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Office of Civilian Radioactive Waste Management

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Corrosion Resistance of Alloy 22

Presented to:
Nuclear Waste Technical Review Board

Presented by:
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Corrosion: Outline/Sections

- Alloy 22 is Highly Corrosion Resistant
- Yucca Mountain from a Corrosion Perspective
- Corrosion Rate of Passive Metal-Experimental Measurements
- Corrosion Background and Perspectives
- Corrosion Conditions at Key Time Periods in Repository
- Localized Corrosion
  - Corrosion Processes and Controlling Parameters
  - Localized Corrosion: Experimental Measurements of Corrosion Resistance
- Corrosion Analysis During Period IV-Cool Down/Dripping and Seepage Possible
- Conclusions

Alloy 22 is Highly Corrosion Resistant

Alloy 22 is Highly Corrosion Resistant

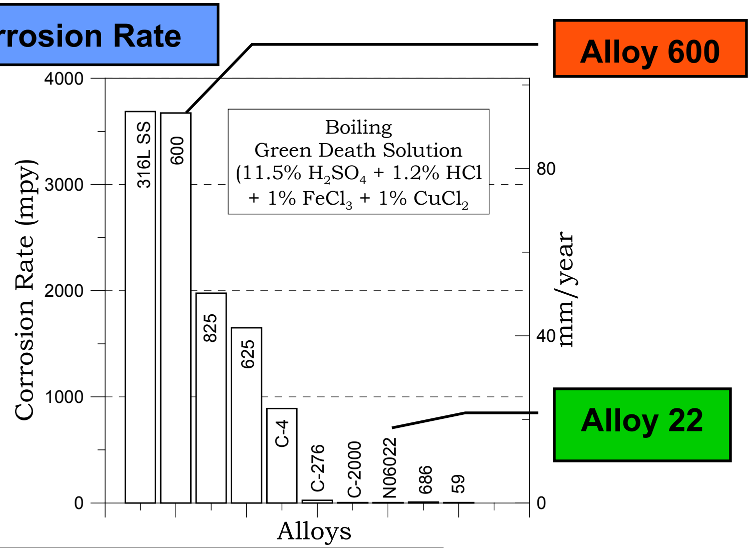
- **Corrosion behavior is controlled by <u>corrosion resistance of material</u> of construction and <u>corrosivity of the environment</u>.**
  - **Alloy 22 for waste packages and titanium for drip shields are highly corrosion resistant materials**
  - **Ambient environment at Yucca Mountain Repository is benign**
    - **Waste packages sit in air; full immersion in water will not occur**
    - **Dilute waters in mountain are non-corrosive**
  - **Highly concentrated waters at elevated temperature show a range of corrosivity**
- ***Determine the corrosion resistance of Alloy 22 exposed to realistic conditions within the repository***

Background on Ni-Cr-Mo Alloys

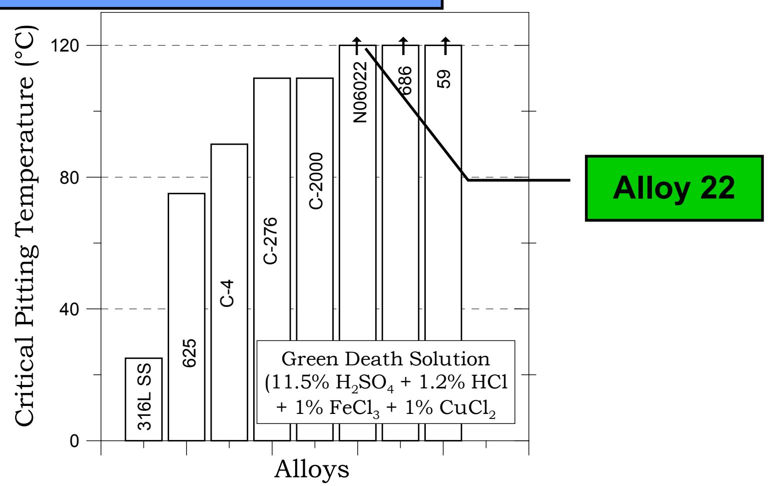
- **Alloy 22 belongs to a family of Ni-Cr-Mo alloys**
  - Earlier alloys include C-276 and C-4 and later alloys include: Inconel 686, Alloy 59, Hastelloy C-2000 and MAT-21
  - Alloy 22 (N06022) is a solid solution of Ni, Cr, Mo and W as the main alloying elements
  - Cr-Mo-W in Alloy 22 act synergistically 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

Alloy 22 is Highly Corrosion Resistant

Corrosion Rate



Critical Pitting Temperature



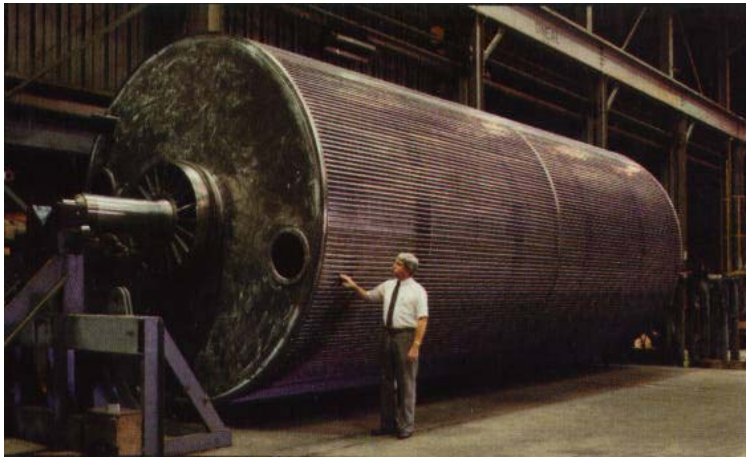
Alloy 22 has one of the lowest corrosion rates, in the same order of 686, 59 and C-2000

- At 0.1 µm/yr, over 10,000 years per mm
- At 0.004 mils/yr, over 30,000 years per 1/8 inch
- Alloy 600, widely used in steam generators in nuclear power plants. In highly aggressive solutions tested here, Alloy 600 suffers severe pitting and a high corrosion rate

Alloy 22 offers the highest resistance to pitting corrosion (greater than 120°C)

- Critical Pitting Temperature (CPT) defines lower limit; no pitting corrosion at lower temperatures
- Test Solution called "Green Death"
  - Highly oxidizing (Fe^{3+} and Cu^{2+})
  - Highly acidic (pH <0)
  - Concentrated chlorides (0.7 M)
- Green Death decomposes above 120°C

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

FGD Scrubber in the UK
Drax Power Station and Others

- 4000 MW, the largest in the UK
- The first fitted with a FGD (Flue Gas Desulfurization) to eliminate SO_2 and NOx
- Coal contains up to 2.8% S and 0.4% Cl
- Gases from 130°C to 80°C, 30,000 ppm Cl (~1M)
- C-22 lining (wall papering) of 9 m diameter ductwork. More than 1,000,000 lb of C-22 Used

Flue Gas Desulfurization (FGD Scrubbers)

- Cleans exhaust from coal-fired power plants
- Scrubs acid gases: SO_2, NOx, …
- High temperature, oxidizing, acidic solutions
- Periodic table of elements in coal
- Multi-species and complex solutions

Electrochemical tests predicted high corrosion resistance and correct ranking of metals

Heat Exchanger in Wet Scrubber in Hamburg, Germany

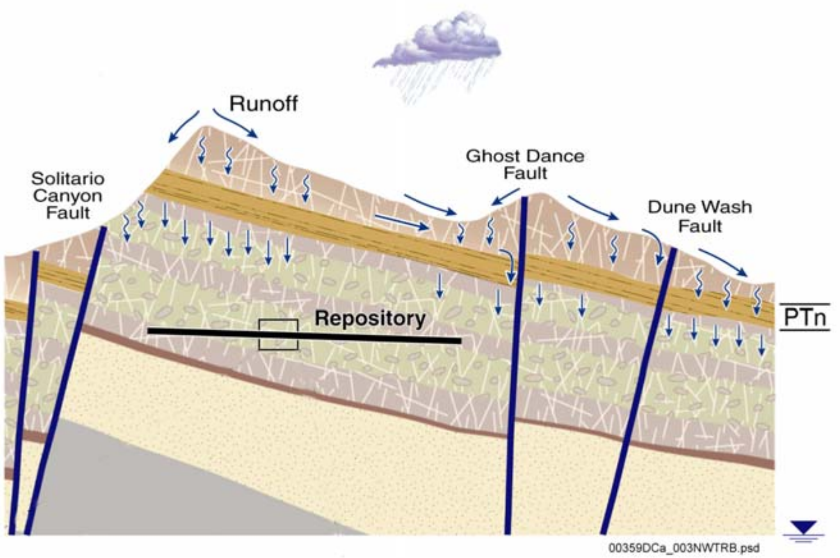
Tube Sheet in Heat Exchanger for Municipal Incinerator
Wet Scrubber to Clean Stack Gases, Chloride, Fluoride, Sulfide
Effluent Gases from 220°C to 350°C
Scrubbed Gases are reheated to 100-140°C using C-22 Heat Exchangers

Lower Colorado River Scrubber

434 MW Plant in the Lower Colorado River Authority
Started Operations in March 1988
Wet Limestone Scrubbing System to Remove 70% of SO_2
Over 31,000 sq ft of C-22 used (95,000 lb)
C-22 used to line the scrubber absorber inlet and outlet ducts

Yucca Mountain from a Corrosion Perspective

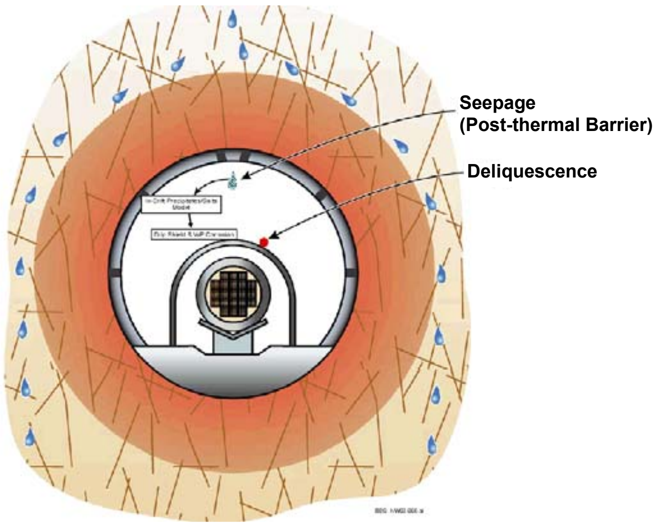
Natural System of Yucca Mountain

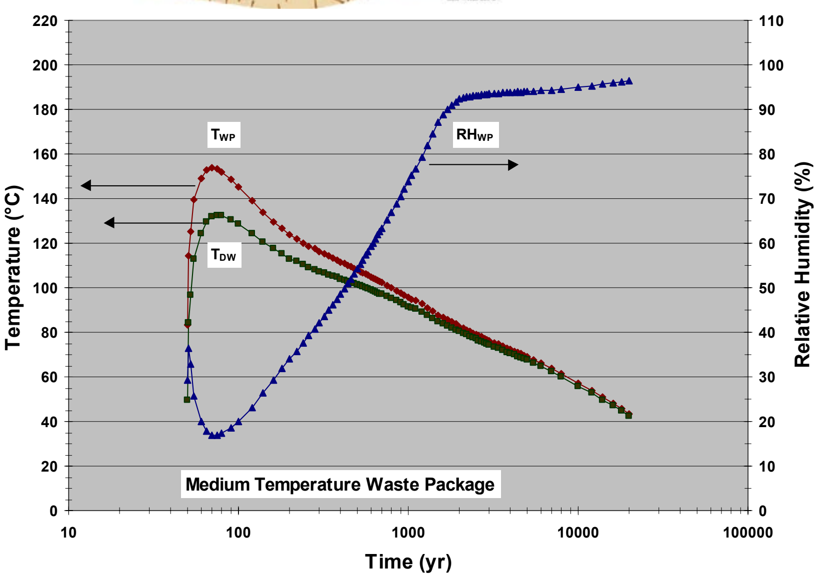


Important Factors

- Waste packages are isolated beneath ~300 meters of rock and 300 meters above the water table.
- Repository in Unsaturated Zone
  - Fractured porous rock
  - Pores partially filled with water
- 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

Attributes of Yucca Mountain Repository

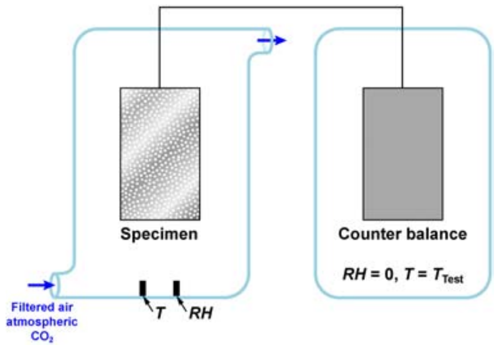




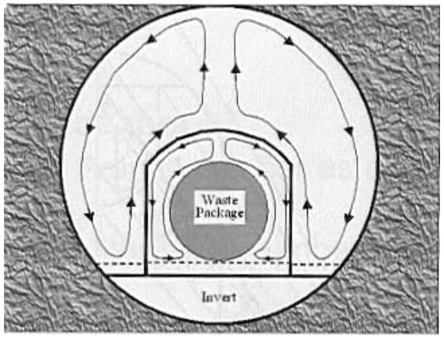
- One long, slow cycle of heating to modest temperature and cooling to ambient
- Waste packages sit in air on support pallets
- No imposed loads; no internal pressure and no moving parts
- No rapid thermal expansion and contraction
  - Low heat fluxes
  - Slow heating and cooling
  - Modest thermal gradients
- 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

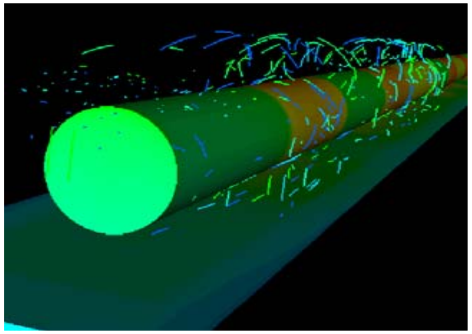
Relevance of Corrosion Test Methods

Thermogravimetric Analyzer (TGA)



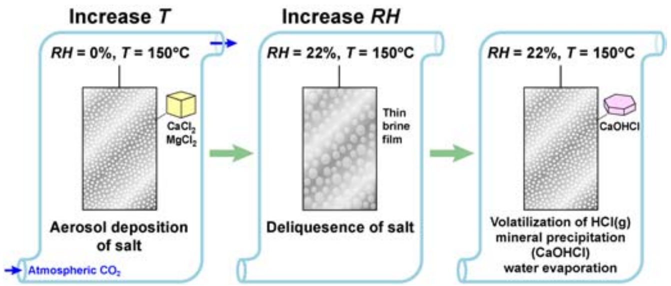
Open; air circulation; Temp controllable to 150°C and higher; RH controllable 20-100%;,



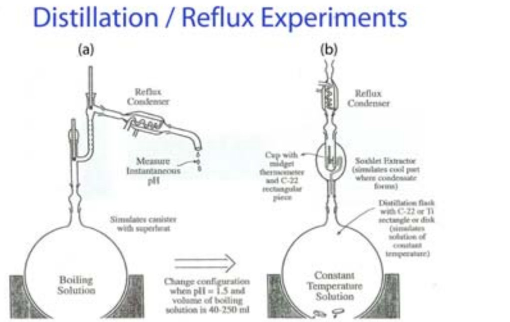


Open, air circulation; Wide range of Temp, RH of interest; Temp to 150°C; RH 20-100%

TGA is relevant to Repository conditions



TGA monitors absorption of water by salt minerals, solution stability and corrosion.



Distill/Reflux

Irrelevant to Repository conditions

Closed; Refluxing; 100% RH-Saturated, Condensing, no CO_2, boiling temp

Attributes of Yucca Mountain Repository

- A particular challenge for the analysis is the extraordinarily long time period required for performance
  - Operational phase of 50 years for emplacement of waste packages
  - Monitoring phase up to 300 years.
  - Closure phase and Regulatory period of 10,000 years. Projected performance to 20,000 yrs and longer
- Important to consider not only the conditions that could initiate a process, but also the time period over which those conditions persist
- Relevant Periods:
  - 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 Temperature for Corrosion

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?

1600 to 160,000 years to penetrate the thickness of one U.S. Quarter

For realistic passive corrosion rates of 1 µm/yr to 0.01 µm/yr and less

Corrosion Rate of Passive Metal
Experimental Measurements

Extensive Corrosion Test Facilities

Thousands of corrosion samples are exposed to high-temperature saturated brines in the Long Term Corrosion Test Facility

Number of Corrosion Tests

Localized Corrosion	
Long Term OCP	>200
Cyclic Polarization	>300
General Corrosion	
Weight Loss	>13,000
Linear Polarization	>100

Arrays of potentiostats are used to measure threshold potentials for localized corrosion & the time-evolution of the corrosion potential

Long-term open circuit potential testing

Measuring General Corrosion Rates

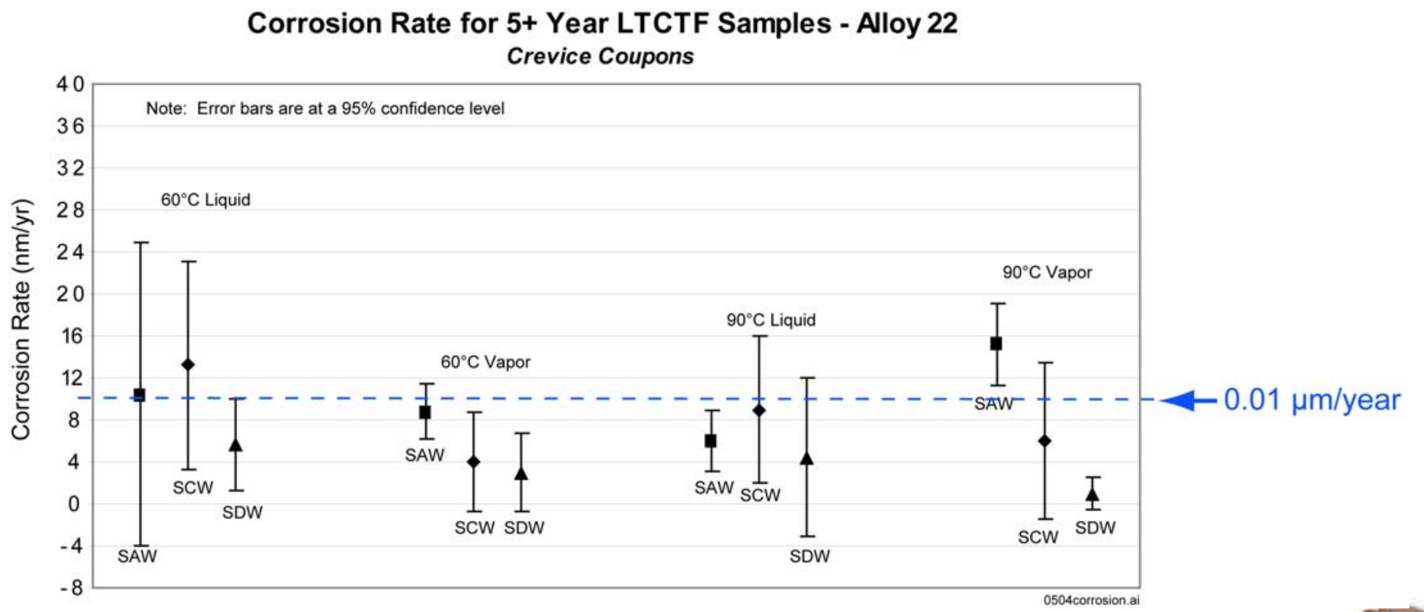
- Immersion Tests
  - Weight (mass) loss
  - Accepted broadly in industrial applications
- Electrochemical Tests
  - Measurement of R_p (Polarization Resistance ASTM G 59 or
    AC Impedance G 106)
  - Constant Potential Tests
- Electrochemical testing may be a fast tool, for example, to determine the effect of environmental variables such as temperature, nitrate, etc., but often yields corrosion rates higher than the actual values for longer exposures

Ranges of Corrosion Rates

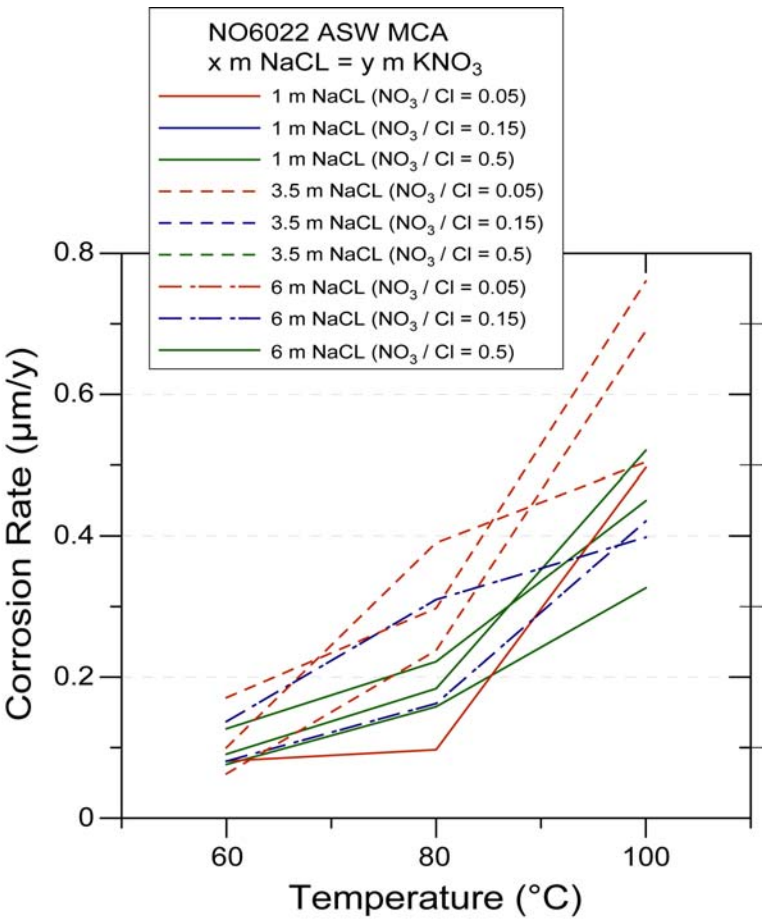
- In 1000X Ambient Water, ~0.8mCl, ~0.4m NO_3, Acidified to pH2.8 (SAW) Corrosion Rate at 90°C
  - 1-h Immersion (Deaerated), freshly polished rate = 1.5 µm/year
  - 1 week in aerated solution rate = 0.1 µm/year
- In Aerated 1 M NaCl, pH 2 Solution at 95°C
  - 1-h immersion rate = 2.1 µm/year
  - 30-h immersion, rate = 0.2 µm/year
- Boiling 3.5% NaCl, 96 h Immersion Testing
  - rate = < 2.5 µm/year

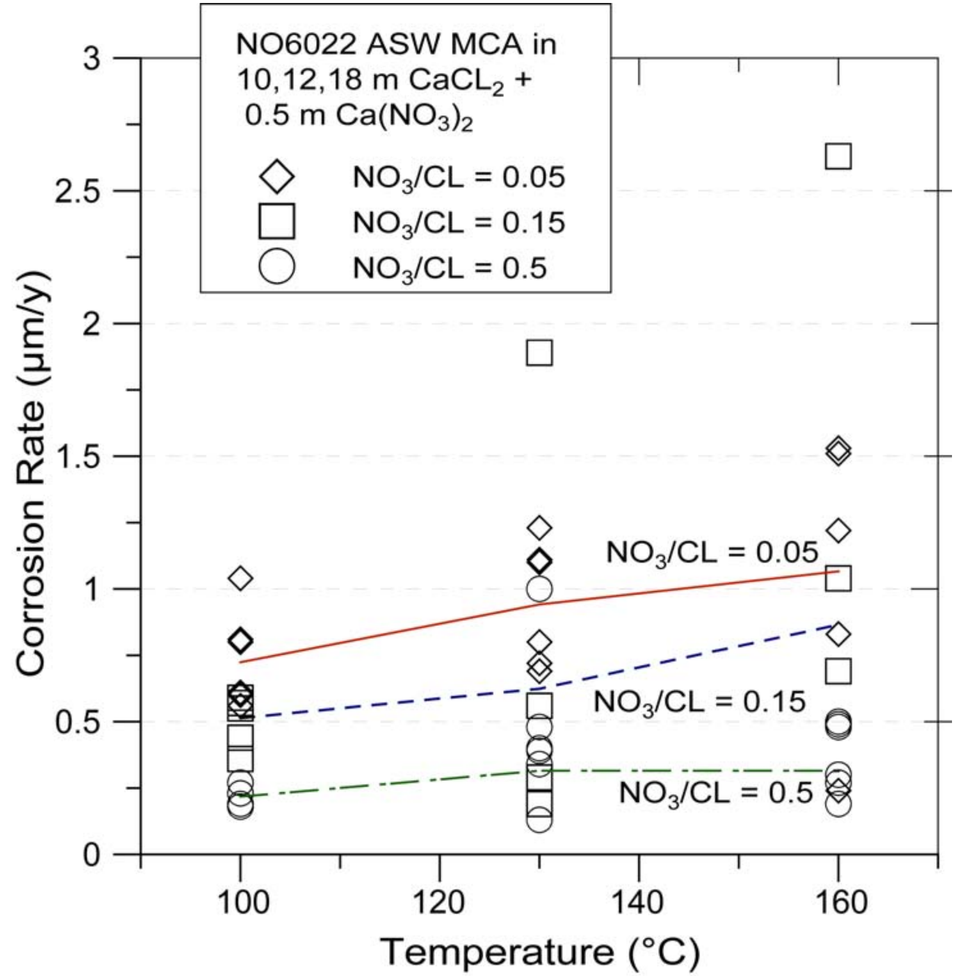
Low Passive Corrosion Rate (5+ year tests)

- Simulated Acidified Water SAW => 1000X Ambient Water, ~0.8mCl, 0.4 mNO_3 Acidified to pH 2.8 (SAW)
- Simulated Concentrated Water SCW => 1000X Ambient Water, ~0.2mCl, 0.1 mNO_3 pH 10 (SCW)
- Basic Saturated Water BSW => 18,000X Ambient Water, ~3.7 mCl, 2.4mNO_3 pH 11-13 (BSW)
- Corrosion rate approximately 0.01 μm/year and independent of temperature and solution composition.



Passive Corrosion Rates Remain Low Up to 160°C in the Presence of Nitrate





Alloy 22 Corrosion Rates by Weight Loss in Autoclave Testing

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

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

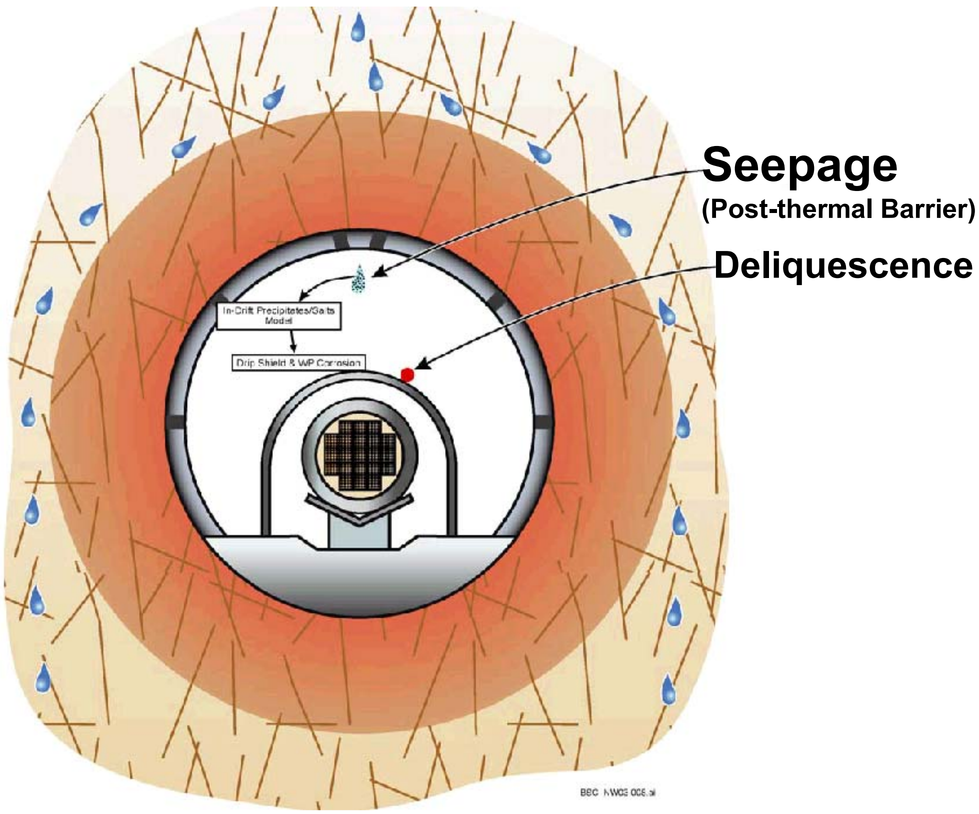
There is no significant general corrosion of Alloy 22 in saturated salt brines at temperatures between 120°C and 220°C

Conclusions From Passive Corrosion

- In a wide range of temperatures (to 160°C and above) and solution composition (even concentrated brines), the short term corrosion rate is 2 μm/year and much less
- Corrosion rate decreases with time to the order of 0.01 μm/year and less
- Nitrate not only inhibits localized corrosion, it also reduces the general corrosion rate
- All corrosion testing methods consistently measure comparable corrosion rates

Corrosion Background and Perspectives

Factors that Protect Against Corrosion



- **Thermal barrier**
  - Drift wall above boiling temperature
  - No drips onto waste package
- **Capillary barrier**
  - Water retained by unsaturated rock
  - No drips onto waste package
- **Drip shield**
  - No drips onto waste package
- **Highly corrosion resistant Alloy 22**
  - No significant corrosion in absence of dripping
  - No corrosion in a wide range of waters resulting from dripping

Limited Amount of Water for Damage to Waste Packages and Transport of Radionuclides

- **No large accumulation of water is formed above repository**
  - **Less than 1 liter per meter length of drift**
  - **Fractures near the dry zone are not filled with water**
  - **Increase from ambient of 5-10 % saturation to ~15% saturation during the thermal period**
- **Drips or seepage into drifts is limited**
  - **10-30% of packages would see seepage if no drip shield**
  - **Seepage water per year over a waste package**
    - **0-600 years <2 liter/yr 1000:1 = 2 ml/yr (current climate)**
    - **600-2000 yrs ~20 liter/yr 1000:1 = 20 ml/yr (climate change)**
    - **After 2000 yrs ~40 liter/yr 1000:1 = 40 ml/yr (climate change)**

Note: 15 ml/yr = 1 table-spoon/year solution on waste package

Two Relevant Moisture Conditions for Corrosion

- **Deliquescence/Condensation Conditions**
  - Describe behavior when there is no dripping of water onto a waste package
  - Effective control by thermal barrier, capillary barrier and drip shield
  - Pertains when any of the three above are operative
- **Dripping and Seepage Conditions**
  - Describe behavior when water may drip onto waste package
  - Only pertain when thermal barrier, capillary barrier and drip shield are simultaneously inoperative

Consider these conditions through the thermal pulse period at the repository

- *Evolution of environment (waters on metal surface)*
- *Evolution of corrosion damage (likelihood, extent and distribution of corrosion, and consequences of any penetrations)*

Temperature/Relative Humidity for 10,000 Years and Beyond

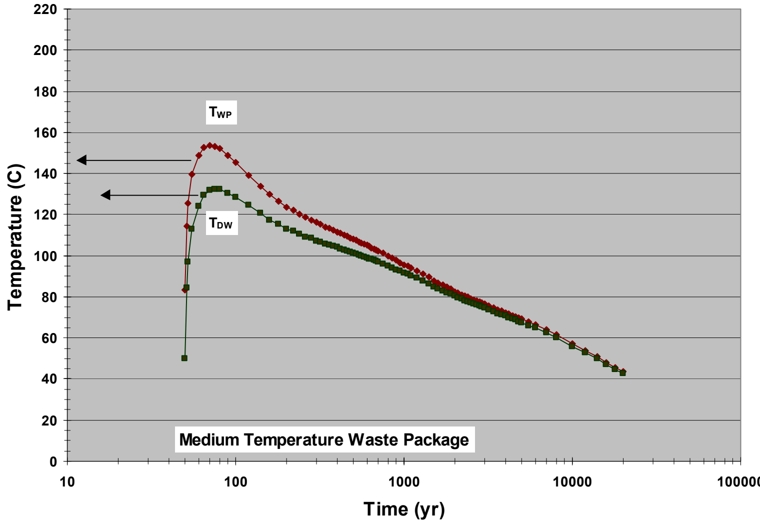
- **Relevant periods regards corrosion:**
  - I - Emplacement of waste packages and preclosure
  - II - Heat up after closure
  - III - Cool down/thermal barrier (drift wall above boiling temperature)
  - IV - Cool down/dripping and seepage possible
  - V - Waste packages below critical temperature for corrosion

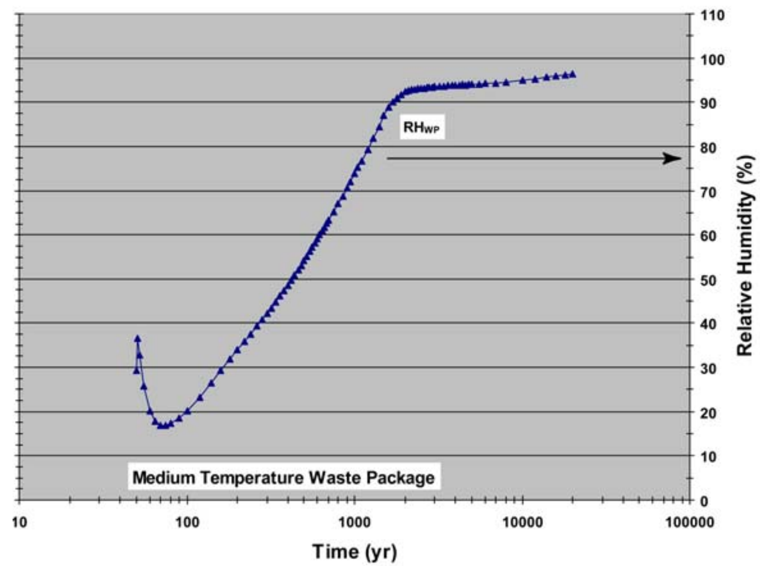
Periods are determined by

(a) Temp-RH over time,

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

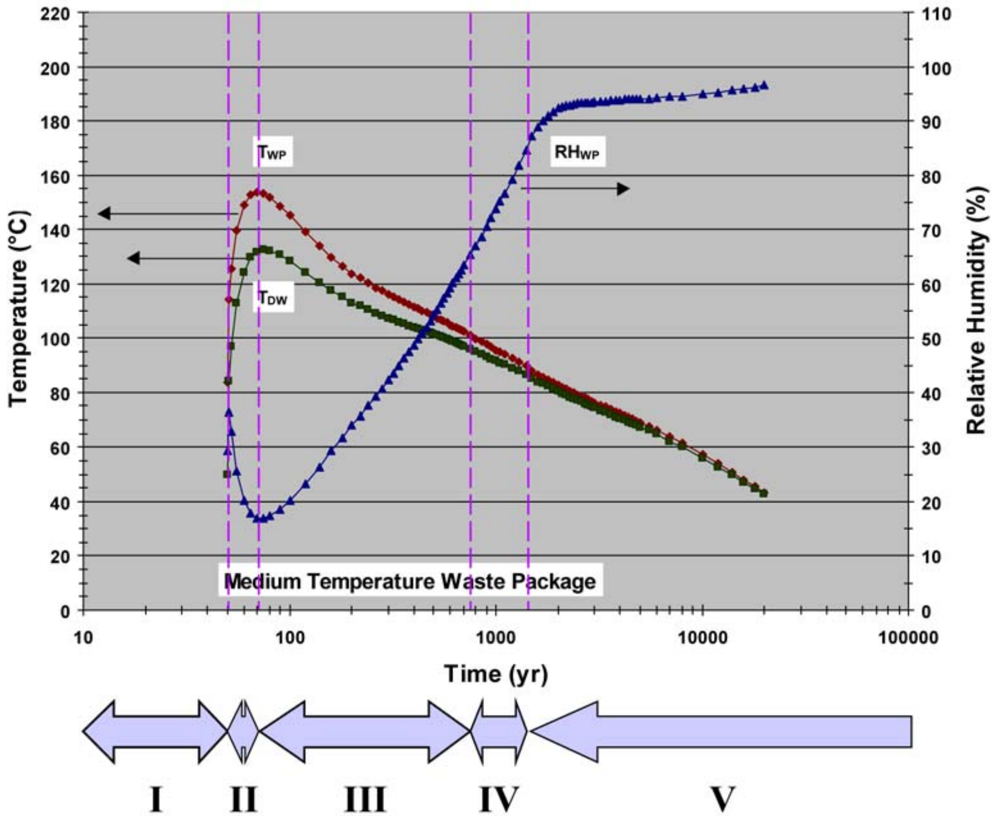
(c) Critical Corrosion Temp for Alloy 22





Corrosion Conditions at Key Time Periods in Repository

Relevant Time Periods Regards Corrosion



- **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 temperature**
  - Year 1375 and beyond

For Conditions Below

Temp-Relative Humidity behavior as shown

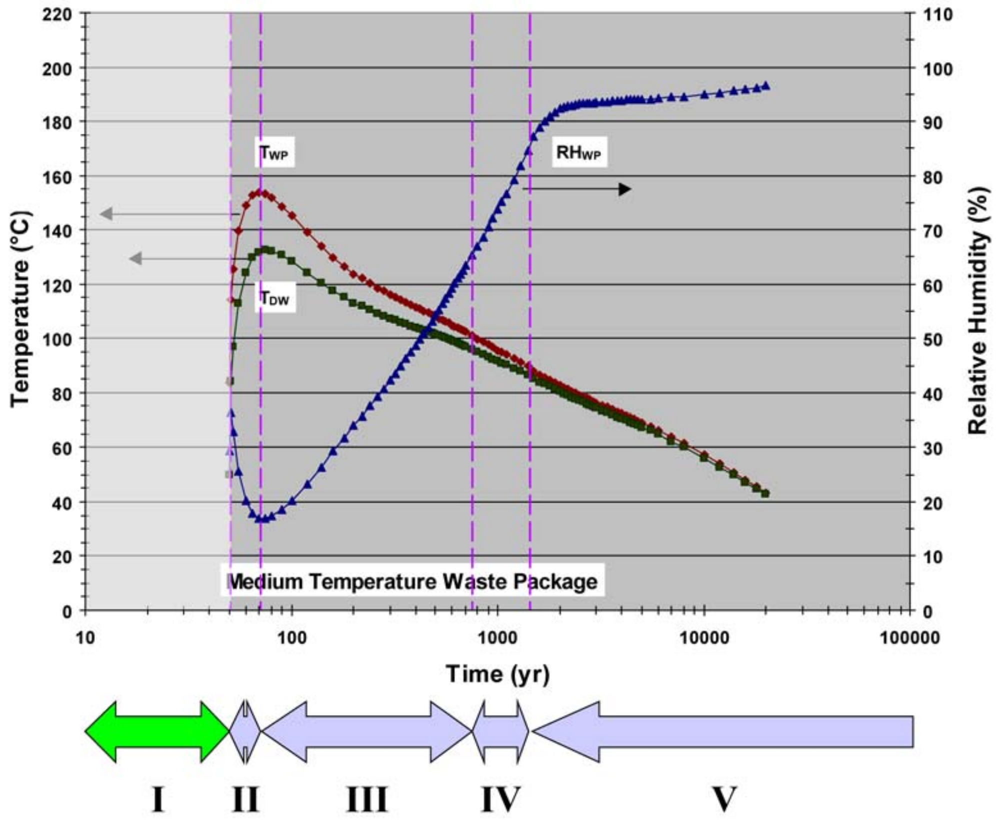
Waste Package at 101°C when Drift Wall cooled to 96°C

Critical Corrosion Temp 90°C

Key Time Periods
I - Emplacement of Waste Packages and Preclosure

0 to 50 years; preclosure

- Ventilation throughout period
- Waste packages are cool
- Dust can accumulate from tunneling and emplacement
- Dust can be ingested during ventilation
- Metal surfaces dry
- No corrosion



Key Time Periods
II-Heat Up After Closure

Dry-zone from ventilation

Thermal barrier (when rock above boiling)

Capillary barrier + drip shield

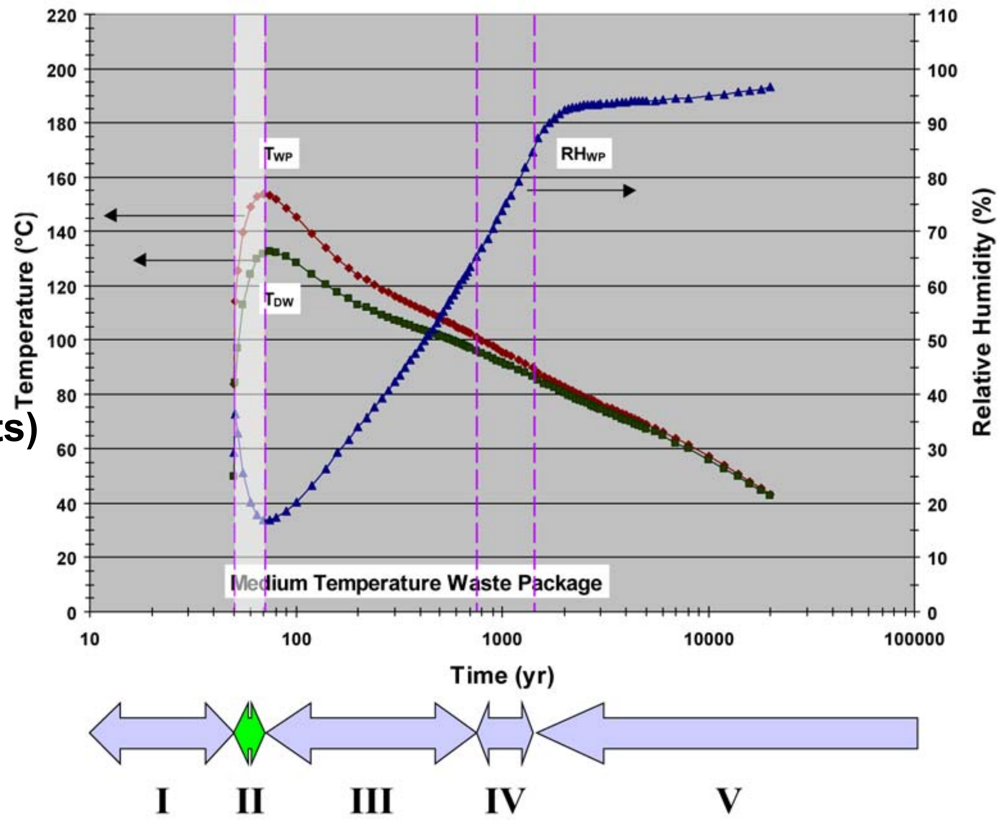
Highly corrosion resistant alloy

- No dripping or seepage onto waste package
- Dust from preclosure on metal surfaces
- Only source of “new” dust is drift degradation (limited amounts)
- Temp low and increasing
- Relative humidity decreasing

Consider deliquescence effects

- Dust constituents alterations
- Corrosion - None to negligible

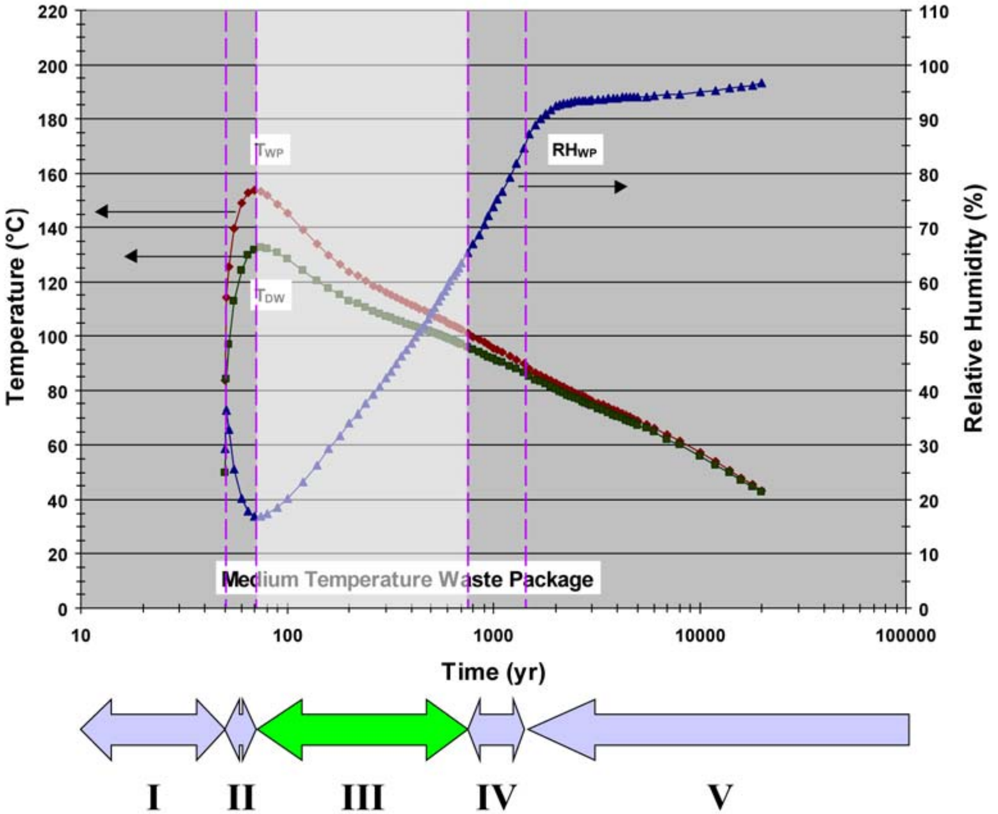
Year 50 for 10-15 yrs: Heat-up



Key Time Periods
III-Cool Down/Thermal Barrier (Drift Wall Above Boiling Temperature)

- Thermal barrier active
- No dripping/seepage onto waste package
- No condensation; waste package hotter than drift wall
- Deliquescence conditions pertain
- Dust only source of salts for formation and evolution of waters
- Corrosive salts limited
- Calcium/Magnesium chloride solutions unstable
- Nitrates in dust
- No significant corrosion

Drift Wall cooled to 96°C;
Waste Package at 101°C at year 750



Key Time Periods

IV-Cool Down/Dripping and Seepage Possible

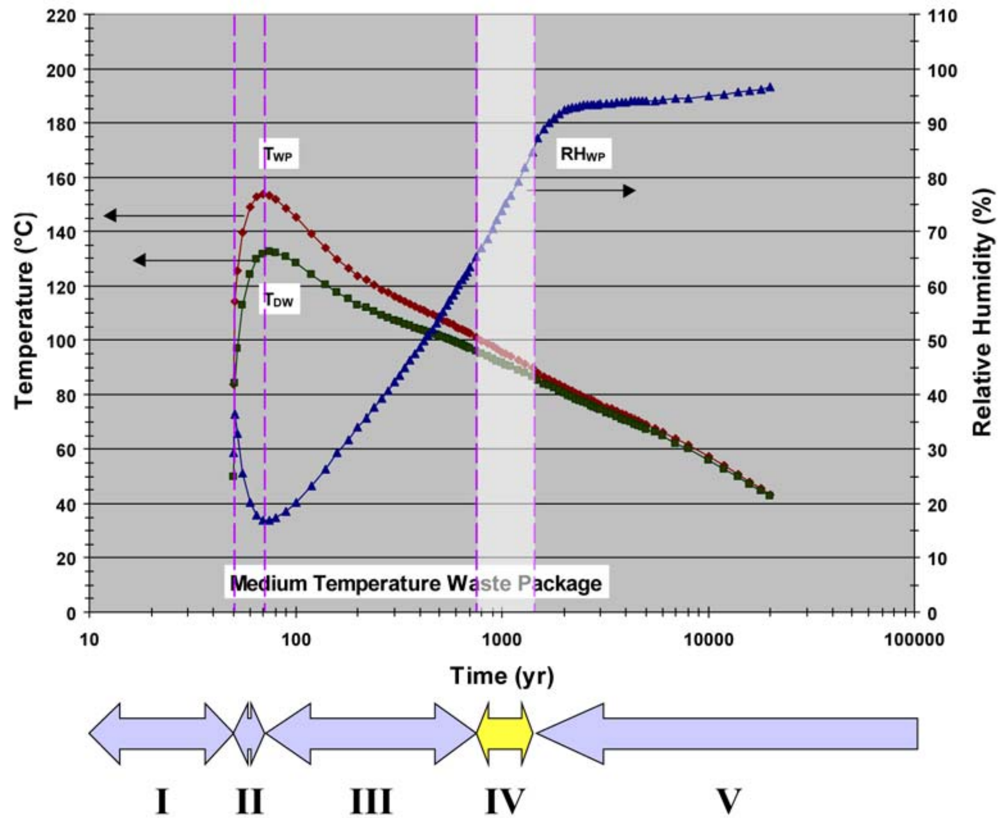
Capillary barrier + Drip Shield +Highly corrosion resistant alloy

- **When drift wall below boiling temperature (96°C) dripping and seepage can occur**
  - **Isolated locations along drifts**
  - **Time variant and episodic**
- **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 and If waste package temperature above critical corrosion temperature**
  - **Then, follow local corrosion logic/fault tree for damage evolution**

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%

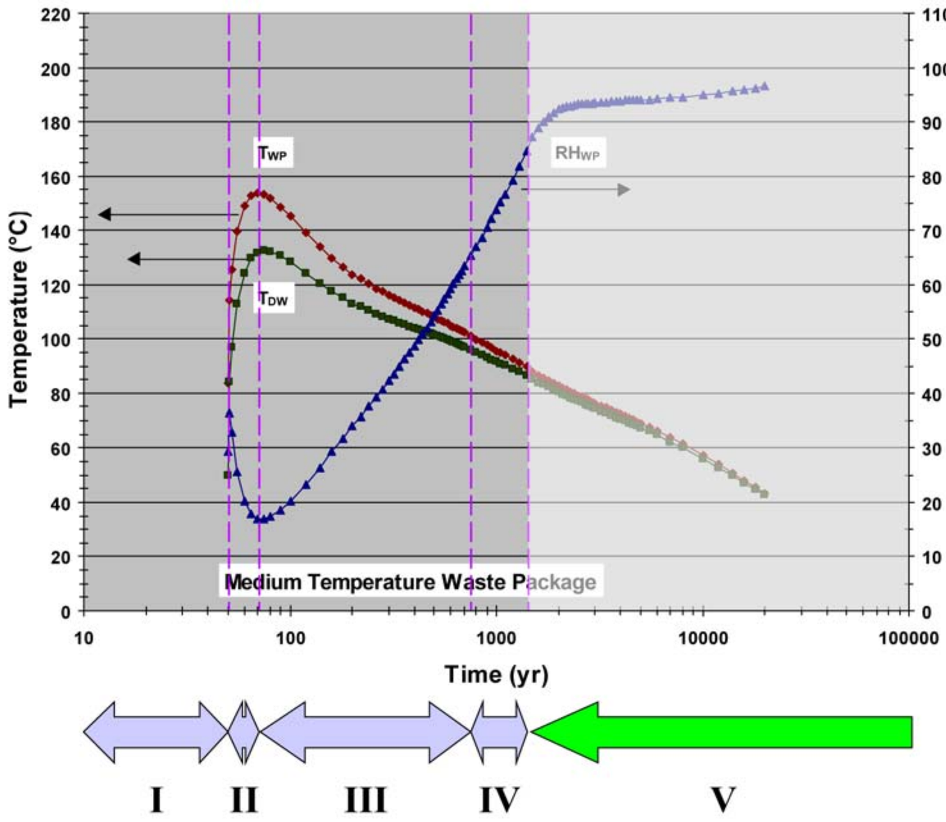
For drift wall at boiling at year 750; Critical Corr Temp 90°C year 1375



Key Time Periods
V-Waste Packages Below Critical Temperatures for Corrosion

- Waste package surface below critical corrosion temperature
- No localized corrosion of Alloy 22
- Passive corrosion rate pertains
  - *16,000 years to penetrate the thickness of one U.S. Quarter (at 0.01 µm/yr)*
  - Even lower rates feasible

For Critical Corrosion Temperature 90°C
Passive Corrosion only after year 1375



Summary of Corrosion Analysis for Key Time Periods in Repository

I-Preclosure (e.g. Start to Year 50) **No corrosion***

II-Heat up (e.g. Year 50 to ~65) **No corrosion***

III-Thermal barrier (e,g. Year ~65 to 750) **No corrosion***

IV-Cool Down Post-Thermal Barrier (e.g. Year 750 to 1375)

- **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 and if waste package surface is above critical corrosion temperature**
- **Then, follow *Crevice Corrosion Logic Tree* and *Localized Corrosion Logic/Fault Tree* to determine damage evolution**

V-Packages below Critical Corrosion Temp (e.g. Year 1375 and beyond)

No corrosion*

*** No Corrosion = no significant damage to waste package**

Localized Corrosion

Corrosion Processes and Controlling Parameters
Experimental Measurements of Corrosion Resistance

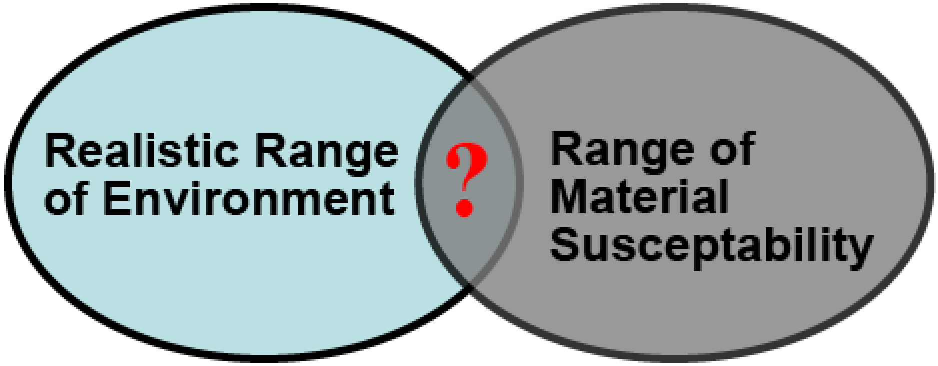
Susceptible Zone for Localized Corrosion

"?" Zone

Correlate with Repository Conditions

- How do these form?
- When, where, how much?
- Will environments persist?
- Can they reform?

"?" Defines the Susceptible Zone



Additional Requirements for Corrosion

- Water must contact waste package
- Water must remain on waste package
- Corrosive species must be present to form electrolyte
- Material must be susceptible to corrosion under these conditions
- Conditions must persist over sufficiently long time

Susceptible Zones Only at Intermediate Temperatures

Lower Temperature

T1-Metal surface is dry, no corrosion

T2-Aggressive solutions possible

T3-Aggressive solutions possible

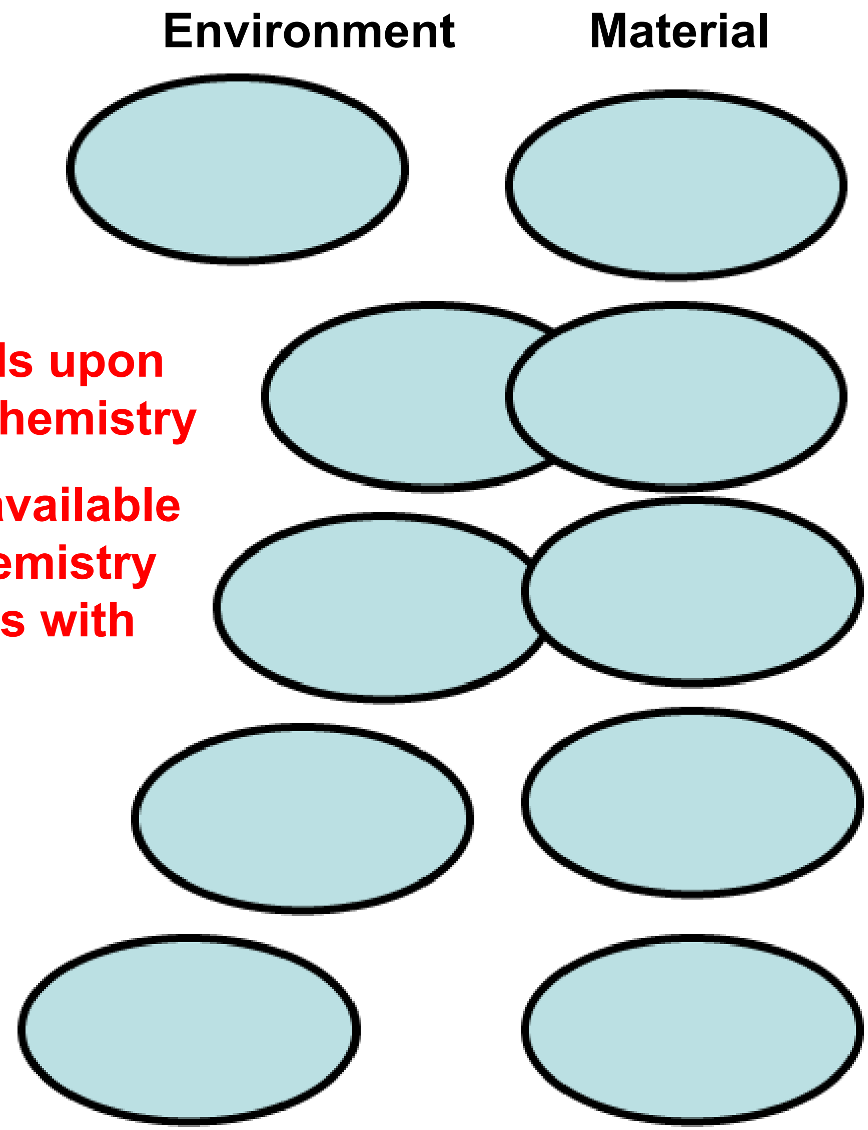
T4-No localized corrosion

T5-No localized corrosion

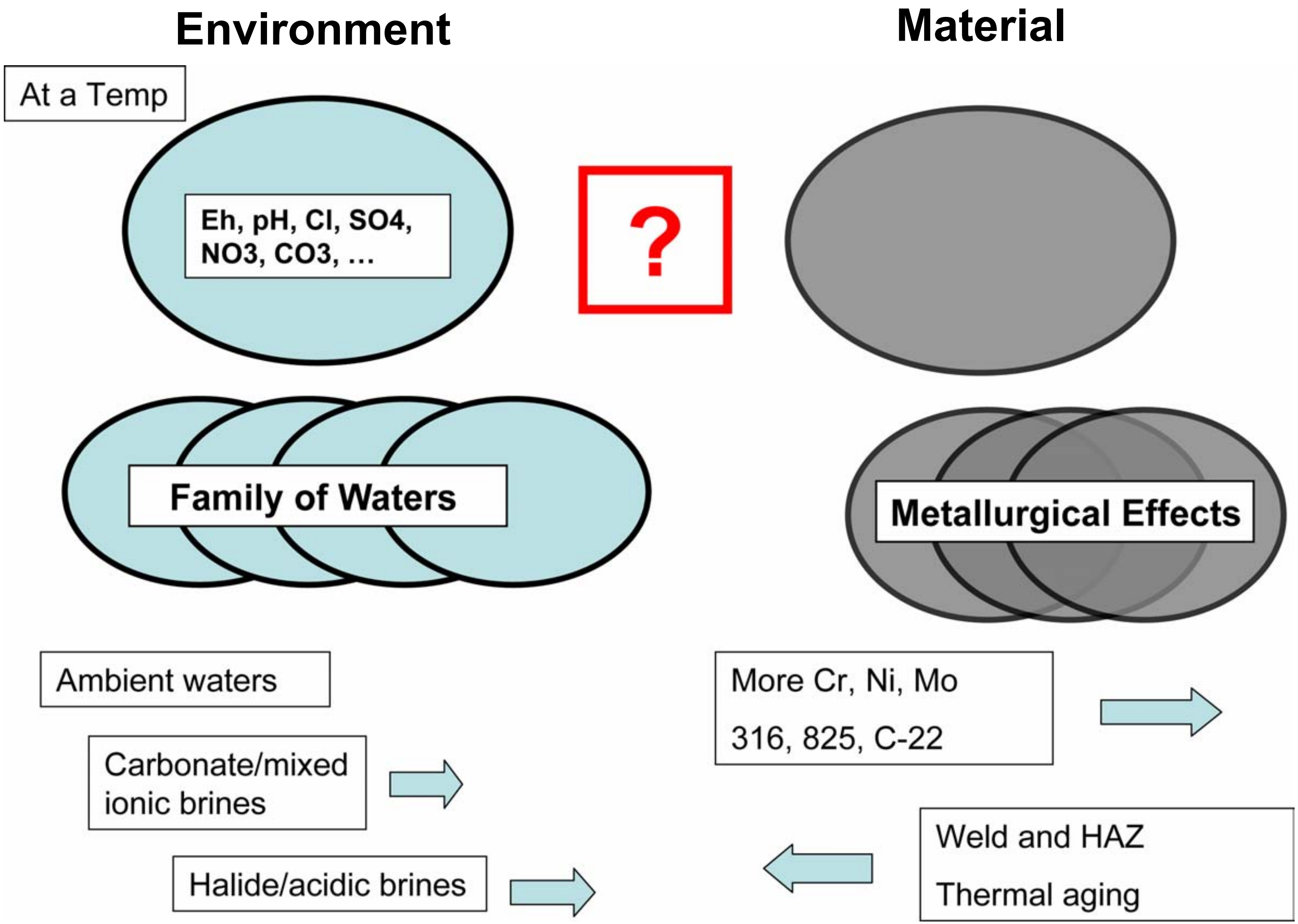
???

Depends upon water chemistry

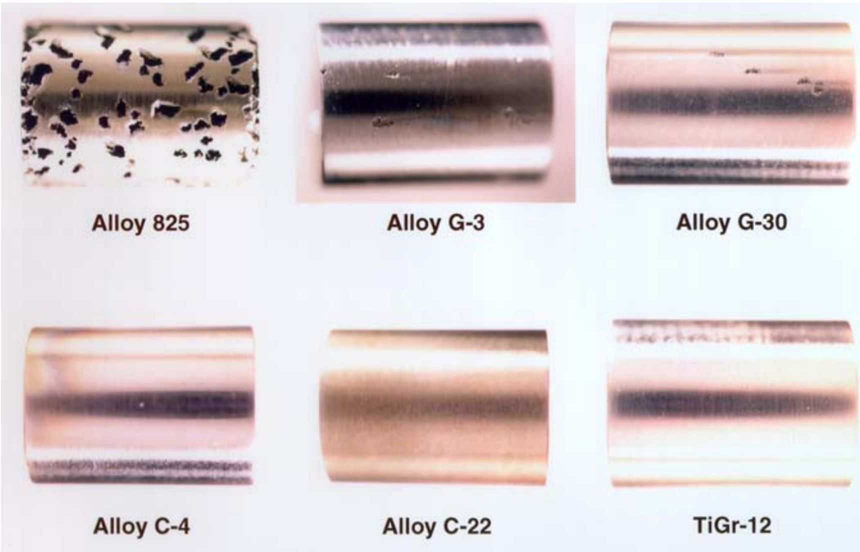
Water available and chemistry changes with time

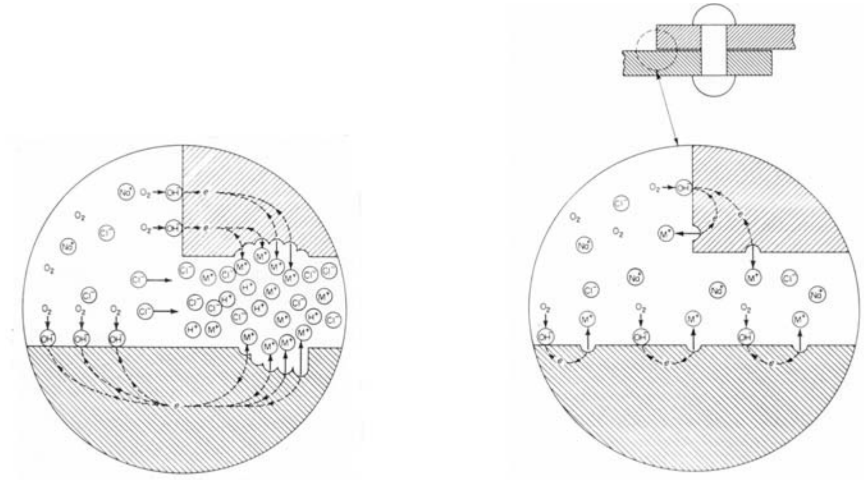


Environment and Materials Factors Affect the Susceptible Zone

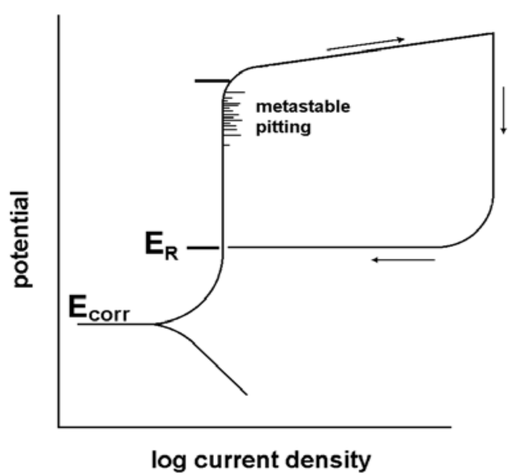


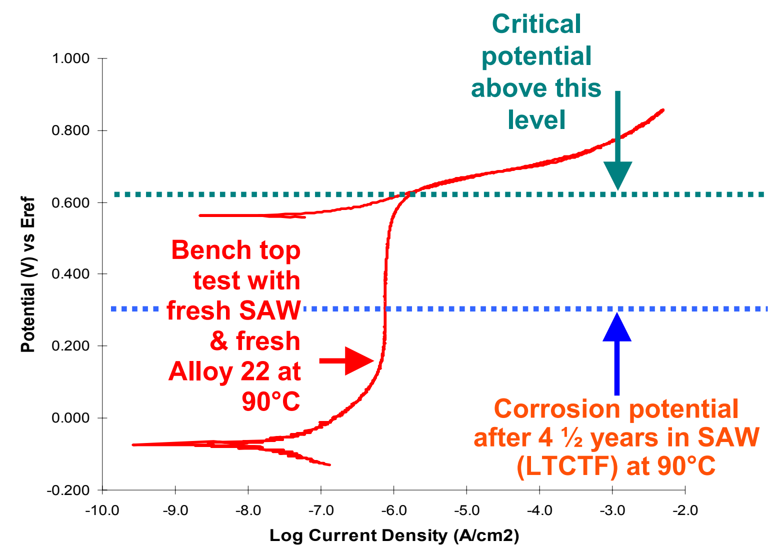
Localized Corrosion Processes





After Fontana *Corrosion Engineering*

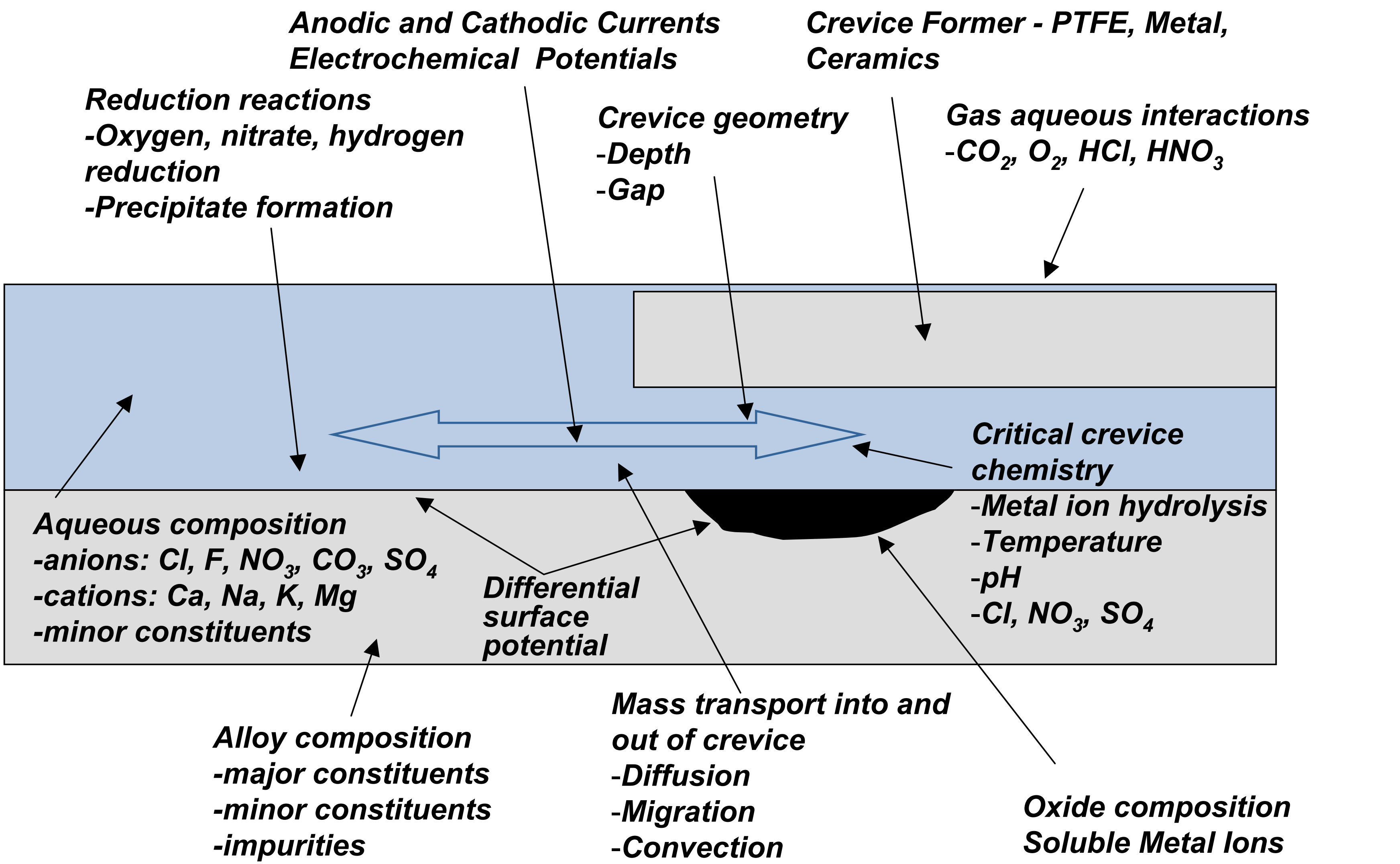




Variables for Crevice Corrosion

- Passive metals such as Alloy 22 and Titanium are susceptible to crevice corrosion under extreme conditions
- Crevice corrosion depends strongly on
  - Chloride concentration (Cl^-)
  - Temperature (T)
  - Potential (E)
  - Acidity (pH)
  - Crevice geometry (tightness)
- The higher the Cl, T, E, the lower the pH, and tighter the crevice geometry, lower the resistance of alloys to crevice corrosion

Factors Affecting Localized Corrosion Processes



Localized Corrosion: Initiation, Propagation, Stifling and Arrest

- Identify factors affecting localized corrosion processes
- Assess requirements in form of Logic/Fault Tree
- Consider initiation, propagation, stifling and arrest
  - Crevice formers: Teflon, metal/metal, rock-dust-ceramic
  - Formation and retention of critical crevice chemistry
  - Power Law for Corrosion Rate

Crevice Formers

- **Critical crevice temperature testing of Alloy 22 in Ferric Chloride showed**
  - **Crevice corrosion with PTFE washers (more severe)**
  - **Absence of crevice corrosion using metal-metal washers**
- **Crevice Corrosion in Alloy 22 found using ceramic washers covered by PTFE tape or coated with PTFE with a torque applied of 70 lb.inch**
- **Dust accumulation or rocks on Alloy 22 do not produce the same extent of crevice corrosion as severe crevice formers in the laboratory**

Crevices do not exist over the great extent of the waste package surface

Critical Crevice Solution Measurements

- **Critical crevice solution measurements indicate solution severity, (i.e. lower pH, higher [Cl^-]) needed for crevice propagation increases with Cr, Mo and Ni content**

Alloy	%Cr-%Mo-%Ni	Critical pH	Critical Cl^-, M	Reference
430 Stainless steel	16Cr-0Mo-0.2Ni	2.90	1*	Lillard et al
304 Stainless steel	19Cr-0Mo-9Ni	2.10	2*	Lillard et al
316 Stainless steel	18Cr-2.5Mo-10Ni	1.65	4	Oldfield & Sutton
Alloy 625	21.5Cr-9.0Mo-61Ni	-0.5 to 0	6 - 8	Oldfield & Sutton

* Calculated

- ***Alloy 22 is more corrosion resistant than Alloy 625***
- ***Extremely aggressive solution required for crevice corrosion of Alloy 22, and extremely tight crevices are required to sustain the severe solution***

Power Law Model for Stifling

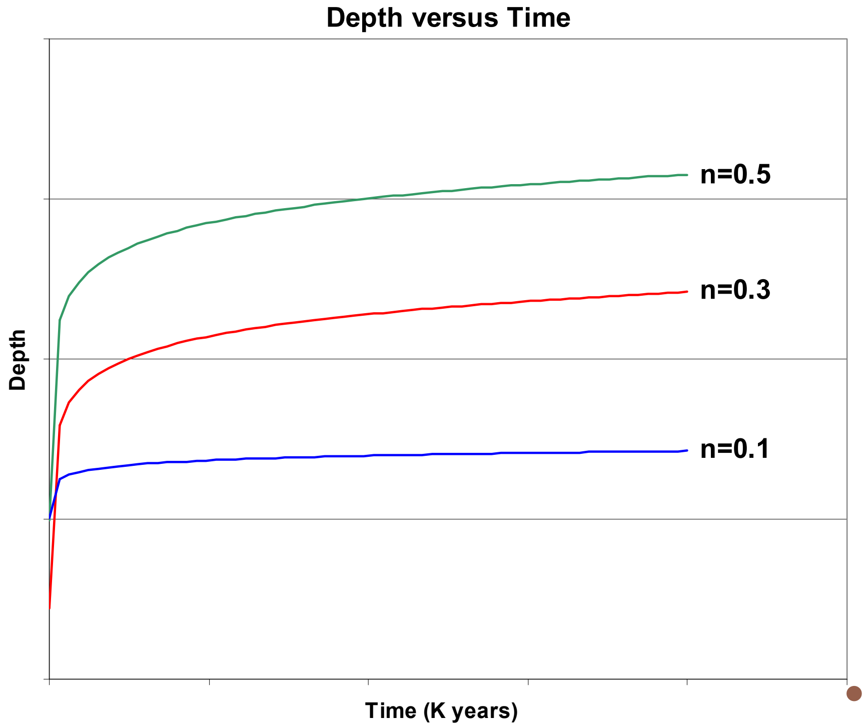
- This is an empirical model where the depth of penetration by localized corrosion decreases with time according to

$$P = kt^n$$

  Where P is maximum depth of penetration, and k and n are empirical coefficients

- The values for the coefficients have been determined from corrosion data available on alloys such as C-4, C-276 and C-22.
  - k is growth constant parameter dependant upon material characteristics
  - n is time exponent with typical values ranging from 0.1 to 0.5 with lower values accounting for repassivation of the corroding sites

Expected Localized Corrosion Propagation Rate



- Literature consistent with time dependent crevice (and pitting) corrosion propagation rate. The rate slows significantly with time.
  - Depth = kt^n
    - Where k and n are constants related to alloy and environmental conditions
  - For a diffusion controlled corrosion process, n = 0.5
    - However, for many alloy/environment systems, n < 0.5 due to processes such as
      - corrosion product plugging,
      - inability to maintain critical crevice chemistry with increasing depth
      - cathodic area limitations
      - limited brine solution availability
- Alloy 22 propagation results limited, but wide range of alloys show similar behavior, e.g. Alloy 600, Titanium Gr 2, & carbon steel

‘n’ found to vary from ~0.02 to 0.5 for range of conditions

Localized Corrosion Logic/Fault Tree

A) Determine corrosion behavior in types of waters

B) Determine types of waters during relevant periods

T-RH formation of water over time

Seepage waters and Deliquescent waters

Evolution of waters with time; Trajectory of corrosiveness of waters

Waters in dust, deposits, crevices

If A) and B) allow local corrosion:

C) Is Ecorr positive enough to initiate and support local corrosion?

If A), B) and C)

D) Are crevices present of sufficient severity

If A), B), C) and D)) support local corrosion:

E) Will localized corrosion persist?

Consider propagation, stifle and arrest

If from E) corrosion persists

What is evolution of damage?

-rate of corrosion and penetration

-damage size, shape, distribution

Requirements for Damage

Do conditions exist?

Will corrosion occur?

Will corrosion persist?

What damage results?

Consider all of the above during the Five Relevant Periods of the Repository

Localized Corrosion

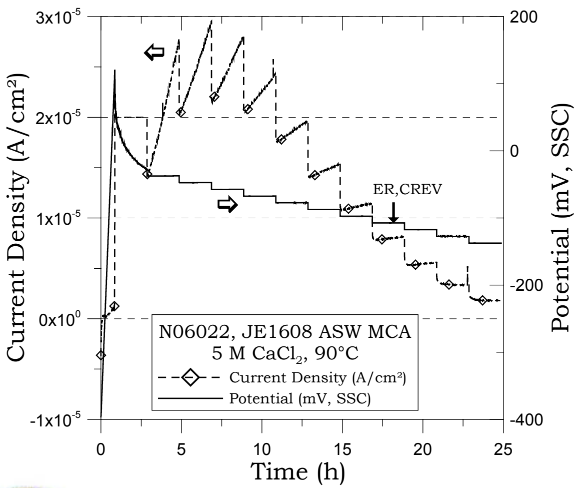
Experimental Measurements of Corrosion Resistance

Localized Corrosion Testing

Immersion Testing

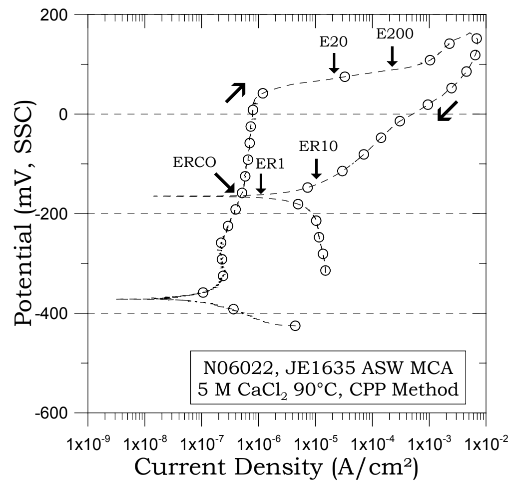
ASTM G 31

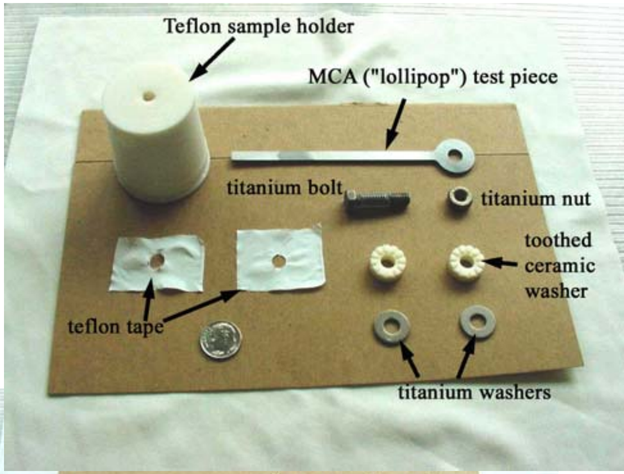
Long Term Corrosion Test Facility (LTCTF)

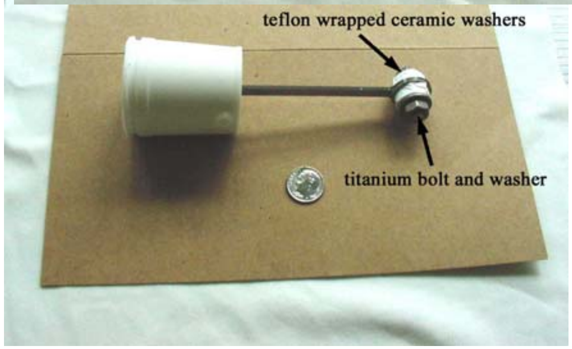


Electrochemical Methods

- **Cyclic Potentiodynamic Polarization (CPP) (ASTM G 61)**
- **Tsujikawa Hisamatsu Electrochemical (THE)**







Specimens

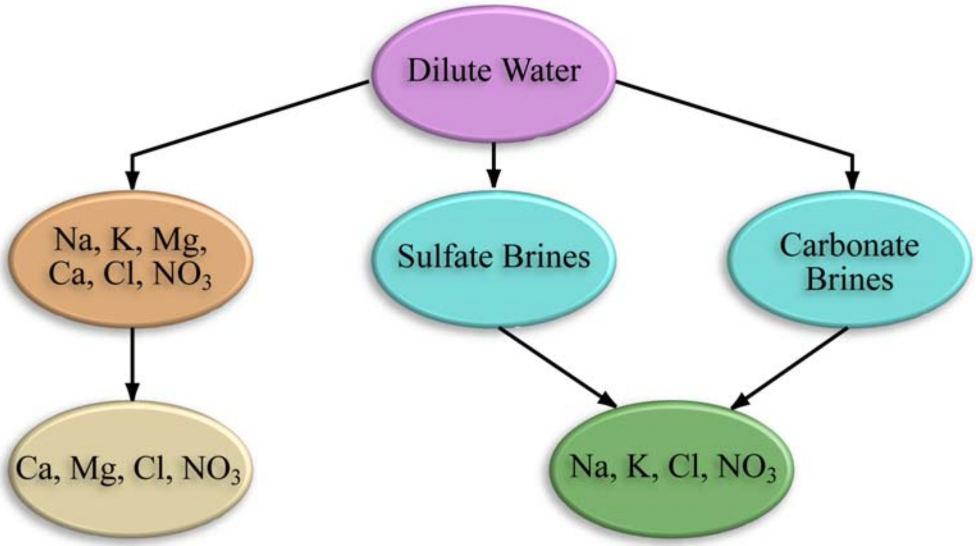
Ceramic + PTFE

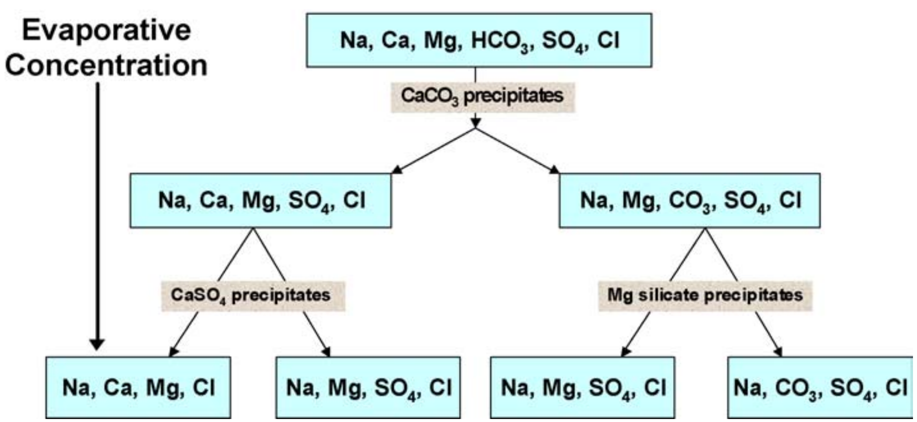
70 lb.in Torque

Multiple Crevice Assemblies (MCA or PCA)

Welded (GTAW) and Non-Welded

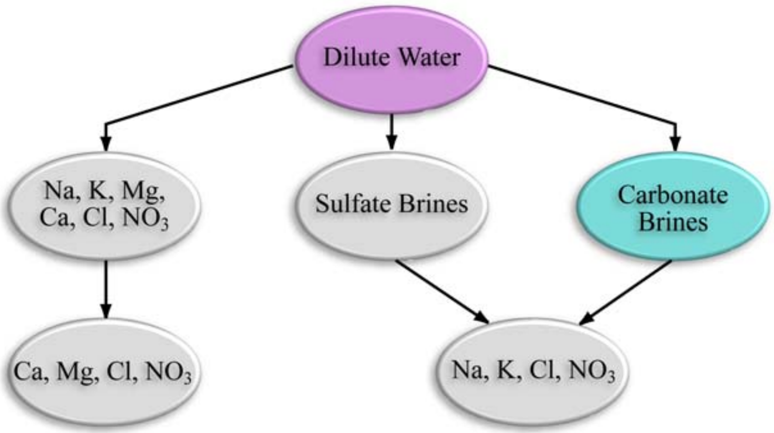
Aqueous Solution Types

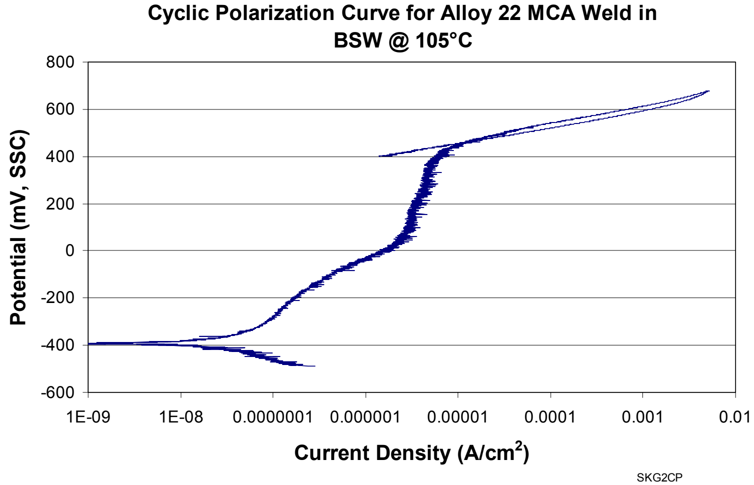




- **Ambient Waters:**
  - **Dilute solutions**
  - **Na-Ca-Mg-HCO_3-CO_3-Cl-NO_3-SO_4**
  - **Near neutral pH**
- **Waters can be concentrated**
  - **Modified during movement**
  - **Thermal-chemical processes**
- **Modifications on waste package surface**
- **Chemical and electrochemical processes**

Corrosion Behavior of Alloy 22 Welds in Dilute and Carbonate Brines



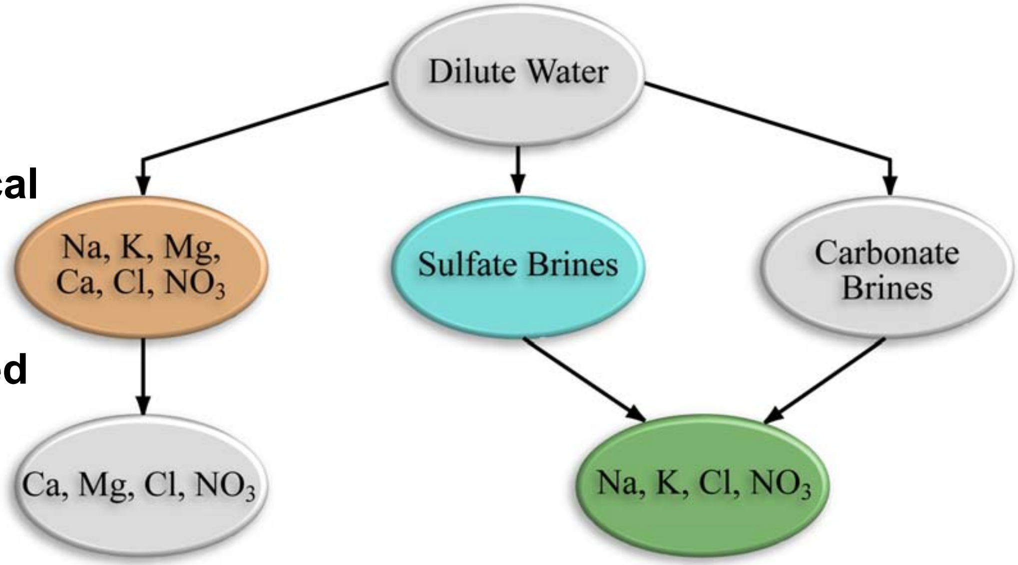


pH 10 1000x ambient water ~0.2 m Cl, 0.1 m NO_3 (SCW)	**No localized corrosion observed using both cyclic polarization and Tsujikawa-Hitsamatsu methods**
pH 11-13 18,000x ambient water ~3.7 m Cl, 2.4 m NO_3 (BSW)	**No localized corrosion observed using both cyclic polarization and Tsujikawa-Hitsamatsu methods**
Industrial Experience	**These are noncorrosive and benign waters. Highly corrosion resistant Alloy 22 is not required**

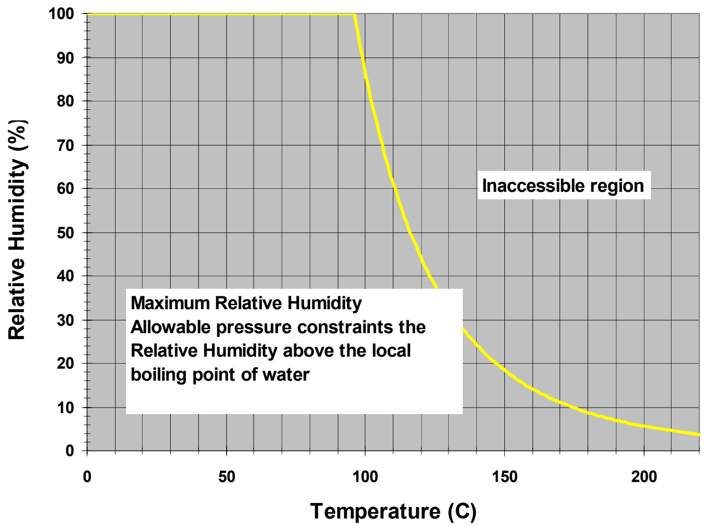
No Localized Corrosion

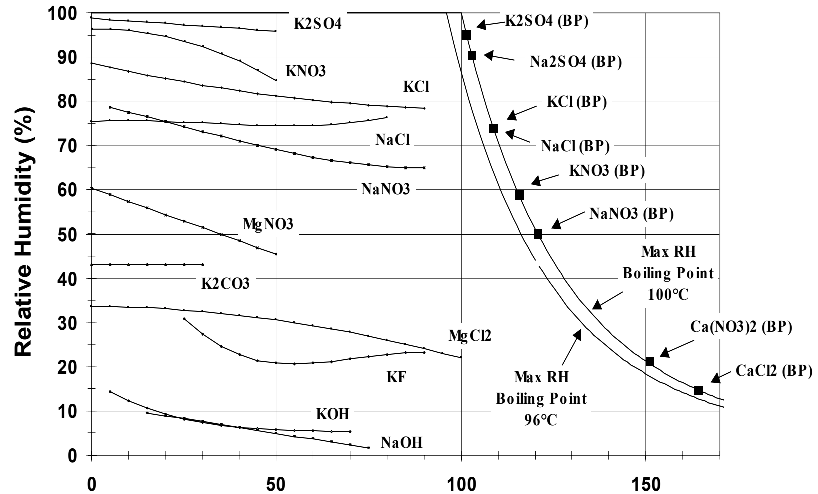
Expected Corrosion Behavior in Na, K, Cl, NO_3 Brines, and Sulfate Brines

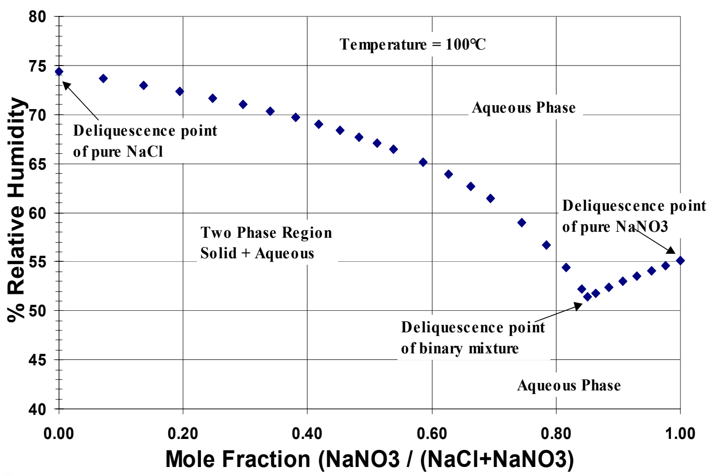
- **Waters with modest nitrate levels**
  - **Localized corrosion not observed**
  - **As-welded Alloy 22 long-term corrosion potential below critical crevice potential for nitrate: chloride between 0.05 to 0.5**
  - **No localized corrosion observed in cyclic polarization testing of Alloy 22 welds in high-nitrate brines**
- **Waters with low nitrate levels**
  - **Localized corrosion is possible**
    - **Crevice corrosion was initiated by polarization into susceptible zone**
  - **When initiated, crevice corrosion current decreased markedly with time (stifling observed)**

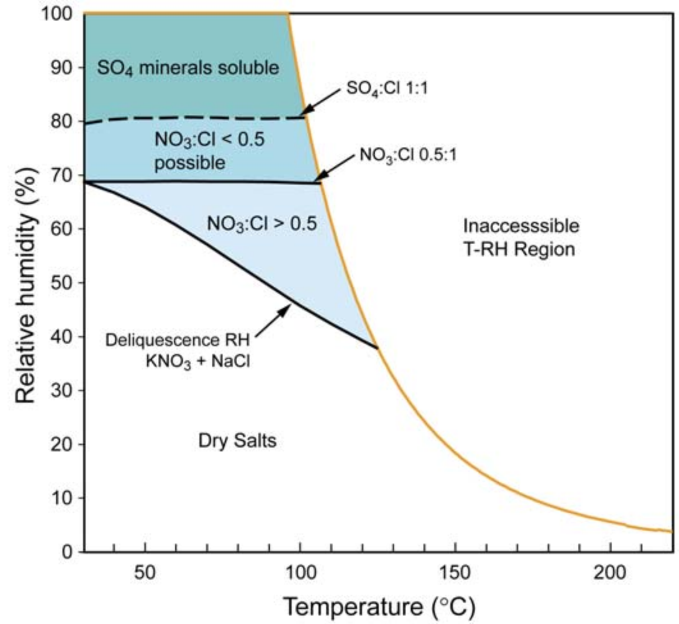


Solution Chemistry Principles



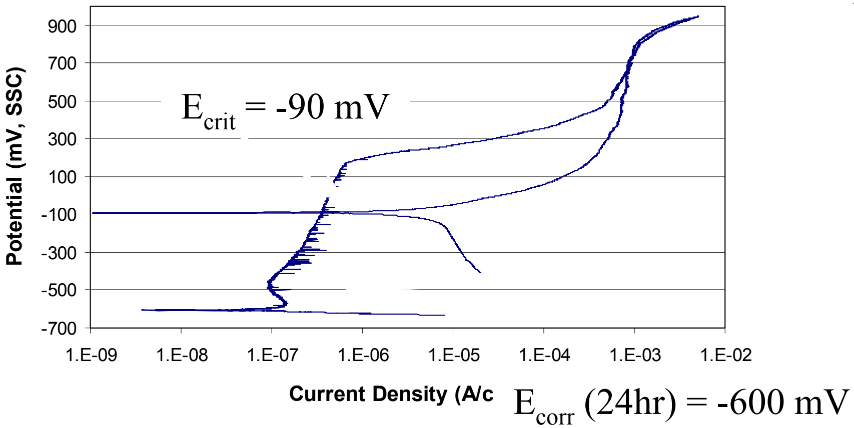






Nitrate Inhibition of Localized Corrosion in Alloy 22 Welds

Cyclic Polarization Curve for Alloy 22 MCA Weld in 6 m NaCl + 0.3 m KNO_3 @ 100°C



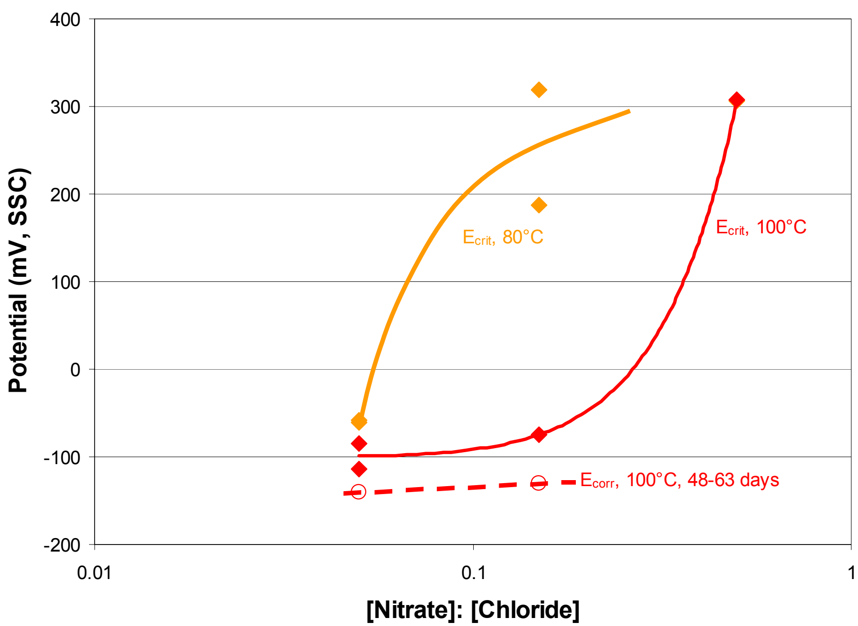
NaCl	NaNO3	Cl:NO3	Temperature (°C)	E_{corr} (V, SSC) (at 24hr)	E_{crit} (V, SSC) (at 1µAcm-2)
1	0.05	0.05	80	-0.438	0.034
1	0.15	0.15	80	-0.494	0.304
1	0.5	0.5	80	-0.462	0.329
1	0.05	0.05	100	-0.526	-0.110
1	0.15	0.15	100	-0.497	-0.014
1	0.5	0.5	100	-0.470	0.306
3.5	0.175	0.05	80	-0.489	-0.054
3.5	0.35	0.1	80	-0.549	0.187
3.5	0.525	0.15	80	-0.477	0.410
3.5	0.7	0.2	80	-0.516	0.301
3.5	1.05	0.3	80	-0.469	0.312
3.5	1.75	0.5	80	-0.466	0.320
3.5	0.175	0.05	100	-0.553	-0.110
3.5	0.525	0.15	100	-0.524	-0.065
3.5	1.75	0.5	100	-0.446	0.345
6	0.3	0.05	80	-0.472	-0.059
6	0.9	0.15	80	-0.478	0.253
6	3	0.5	80	-0.391	0.418
6	0.3	0.05	100	-0.531	-0.099
6	0.9	0.15	100	-0.505	-0.048
6	3	0.5	100	-0.298	0.308

- **Inhibition with**
  - **NO_3:Cl > 0.5 at 100°C**
  - **NO_3:Cl > 0.15 at 80°C**

Nitrate Inhibition of Localized Corrosion in Alloy 22 Welds

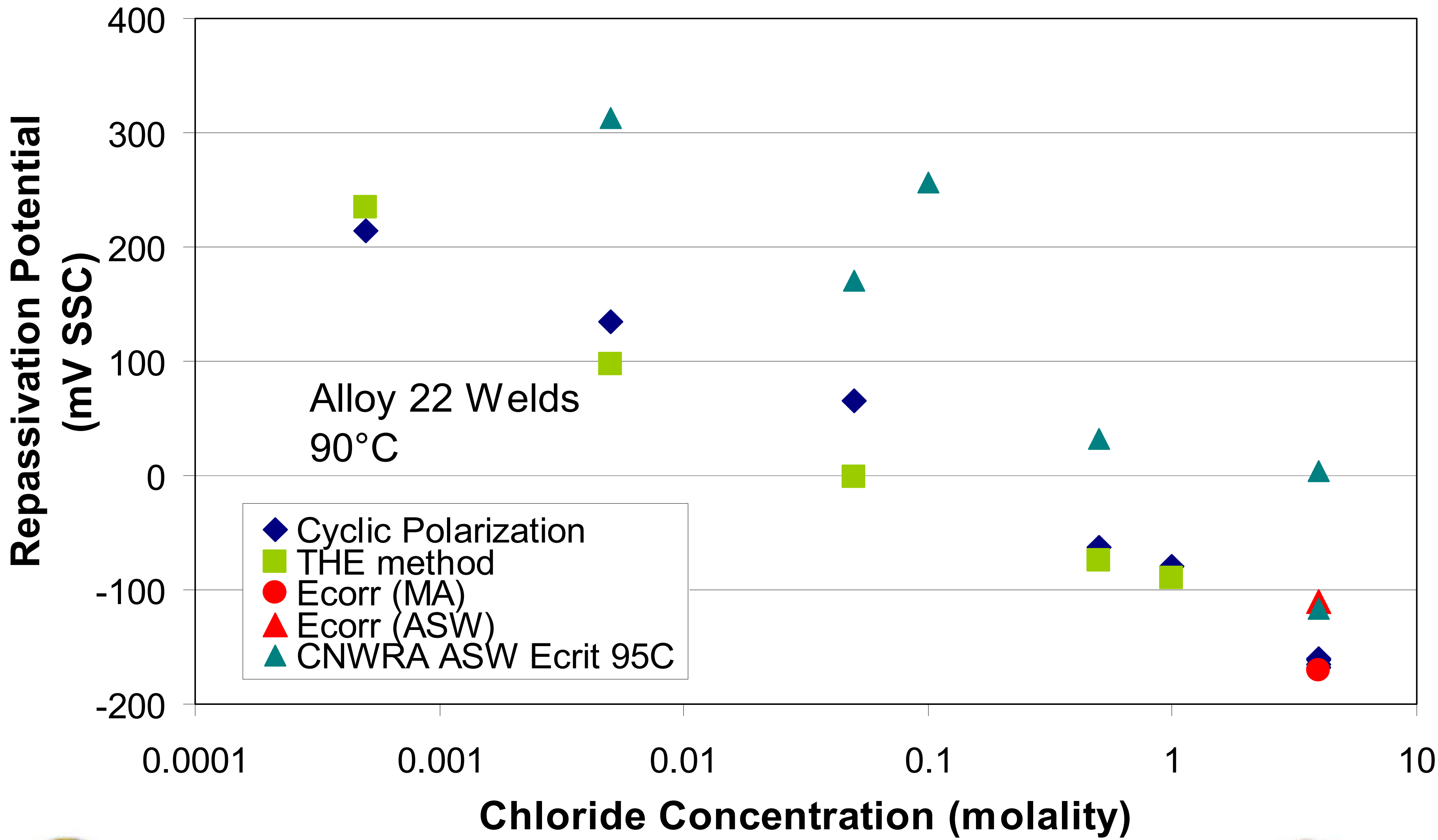
(Continued)

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

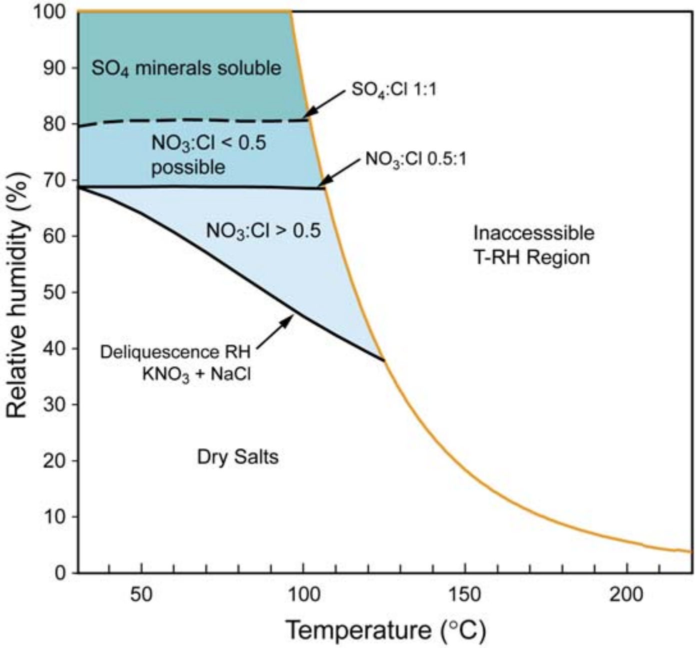


- Inhibition with
  - NO_3:Cl > 0.5 at 100°C
  - NO_3:Cl > 0.15 at 80°C
- Chloride concentration (1m, 3.5m and 6m) had only secondary effect on Ecrit
- Long-term corrosion potential approaching Ecrit at low NO_3:Cl and high temperature
- Sulfate, if present, can be beneficial

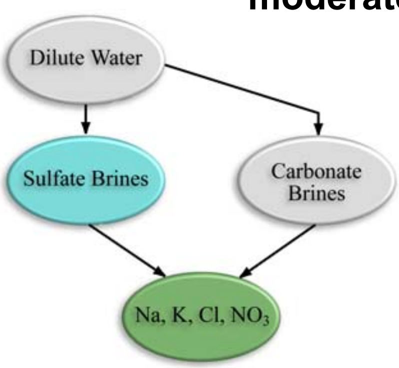
Project Values of Repassivation Potential Compare Conservatively to CNWRA Values



No Localized Corrosion Observed in High-Nitrate, NaCl Brines



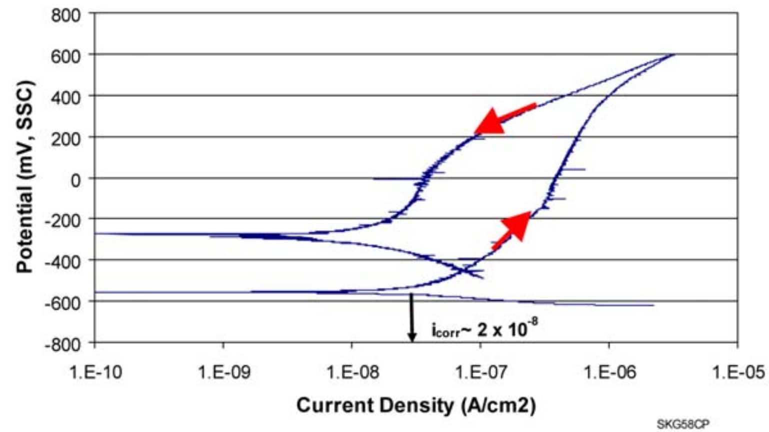
Highly concentrated waters at moderate Relative Humidity



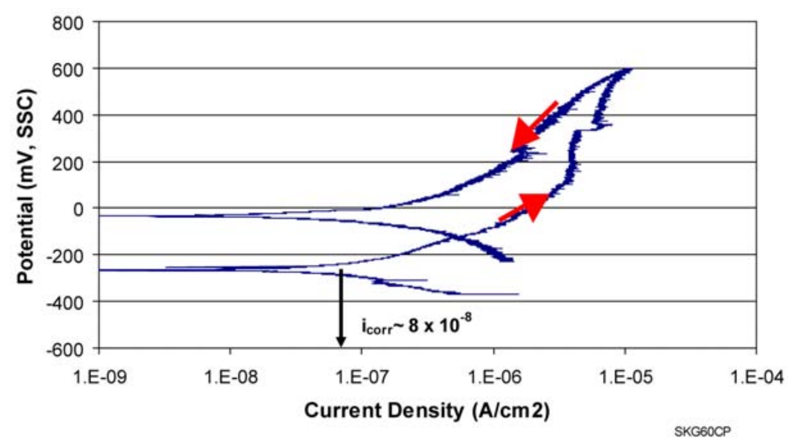
115°C Condition represents:

- **1st wet (deliquescence)**
- **Last dry (evaporation)**

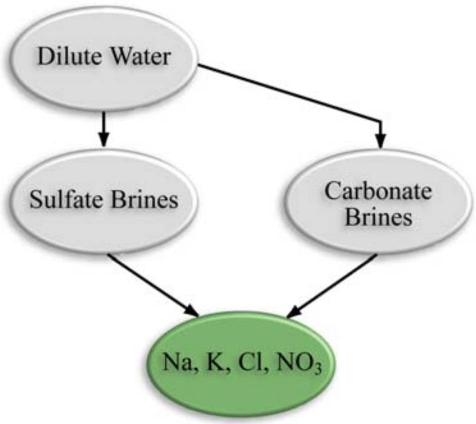
Cyclic Polarization Curve for Alloy 22 MCA Weld in 5.8 m NaCl + 18.2 m KNO_3 + 2.4 m $NaNO_3$ @ 100°C



Cyclic Polarization Curve for Alloy 22 MCA Weld in 5.8 m NaCl + 18.2 m KNO_3 + 2.4 m $NaNO_3$ @ 115°C

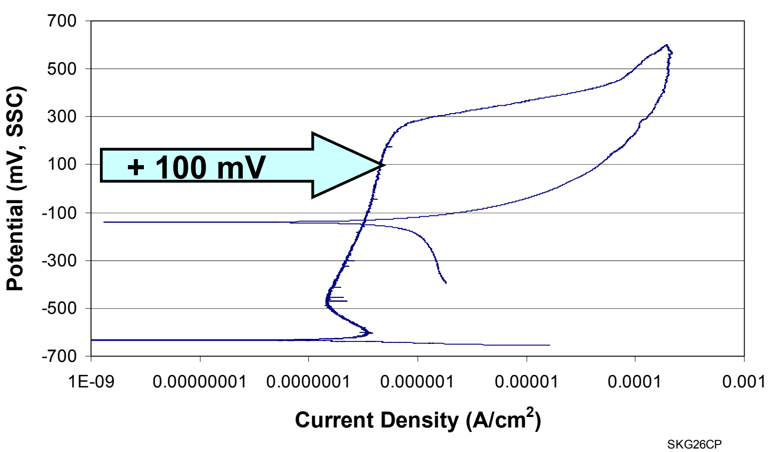


Evidence of Crevice Corrosion Stifling in Solutions with Low Nitrate, NaCl Brines

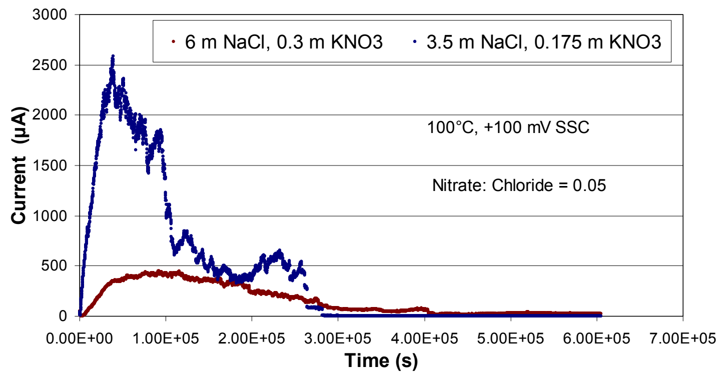


- Localized corrosion initiated by potentiostatic polarization above Ecorr and into susceptible range
- Crevice corrosion current decreased after initial spike indicating sharp drop in crevice corrosion rate

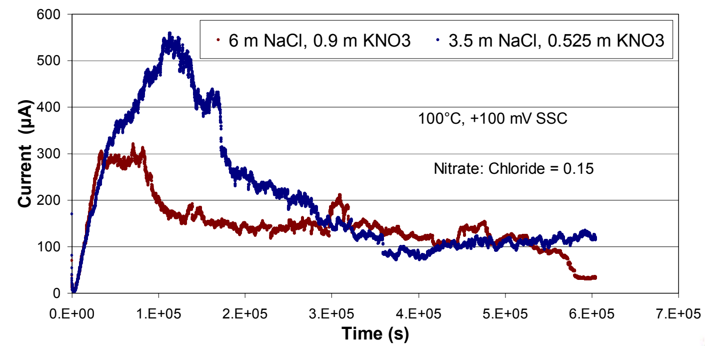
Cyclic Polarization Curve for Alloy 22 MCA Weld in 3.5 m NaCl + 0.175 m KNO_3 @ 100°C



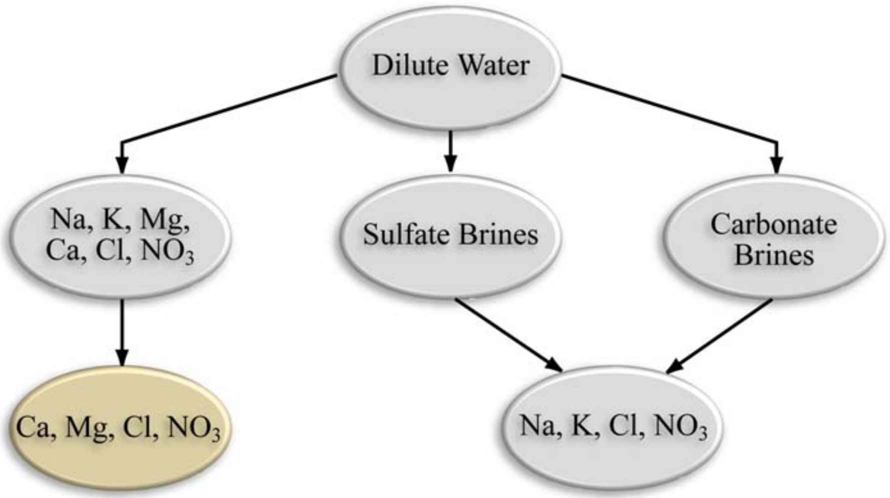
Evidence of Crevice Corrosion Stifling in Alloy 22 Welds in NaCl Brines



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

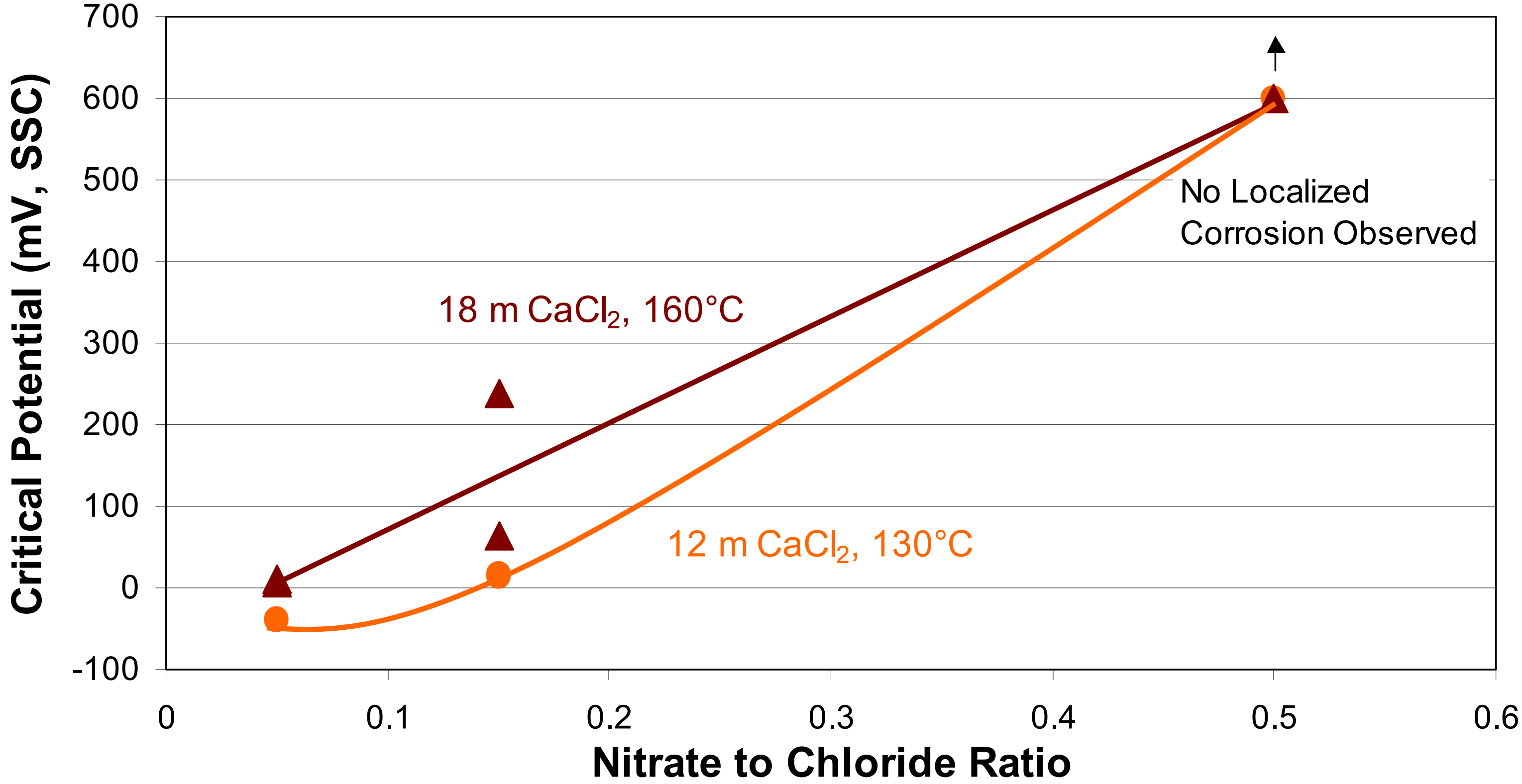


Expected Corrosion Behavior in Calcium Chloride Brine

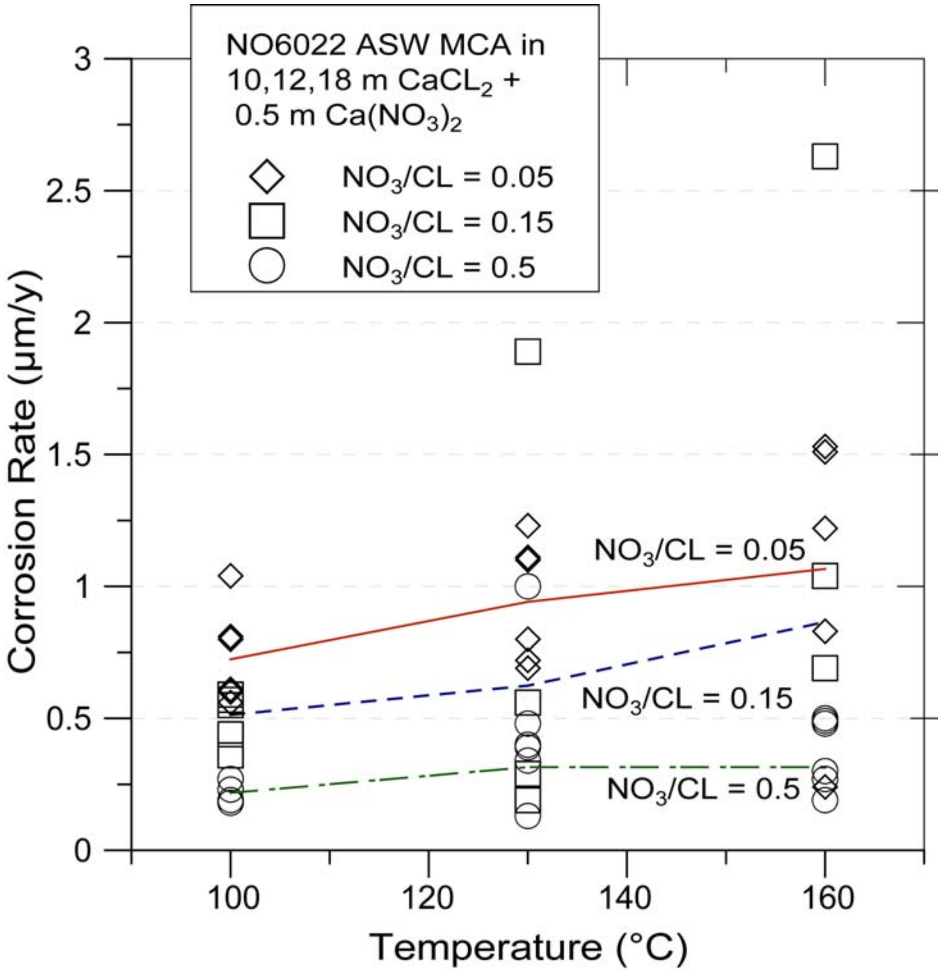


- **Localized Corrosion not expected for nitrate: chloride greater than 0.5**
- **Ca, Mg, Cl, NO_3 brines are highly unlikely in the repository**
- **Even in these aggressive brines, nitrate is found to inhibit localized corrosion at nitrate to chloride levels of about 0.5**
- **Localized corrosion possible when nitrate: chloride is below ~0.5**
- **Nitrate found to inhibit localized corrosion even up to 160°C**

Localized Corrosion Resistance of Alloy 22 Creviced Welds in $CaCl_2$ Brines at High Temperature



Effect of the Temperature and Nitrate
(Passive Corrosion Rate)



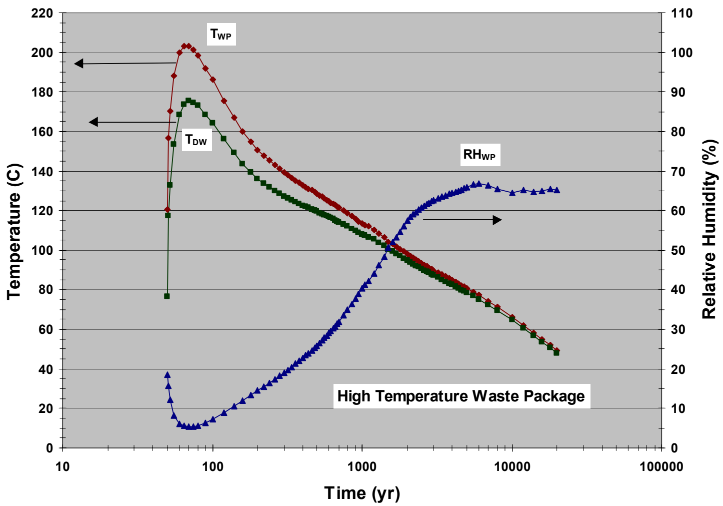
- **Rp via the Polarization Resistance Tests (G 59)**
- **Highly Concentrated $CaCl_2 + Ca(NO_3)_2$ Brines**
- **Temperatures between 100°C and 160°C**
- **The Corrosion Rate increases with the Temperature**
- **The Lower the Cl^-/NO_3^- Ratio at each Temperature the Lower the Corrosion Rate**

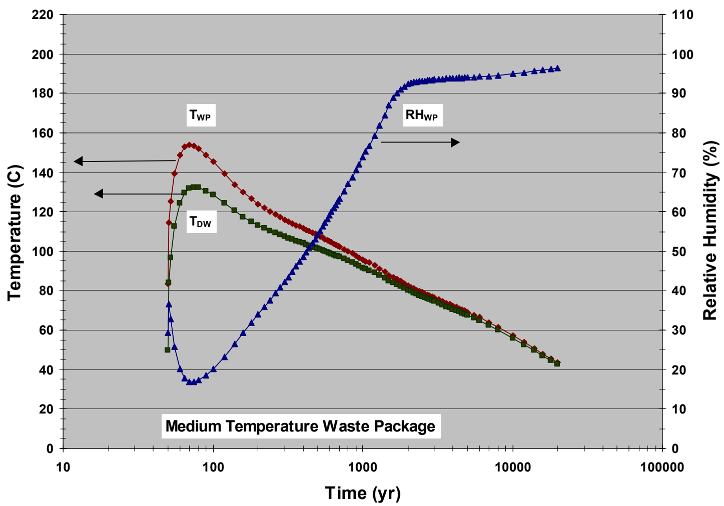
Corrosion Analysis During Period IV-Cool Down/Dripping and Seepage Possible

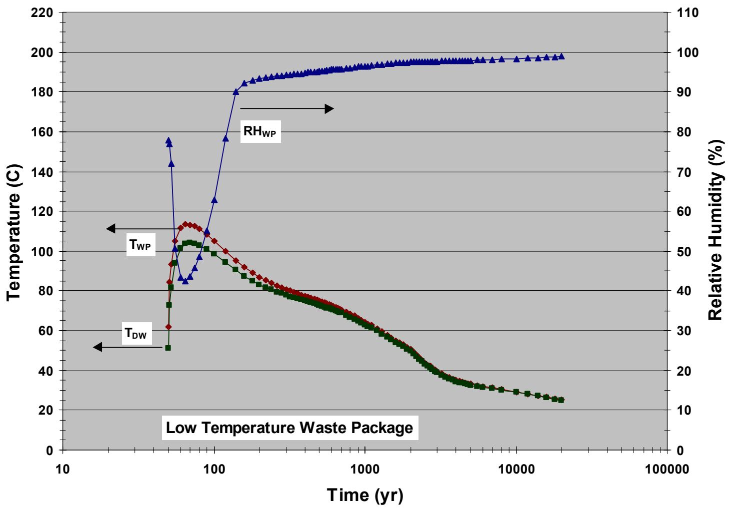
Corrosion Considerations during Period IV

- Capillary barrier and drip shield prevent corrosion
- Seepage, distribution, % Waste Packages and amount
- Composition of waters seeping—composition, concentration, total molality
- Behavior at waste package surface
- Local corrosion logic/fault tree
- Crevice corrosion decision tree
- Initiation-stifle-arrest
- Damage evolution

Period IV Conditions for Mid, Hot and Cool Waste Packages

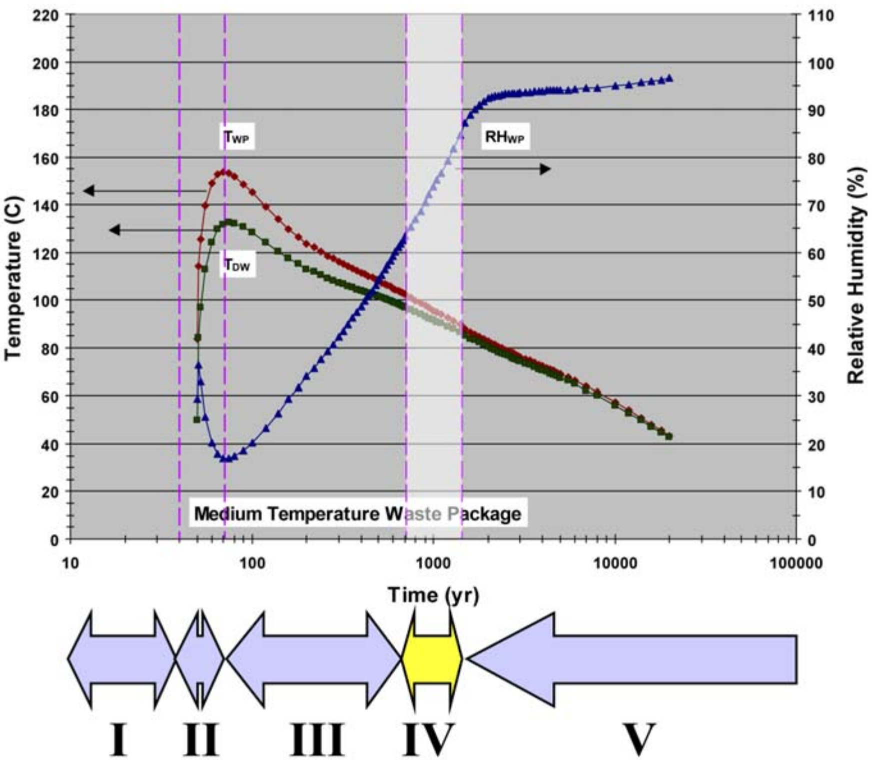


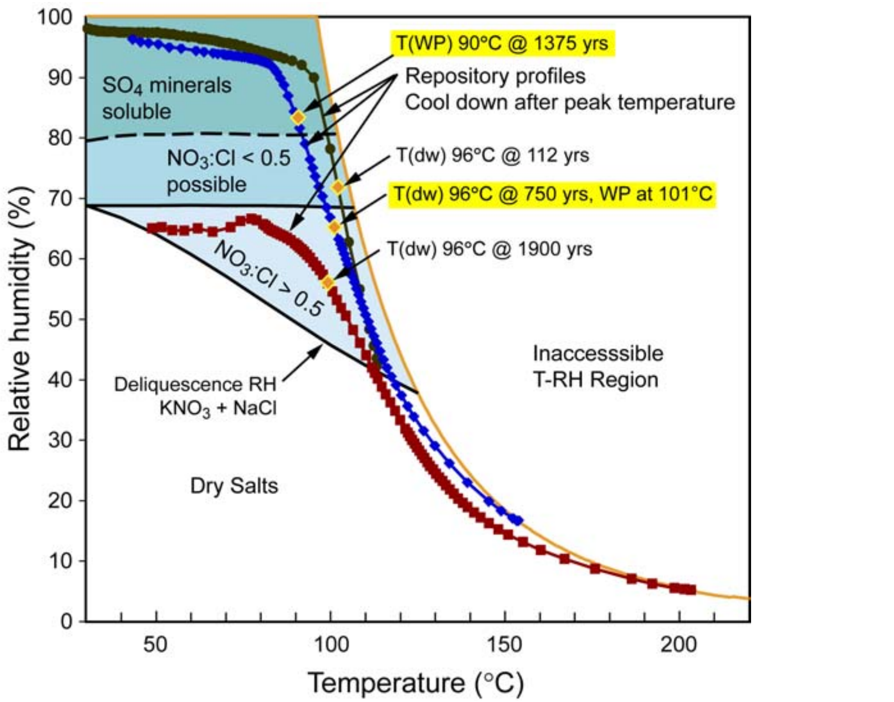




	Drift Wall 96°C			Waste Package at 90°C
	Year	Waste Package Temp °C	Relative Humidity	Year
Mid WP	750	101	65	1375
Hot WP	1900	99	56	3000
Cool WP	112	102	72	175

Period IV Analysis of T-RH-Solution Composition





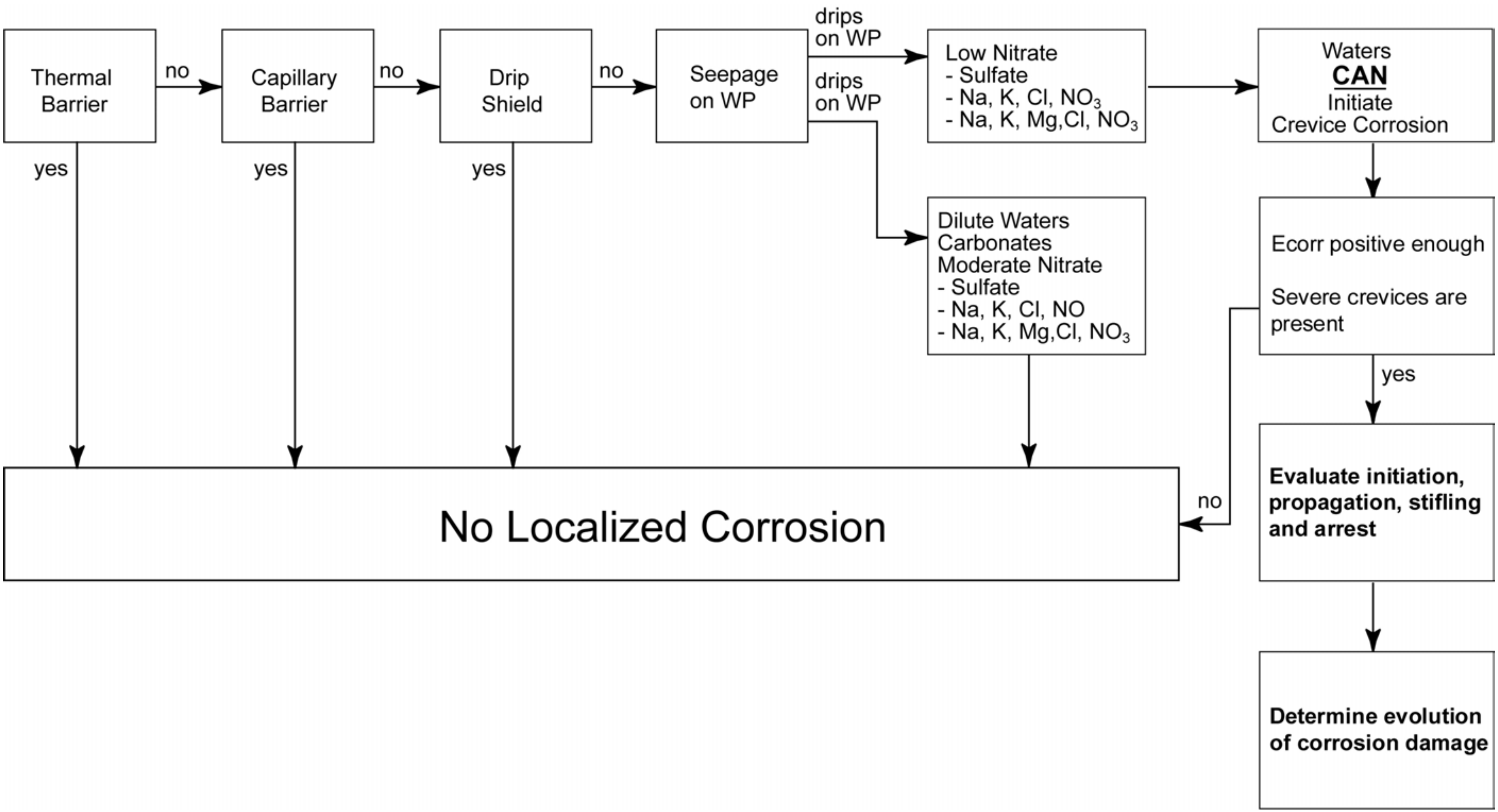
The Temp-RH at any time fixes the possible waters. Can follow the trajectory with time.

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%

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

Crevice Corrosion Decision Tree



Key Time Periods
IV-Cool Down/Dripping and Seepage Possible

- ***Follow local corrosion logic/fault tree for this;*** ***always/everywhere is unrealistic but never/anywhere is not certain; so issues are how much?, where? and damage evolution and consequences.***
- ***Use the Temp-RH behavior for waste package to determine time trajectory during this period***
- ***Use thermodynamic solution constraints for aqueous phase***
- ***Analyze conditions on waste package—consider temps; RH; amount of salts and water; mass balances***
- ***Number of non-corrosive solutions; Sodium chloride with low nitrate solutions can be corrosive***
- ***Conclusion: (a) Large areas--No significant corrosion (b) Isolated waste packages affected—Where, how much?***

Conclusions

Conclusions
Corrosion Resistance of Alloy 22

- **Alloy 22 is a highly corrosion resistant metal**
  - **Confirmed by laboratory evaluations in harsh environments**
  - **Verified by industrial experience, e.g. Flue Gas Scrubbers with high temperature, oxidizing strong acids, chlorides and complex, multi-species solutions**
- **Yucca Mountain Repository Conditions**
  - **Waste Packages sit in air**
  - **Ambient waters are dilute and non-corrosive**
  - **Highly concentrated waters can form under repository conditions**

Conclusions
Corrosion Resistance of Alloy 22
(Continued)

- **Corrosion resistance is crucial to waste package performance**
- **Passive metals (Alloy 22 and Titanium) have extremely low corrosion rates**
  - Corrosion rates of passive Alloy 22 are measured to be 0.1 to 0.01 micron per year in long term exposures
  - At these rates, the thickness of a U.S. quarter lasts 1,600 to 160,000 years and waste packages are 12 quarters thick
  - Alloy 22 is passive over a wide range of realistic, repository conditions
  - Major effort was undertaken to examine the potential for damage by corrosion

Conclusions Corrosion Resistance of Alloy 22

(Continued)

- A hierarchy of factors prevent dripping onto waste packages
  - Thermal barrier, capillary barrier, and drip shield
  - Dripping is over a fraction of waste packages and the amount of seepage is small
- Where no drips fall upon waste packages
  - Deliquescent corrosion conditions pertain
  - No significant corrosion damage results
- Where drips fall upon waste packages
  - Evaluate the environment (waters) on the waste package and the likelihood of localized corrosion
  - Apply these evaluations to the relevant time periods of the repository

Conclusions
Corrosion Resistance of Alloy 22
(Continued)

- Five relevant time periods were identified for repository
- Conditions to support localized corrosion are possible only during Period IV
  - Drift wall is below boiling
  - Waste package above critical corrosion temperature
  - No corrosion when capillary barrier or drip shield are operative
- Analyze conditions on waste package
  - Number of non-corrosive waters form
  - Sodium chloride waters with low nitrate can be corrosive
- Follow the logic/fault analysis for cases with corrosive waters

Conclusions
Corrosion Resistance of Alloy 22
(Continued)

- No significant corrosion outside of Period IV
- Environments during Period IV
  - Potential to form corrosive waters on waste package restricted by Temperature-Relative Humidity
  - Distribution and volume of corrosive waters are limited
- Corrosion behavior for Period IV conditions
  - Alloy 22 has high corrosion resistance in many waters
  - Currently, localized corrosion is highly restricted, but can not be ruled out in all cases
  - Several factors stop and impede localized corrosion damage to Alloy 22
- Overall conclusion: (a) Large areas—no significant corrosion (b) Isolated waste packages may be affected
  - Always/everywhere is unrealistic
  - Never/anywhere is closer to reality but not certain