U.S. Department of Energy
Office of Civilian Radioactive Waste Management

Question 1: Alloy 22 Corrosion Rates: Current Status, Uncertainties and Approach for Extrapolation to Long Times

Presented to:
Nuclear Waste Technical Review Board

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YUCCA MOUNTAIN PROJECT

Outline

- **Basis for Alloy 22 selection for current waste package**
- **Current status**
  - **General Corrosion over long times**
  - **Localized Corrosion**
  - **Waste Package Environment**
  - **Long Term Passive Film Stability**
- **Path Forward to reduce remaining uncertainties**
- **Conclusions**
- **Backups**

Question No. 1

- What is current theoretical and empirical basis for extrapolating the behavior of Alloy 22 for extremely long periods (e.g. 10,000 years)?
  - Alloy 22 corrosion behavior is currently empirically extrapolated from a large data base of weight loss corrosion rate measurements out to 2.3 years exposure in a range of repository relevant environments.
  - Theoretical considerations on the margin that will be maintained over time against the initiation of localized corrosion (higher rates) include
    - the expected increasing potential difference between the expected slight increase in corrosion potential (due to increasing oxygen solubility) as the repository temperature drops as compared to the greater observed increase in passive film breakdown potential will increase margin with time.
    - also, the maximum corrosion potential is upper-bounded by the oxygen evolution potential in aerated water and that potential tends to lie below the passive film breakdown potential.
    - In addition, the corrosion potential is set by the mixed potential on the metal surface from the likely reactions due to metal oxidation and oxygen reduction. Since the observed corrosion rate vs. time decreases and appears to be approaching a very small, steady state value, any increase in mixed potential should remain small.

Question No. 1

- What are significant gaps in understanding that exist?
  - Potential gaps in understanding relate to issues such as mechanisms that could degrade the protective nature of the passive film over time, minor element effects on localized corrosion under repository conditions, the possibility that some unknown mechanism could increase corrosion potential to passive film breakdown potential levels, the possibility that residual stress mitigation processes to preclude stress corrosion could unduly degrade the alloys corrosion resistance.
- How might gaps be closed and how long would it take?
  - As described in presentation, there is an extensive path forward effort focused on providing experimental and theoretical support to further increase confidence and decrease uncertainties in each of these areas. This effort will yield a significant supporting body of data by Site-Recommendation and additional data by License Application.
- How much of a reduction in uncertainty is likely to take place if that additional work is performed?
  - Although, as described in presentation, there is a good basis for current confidence in expected long term performance, as results become available from these efforts, the degree of confidence will continually increase.

Question No. 1

- Is that additional work necessary for making a site-recommendation decision? Why or why not?
  - As described previously under “Gaps in Understanding”, there are potential life shortening issues that are not expected, based on currently available results. However, path forward efforts will provide significant additional confidence in these areas by site-recommendation and even more confidence by License Application.

Question No. 1

- For example, TSPA predicts that localized corrosion of Alloy 22 will never occur in Yucca Mountain because the models used in TSPA rely on the open circuit potential of Alloy 22 never approaching or exceeding a certain critical localized corrosion potential. What theory, data, analysis, etc. form the basis for believing that open circuit potential will not change significantly over extremely long periods?
  - This theory and data are summarized under the previous answer to the first part of this question and is covered in more detail through the balance of the presentation. Of course, the confidence in any long term prediction of corrosion potential trend and passive film stability will increase as longer term data become available. As described in the Path Forward efforts (backup slides), it is planned to obtained 5 and 10 year LTCTF results and much longer term corrosion measurement results as part of the planned performance confirmation program (that will last up to repository closure) along with extensive supporting information and mechanistic model development that will provide a better basis for extrapolation over time

Basis for Alloy 22 Selection

- **Alloy 22 is fourth generation in C-family of increasingly corrosion resistant Nickel-base alloys**
  - Haynes and others discovered Ni-Cr alloys ca. 1898
  - Alloy C* developed by Union Carbide in 1930's (Ni-Cr-Mo-W alloy with <0.15% C)
    - Alloy C maintains passivity (retains mirror finish) after ~57 years seaside exposure at Kure Beach test facility
  - Alloy C-276 developed by BASF in early 1960's (Ni-Cr-Mo-W alloy with <0.02% C)
  - Alloy C-4 developed in 1973 (Ni-Cr-Mo alloy with <0.015% C)
  - Alloy C-22 developed in 1981 (Ni-Cr-Mo-W alloy with <.015% C)
- **Major Alloy 22 applications in highly corrosive environments (flue gas scrubbers, chemical process fluids, down hole tubing, pulp bleach systems, etc.)**

*** Compositions listed in backup charts**

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

Basis for Alloy 22 Selection

- **YMP test results (to be reviewed) under broad range of repository relevant environments provide basis to describe expected corrosion behavior**
- **Combination of industry plus project results provide basis for confidence in empirically projected long-term performance**
- **Detailed experimental program and theoretical corrosion model development and qualification underway to reduce remaining uncertainties associated with long-term performance**

Current Status

- General Corrosion over long times
- Localized Corrosion
- Waste Package Environment
- Long Term Passive Film Stability

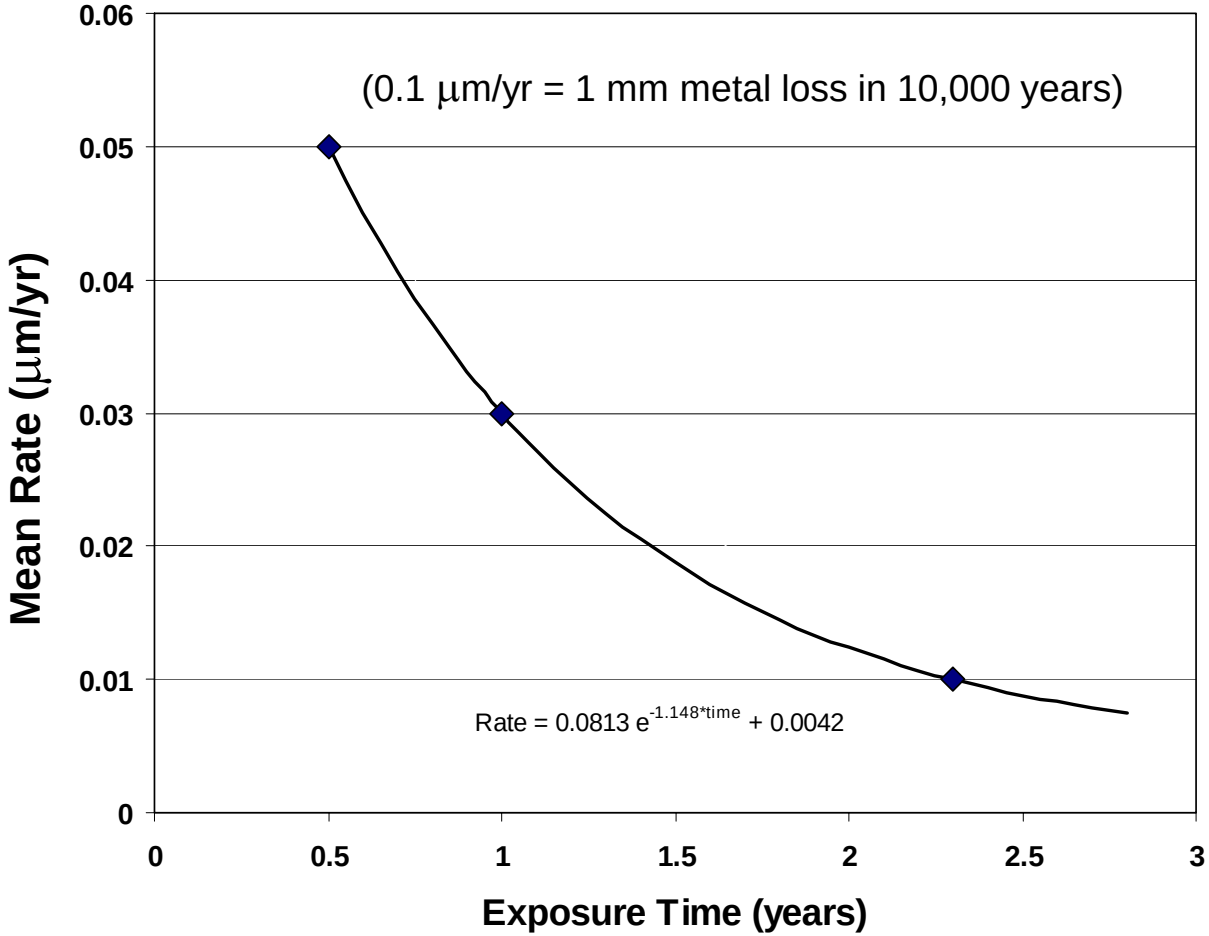
General Corrosion — Status

- **Available long-term (LT) and short-term (ST) corrosion test results generated on uncreviced, creviced, annealed and welded Alloy 22 in a range of concentrated J-13 environments**
  - **J-13 concentrated by ~10X to 3000X (LT), to 50,000X (ST)**
  - **pH adjusted over range of ~ 2.7 to 9.9 (LT), to 13 (ST)**
  - **Carbonate (e.g. concentrated J-13 waters) and carbonate-free (e.g. concentrated pore waters) environments**
  - **Test temperatures of 60 and 90°C (LT), 30 -120°C (ST)**
- **Upper bound rate of 0.07 µm/year measured after 2.3 years in long term corrosion test facility (LTCTF)**
  - **mean rate = 0.01 µm/year or 100 angstroms/year**
- **Measured rate decreasing with time as expected**

Alloy 22 Corrosion Rate vs. Time

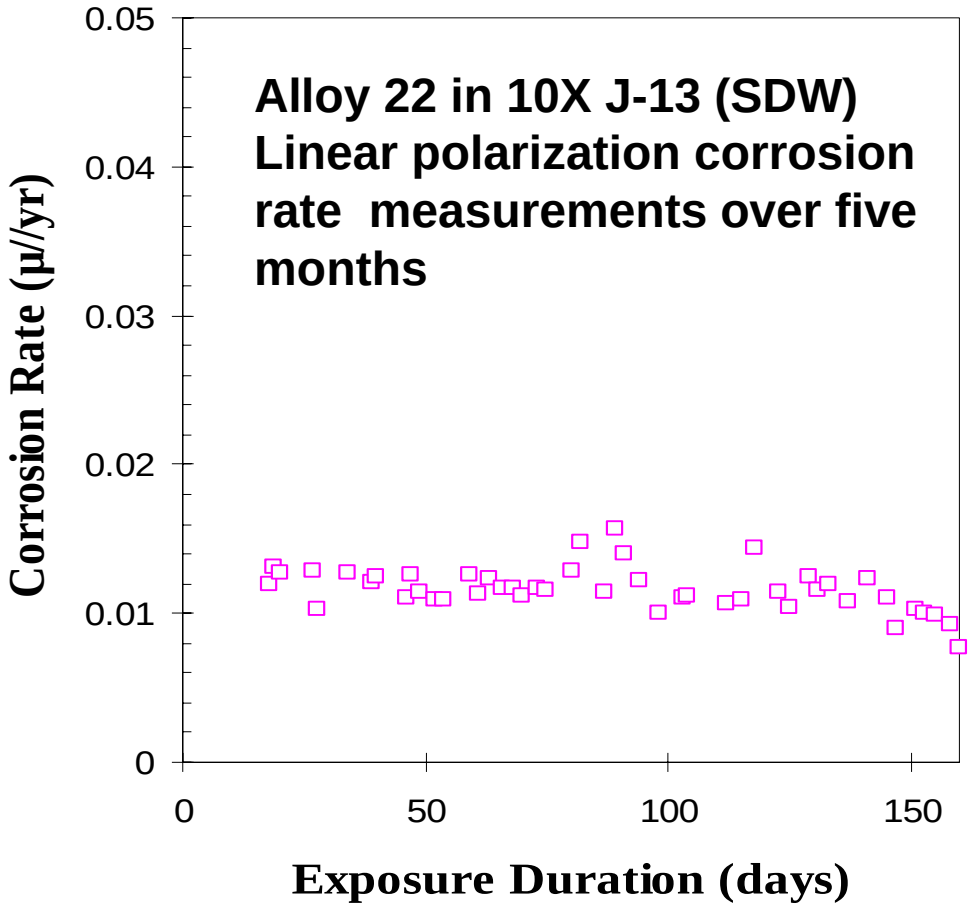
Alloy 22 Mean Corrosion Rates Measured at 60ºC and 90ºC in Long-Term Corrosion Test Facility (LTCTF) in Range of Relevant Environments

(Each data point mean of measurement on at least 144 specimens)



Two year rate conservatively selected as basis for extrapolation over time

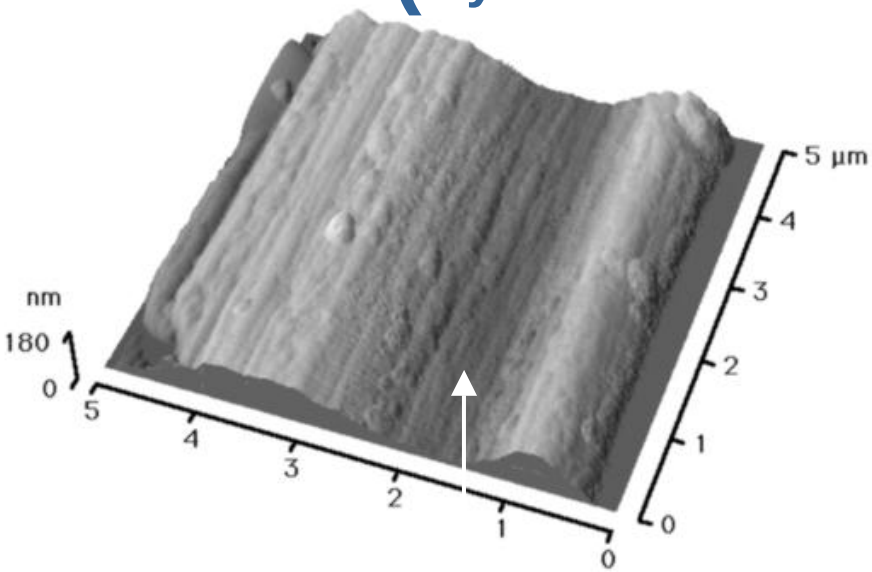
Electrochemical Confirmation of Weight Loss Rate Measurements



Electrochemically measured rate (~0.011 µm/yr) equivalent to two-year mean rate measured by weight loss

Atomic Force Microscopy of Alloy 22 Surface Exposed to Vapor Phase

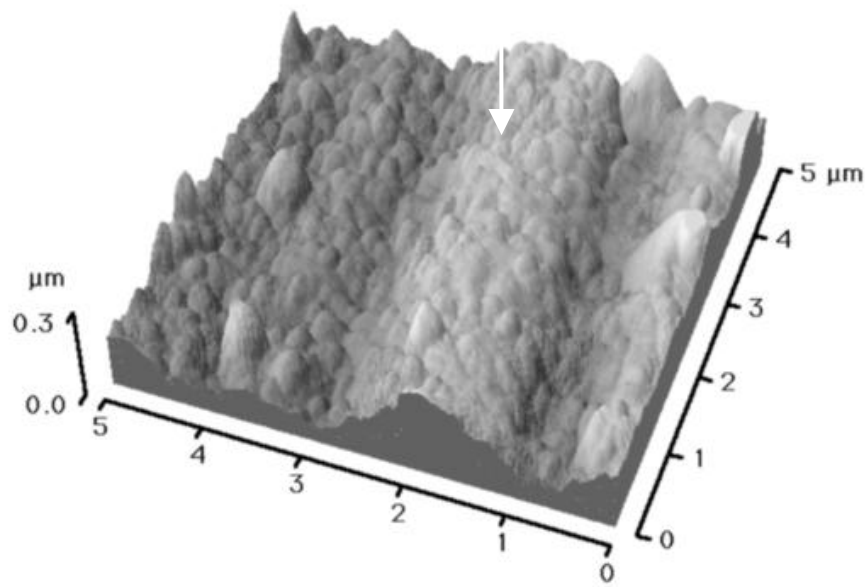
(1 year at 90°C in simulated acidic water)



Scratch from surface finishing

No Exposure
(control sample)

General corrosion



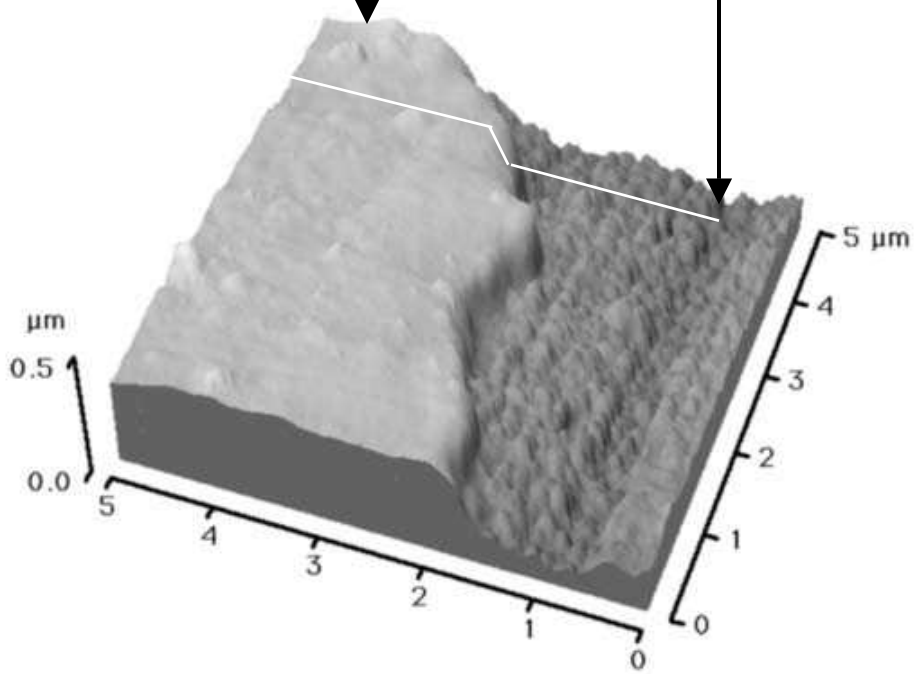
One year oxide thickness from weight loss measurements (~0.01 to 0.1microns) consistent with microscopic observations

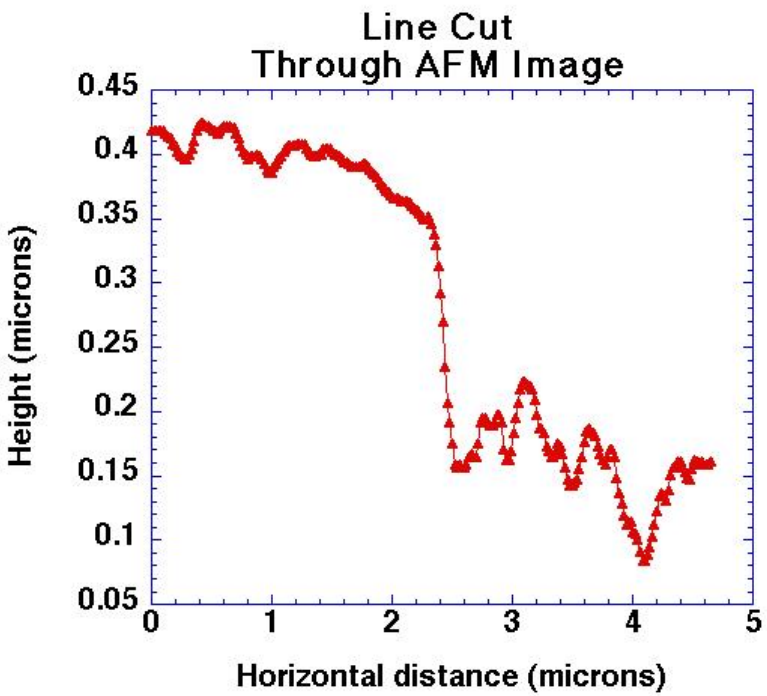
Atomic Force Microscopy of Alloy 22 Surface Exposed to Liquid Phase

(1 year at 90°C in simulated acidic water pH = 2.7)

Silica rich surface deposit observed on some weight loss specimens

Scratch from surface finishing

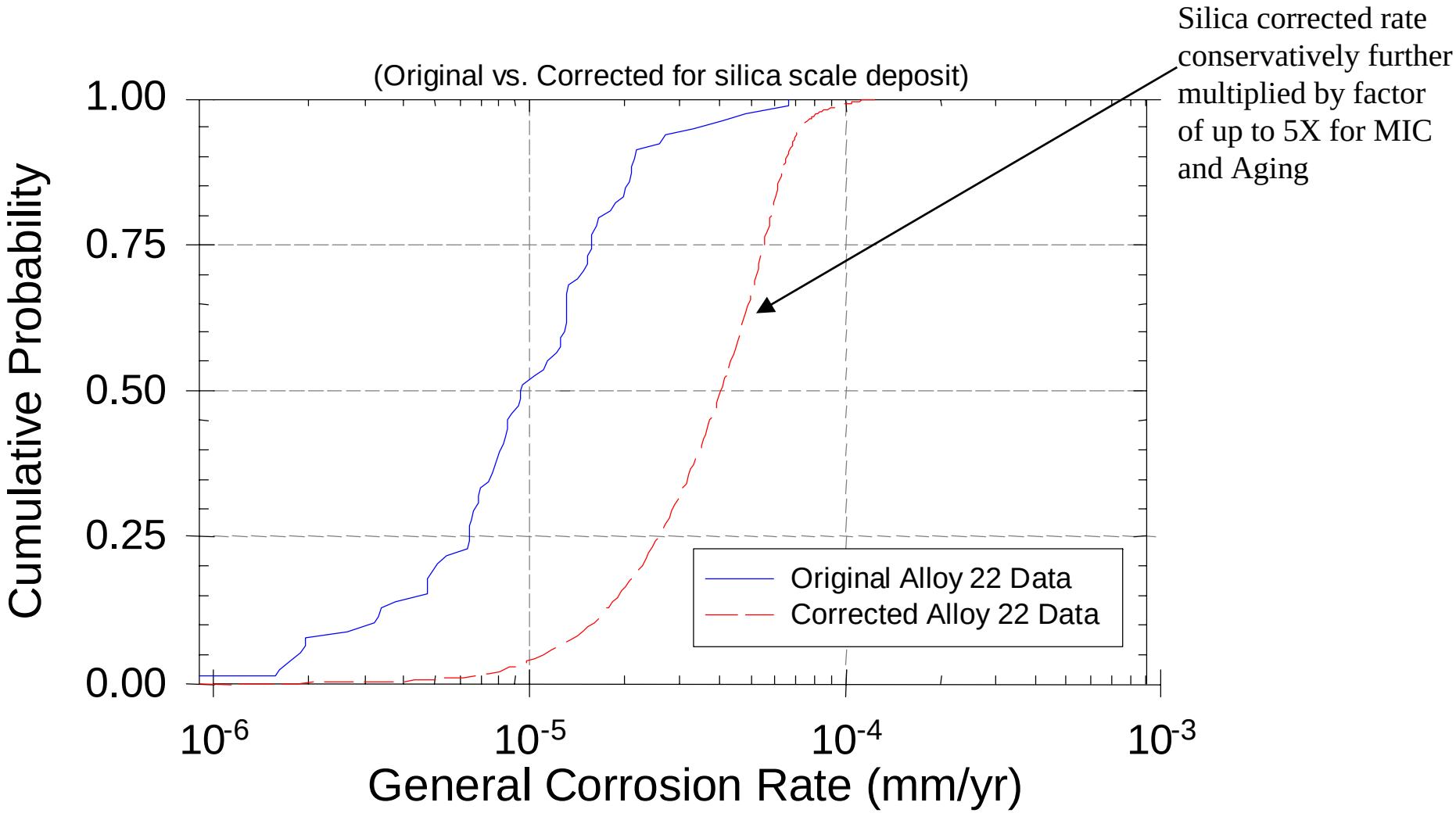




Maximum silica deposit thickness measurement of ~ 0.25 microns equivalent to incremental corrosion rate of 0.063 microns/year

Cumulative Probability Distribution of Two-Year General Corrosion Rates

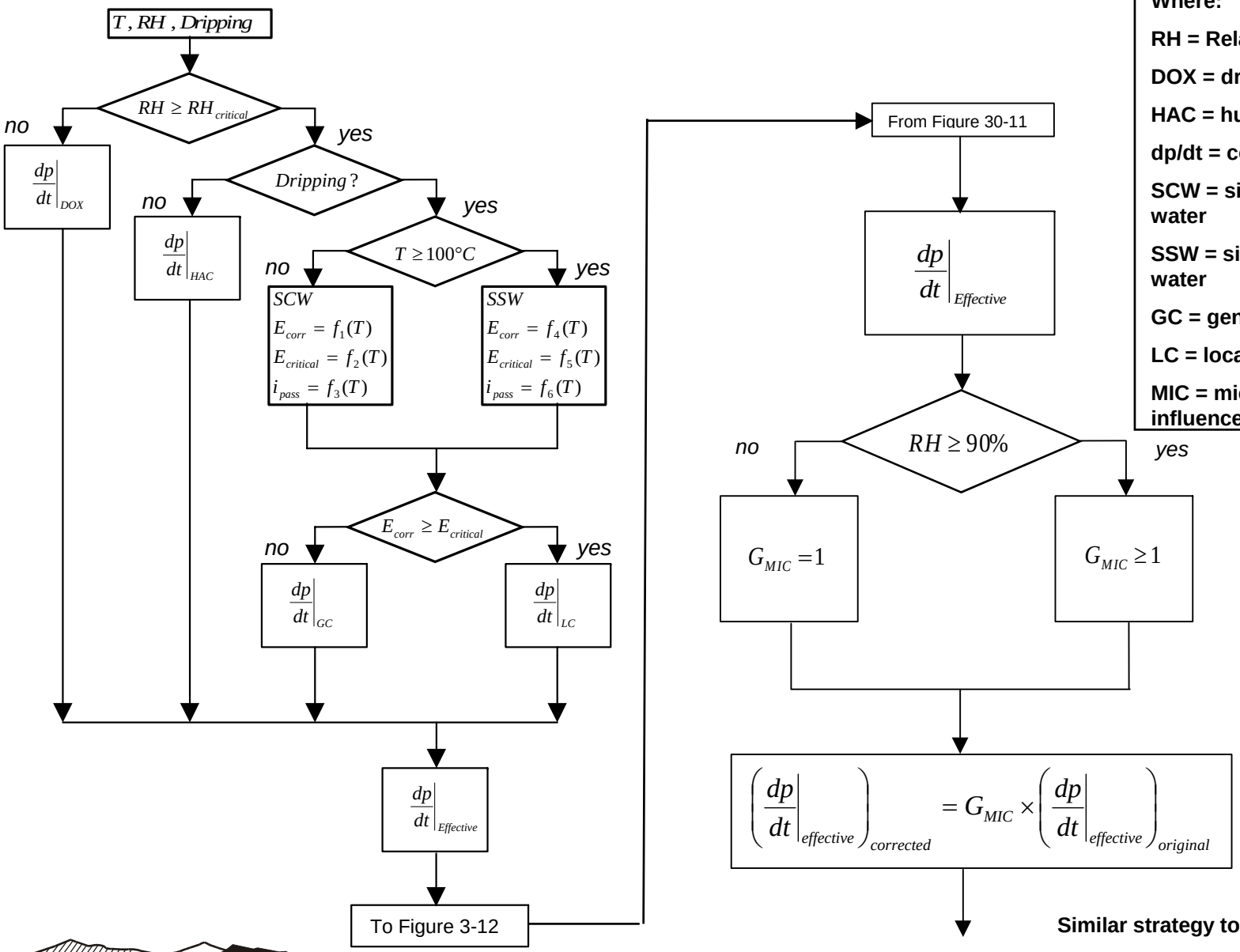
(Rate distribution and uncertainties accounted for in corrosion model)



Introduced Conservatism's

- **Measured rates conservatively increased in corrosion model used to account for unexpected but possible accelerating factors**
  - **Corrosion rate increased by**
    - **0.063 µm/year to account for possibility of silica deposition affecting weight loss measurement**
    - **factor of 2X for microbiologically influenced corrosion possibility**
    - **factor of 2.5X for thermal aging possibility**
- **Environment on waste package surface also conservatively assumed to be same as on drip shield with dripping if relative humidity ≥ 50%**

Schematic of Corrosion Model



Where:

RH = Relative humidity

DOX = dry air oxidation

HAC = humid air corrosion

dp/dt = corrosion rate

SCW = simulated concentrated water

SSW = simulated saturated water

GC = general corrosion

LC = localized corrosion

MIC = microbiologically influenced corrosion

Similar strategy to account for aging

General Corrosion — Status

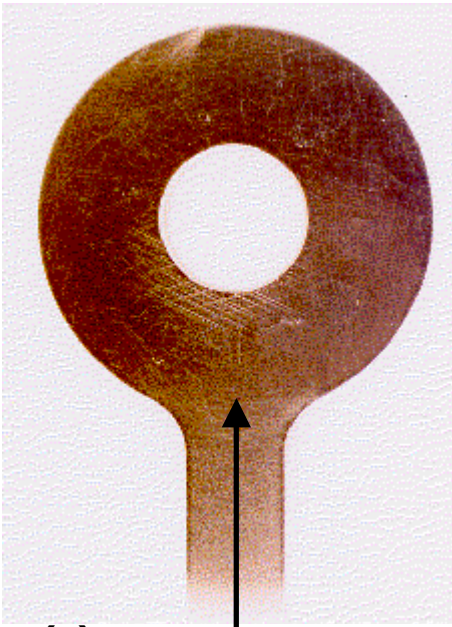
- **In addition to excellent but relatively shorter-term Alloy 22 LTCTF experimental results and commercial alloy analog performance,**
  - **longer term exposure of less corrosion resistant nickel-iron alloy "mineral", Josephinite (Ni_3Fe), indicates passivity can apparently be maintained for many millennia**
  - **Therefore, confident that significantly more corrosion resistant Alloy 22 will maintain passivity for required period under repository exposure conditions**
  - **However, extensive 'Path Forward' efforts underway to further decrease uncertainties**

Localized Corrosion Status

- **Localized corrosion not expected under range of potential repository aqueous conditions [buffer/inhibitor ion(s) always present, $E_{corr} < E_{crit}$]**
  - **Resistance confirmed by extensive project and literature data**
  - **However, as expected, localized corrosion of Alloy 22 can occur under very oxidizing conditions (high applied potentials) in concentrated chloride solutions without beneficial buffer/inhibitor ions (NO_3^-. $CO_3^=$, $SiO_4^=$, $SO_4^=$, etc.)**

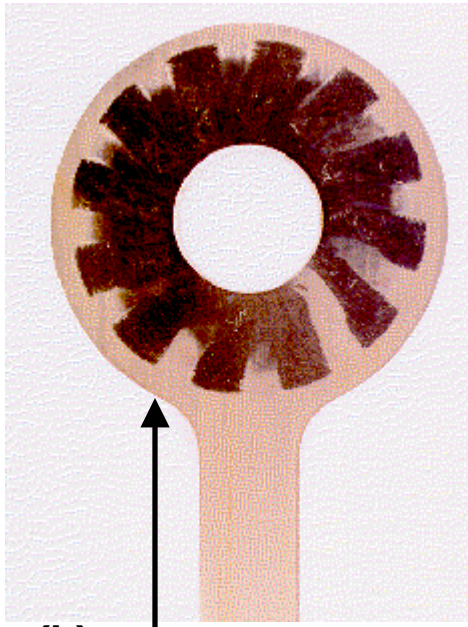
Crevice Corrosion in Relevant Environment (BSW) and in NaCl

Alloy 22 Crevices
Ceramic Washer
Ramped to 550 mV
~ 100°C BSW



(a)
No crevice attack

Alloy 22 Crevices
Teflon Washer
Ramped to 800 mV
~ 110°C BSW



(b)
Stain but no crevice attack in BSW

Alloy 22 Crevices
Ceramic Washer
350 mV for 2 hours
~ 100°C 4M NaCl

(c)
Severe crevice attack of sample

[BSW test solution contains ~9% Cl^-, 9% NO_3^-, 0.6% $SO_4^=$, 0.1% F^-, 0.1% S $iO_4^=$]

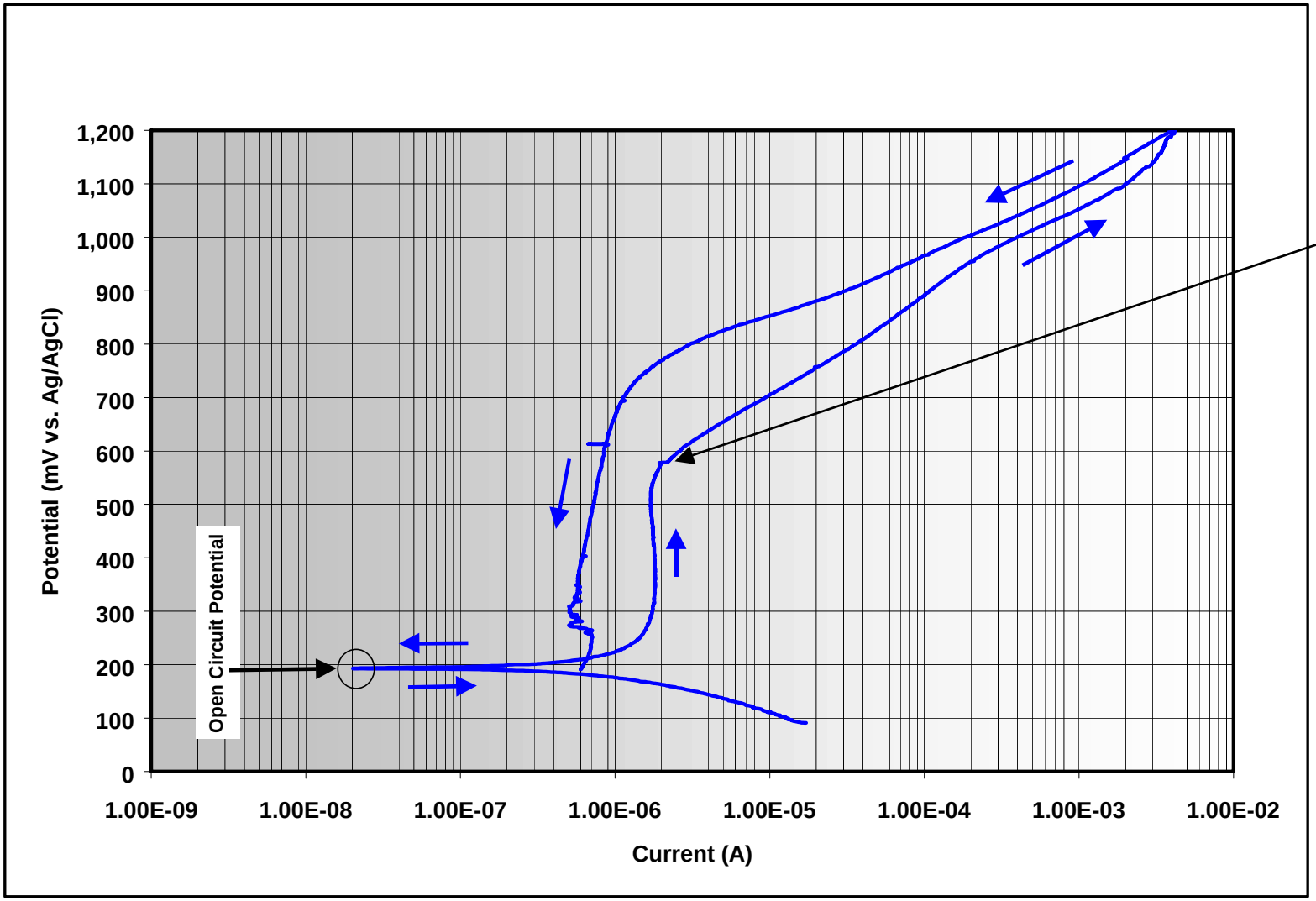
Crevice corrosion not observed with repository relevant buffer ions

Localized Corrosion Status

(Continued)

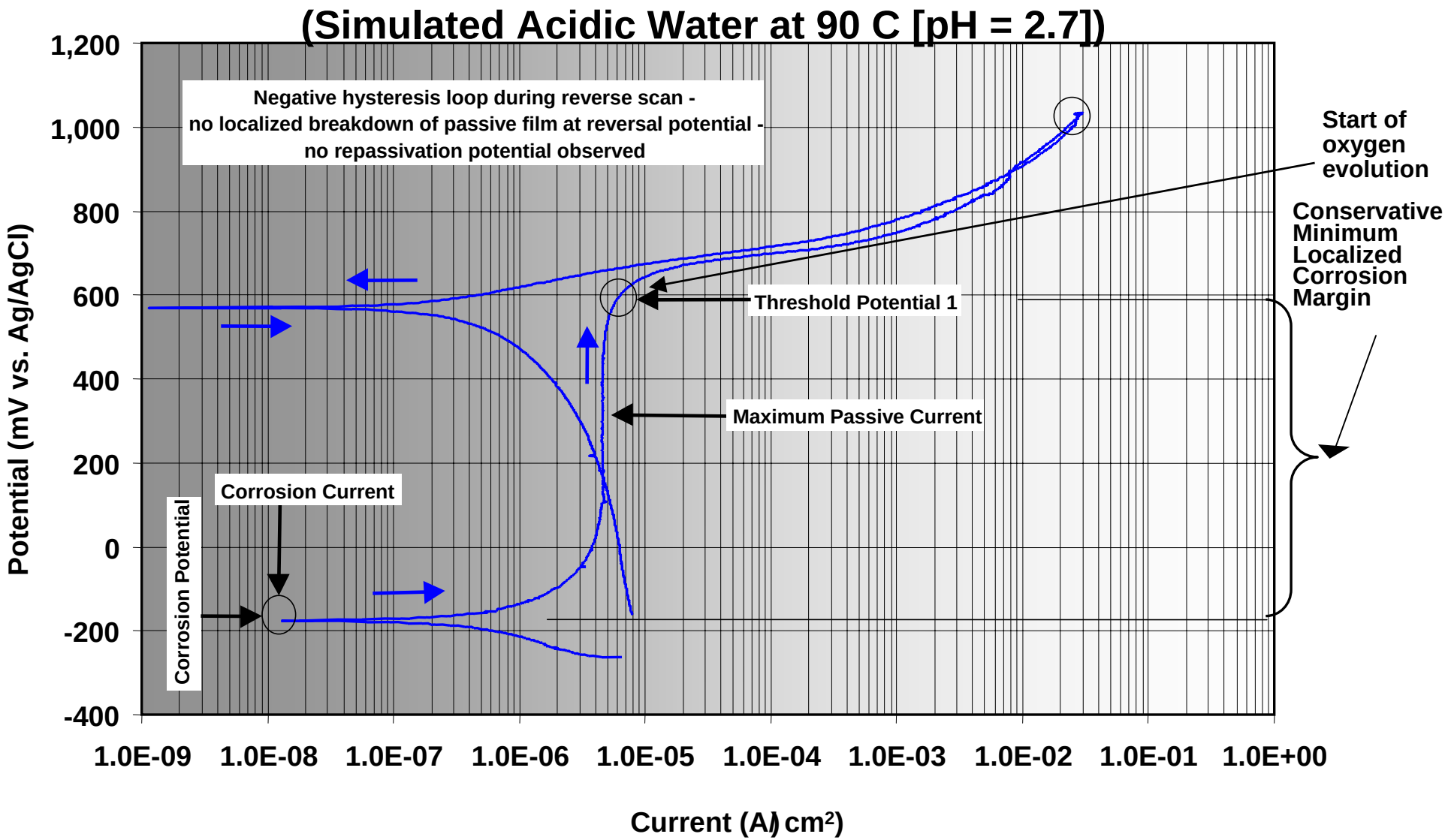
- Crevice corrosion can occur when corrosion potential exceeds passive film breakdown potential, i.e. critical potential or repassivation potential
- Significant margin observed between measured corrosion potentials and passive film breakdown potentials over range of relevant environments
  - Cyclic polarization measurements of crevice corrosion resistance consistent with measurements taken on creviced specimens in long-term corrosion tests where no crevice corrosion observed

Cyclic Polarization of Platinum in Simulated Concentrated J-13 at 90°C



Start of oxygen evolution

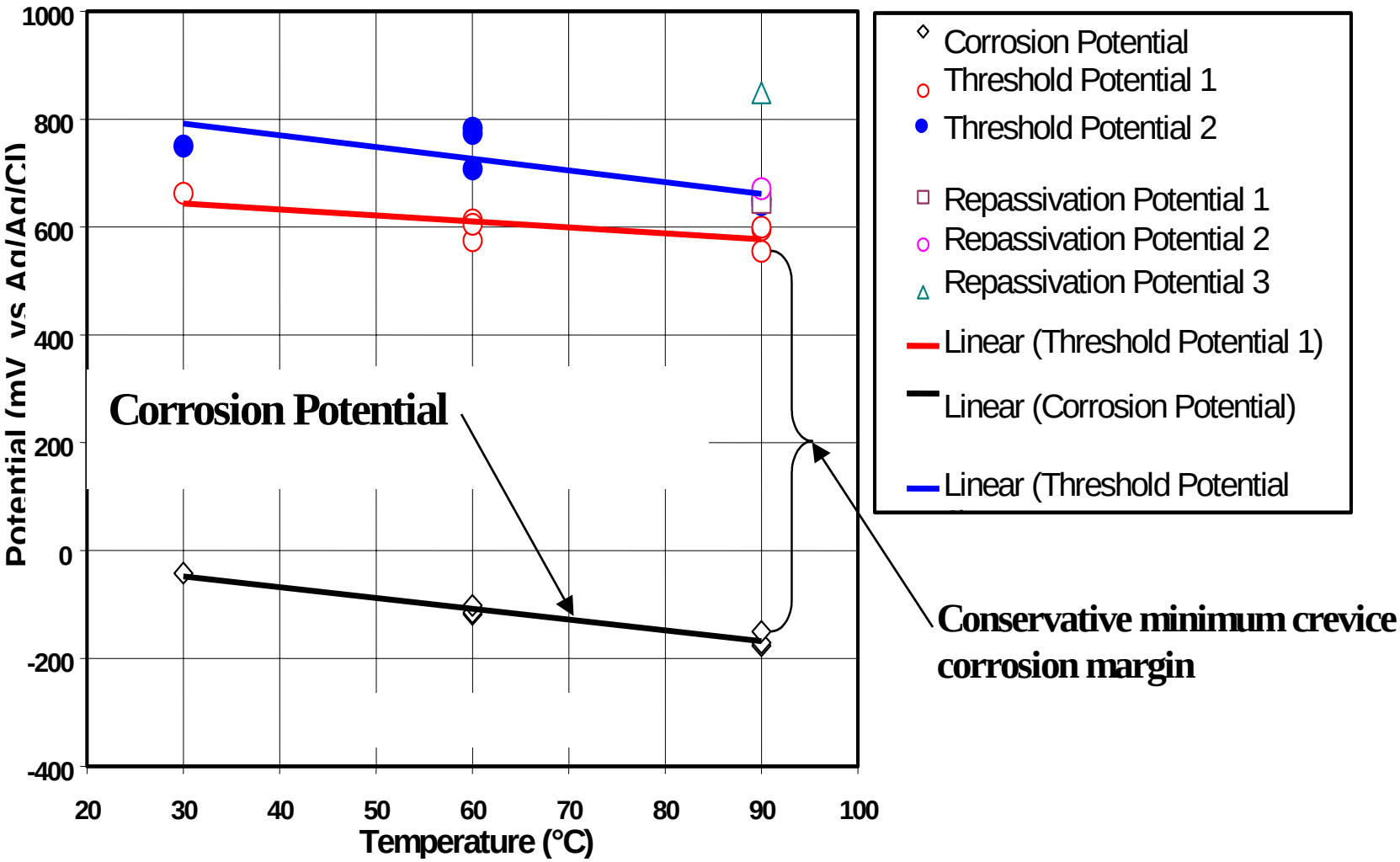
Typical Alloy 22 Cyclic Polarization Curve



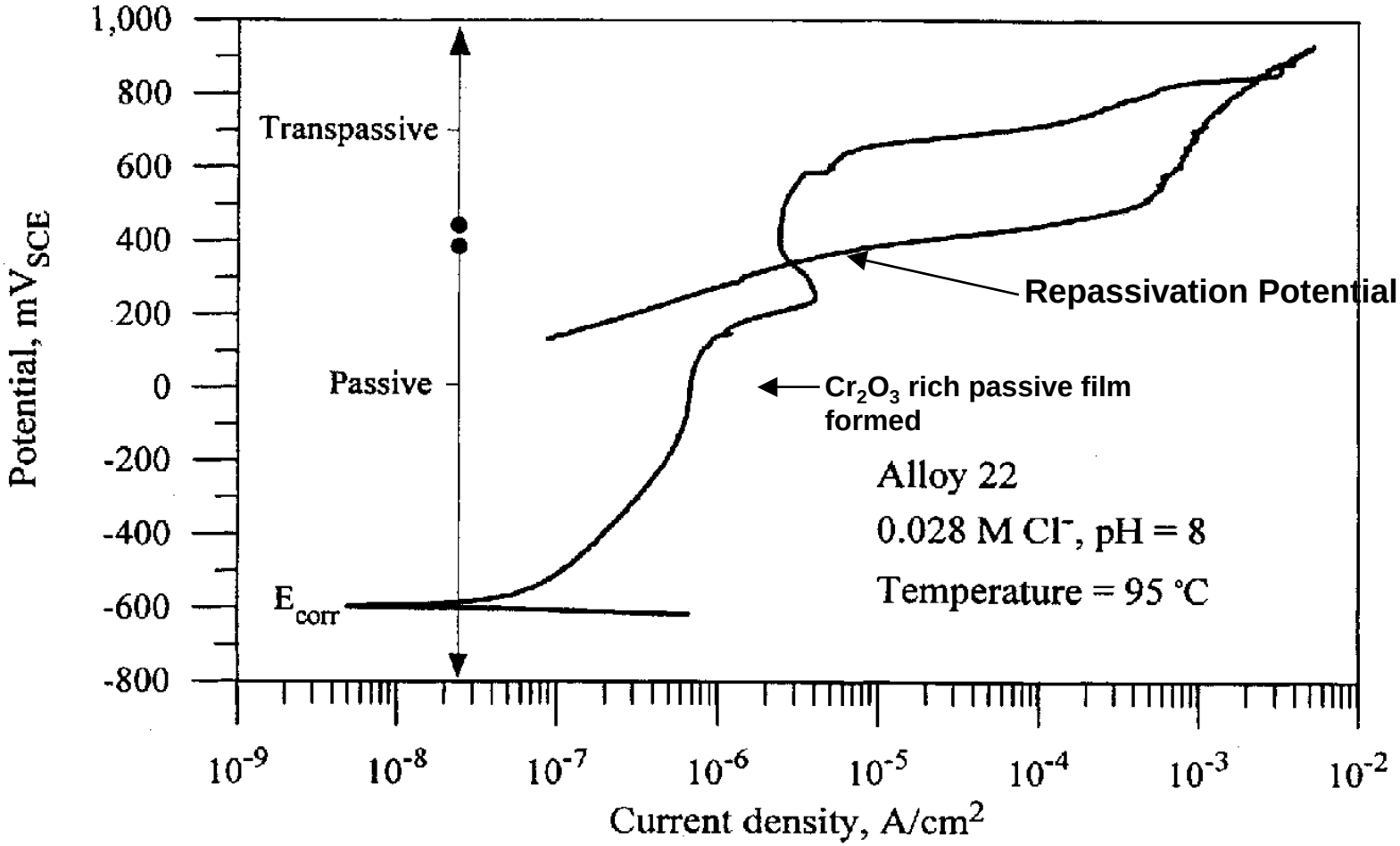
No localized corrosion observed at potentials < 1000 mV vs. Ag/AgCl in relevant acidic environment

Alloy 22 Potentials vs. Temperature

Tested in Acidic [pH = 2.7], Concentrated J-13 (Simulated Acidic Water)



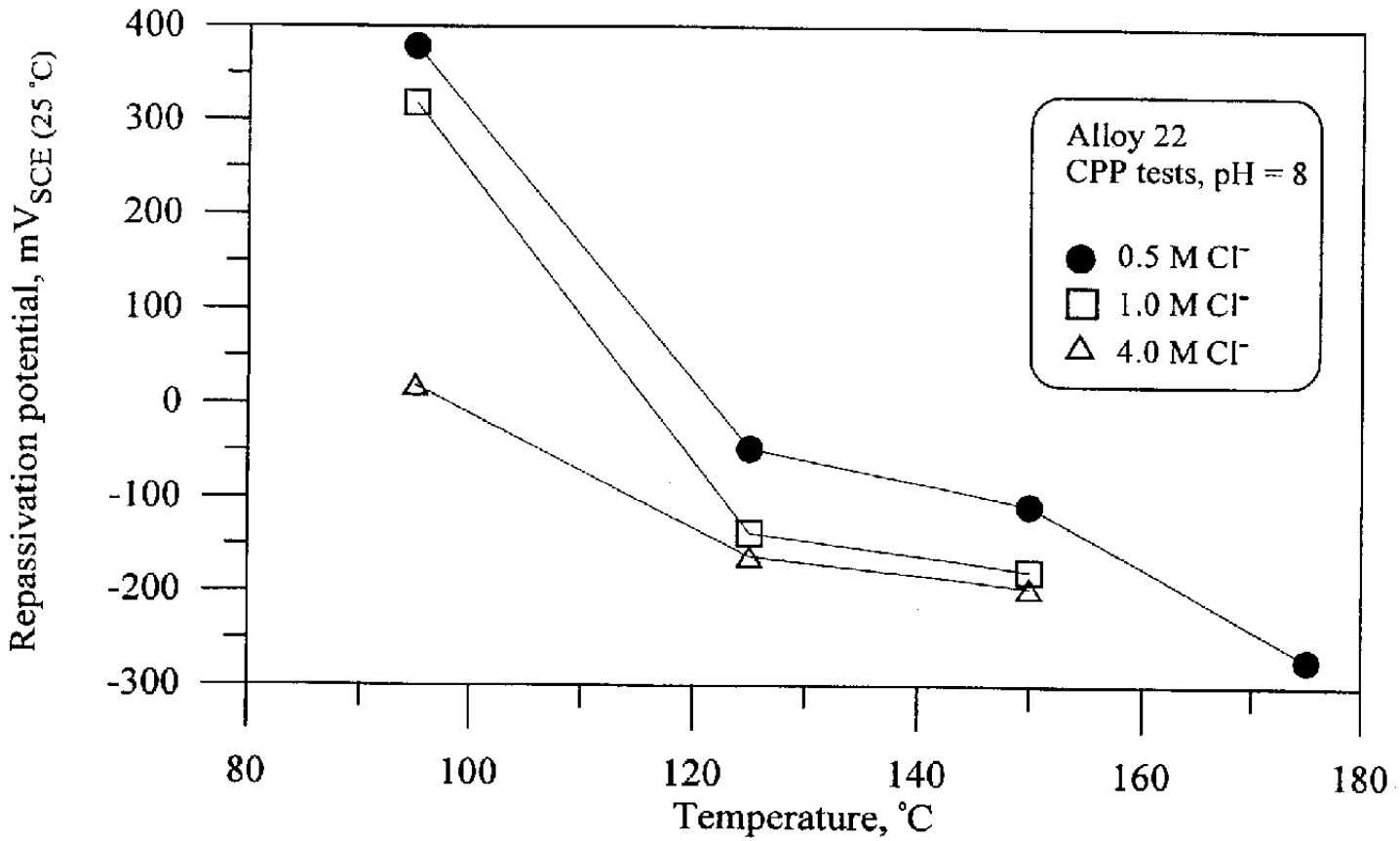
Typical Alloy 22 Cyclic Polarization Curve in NaCl Solutions



Repassivation potential: lowest potential at which crevice corrosion can occur once initiated at higher potentials

[Cyclic polarization results obtained by USNRC (CNWRA 99-004)]

Alloy 22 Repassivation Potential vs. Temperature in NaCl Solutions



Repassivation potential increases rapidly as temperature drops leading to increased crevice corrosion margin

(Alloy 22 data from USNRC CNWRA 99-004)

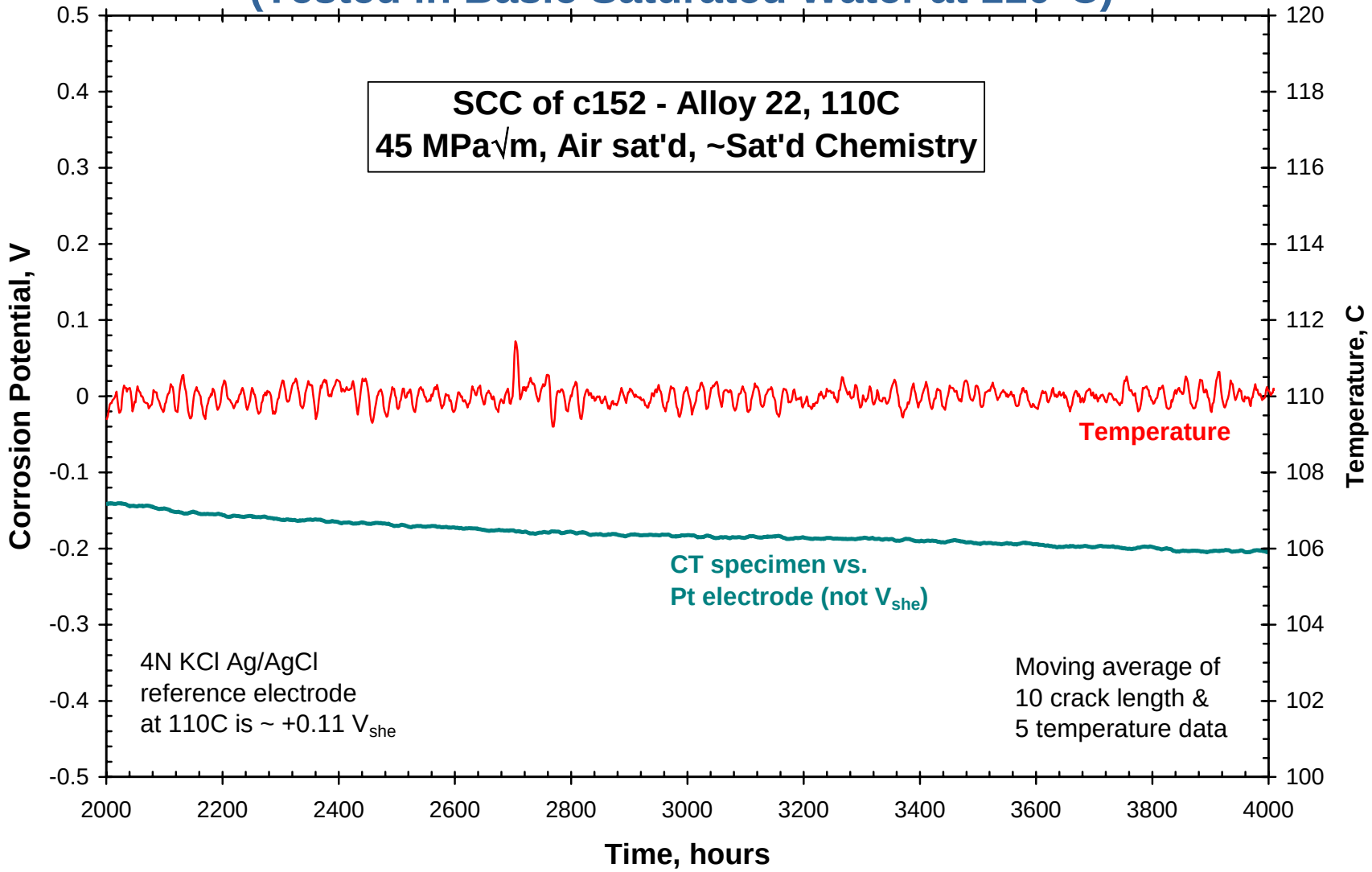
Localized Corrosion Theoretical Considerations

- **As temperature drops over time**
  - **oxygen solubility increases somewhat resulting in small corrosion potential increase per Nernst Equation**
    - **consistent with observed behavior**
  - **repassivation potential also increases with steeper slope than for corrosion potential**

- **Very low Alloy 22 corrosion rate approaching steady state after ~ 2 years**
  - **will minimize tendency for corrosion potential to drift upward with time, i.e. mixed potential should remain relatively stable**
    - **No upward drift noted in basic saturated J-13 water at 110°C after ~4,000 hours exposure**
    - **In process of measuring corrosion potential after three years exposure in LTCTF to confirm absence of significant upward drift with time**

Alloy 22 Corrosion Potential vs. Time

(Tested in Basic Saturated Water at 110°C)



Corrosion potential at a given temperature drifting slowly downward over time

Localized Corrosion Theoretical Considerations
(Continued)

- **Maximum corrosion potential in repository relevant environments limited to oxygen evolution potential (highest relevant redox system) which lies below passive film breakdown potential**
- **Literature indicates Ni-Cr-Mo alloy corrosion films consist of two layers,**
  - **a very thin (~100 angstroms), thermodynamically stable Cr_2O_3 rich, molybdenum, nickel containing protective inner layer**
  - **a less protective hydroxide containing outer layer**

Localized Corrosion Status

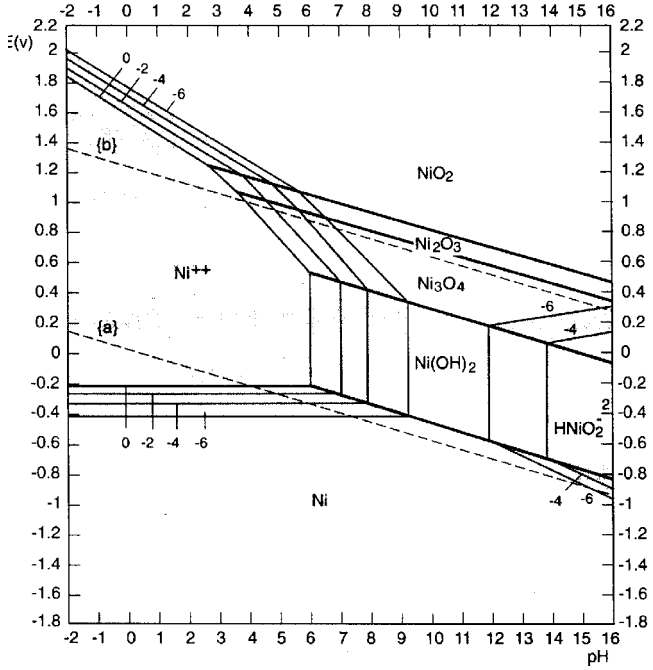
(Continued)

Theoretical considerations (continued)

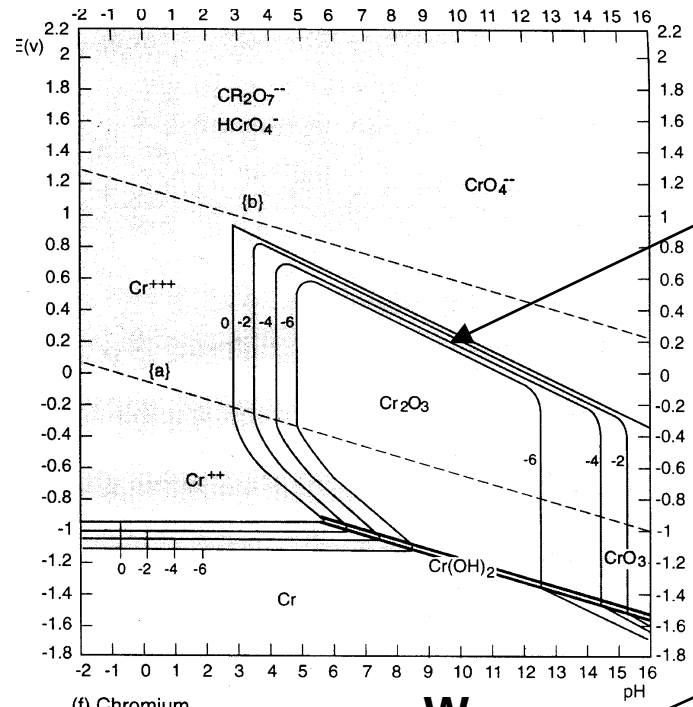
- **Pourbaix diagrams indicate rate controlling corrosion film (Mo and W containing Cr_2O_3) is thermodynamically stable over a range of pH and corrosion potential and thus would not be expected to change composition over time**
  - **detailed calculation of Alloy 22 specific Pourbaix diagram in Path Forward effort**

Thermodynamic stability domain of Cr_2O_3 corrosion film on Alloy 22 (Ni-22 Cr-13 Mo-4 W) indicated by Pourbaix Diagrams

Ni



Cr

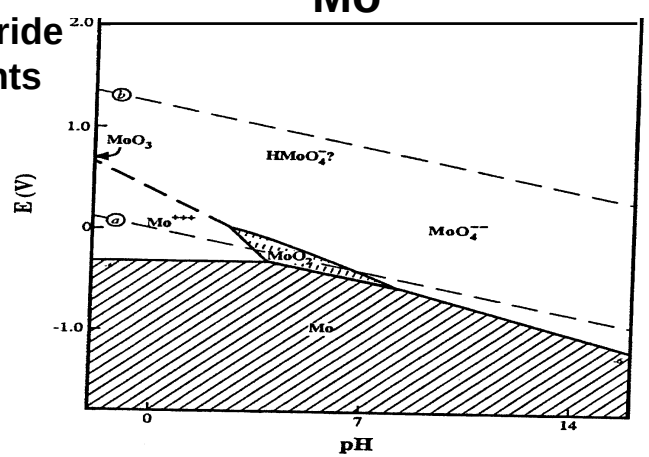


(f) Chromium

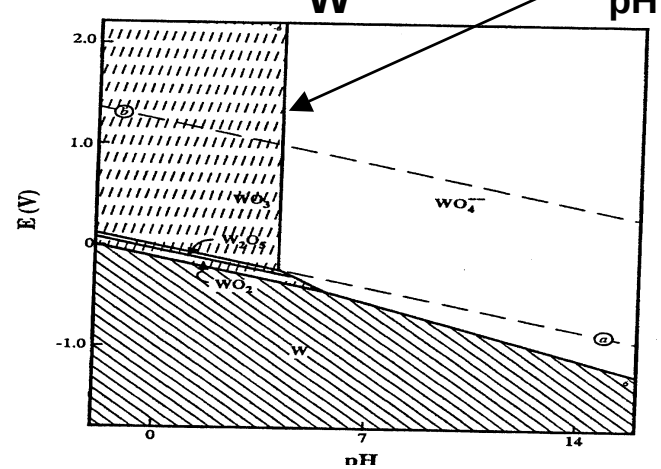
Cr_2O_3 oxide stability domain

Mo stabilizes film in chloride environments

Mo



W



W stabilizes film at low pH

Localized Corrosion Status

(Continued)

- **Based on previous experimental and theoretical considerations, the observed localized corrosion margin expected to be maintained or to increase in repository relevant environments as temperature drops over time**
- **Path forward efforts underway will provide added confidence**

Waste Package Environment — Status

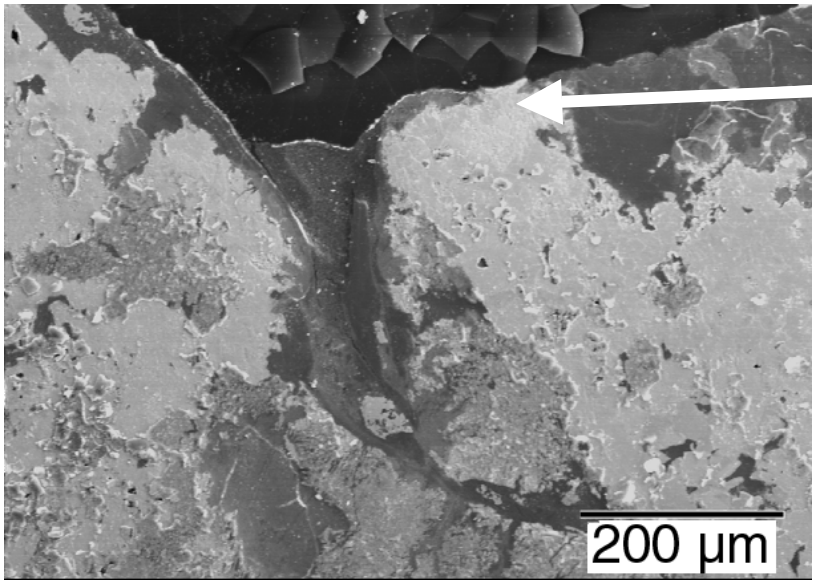
- **Corrosion testing has been performed over a broad range of potential waste package surface environments (including recently identified Simulated Saturated Water at 120°C and Basic Saturated Water (pH = 12-13) at 110°C)**
  - **Test environments evaluated are bounding in pH, temperature, chloride concentration, dissolved oxygen, etc.**
  - **Recent tests in unbuffered water containing lead (1% $PbCl_2$ added) at 75°C indicate no deleterious effects on localized corrosion or stress corrosion ***
  - **Additional testing underway to evaluate other minor elements such as arsenic and mercury**

***See backup chart**

Long Term Passive Film Stability — Status

- **Passive film on Alloy 22 in relevant repository environments appears thermodynamically stable**
- **Josephinite, a natural mineral containing Ni_3Fe alloy has survived many millennia in ambient environments providing potential confirmation of long term passivity**
  - **Awaruite (Ni_3Fe metallic alloy) present in Josephinite, a rock found in southern Oregon and northern California, is believed to have formed during serpentinization (Mg silicate reaction) of igneous rocks in the region**
  - **During serpentinization, hydrogen evolved leads to reduction of Ni- and Fe-bearing oxides and sulfides. As process continues, temperature decreases and conditions become less and less reducing. As a result, the outer layers of Josephinite tend to be nonmetallic but contain areas that appear to be metallic**

Characterization of Natural Analogues



- **Apparent metallic area on surface (SEM and raman microscopy currently planned)**
- **Identification of minerals and thickness and area coverage measurements of nonmetallic layer currently planned**

- **An investigation of the character of Awaruite found in other regions of the world is being made for comparison to Josephinite.**
- **The Fe-Ni metal found in meteorites is also of interest.**

Path Forward to Reduce Remaining Uncertainties

- **Current state of knowledge provides confidence in our understanding of relevant Alloy 22 corrosion degradation behavior over time**
  - **However, it is important to reduce remaining uncertainties to further increase confidence in long term behavior**
  - **Extensive "path forward" experimental/modeling program (see backups for details) to reduce uncertainties underway in**
  - **General corrosion**
  - **Localized corrosion**
  - **Waste package environment**
  - **Long term passive film stability**
- **Long term passive film stability is particularly important to successful long term performance of waste package**

Long Term Passive Film Stability Path Forward

- **To decrease uncertainty, need to better understand fundamental mechanisms that, although unlikely for Alloy 22 in repository conditions, could degrade passive layer protectiveness over time**
  - **defect accumulation as layer sweeps through metal**
  - **debris accumulation — long term corrosion product effects on layer**
  - **quasi-transpassive dissolution — if corrosion potential increases over time, transpassive dissolution may occur aided by high Mo content**
  - **diffusion induced grain boundary migration**
  - **changes in film amorphous or crystalline structure or composition (metastable phases)**
- **Extensive experimental and modeling program underway (see following chart) to increase understanding**

Plan to Verify Long-Term Corrosion Performance

Technical Oversight and Direction
DOE/M&O Waste Package Department

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Prof. Denny Jones
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Drs. McCright, Gdowski, Summers, Lawrence Livermore National Lab.

Confirm Long-Term Passive Film Stability

- Demonstrate film is thermodynamically stable = f (Δ x, environment, t, T, ECP, etc.)
  - Calculate Pourbaix diagram and compare to measured film compositions
- Compare passive films on Josephinite and commercial alloy analogs with Alloy 22
- **Utilize mechanistic model to extrapolate expected behavior over time**

Characterize Corrosion Mechanism(s)

- Develop mechanistic model (e.g. Point Defect or Mixed Conduction Models)
  - Characterize film structure = f(Δx, t, T, ECP, etc.)
    - Evaluate film structure on specimens from LTCTF, CP, potentiostatic exposures, higher temp. autoclave exposures, Josephinite, etc.
      - AFM, TEM. AES, XPS, SIMS, etc.
  - Evaluate film defect structure, diffusing species and diffusivities
    - CP, CER, EIS, TEM, etc.
- Characterize solution interface reactions

Confirm Expected Corrosion Rates

- Characterize LTCTF weight loss specimens
  - Evaluate E_{corr} of 2-3 year specimens in each environment and compare to E_{corr} during initial exposures
- Add new LTCTF tanks with BSW @ 110°C and SSW @ 120°C
- Add high sensitivity weight loss and on-line monitoring of specimens in LTCTF
- Measure rates in situ in AFM = f(Δx, t, T, ECP, etc.using photolithographic height grid
- Run long-term potentiostatic tests = f(ECP, t, environ.,T, welded, aged, etc.) to measure corr rate & E_{rp} = f(time)
- Confirm that environments evaluated to date represent bounding environments

Long Term Passive Film Stability Path Forward

- **Need to Benchmark passive film mechanistic model (Point Defect Model, Mixed Conduction Model, etc.)**
  - **If appropriate, will use model to extrapolate expected long term corrosion performance**
- **DOE plans to hold a Peer Review and/or Workshop with a number of international corrosion/passivity experts to review path forward program and identify any key missing elements**

Conclusions

- **Current extrapolation of relatively short-term corrosion data for passive Alloy 22 to longer periods (>10,000 years) based on extensive data base that contains several conservatism's**
- **Other multiple lines of evidence such as commercial analogs and Josephinite performance tend to support basis of extrapolation**
- **Comprehensive experimental and modeling program defined and underway to decrease remaining uncertainties**
  - **Extensive confirmatory experimental results expected by October-December, 2001**
  - **Performance projections expected to improve as bases for removing many conservatism's used becomes better supported**