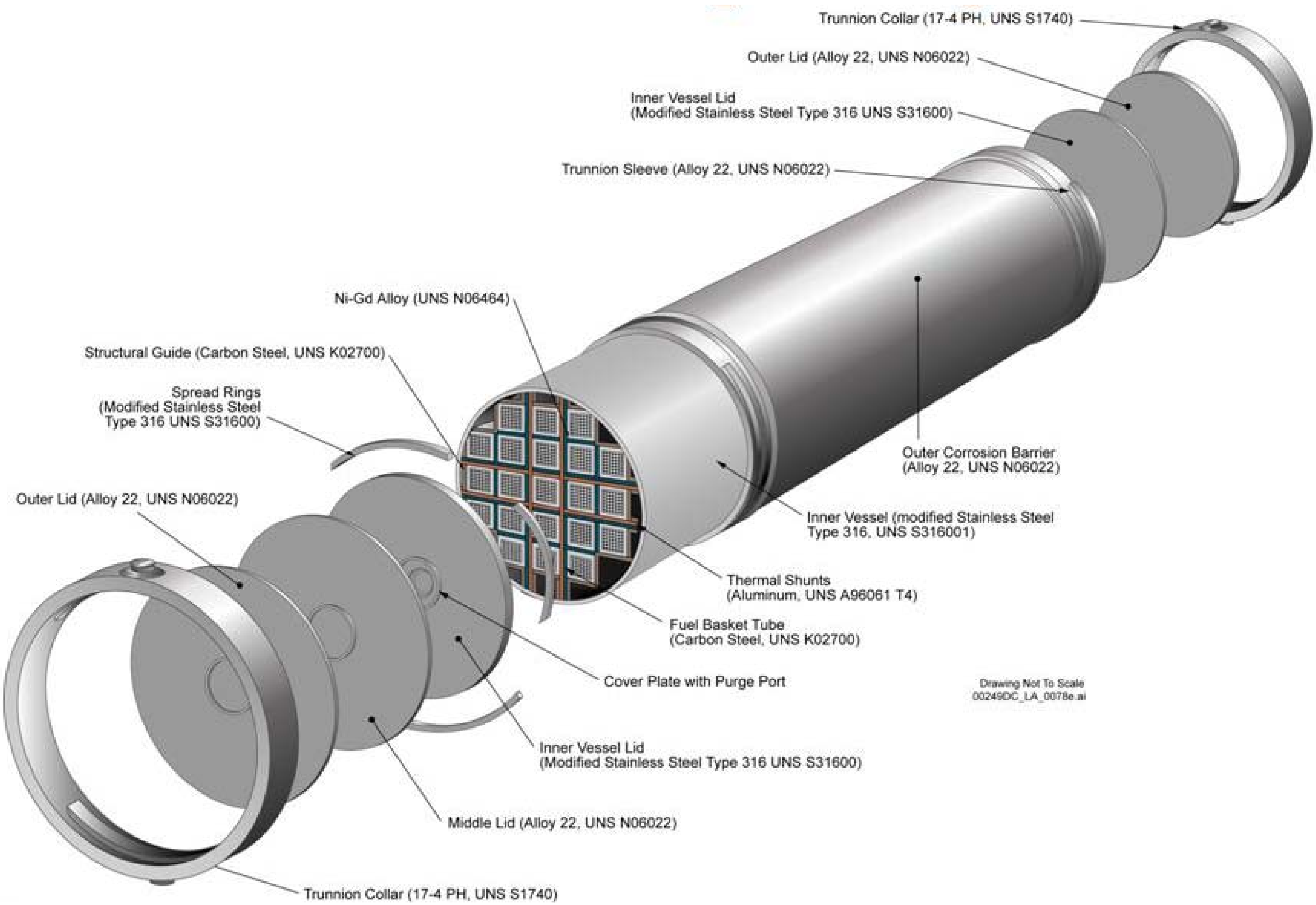


- About 300 m below the surface and 300 m above the water table
- In the unsaturated zone, i.e. fractures and pores in rock are partially filled with water
- Desert area with about 5 cm of rain per year
- Most of water runs off or evaporates; however, some infiltrates to rock and moves through the mountain to the water table
- Repository is at atmospheric pressure
- Relative Humidity ranges from low to high; limited dripping
- Ambient waters are dilute and near neutral pH
- Highly concentrated waters can form under repository conditions

Proposed Emplacement Drift



Waste Package Design



Background on Ni-Cr-Mo Alloys

- **Alloy 22 belongs to a family of Ni-Cr-Mo alloys**
  - Earlier alloys include C-276 and C-4 and later alloys include: Inconel 686, Alloy 59, Hastelloy C-2000 and MAT-21
  - Alloy 22 (N06022) is a solid solution of Ni, Cr, Mo and W as the main alloying elements
  - Cr-Mo-W in Alloy 22 act synergistically to provide resistance to localized corrosion such as crevice corrosion
- **Large Industrial equipment in service for many years in harsh environments without corrosion**
  - Alloy 22 has great toughness and over 50% elongation before failure
  - Can be hot or cold formed and is weldable by many methods
  - Can be fabricated into large structures and components

Industrial Experience in Harsh Environments

Pulp and Paper Bleach Washer

- Fabricated in 1987 using C-22 material
- Went into service for International Paper plant in Texarkana
- Operation in highly oxidizing wet chlorine and chlorine dioxide solutions

Agitator in Bleach Plant

C-22 Agitator installed in 1985

Environment with Chlorine and Chlorine Dioxide, up to 5000 ppm Chloride, temperature up to 60°C

Other alloys such as 904L, 317L SS and 254SMO corroded rapidly

Mixed Waste Incinerator at Los Alamos

Alloy Selected by Waste Management Group of the Department of Energy (DOE)

Gaseous Effluents from Incinerator are treated in a Spray Quench Tower, a venturi scrubber and a packed absorber tower

Tests were carried out in "worst case scenario" to replace previous fiberglass reinforced polyester (FRP)

3 M NaCl + 0.1M$FeCl_3$ + 0.1 M NaF adjusted to pH 1 with 10 M HCl/1 M $H2SO_4$ at 75°C for 39 days
Best combination: C-22 welded with C-22

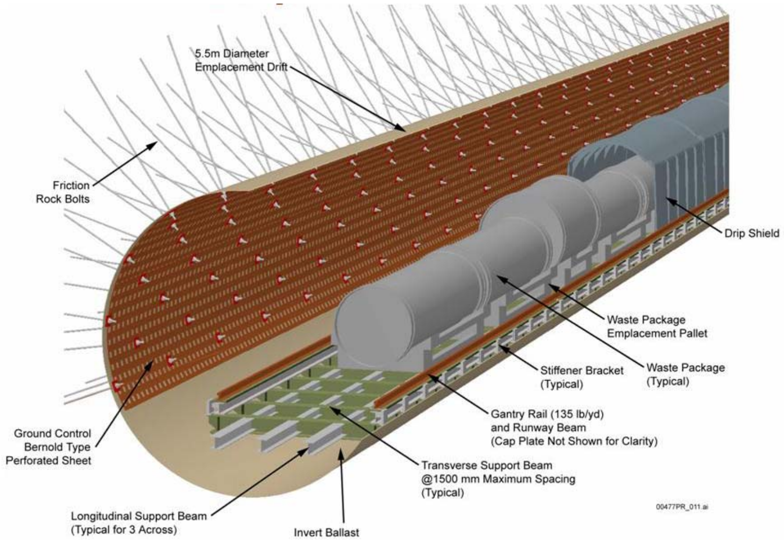
Corrosion Resistance is Crucial to Waste Package Performance

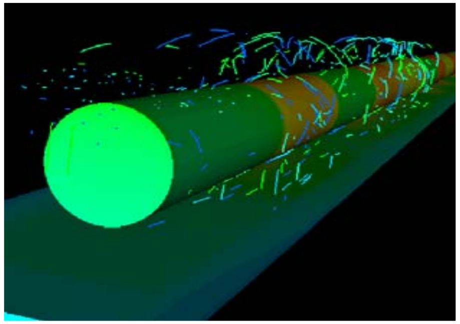
- Radionuclides are fully isolated if there are no penetrations
  - Even penetrated package can limit radionuclide movement
- Corrosion rate of passive metals are extremely low
  - Realistic rates are less than 1 µm/yr (a millionth of a meter per year) and much less
  - Alloy 22 layer is 2-cm thick (a stack of 12 U.S. Quarters)
- Analysis of the potential for damage by corrosion is crucial and a major effort has been undertaken
  - Can corrosive environments form and persist
  - Will localized corrosion start and persist
  - What damage would result

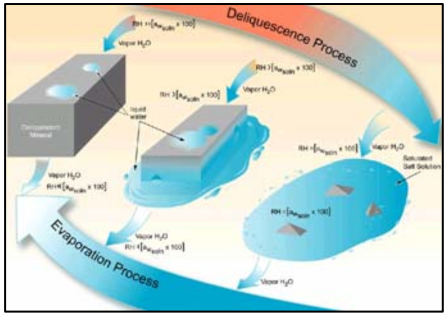
16,000 to 160,000 years to penetrate the thickness of one U.S. Quarter for a corrosion rate of 0.1 to 0.01 µm/yr.

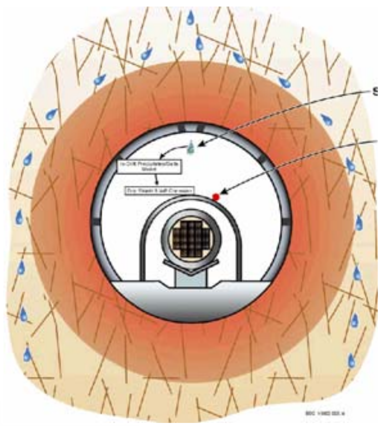
Corrosion rates of approximately 0.01 µm/year are measured in exposures of over 5-years at LLNL Long Term Test Facility.

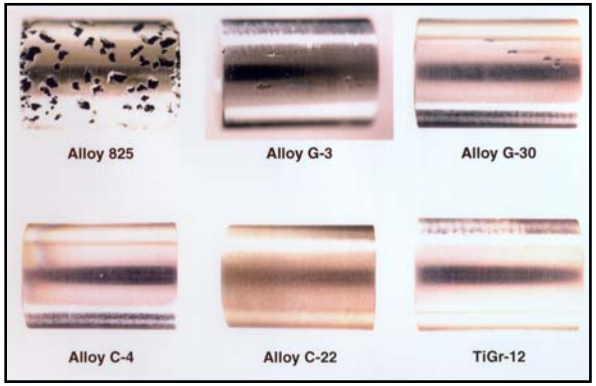
Corrosion and Materials Performance

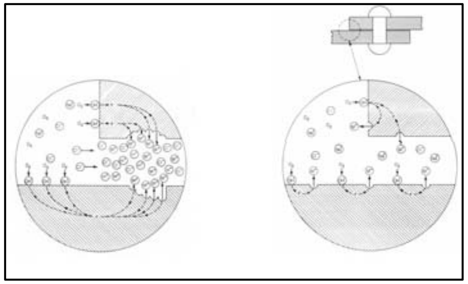




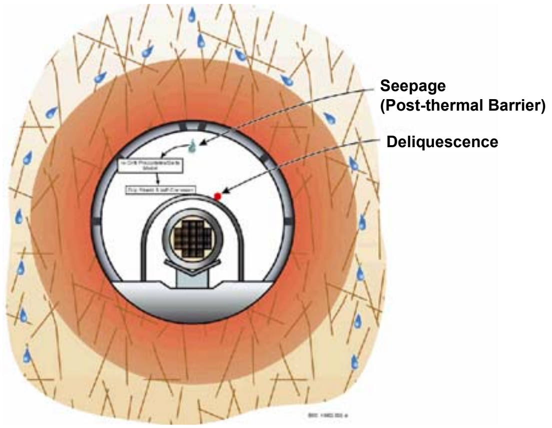


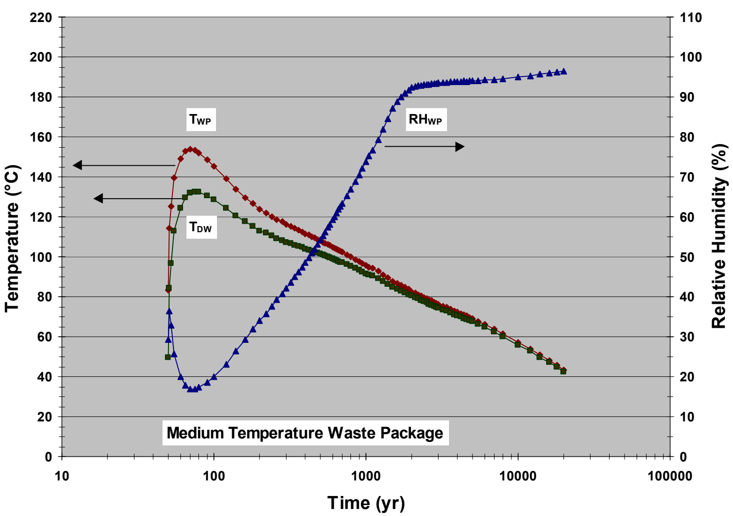






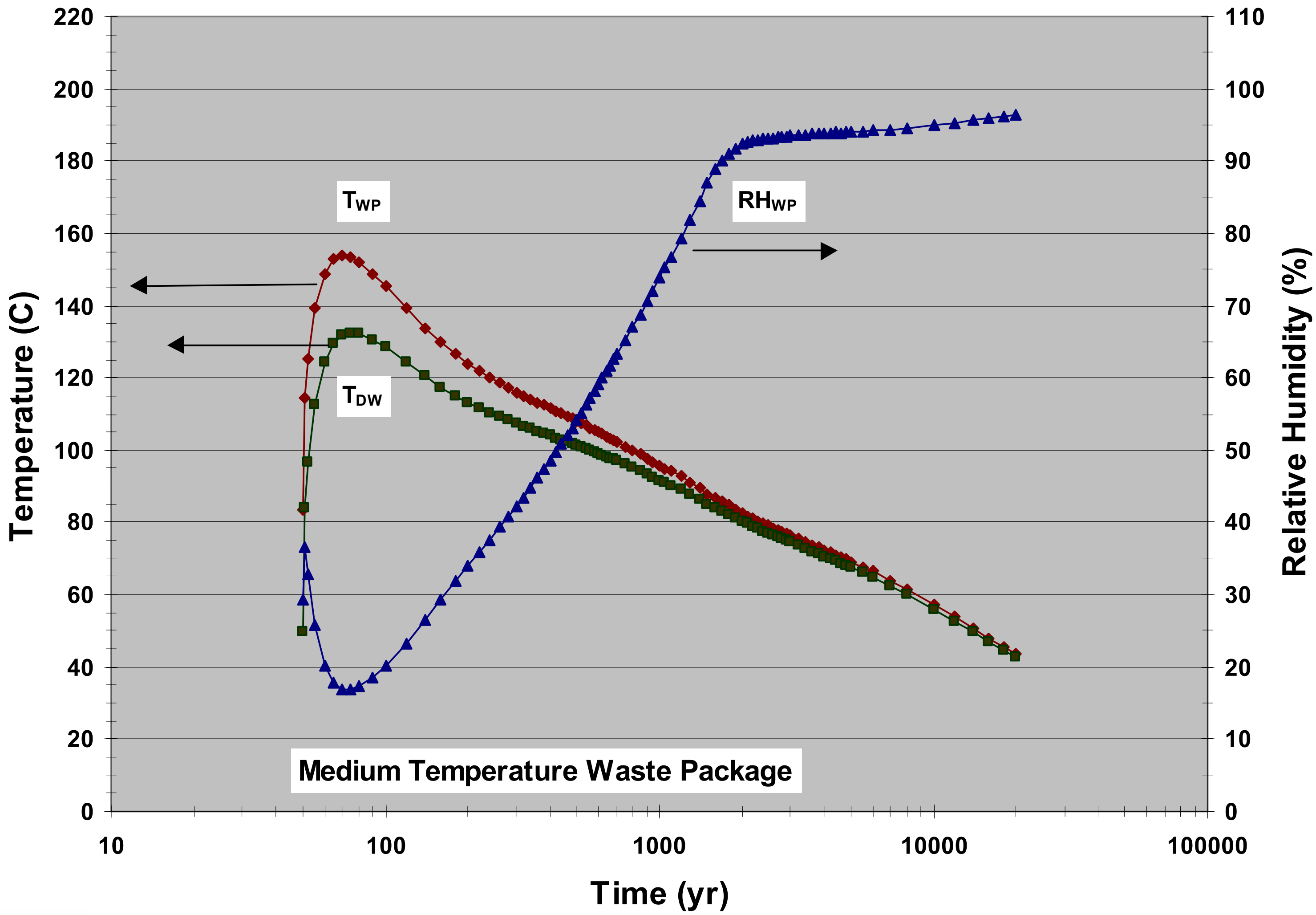
Attributes of the Proposed Yucca Mountain Repository





- One long, slow cycle of heating to modest temperature and cooling to ambient
- Waste packages sit in air on support pallets
- No imposed loads; no internal pressure and no moving parts
- No rapid thermal expansion and contraction
  - Low heat fluxes
  - Slow heating and cooling
  - Modest thermal gradients
- Heat and radiation from waste decrease with time
  - Radiation effects at waste package surface negligible after a few hundred years
  - Packages cool to ambient over several thousands of years
- Limited amount of water moving through the rock
- Limited salts and minerals carried into drifts by incoming water and dust

Predicted Temperature and Relative Humidity for Medium Temperature Waste Package



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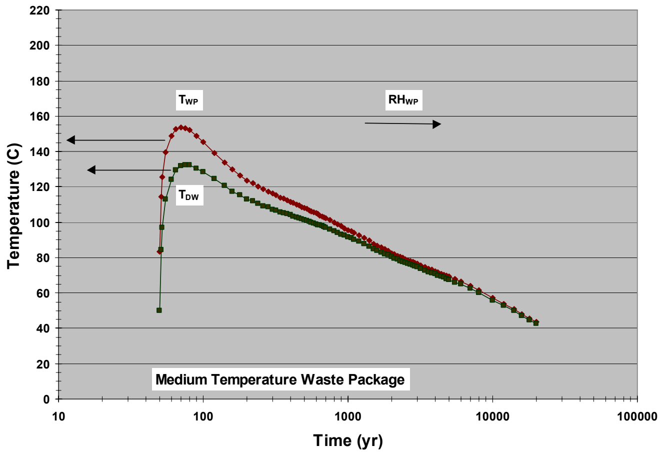
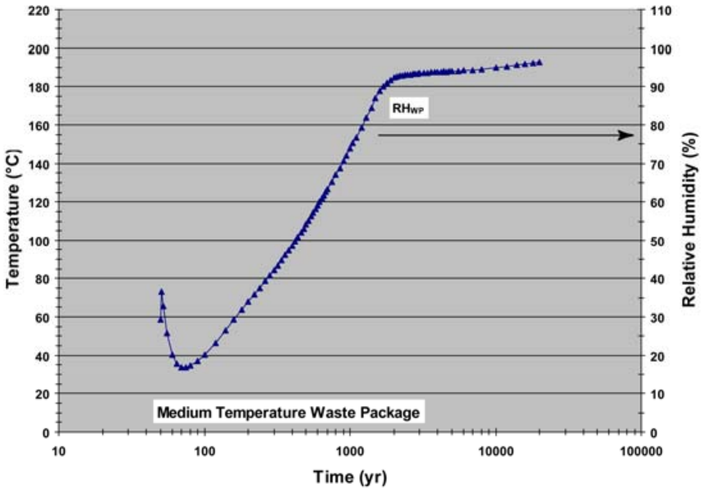
Temperature/Relative Humidity for 20,000 Years

- **Relevant Periods regards Corrosion:**
  - **I - Emplacement of waste packages and preclosure**
  - **II - Heat Up after closure**
  - **III - Cool down/Thermal Barrier (drift wall above boiling temperature)**
  - **IV - Cool Down/Dripping and Seepage Possible**
  - **V - Waste Packages below Critical Temp for Corrosion**





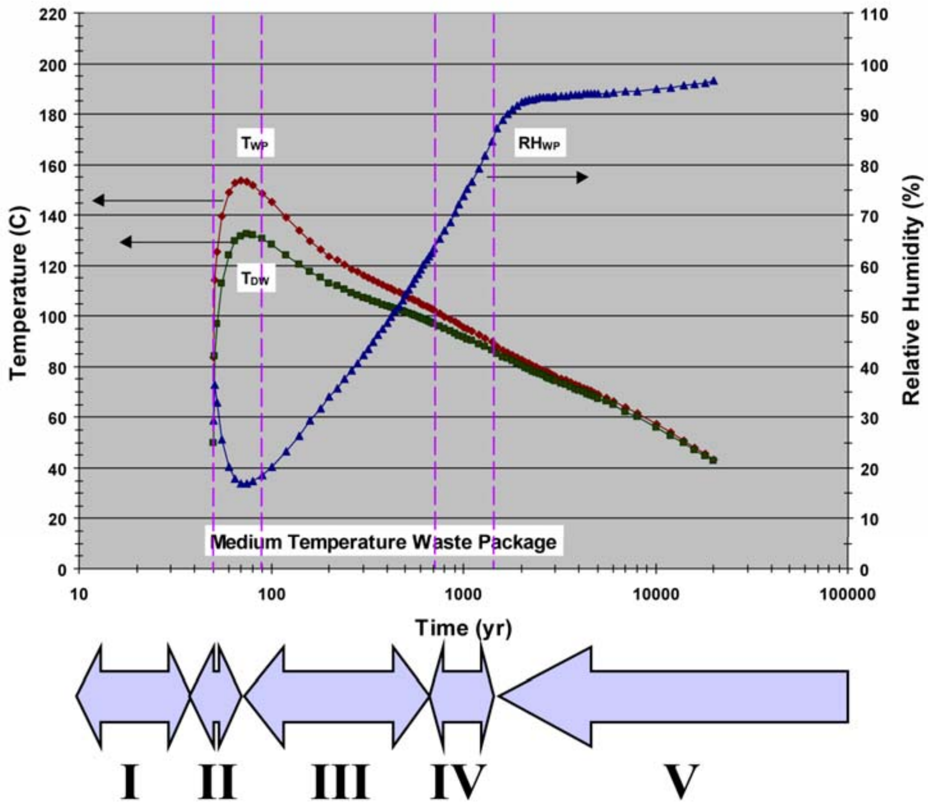
Periods are determined by

(a) Temp-RH over time,

(b) Time when drift wall reaches 96°C and

(c) Critical Corrosion Temp for Alloy 22

Relevant Time Periods Regards Corrosion



For Conditions Below

Temp-Relative Humidity behavior as shown

Waste Package at 101°C when Drift Wall cooled to 96°C

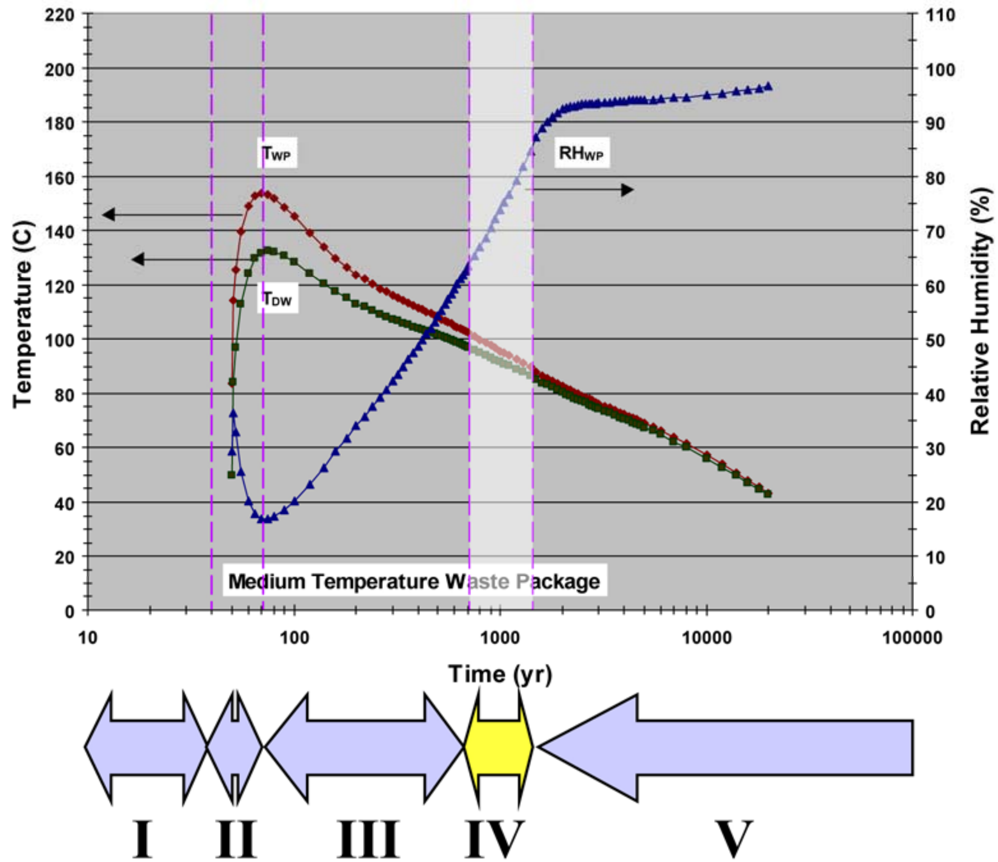
Critical Corrosion Temp 90°C

- **I-Preclosure**
  - Start to Year 50
- **II-Heat Up**
  - Year 50 to ~65
- **III-Thermal Barrier**
  - Year ~65 to 750
- **IV-Cool Down Post-Thermal Barrier**
  - Year 750 to 1375
- **V-Packages below Critical Corrosion Temp**
  - Year 1375 and beyond

Period IV-Dripping and Seepage Possible

- When drift wall below boiling temperature (96°C) Dripping and Seepage can occur
- Dripping onto waste package can occur
  - Where both capillary barrier and drip shield are inoperative
  - And dripping location is in alignment
- When these conditions are met
  - If waste package temperature above critical corrosion temperature
  - Then, follow local corrosion logic/fault tree for damage evolution

For drift wall at boiling at year 750;
Critical Corr Temp 90°C year 1375



Drift wall boiling at year 750; Waste Package at 101°C: Relative humidity 65%

Waste Package at 90°C at year 1375: Relative Humidity 84%

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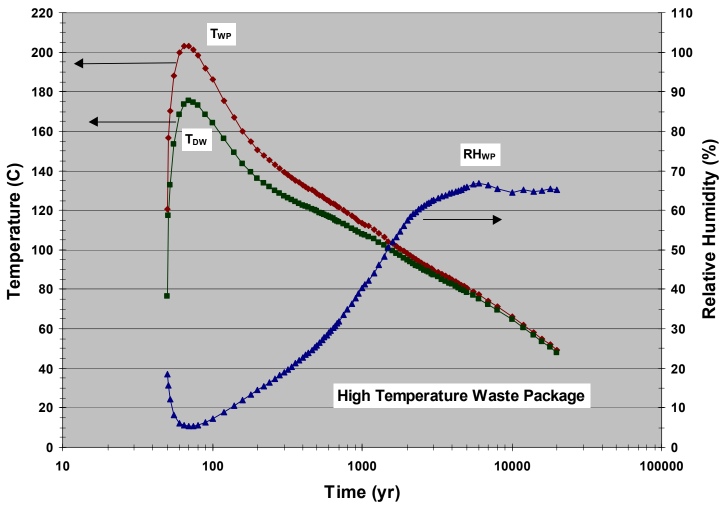
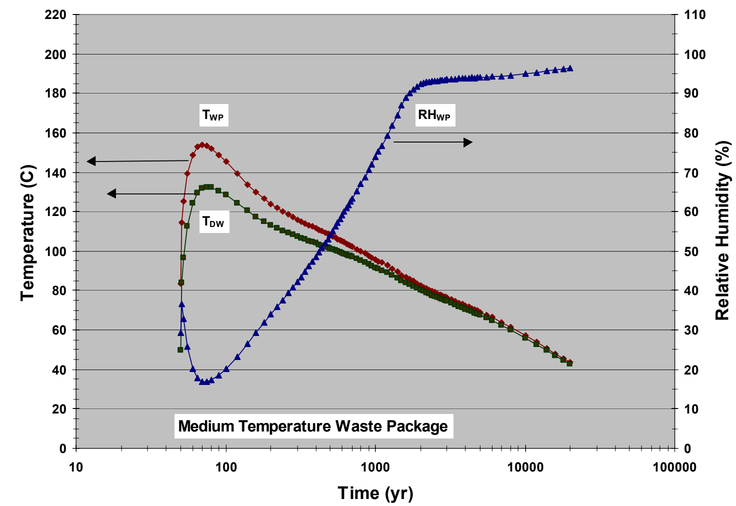
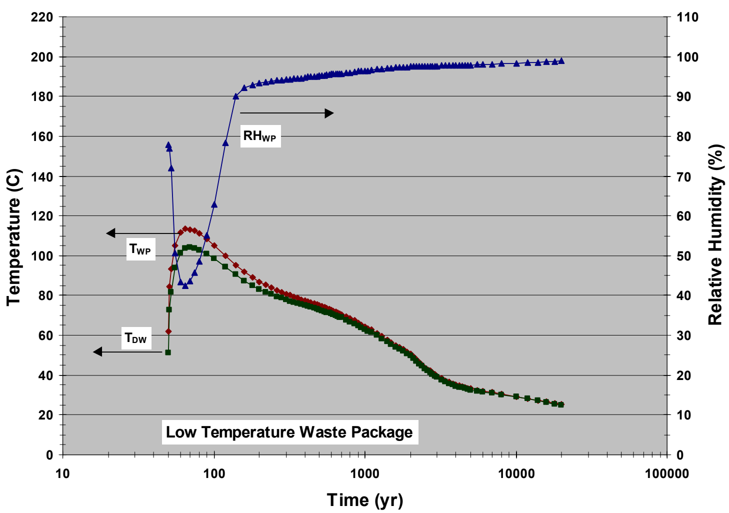
Period IV Conditions for Mid, Hot and Cool Waste Packages

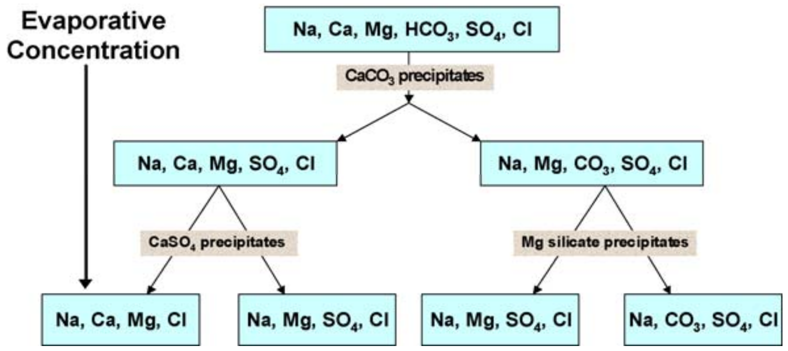


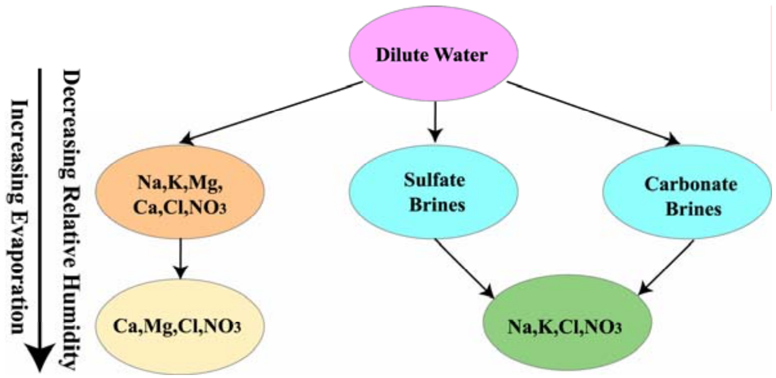




Drift Wall 96°C	Year	Waste Package Temp °C	Relative Humidity	Waste Package at 90°C
Mid WP	700	101	65	1325
Hot WP	1850	99	56	3000
Cool WP	62	102	72	125

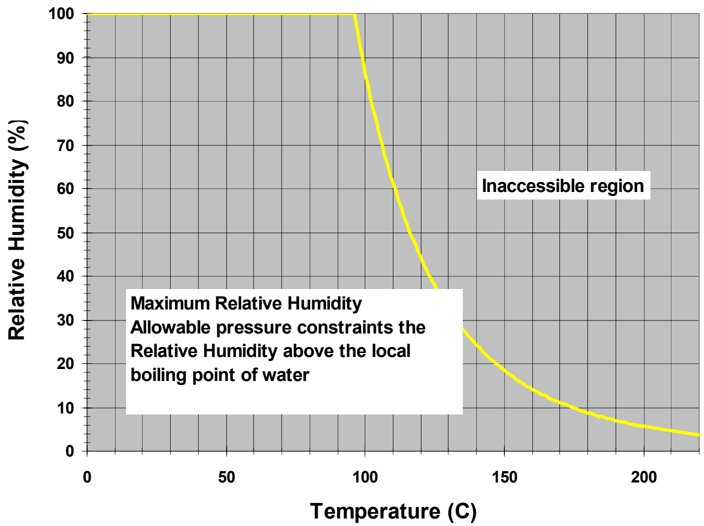
Chemical Divide Processes Determine the Categories of Waters

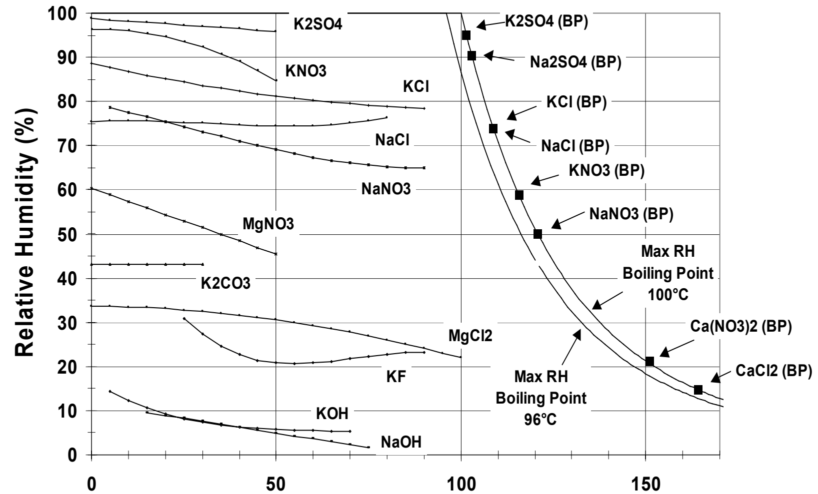


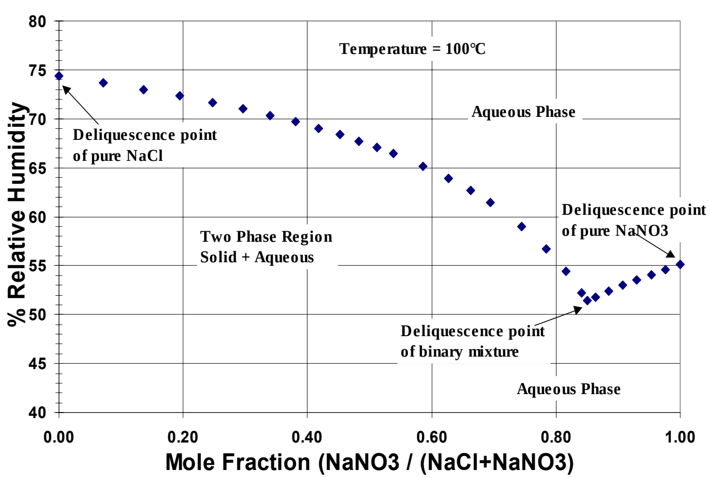


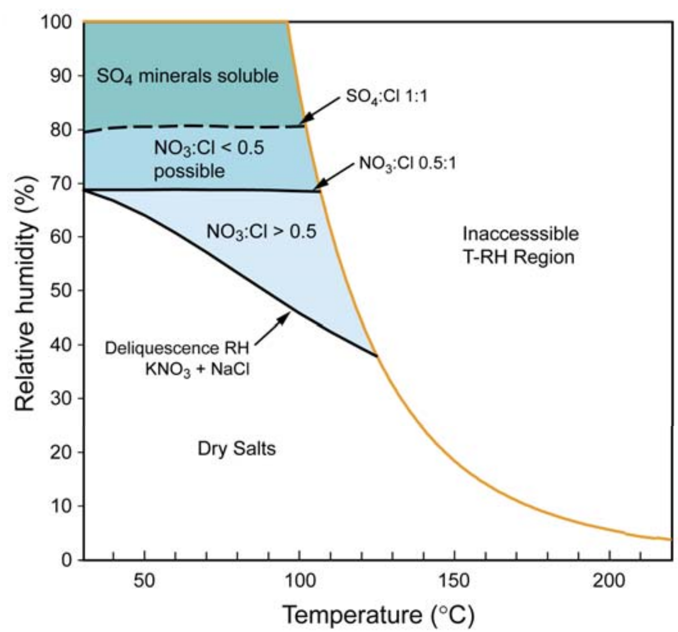
- Ambient Waters:
  - Dilute solutions
  - Na-Ca-Mg-HCO_3-CO_3-Cl-NO_3-SO_4
  - Near neutral pH
- Waters can be concentrated
  - Modified during movement
  - Thermal-chemical processes
- Modifications on waste package surface
- Chemical and electrochemical processes

Solution Chemistry Principles

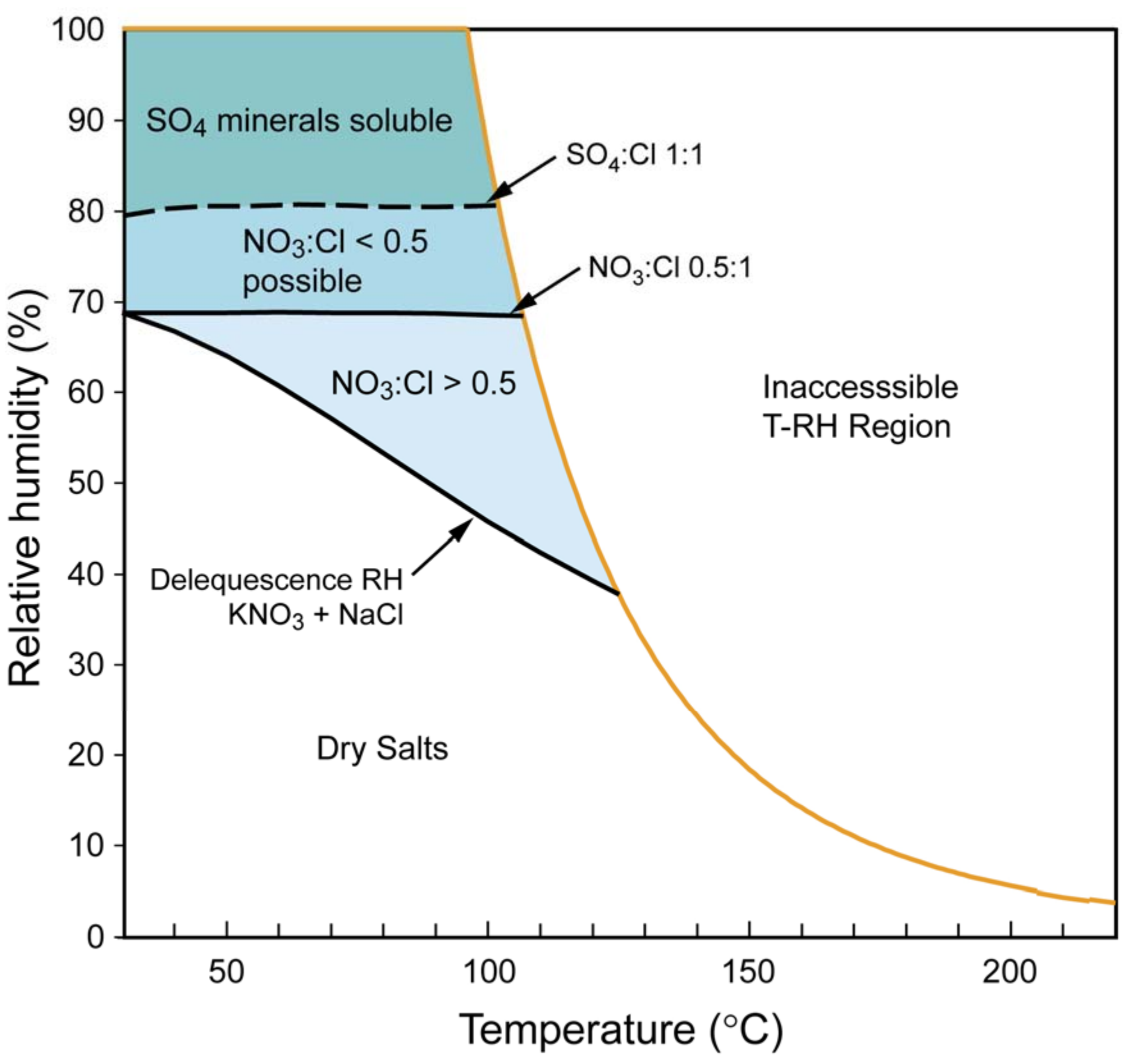






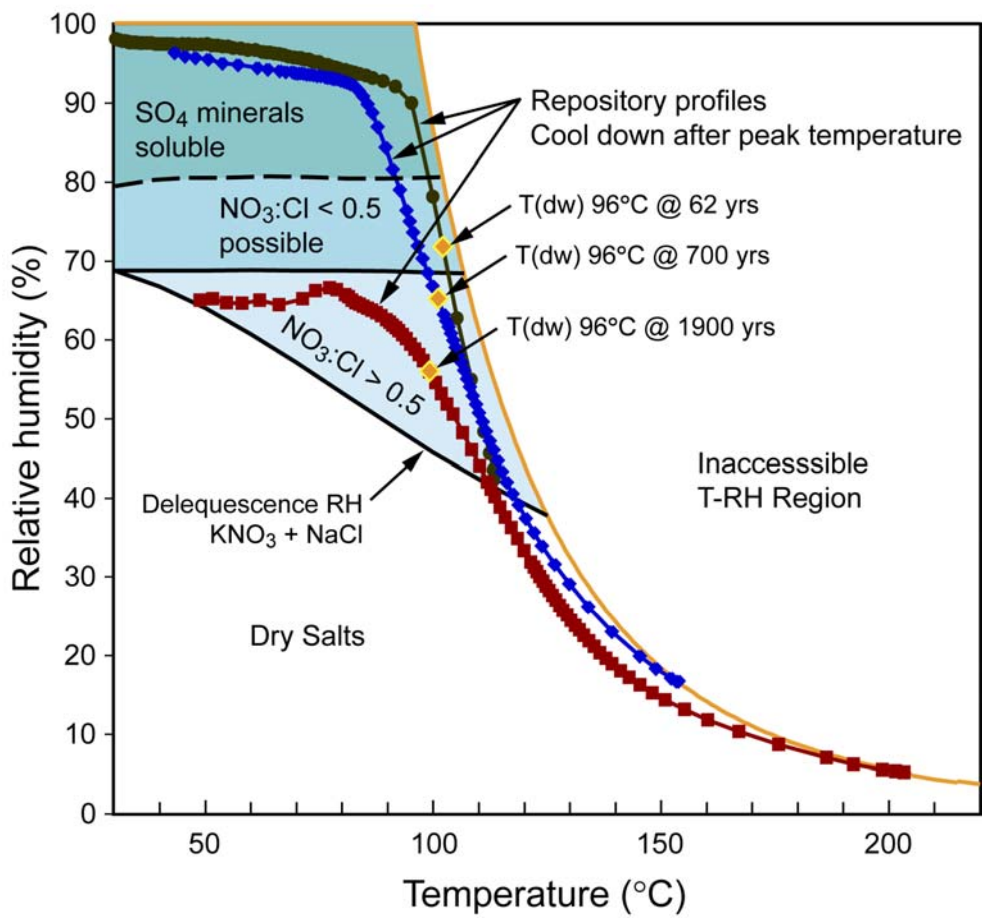


Constraints on Water Compositions for Sodium and Potassium Salts



Water Chemistry Scenarios for Waste Package

- **T-RH Profiles Related to Brine Solution Compositions for Sodium and Potassium Base Salts**



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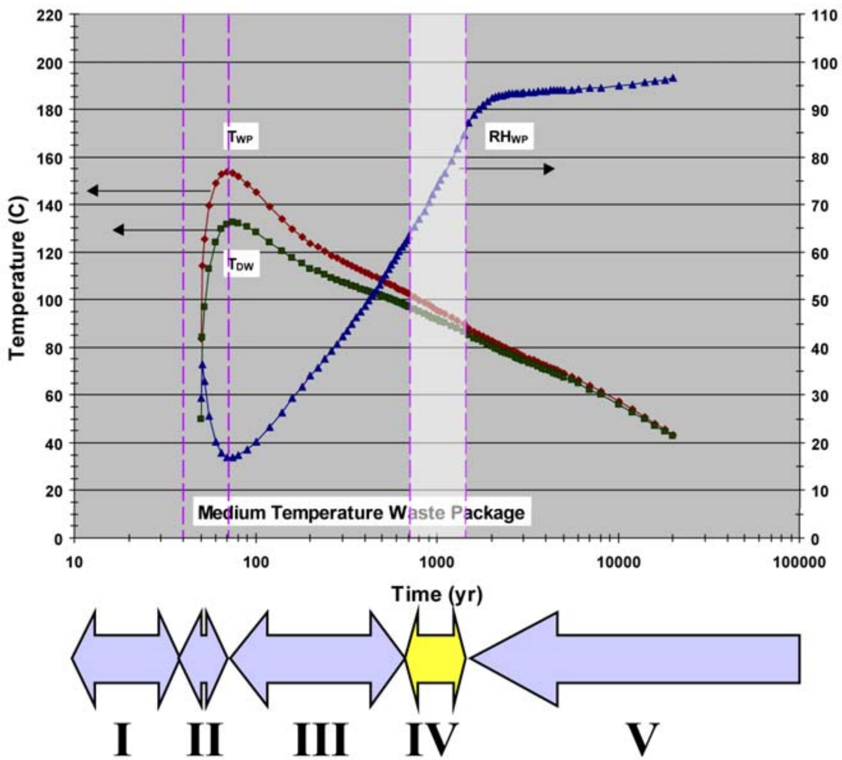
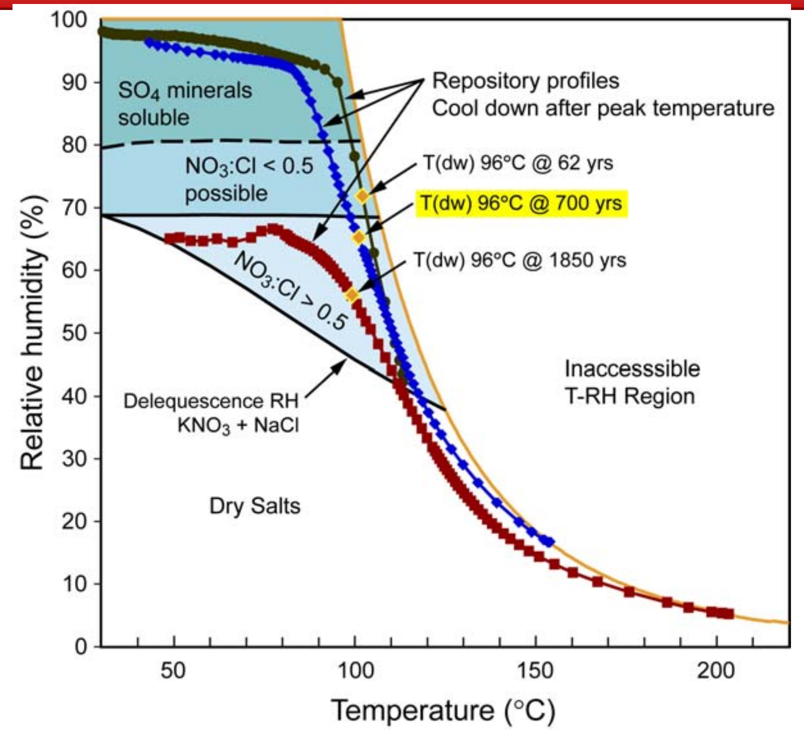
Period IV Analysis of T-RH-Solution Composition





Drift wall 96°C at 750 years;

Waste Package at 101°C;

Relative Humidity 65%

Critical Corrosion Temp 90°C at year 1375; Relative Humidity 85%

The Temp-RH at any time fixes the possible waters. Can follow the trajectory with time

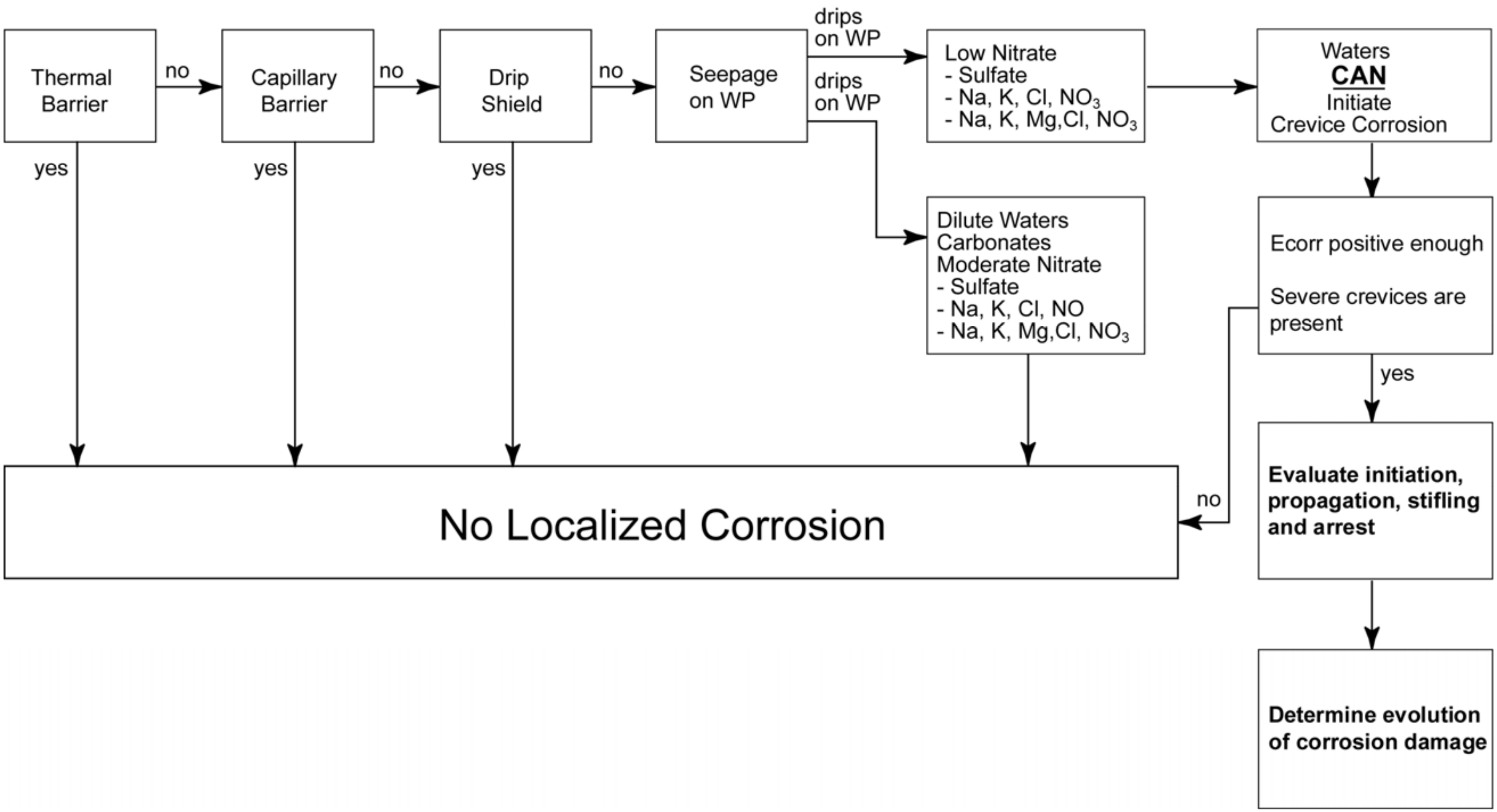
Number of non-corrosive solutions; Sodium chloride with low nitrate solutions can be corrosive

Decision-Tree Analysis

- A decision-tree for localized corrosion
  - Are environments and crevices present to induce localized corrosion
    - Consider conditions in moist layers of particulate and deposits
  - If localized corrosion initiates, will it persist
    - Consider stifling and arrest processes as the corrosion proceeds
  - What amount of metal penetration occurs
  - What is the size and distribution of corrosion sites

Decision-Tree Analysis

- **A decision-tree for localized corrosion**



Overview of OST&I Materials Performance Thrust

- Organized to address important topics:
  - Long-term behavior of protective, passive films
  - Composition and properties of moisture in contact with metal surfaces
  - Rate of penetration and extent of corrosion damage over extremely long times
- Three multi-investigator, coordinated projects
  - Corrosion of metal surfaces under particulate and deposits
  - Evolution of corrosion damage by localized corrosion
  - Evolution of environment on metal surfaces

DOE/OST&I Corrosion Cooperative

University-based research program (5-years started in June 2004)

- Funded by Office of Science and Technology and International; U.S. Dept of Energy; Office of Civilian Radioactive Waste Management
- Multi-University Investigators
- Coordinated with projects at National Laboratories: ANL, LBNL, LLNL, ORNL and with AECL in Canada

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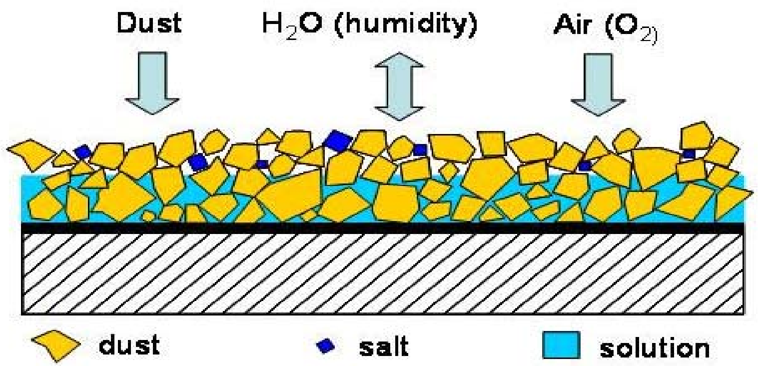
Roger C. Newman, University of Toronto
John R. Scully, University of Virginia
David W. Shoesmith, University W Ontario
William H. Smyrl, University of Minnesota

Task is to increase understanding (underlying science), develop enhanced process models and develop advanced technologies related to corrosion issues in Yucca Mountain

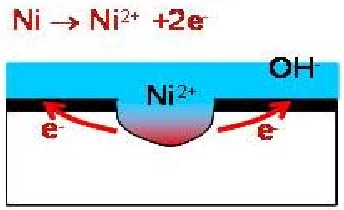
Scope: Major Technical Thrusts

- To enhance the understanding of materials corrosion performance and to explore technical enhancements
- Corrosion processes metal surfaces covered with particulate and deposits
  - Effects of moisture on corrosion performance of metals
- Evolution of corrosion damage by localized corrosion
  - Initiation, propagation, and arrest phenomena particularly for crevice corrosion of metals
- Evolution of the environment on metal surfaces
  - Moisture content, distribution, and chemical composition on metal surfaces

Corrosion in Thin Layers of Particulate

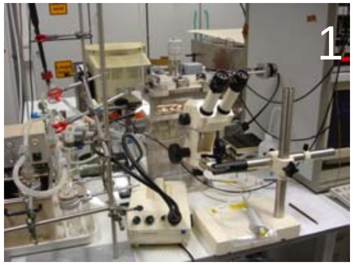


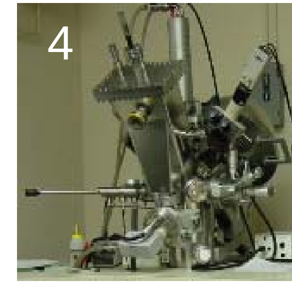
$$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2(OH)^-$$

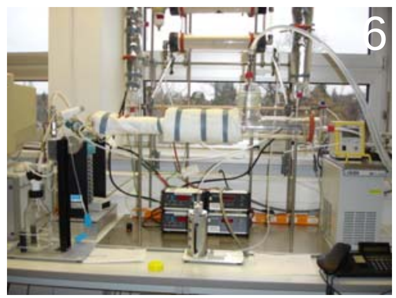


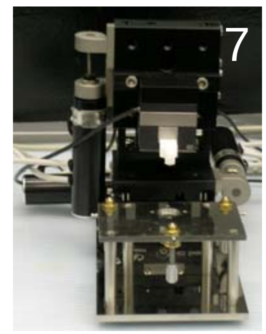
- Dust deposited
- Degree of wetness
- Soluble salts
- Gas composition and property, T, RH
- Particulate layer properties, such as conductivity, temperature, pH, degree of wetness etc.
- Localized environment on the surface
- Anode: $Ni \rightarrow Ni^{2+} + 2e^-$
- Cathode: $H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$

Specialized Capabilities and Facilities









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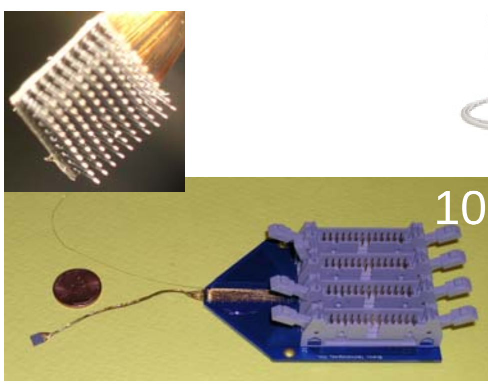
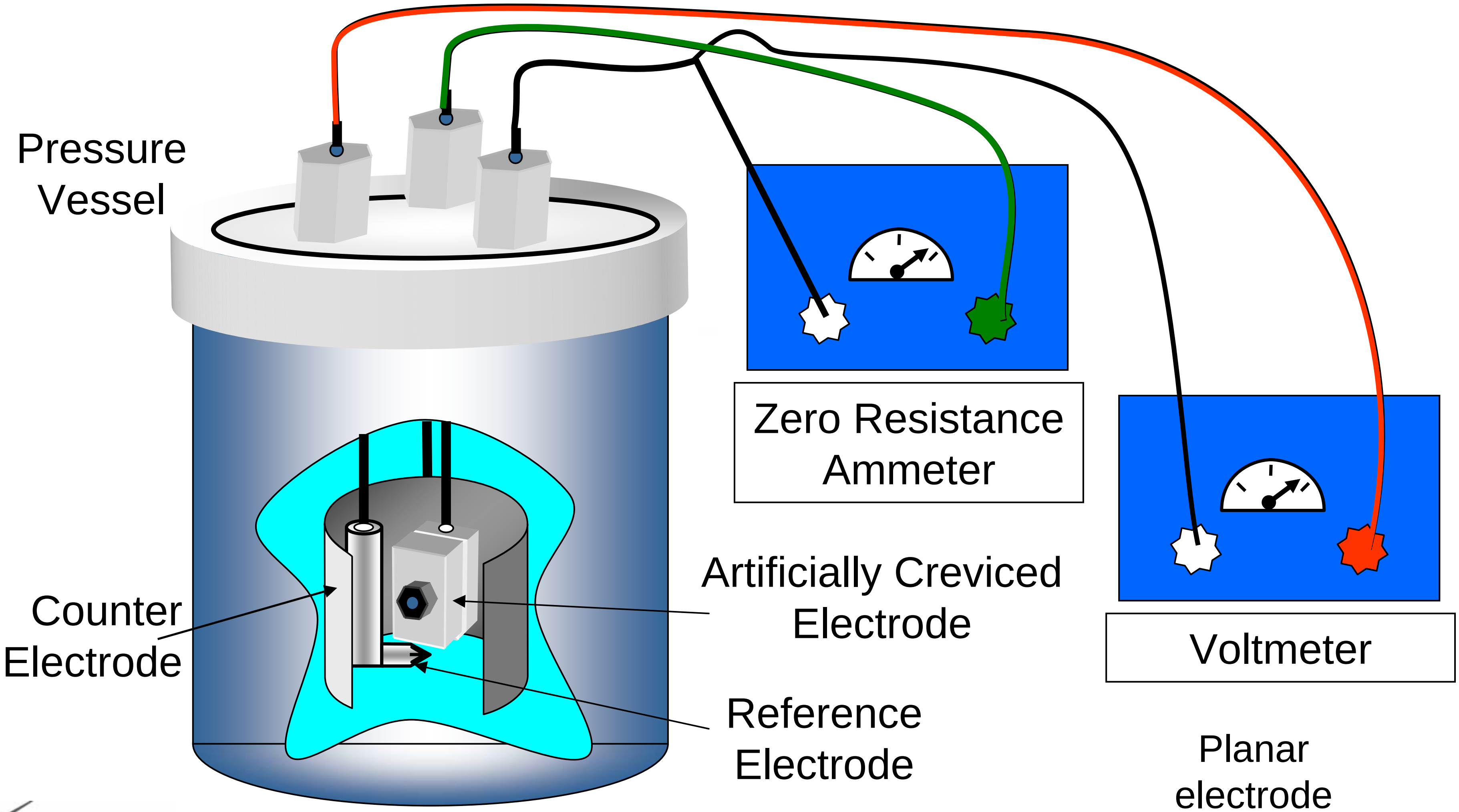
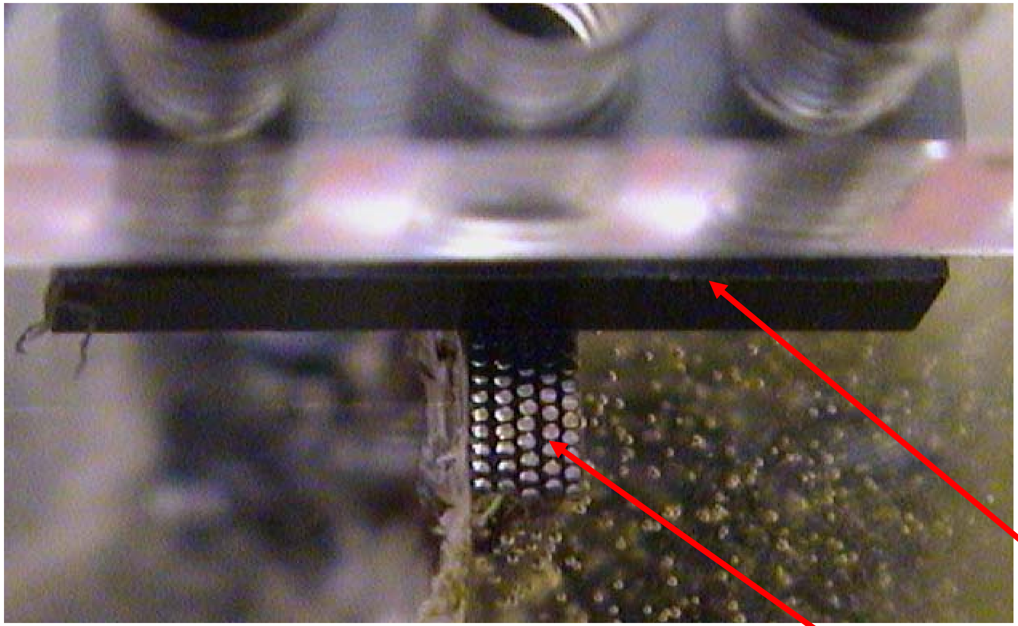


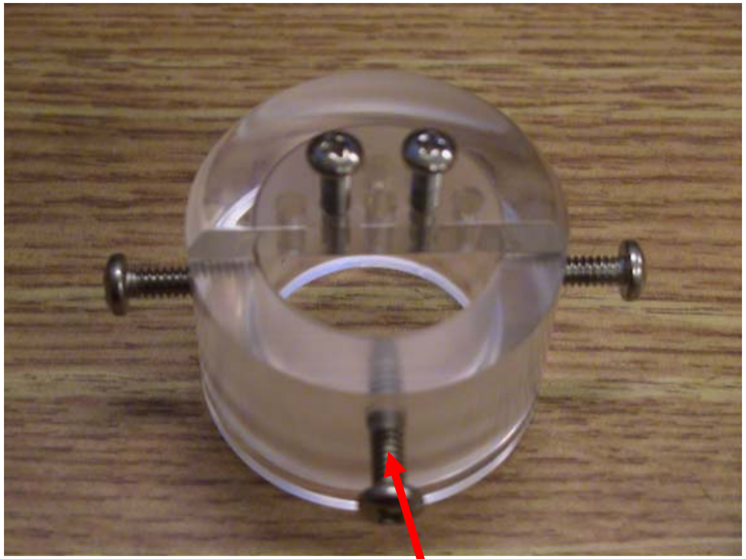
1. Kelvin Probe and Scanning Kelvin Probe
2. Laser-directed powder deposition for graded Ni-Cr-Mo compositions
3. Experimental apparatus for thin-layer electrochemical studies of stability of corrosion sites
4. X-ray Photo-Electron Spectrometry
5. 200KV Transmission Electron Microscope
6. Salt Particle Deposition System
7. Scanning Electrochemical Microscope
8. Thermogravimetric Analysis System at LLNL
9. Electrochemical Quartz Crystal Microbalance
10. Microelectrode Array

Coupled Crevice Experiment



Multi-Electrode Rescaled Crevice

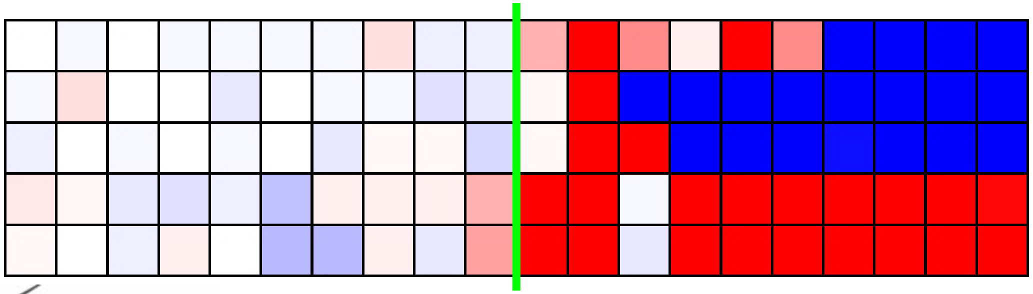




- Each individual wire electrode in MEA is individually addressable for current or potential measurement.

Crevice Former Line

Multi-Electrode Array (MEA)



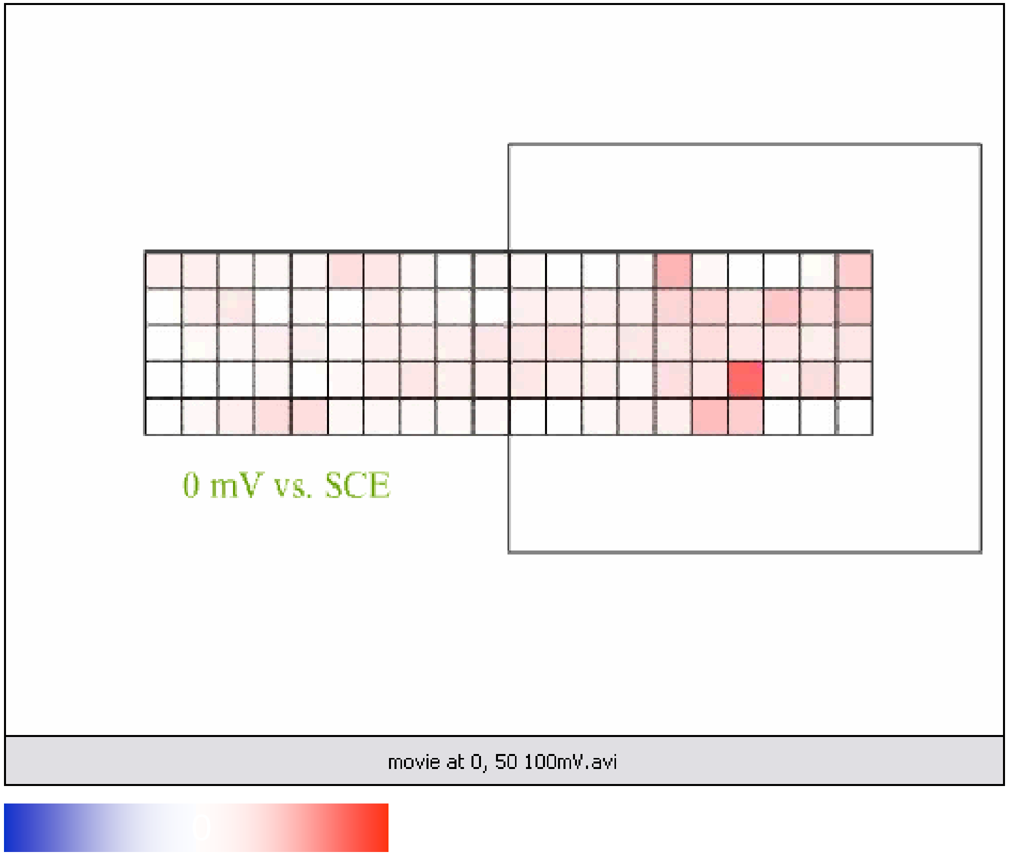
<u>Crevice Former Holder</u>

- Fits over the end of a MEA holding crevice former firmly against the specimen

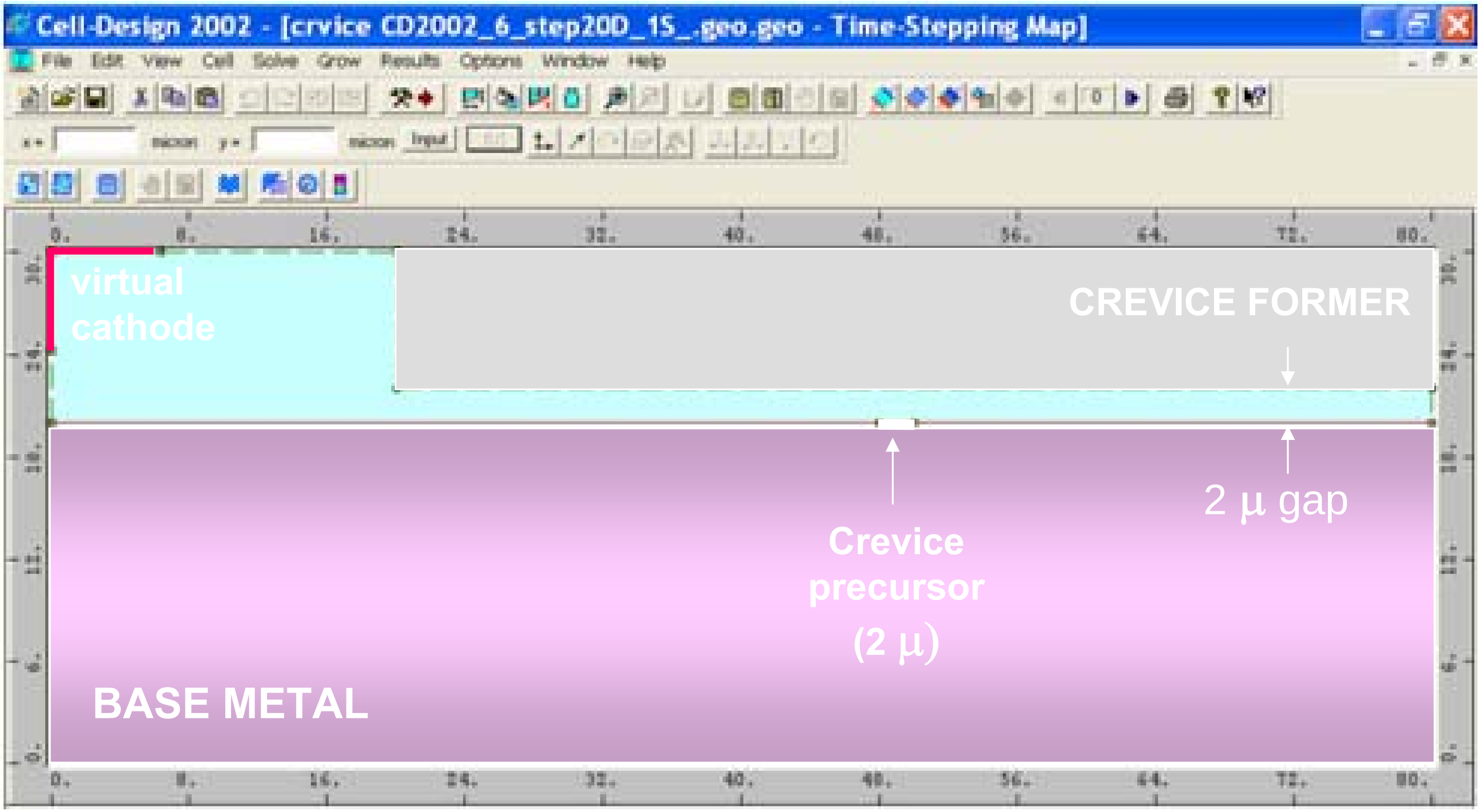
•AISI 316 SS in 0.25 M Fe_3Cl

Crevice Corrosion Damage Evolution

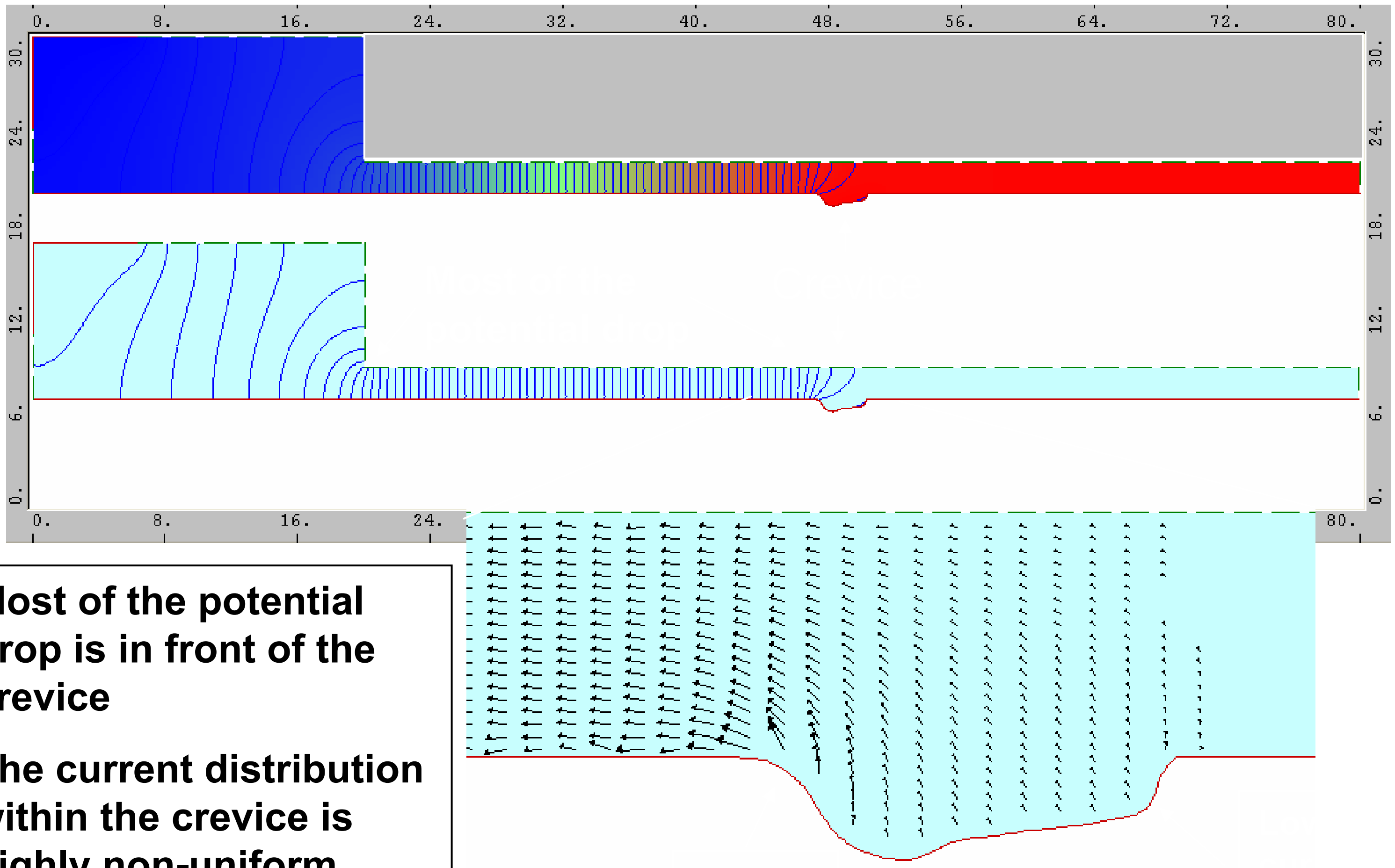
•*316 SS at 47 °C, 1M NaCl, 1 hr at 0 V vs. SCE, 1 hr at 0.05 V vs. SCE and 1 hr at 0.1 V vs. SCE, aerated. SCE is a Saturated Calomel Reference Electrode.*



Simulation of Crevice Propagation

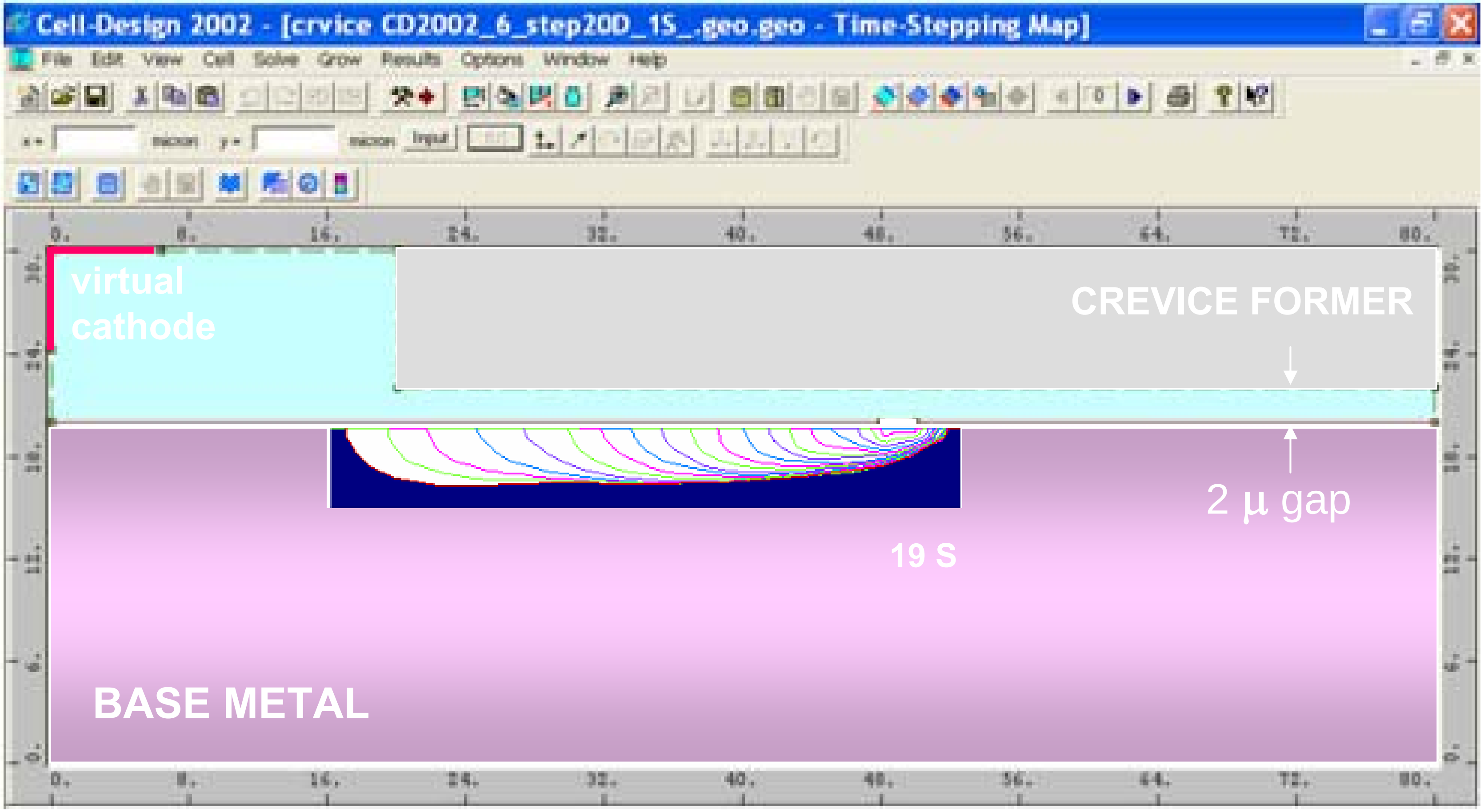


Potential and Current map in a Crevice



- Most of the potential drop is in front of the crevice
- The current distribution within the crevice is highly non-uniform
- The diffusion field is similar to the potential field

Simulation of Crevice Population



Corrosion Perspectives

- Corrosion resistance of the waste package outer canister
- A framework for the analysis of localized corrosion processes
  - Corrosion Conditions at Key Time Periods in Repository
  - Corrosion Analysis during Period IV-Cool Down/Dripping and Seepage
  - A Decision-Tree Analysis for corrosion damage evolution
- Overview of the OST&I Materials Performance Thrust
  - To further enhance the understanding of the role of engineered barriers in waste isolation
  - Office of Science and Technology and International, U.S. Department of Energy, Office of Civilian Radioactive Waste Management