



CASE

CASE WESTERN RESERVE UNIVERSITY



SCHOOL OF ENGINEERING

Role of Corrosion Science in Long-Term Performance Assessment

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Introduction

- **Long-term performance of materials**
 - › **Crucial for safe and reliable systems**
- **Corrosion science has an essential, beneficial role**
- **All sectors affected**
 - › **Infrastructure necessary to support our society**
 - › **Energy, transportation, communication, manufacturing, medical, ...**
- **Role of corrosion science**
 - › **Evolutionary path of progress is documented**
- **Opportunities and recommendations**
 - › **Corrosion community**
 - › **NACE International**

Background

- ***Corrosion Costs and Preventive Strategies in the United States – Report to U.S. Congress***
 - › Preventive strategies to reduce corrosion costs were described in the NACE International study
- **International relevance of a national study (U.S.)**
 - › Strategies, barriers and keys to progress are pertinent to countries around the world
- **A major finding**
 - › Benefit/need for advances to performance assessment and life prediction
- **Achieved through advancement of corrosion science**
 - › Implementation to important societal needs

Main Theme

- **Importance of scientific contributions to the understanding at the molecular level**
 - › Electrochemistry, materials science, chemistry, physics
- **Better science provides a robust technical basis**
 - › Performance assessment
 - › Remaining life assessment
 - › Risk analysis
- **Better science leads to advanced technologies**

Evolution from Problem Recognition to Solution

- **Problem or need recognition**
 - › Phenomenological and empirical
 - › Too often triggered by a catastrophic event
- **Parametric awareness**
 - › Environment: composition, oxidizing power and stress
 - › Material: metallurgy and fabrication
- **Process models development**
 - › Localized corrosion, stress corrosion
- **Performance models implementation**
 - › Life prediction, risk assessment

Illustrations of the Role of Corrosion Science

- **Buried steel storage tanks and pipelines**
 - › **Exemplar of the aging infrastructure**
- **Long-term disposal of nuclear waste**
 - › **Special feature is extremely long time-frame**
- **Reliability of microelectronics, computers and communications**
 - › **Corrosion in adsorbed/condensed moisture**
- **Implantable neuroprosthesis systems**
 - › **To restore standing, stepping, grasping, reaching**

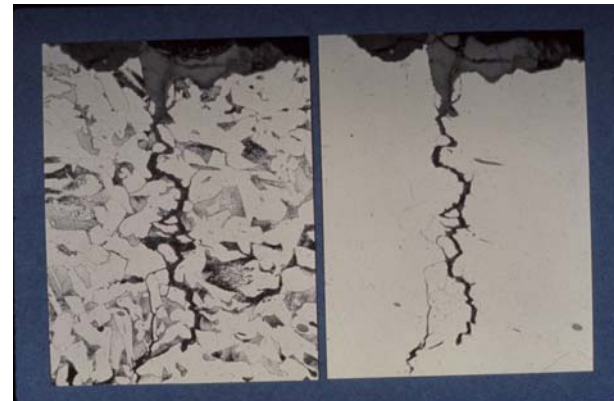
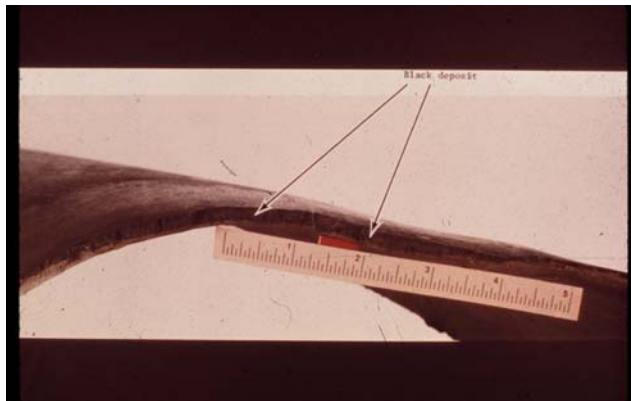
In each area, the essential roles of corrosion science at the molecular level and evolution of progress are noted

Steel Storage Tanks and Buried Pipelines

- **Stress corrosion cracking of steel tanks and buried pipelines**
 - › Severe damage and large costs
- **Phenomenon was hardly recognized and poorly understood in 1950's and 1960's**
 - › Critical environments, metallurgical factors, pipeline operating factors?
 - › Methods to test causes and remedial methods?
 - › Methods to inspect, predict and control?
- **Advances to the understanding and control**
 - › Resulted from sustained efforts
 - › Significant industry/research collaborations
- **Now improved remaining life assessment methodologies**
 - › Failure preventive strategies have emerged and are being put into practice

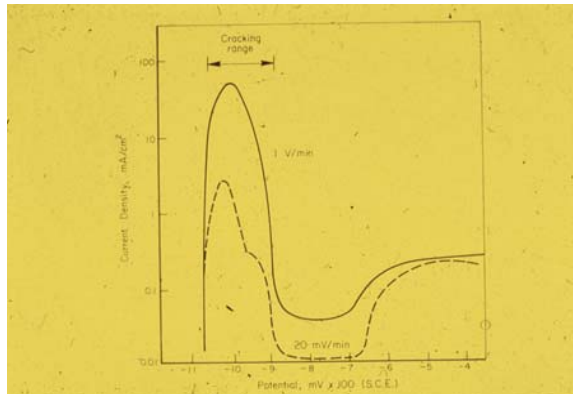
Stress Corrosion Cracking of Buried Pipelines

- Unanticipated, catastrophic failures
- Cracking failures of ductile metal
- Many years of service before failure (10-20 yrs)



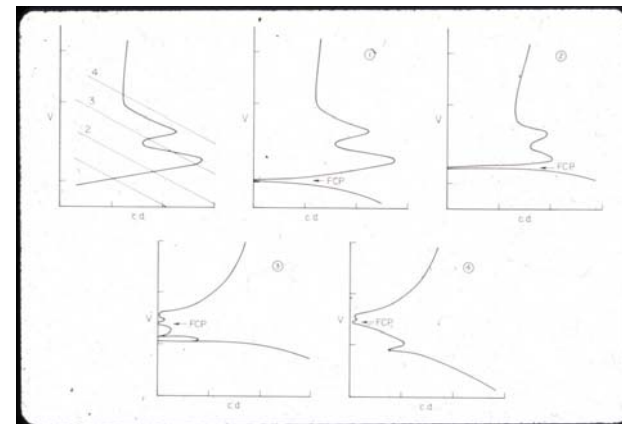
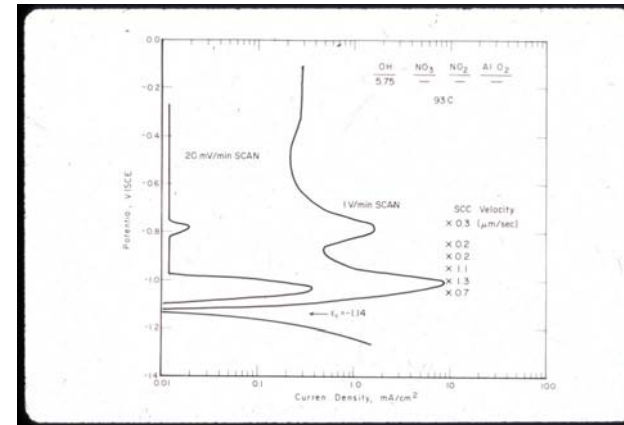
Some Early (1970's) Identification of Controlling Factors

- Critical potential range for SCC
- Electrochemical polarization at fast and slow scan
- Slow strain rate testing for ductile metals

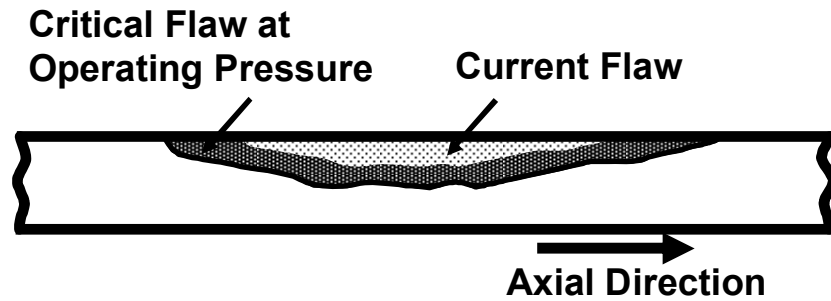


Redvers Parkins: Established a measurable criteria for SCC of steel in caustic.

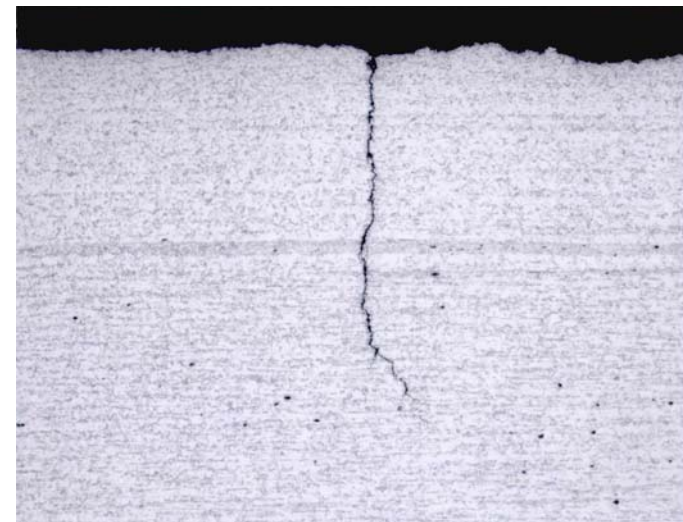
Application to Hot, Multi-species brines



Schematic of a Surface Flaw



Magnetic Particle Inspection for Cracking

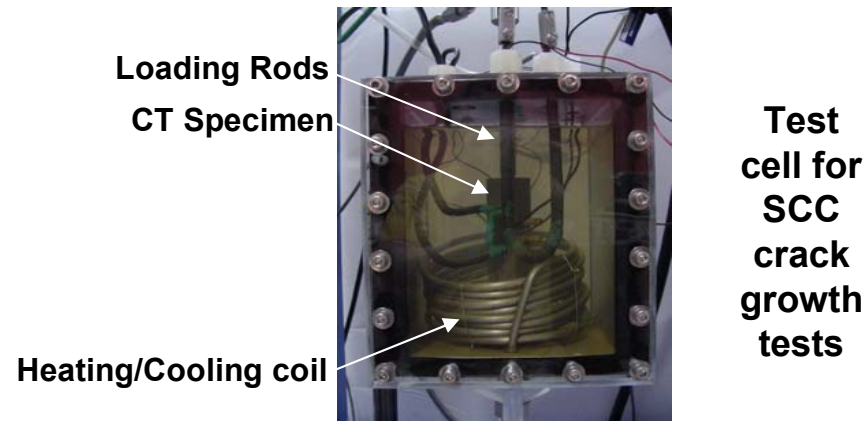


High-pH SCC of Underground Pipeline

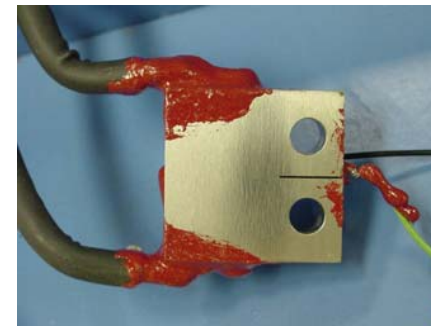
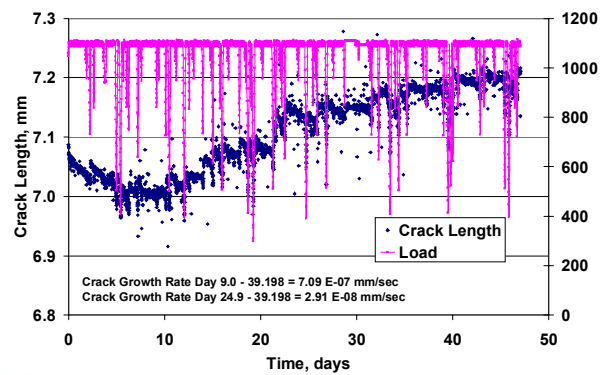
Thanks to John Beavers, CCTechnologies

Laboratory Simulation

- Analyze pressure cycle data for pipeline segment and develop laboratory analog
- Obtain soil/groundwater and pipe steel samples for testing
- Cyclically load compact type specimen of pipe steel in presence of simulated underground environment
- Monitor crack growth by electric potential drop



Crack Length and Load versus Time



Thanks to John Beavers, CCTechnologies

Remaining Life Assessment for Underground Pipelines

- **Life Assessment Uses**
 - › Identify integrity threats to pipeline from flaw growth
 - › Establish safe re-inspection interval for pipeline segments
 - » Incorporate factor of safety
 - › Prioritize pipeline segments for remediation
 - › Establish integrity management budgets
- **Life Assessment Methodology**
 - › **Characterize Existing Flaw Distribution**
 - » In-line inspection
 - » Hydrostatic testing
 - » Direct assessment
 - › **Determine Critical Flaw Size**
 - » Corrosion Flaws: based on plastic instability
 - » Crack Life Flaws: based on fracture toughness or plastic instability
 - › Estimate Rate of Flaw Growth
 - › Estimate Remaining Life

Recent Advances: Life Assessment for Underground Pipelines

- **Improved deterministic models relating crack growth rates and cyclic loading**
- **Probabilistic approaches to integrity management**
 - › **Monte Carlo simulations**
 - » **Distribution of input parameters**
 - Initial flaw dimensions
 - Mechanical property data
 - Flaw growth rates
 - » **Output: cumulative probability of failure versus time**

Long-Term Disposal of Nuclear Waste

- **Several nations have active repository design and analysis programs**
- **Waste packages are a major component of a long-term strategy for safe disposal of nuclear waste**
 - › **First isolate the radionuclides for long times**
 - › **Greatly retard the egress and transport of radionuclides from penetrated packages**
- **Corrosion is a primary determinant of waste package performance**
 - › **Corrosion will control the delay time for radionuclide transport from the waste package**

Cyclic Polarization Provides a Widely Used Criteria for the Susceptibility to Localized Corrosion

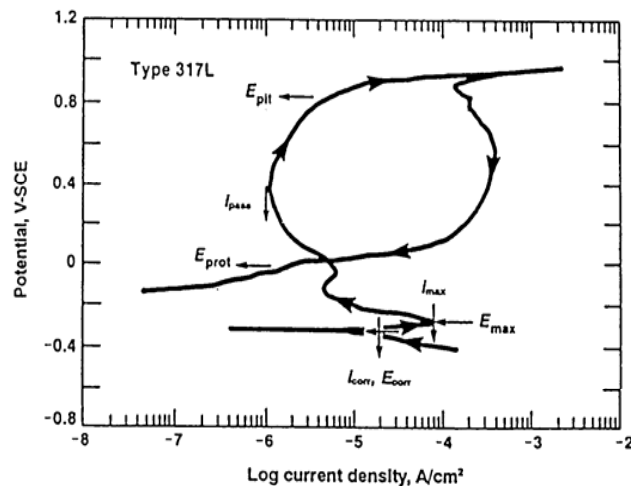


Figure 18. Anodic polarization behavior of type 317L stainless steel in an acid chloride solution.

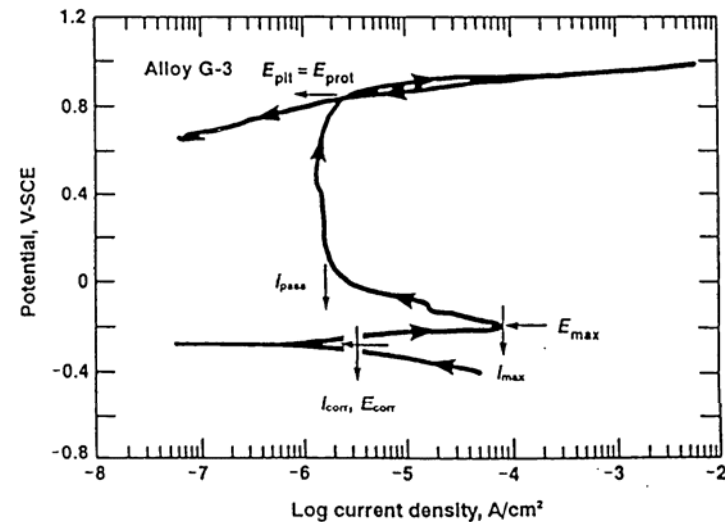


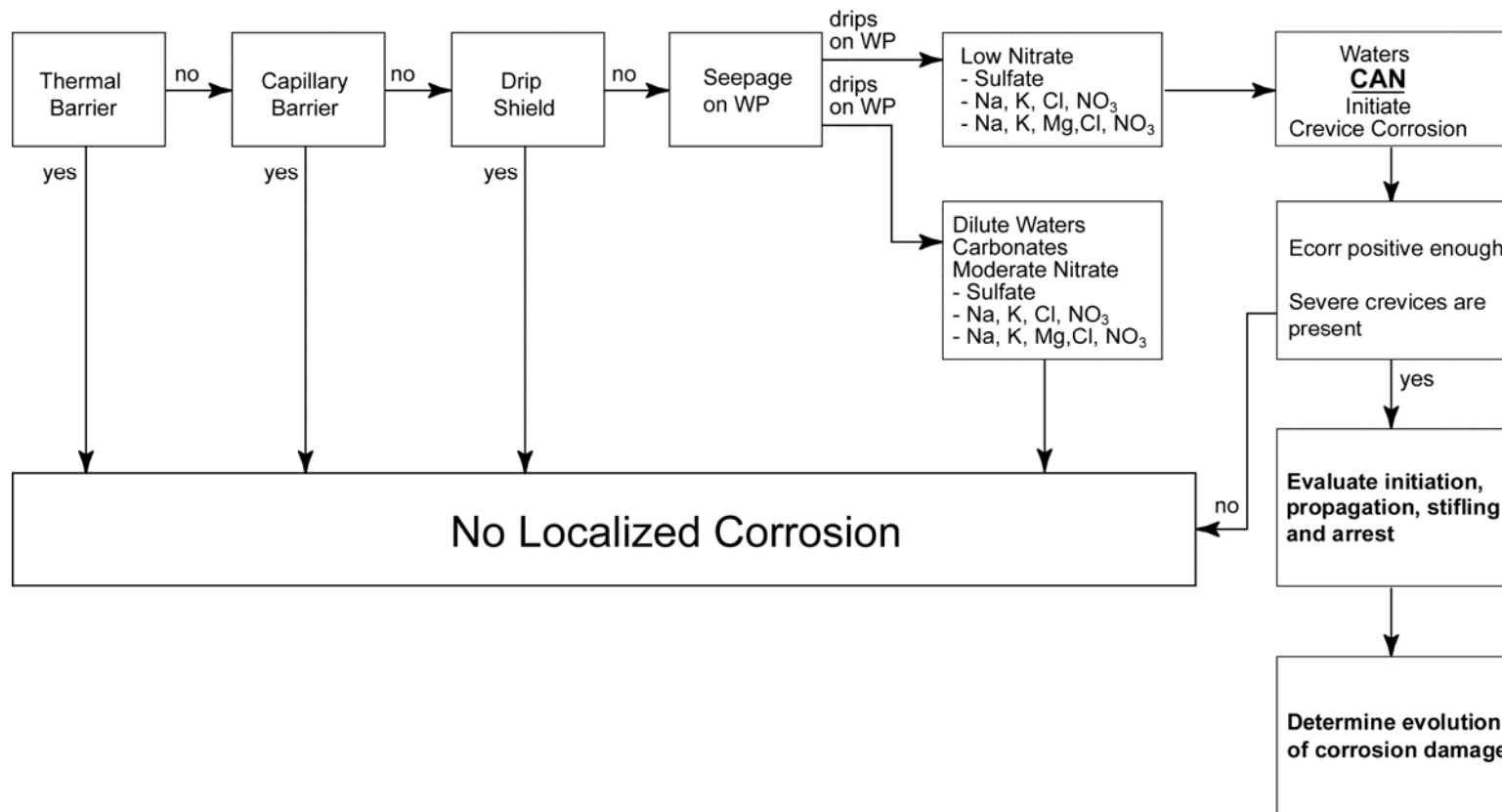
Figure 19. Anodic polarization behavior of alloy G-3 in an acid chloride solution.

- Pitting and crevice corrosion susceptibility based on corrosion potential, breakdown (pit) potential and protection (repassivation) potential
- Figures demonstrate effect of the metal composition in an acid, chloride solution, i.e. higher Ni-Cr-Mo beneficial, Alloy G-3 more resistant than Type 317L
- Direct application presumes that a severe crevice will be present and metal is fully immersed in the test solution

Decision-Tree Analysis

- **A decision-tree analysis goes further than a straight go/no go criteria**
 - › **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 corrosion proceeds**
 - › **What is evolution of corrosion damage?**
 - » **What amount of metal penetration occurs?**
 - » **What is the size and distribution of corrosion sites?**

Decision-Tree Analysis



Corrosion Science for the Proposed Yucca Mountain Repository

- **Brief overview of the proposed repository from a corrosion perspective**
- **Research on localized corrosion and the evolution of corrosion damage**
- **Research on durability of passive films**

Acknowledgements

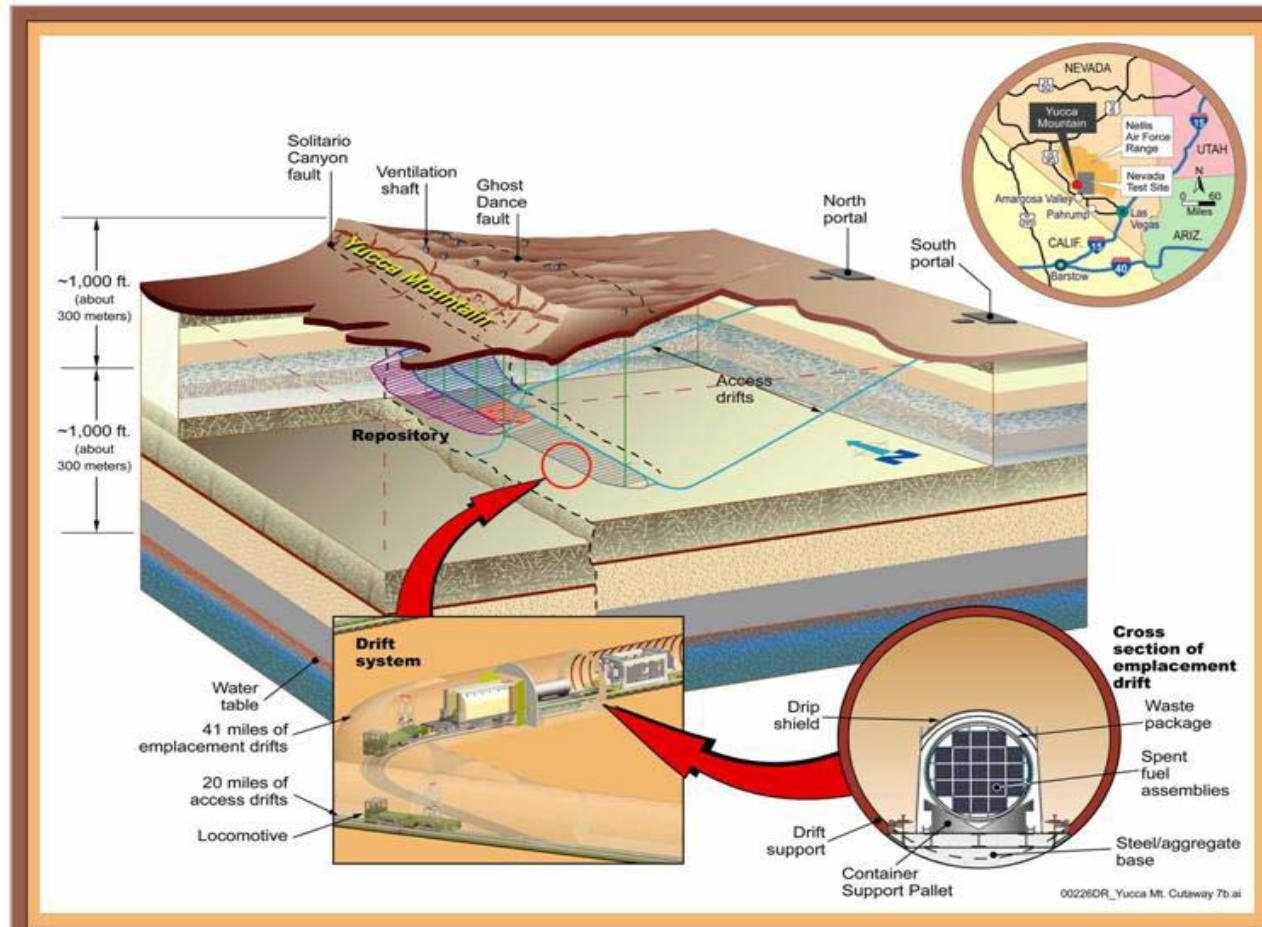
- **Support by the Office of Science and Technology and International (OST&I) of the U.S. Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM) is gratefully acknowledged. The work was performed under the Corrosion and Materials Performance Cooperative, DOE Cooperative Agreement Number: DE-FC28-04RW12252**
- **The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OST&I**

Methodology for Determination of Materials Performance

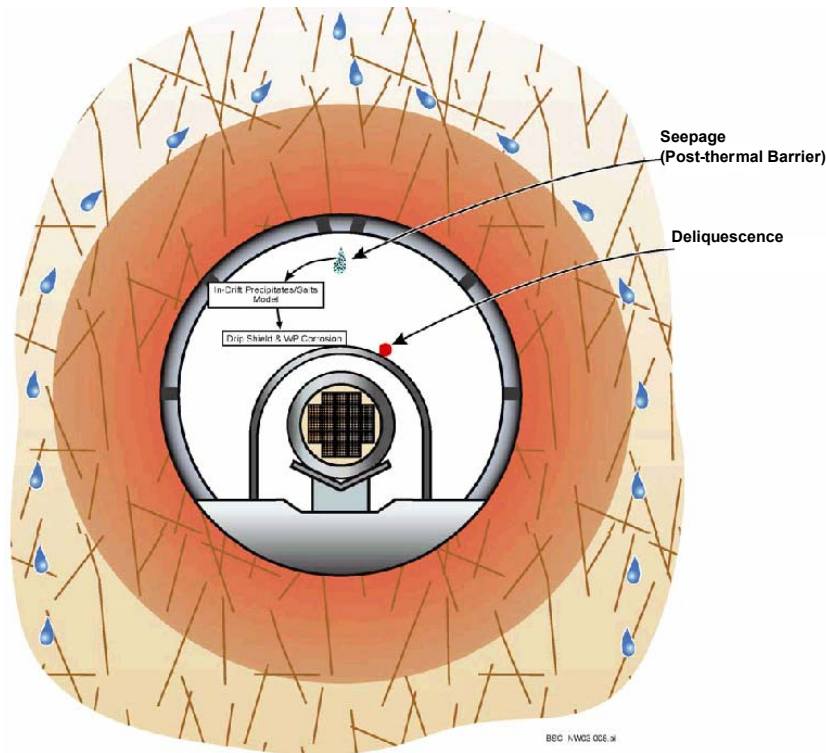
- **Materials performance at the proposed Yucca Mountain Repository is amenable to a familiar and effective analytical methodology**
 - **Widely accepted in the energy, transportation and other industries**
- **Three components comprise the analysis**
 - **Definition of the performance requirements**
 - **Determination of the operating conditions to which materials will be exposed**
 - **Selection of materials of construction that perform well in those conditions**
- **A special feature of the proposed Repository is the extremely long time frame of interest, i.e. 10,000's of years and longer**
 - **Time evolution of the environment in contact with waste package surfaces**
 - **Time evolution of corrosion damage that may result**

The Proposed Yucca Mountain Repository

Repository Reference Design Concept



Attributes of the Proposed Yucca Mountain Repository



- One long, slow heating/cooling cycle
 - > Packages cool to ambient over several thousands of years
- Waste packages on support pallets
 - > No immersion in waters
- No moving parts
- Low heat fluxes, slow heating and cooling, and modest thermal gradients
- Radiation effects at waste package surface negligible after a few hundred years
- Limited amount of water moving through the rock
- Limited salts and minerals carried into drifts by incoming water and dust

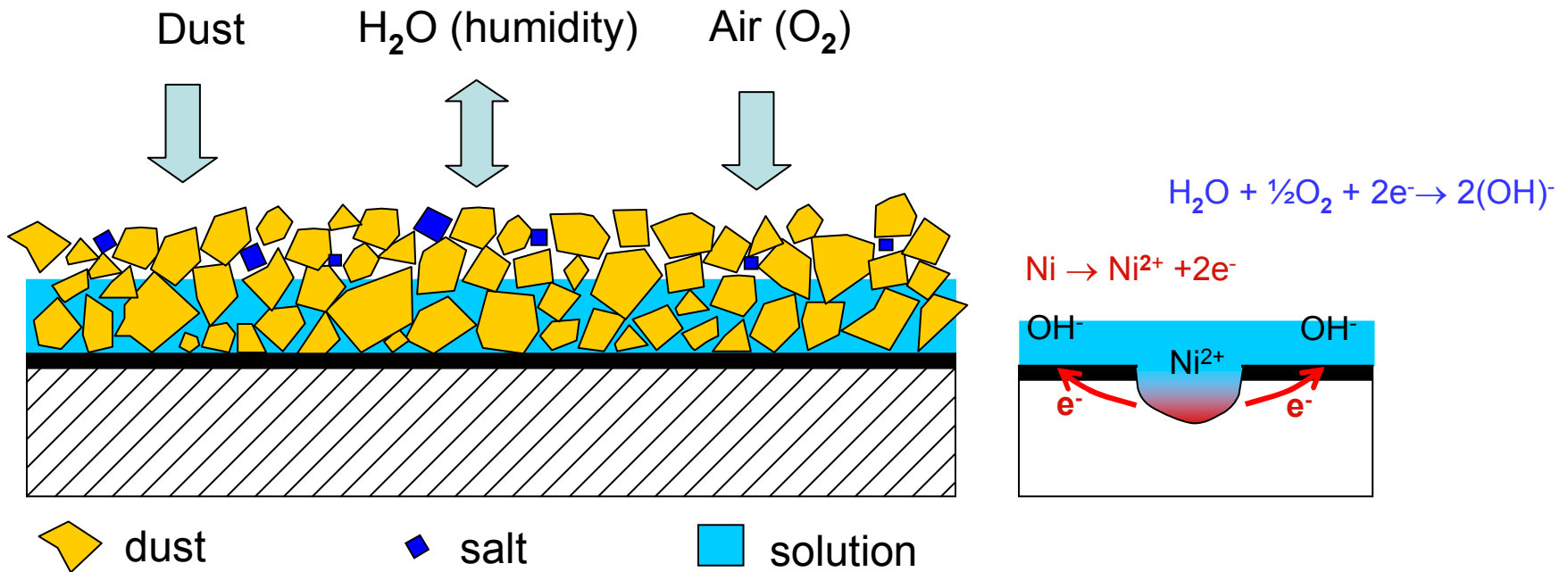
Corrosion Resistance is Crucial to Waste Package Performance

- Radionuclides are fully isolated if there are no penetrations
 - Even penetrated package can limit radionuclide movement
- Corrosion rates of passive metals are extremely low
 - Realistic rates are less than 1 $\mu\text{m}/\text{yr}$ (a millionth of a meter per year) and much less
 - Alloy 22 layer is 2-cm thick (a stack of 12 U.S. quarters)
- Corrosion rates of approximately 0.01 $\mu\text{m}/\text{year}$ are measured in exposures of over 5-years at the Long Term Test Facility at Lawrence Livermore National Laboratory



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 $\mu\text{m}/\text{yr}$

Corrosion in Thin Layers of Particulate



- 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: $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$
- Cathode: $\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow 2(\text{OH})^-$

Participants in Materials Performance Targeted Thrust - Universities

- **DOE/OST&I Multi-University Corrosion Cooperative (CorrCoOp)**
Comprised of some 14 Principal Investigators and approximately 20 grad students and post docs
 - > **DOE CorrCoOp is based at Case Western Reserve University**
 - >> **Arizona State University**
 - >> **Case Western Reserve University**
 - >> **The Ohio State University**
 - >> **Pennsylvania State University**
 - >> **University of California at Berkley**
 - >> **University of Minnesota**
 - >> **University of Toronto**
 - >> **University of Western Ontario**
 - >> **University of Virginia**

Participants in Materials Performance Targeted Thrust - National Laboratories

- **National Laboratories**

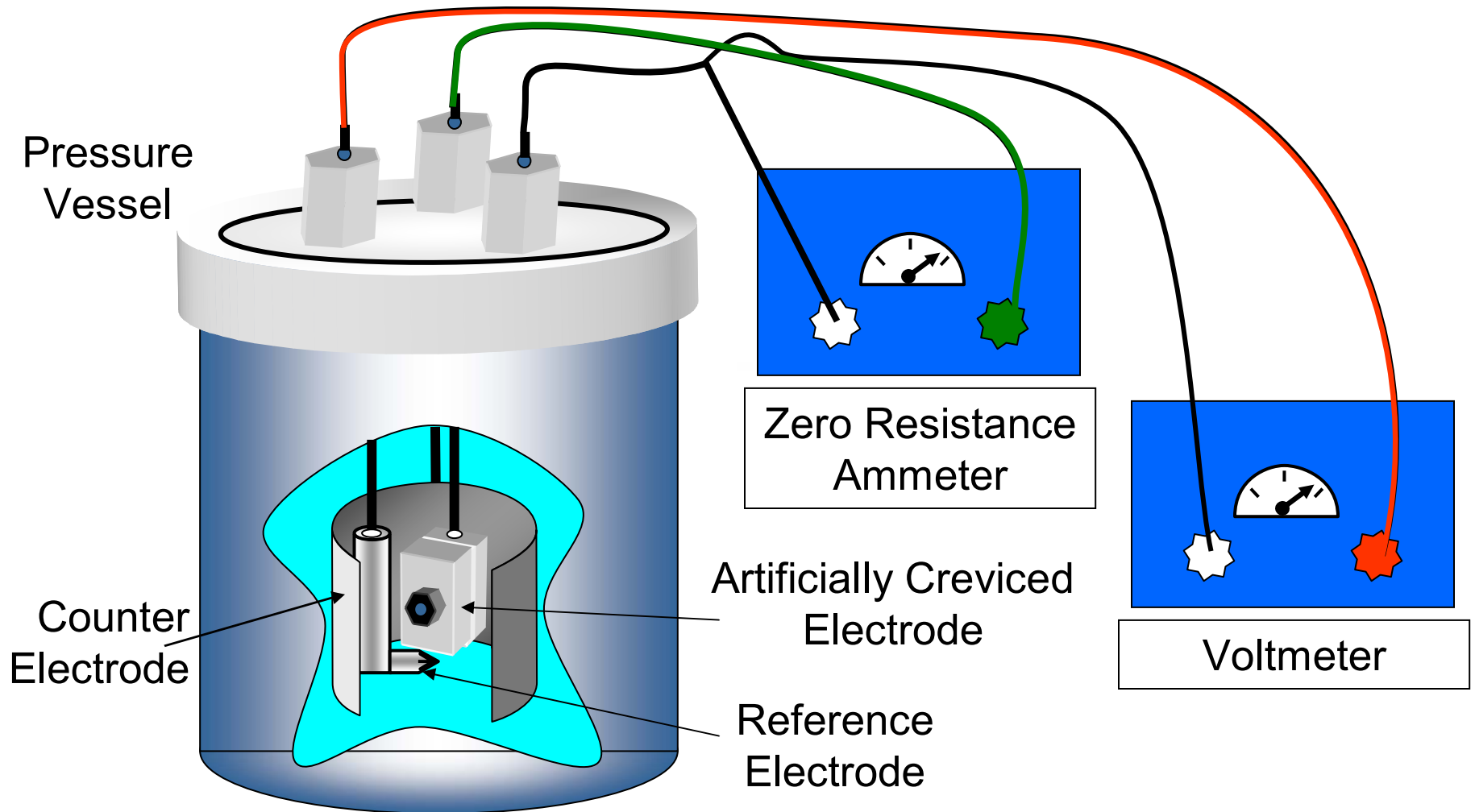
- **Argonne National Laboratory (ANL)**
- **Lawrence Livermore National Laboratory (LLNL)**
- **Lawrence Berkley National Laboratory (LBNL)**
- **Oak Ridge National Laboratory (ORNL)**
- **Pacific Northwest National Laboratory (PNNL)**
- **Atomic Energy of Canada Limited (AECL)**

Outline of Research that Follows

- **Localized corrosion and the evolution of corrosion damage**
 - **Initiation-propagation-stifling-arrest processes**
 - **Role of cathodic region on crevice corrosion**
 - **Role of crevice former and severity of damage**
- **Durability of passive films**
 - **Structure and composition of passive films on Ni-Cr-Mo alloys**
 - **Kinetics of cathodic reduction of oxygen**
 - **Electrochemical behavior and passive film properties**
 - **Mechanism of mixed-ion effects**
 - **Computational model of passivity**

This will be a quick sampling of a multi-investigator effort

Coupled Crevice Experiment



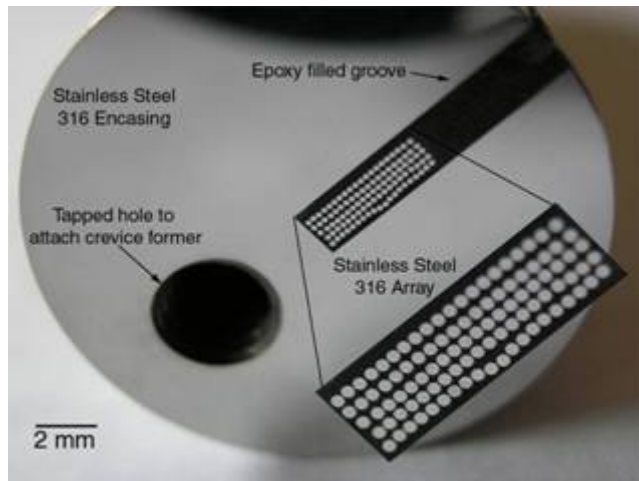
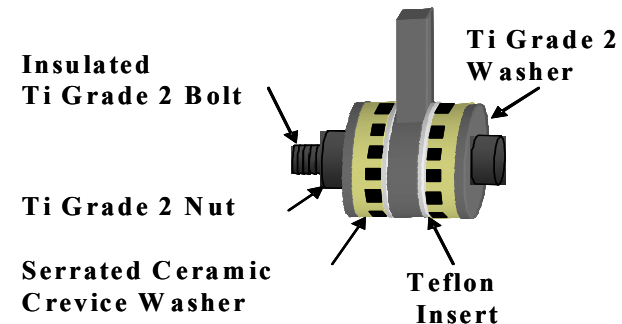
Thanks to Brian Ikeda, Atomic Energy of Canada Limited

Use of Coupled Multi-Electrode Arrays to Advance the Understanding of Selected Corrosion Phenomena

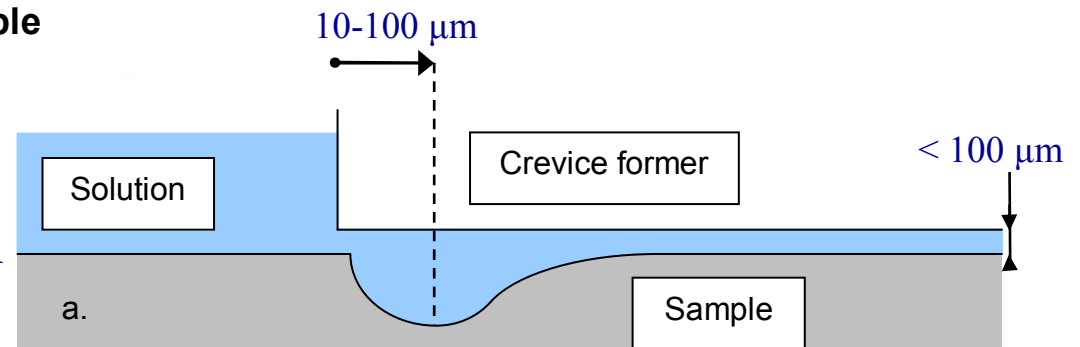
- **Topic is being discussed in more detail at NACE Research in Progress session**
- **Presented by**
 - **N.D. Budiansky, F. Bocher, H. Cong, M. F. Hurley and J. R. Scully**
 - **Center for Electrochemical Science and Engineering
Department of Materials Science and Engineering
University of Virginia**

Multi-Crevice Assembly vs. Multi-Electrode Array

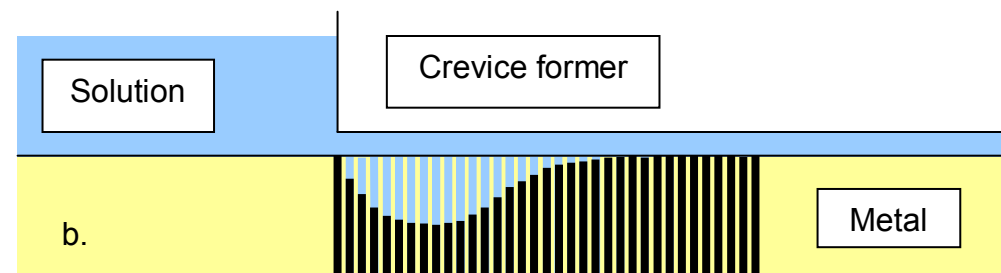
- The array is flush-mounted in a metallic rod of the same material, resulting in a metallic surface-volume ratio similar to that of MCA
- Array provides detailed spatial-temporal resolution, important as crevice corrosion behavior is very dependent on position
- Easier study of effects on initiation and propagation of some factors such as: proximate cathode, limited cathode and semi-permeable crevice former



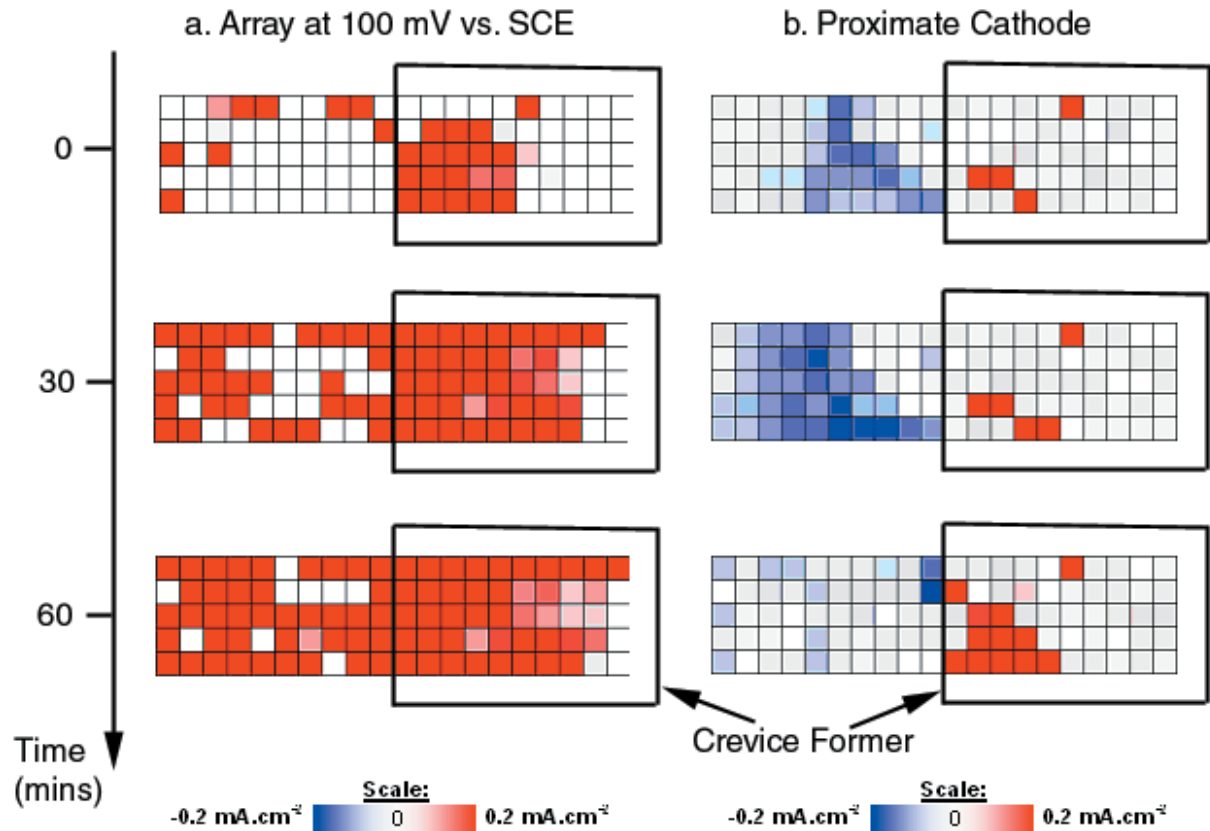
MCA



MEA



Crevice Corrosion & Proximate Cathode



- 316 Stainless Steel
- E_{Applied} stepped 50 mV/hour starting at 0 V_{SCE}
- 1 M NaCl 47°C

- Pitting and Crevice Corrosion
- Pitting occurs randomly outside crevice

- The proximate cathode ($-400 \text{ mV}_{\text{SCE}}$) outside the crevice inhibits the initiation of crevice corrosion at $100 \text{ mV}_{\text{SCE}}$

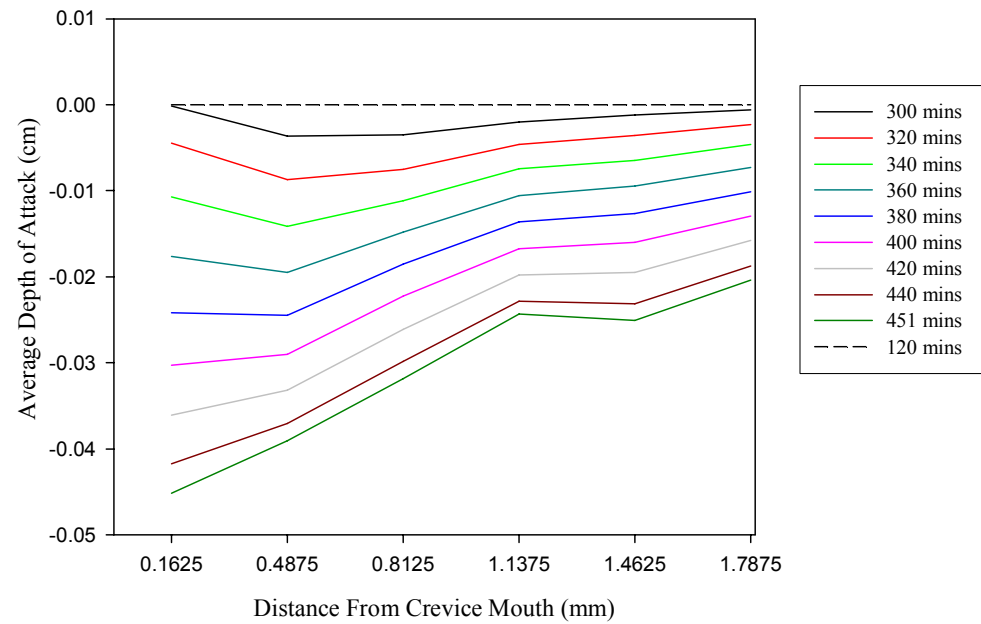
Thanks to John Scully, University of Virginia

Crevice Corrosion Analysis

- From Faraday's Law:

$$d = \frac{C \cdot EW_{316SS}}{F \cdot \rho_{316SS} \cdot \pi \cdot r^2}$$

- With $EW_{316SS} = 25.4$
- and $\rho_{316SS} = 7.87$
- The charge is derived from the net current. Close to the crevice mouth, the cathodic current contribution will be minimal
- The derived depth of attack profile evolution is in agreement with the IR drop model



Effect of Crevice Former on Corrosion Damage Propagation

- Topic is being discussed in more detail at NACE Research in Progress session March 14, 2006
- Presented by
 - > Joe H. Payer, Uziel Landau, Xi Shan, Arun S. Agarwal
Department of Materials Science and Engineering
Department of Chemical Engineering
Case Western Reserve University

Test Cell and Specimen

Test Cell



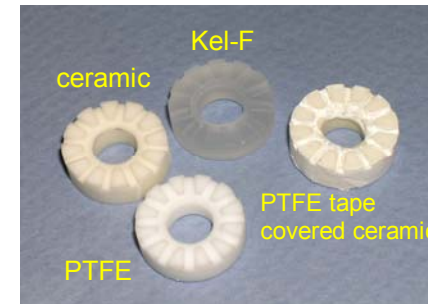
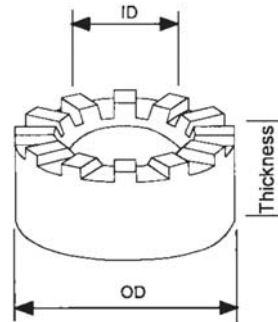
Specimen assembly

Multiple crevice assembly (MCA)



- Two segmented washers
- Applied Torque: 70 in-lb

Crevice formers: after ASTM G48-03



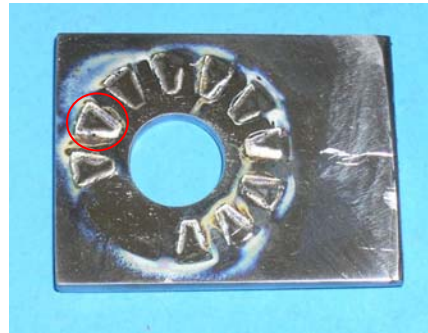
- 12 contact plateaus (feet)
- ID: 9.9 mm OD: 15.9 mm Thickness: 6.3 mm
- Contact area: 6 mm²/contact area (foot)

Effect of Crevice Former on C-22

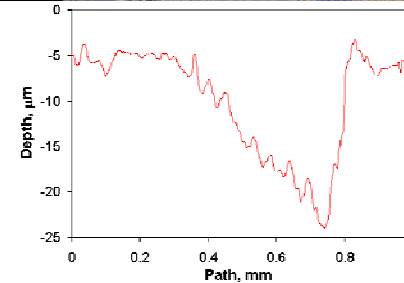
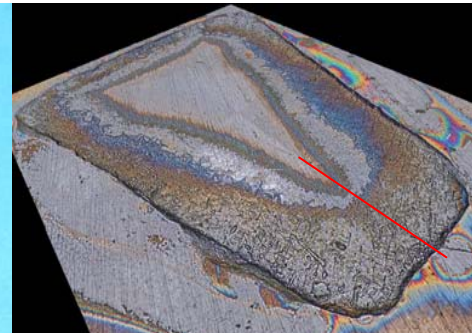
Ceramic vs. PolyTetraFluroEthylene (PTFE) tape covered ceramic



Ceramic side

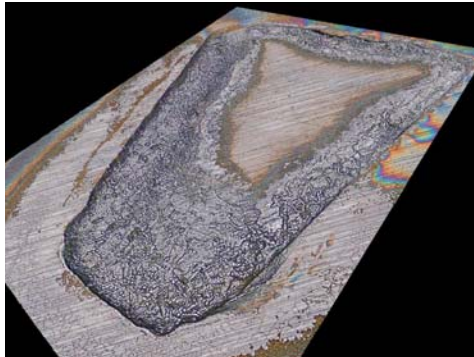


PTFE tape covered ceramic side

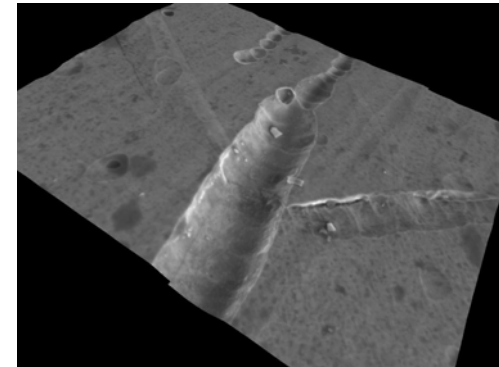


- 4M NaCl, 100°C, potentiostatic, anodic polarization to $E = -0.15$ volts vs. SCE, wet specimens with test solutions before tighten assemblies
- On ceramic side, no crevice corrosion was found
- On PTFE tape covered ceramic side, crevice corrosion to depth of about 25 μm after total flow of charge 10C to the whole specimen (67 hours)

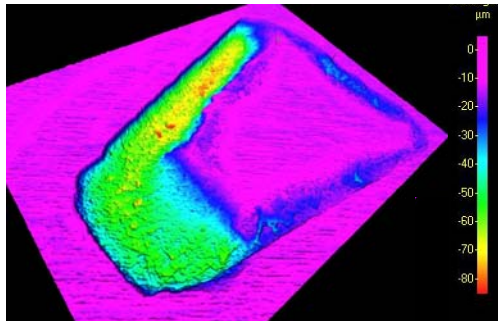
3D Measurement of Corrosion



Optical microscopy
3D reconstruction

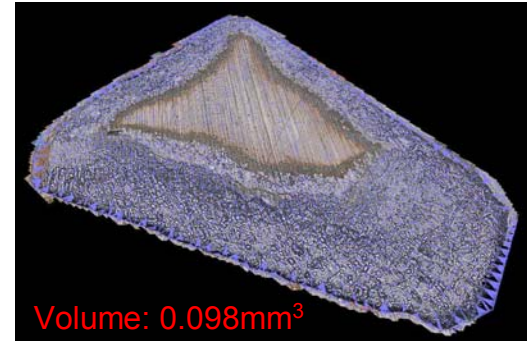


SEM 3D
reconstruction



Depth profile

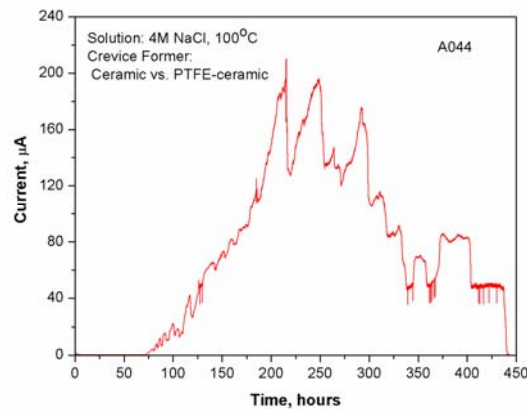
C-22
4M NaCl 100°C
PTFE tape covered ceramic



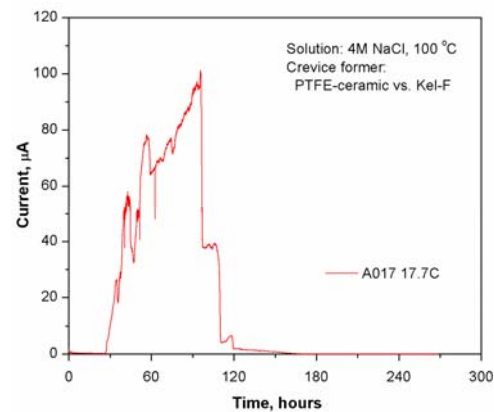
Volume

Effect of Crevice Former

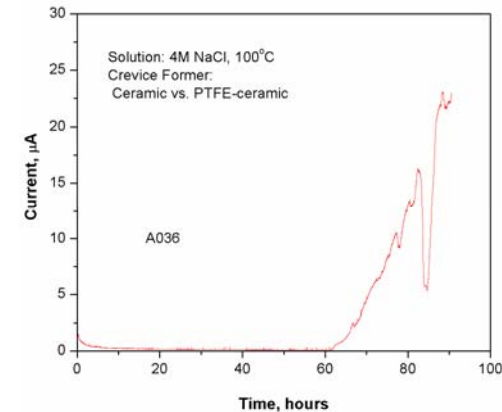
Initiation and arrest of crevice corrosion indicated by specimen current throughout the test



of feet corroded: 9



of feet corroded: 4

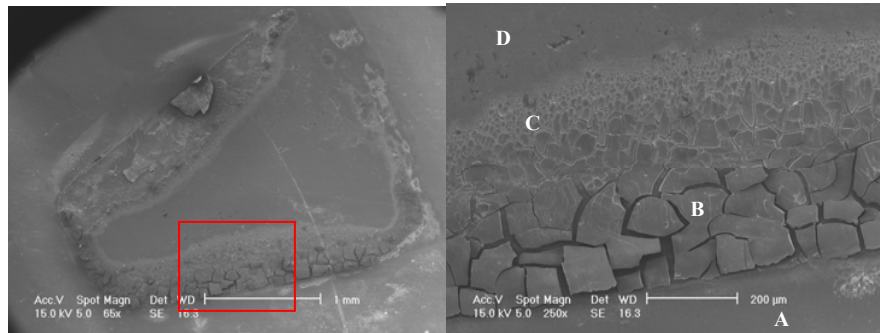


of feet corroded: 1

- Specimens become re-passivated after certain period of test
- Multiple initiation and arrest of crevice corrosion events indicated during the test
- Initiation and arrest events are loosely related to the number of feet corroded; future work will pursue more direct correlation
- Initiation and arrest of corrosion also observed on current response of a single crevice foot

C-22 Corrosion Deposits Within Crevice

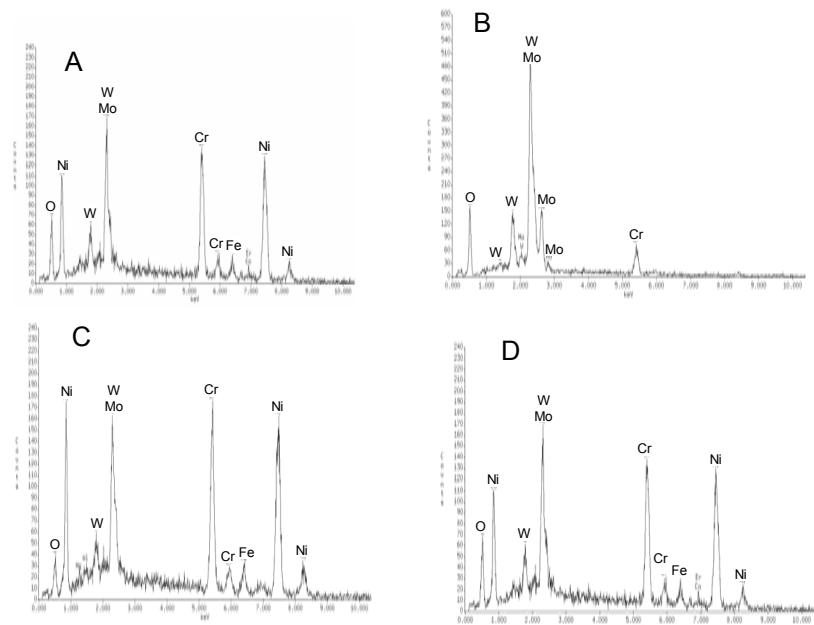
EDS analysis of C-22 corrosion product



| | Cr (at%) | Mo (at%) | W (at%) | Fe (at%) | O (at%) | Ni (at%) |
|----------|--------------|--------------|-------------|-------------|--------------|--------------|
| A | 23.26 | 7.8 | 1.04 | 6.19 | 8.46 | 64.28 |
| B | 7.86 | 20.82 | 3.33 | 0 | 67.23 | 0.78 |
| C | 21.76 | 7.42 | 0.79 | 4.97 | 12.70 | 62.37 |
| D | 19.66 | 7.86 | 1.27 | 4.16 | 22.89 | 44.37 |

C-22 base composition (at%)

| Cr | Mo | W | Fe | O | Ni | Co |
|--------------|-------------|----------|------------|------------|-------------|------------|
| 26.05 | 8.34 | 1 | 3.3 | n/a | 58.7 | 2.6 |

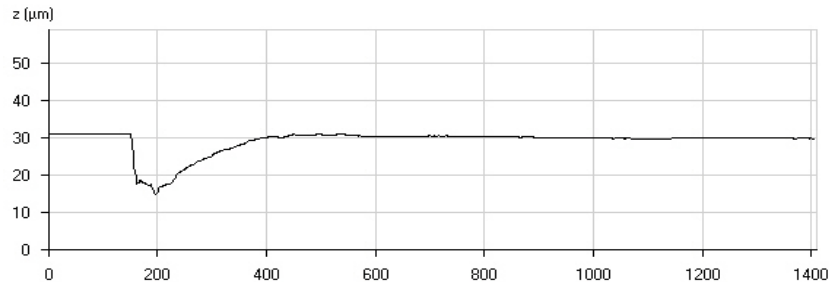


- 4M NaCl, 100°C, potentiostatic, anodic polarization to $E = -0.15$ volts vs. SCE, wet specimens with test solution before assemblies tightened
- Loose, black corrosion products found under the crevice former after test
- Corrosion products are depleted in Ni, Cr and Fe, and enriched in W and Mo; it also contains high amount of oxygen

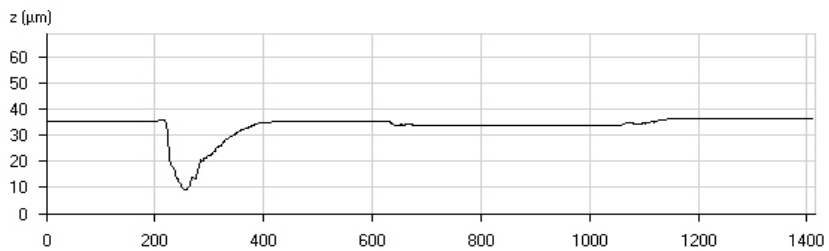
Quantitative Analyses of the Severity of Attack on Crevice Corrosion Surfaces

- Topic is being discussed in more detail at NACE Research in Progress Symposium and Student Poster Session
- Presented by
 - > A. J. Hodges, R. G. Kelly
Center for Electrochemical Science and Engineering
University of Virginia

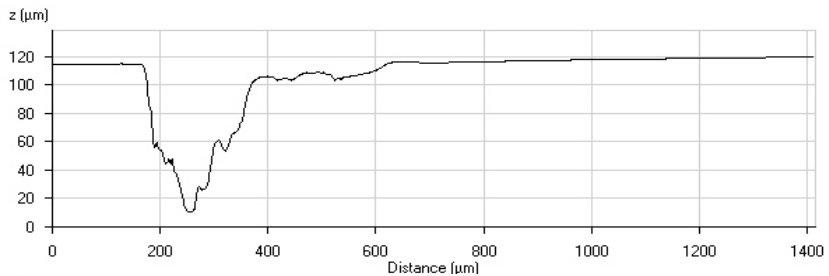
Effect of Charge Passed on Crevice Damage Profile



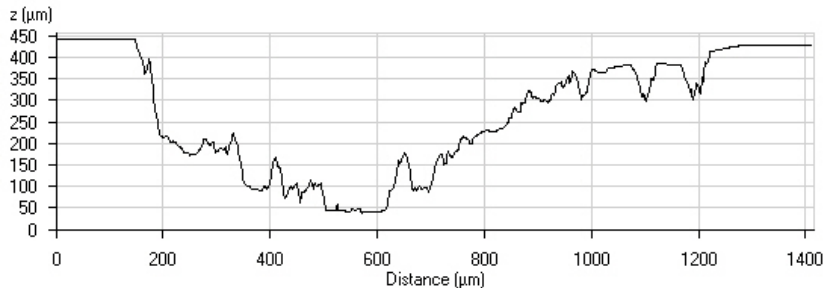
0.530 C/cm²



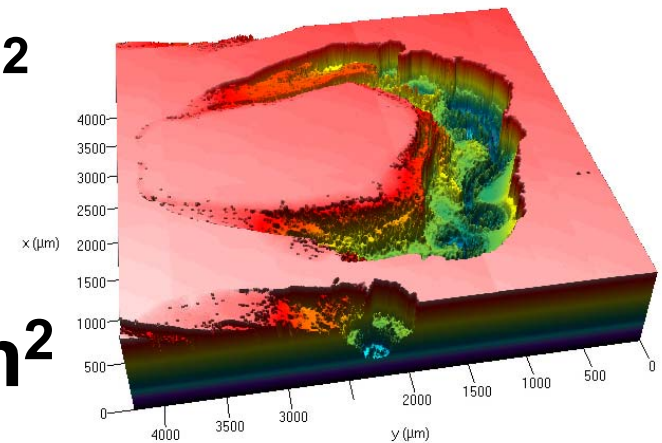
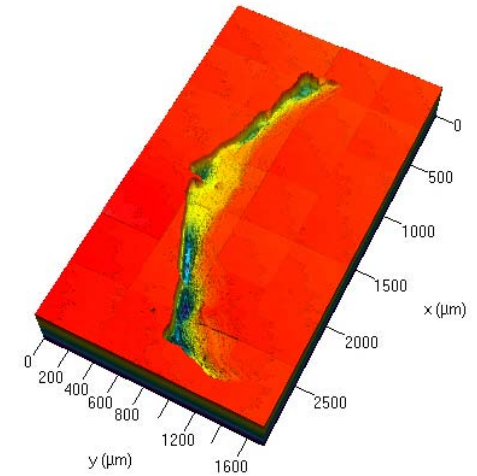
1.60 C/cm²



12.7 C/cm²



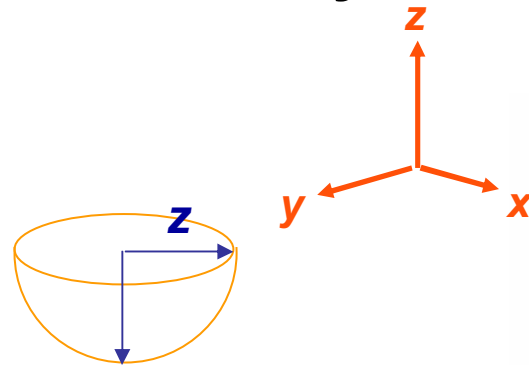
305 C/cm²



Thanks to Rob Kelly, University of Virginia

Crevice Corrosion Growth Laws

- Geometry of damage determined by growth law



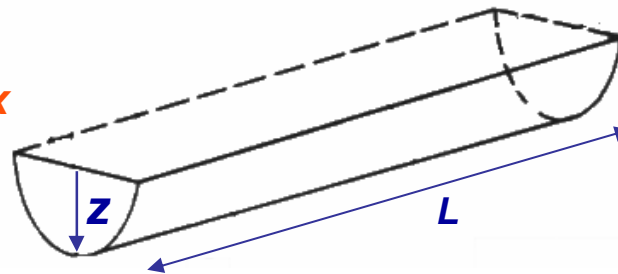
3D growth

$$V_{3D} = \iiint \frac{1}{2}(2\pi z) d\theta d\phi dz$$

$$V_{3D} = \left(\frac{2}{3}\right)\pi z^3$$

$$V_{3D} = C z^3$$

V = volume lost z = Maximum depth

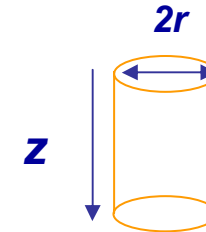


2D growth (x and -z directions)

$$V_{2D} = \iint \frac{1}{2}(2\pi z) dz dy$$

$$V_{2D} = \left(\frac{1}{2}\right)L\pi z^2$$

$$V_{2D} = C z^2$$



1D growth (-z direction)

$$V_{1D} = \int \pi r^2 dz$$

$$V_{1D} = \pi r^2 z$$

$$V_{1D} = C z$$

All result in power law relation between V and z

Role of the Cathodic Region in Localized Corrosion

- **Topic is being discussed in more detail at NACE Research in Progress Symposium**
- **Presented by**
 - **R. G. Kelly, F. Cui, F. J. Presuel-Moreno
Center for Electrochemical Science and Engineering
University of Virginia**
 - **A. S. Agarwal, X. Shan, U. Landau, J. H. Payer
Department of Materials Science and Engineering
Department of Chemical Engineering
Case Western Reserve University**

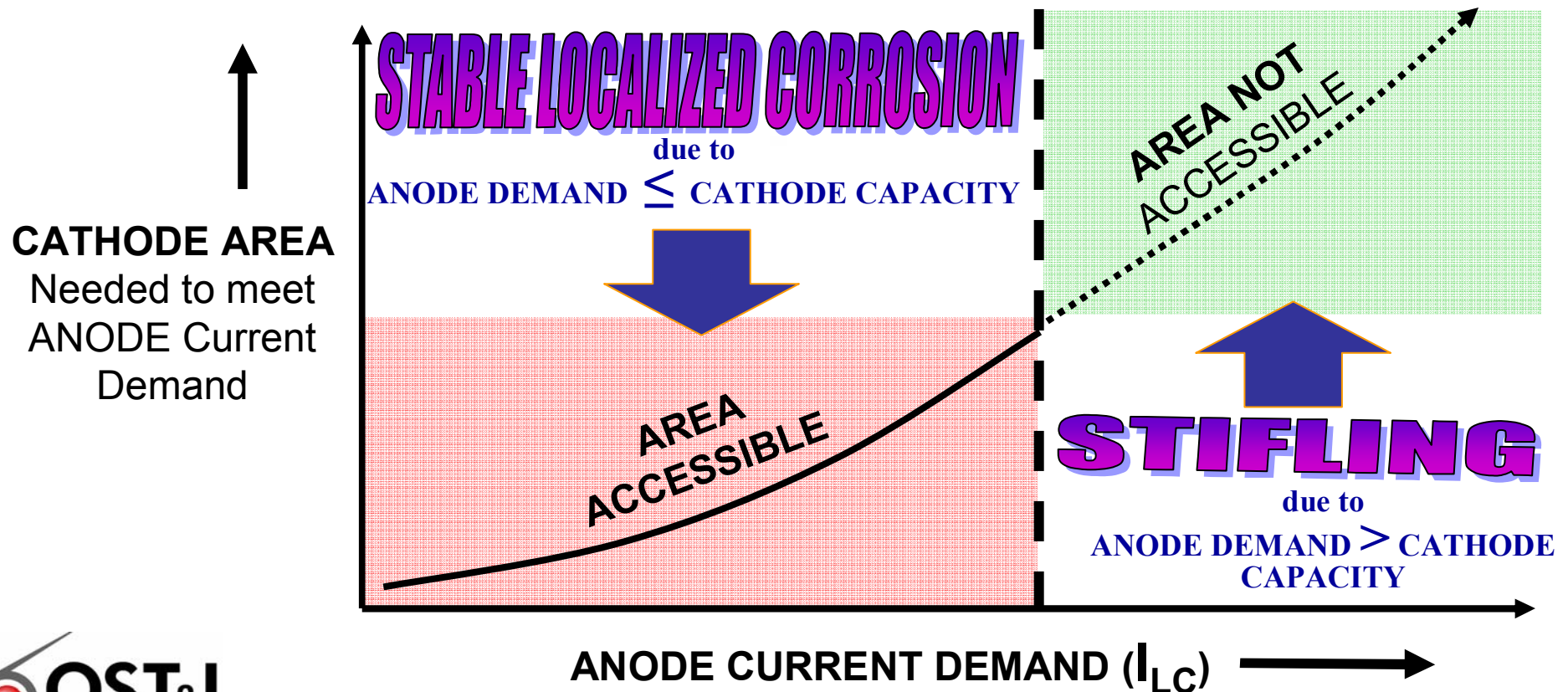
Localized Corrosion can be Stifled by Limits on the Cathodic Processes

- In the proposed repository waste packages will never be fully immersed in solution
- Moisture and particulates may be present on surfaces
- Corrosion behavior in moist particulate can differ from full immersion
 - > Limited size of corrosion site
 - > Limited cathodic area to support localized corrosion
 - > Limited cathodic kinetics could stifle corrosion



Objective

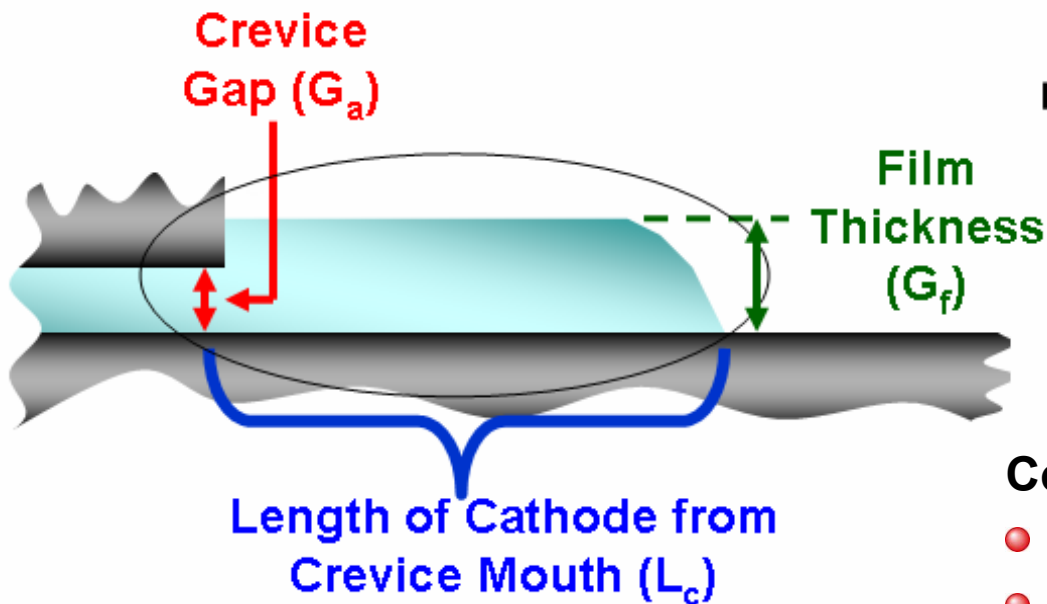
- Quantification of the total cathodic current that a wetted surface of limited area could deliver under a given set of conditions provides a scientific basis for analyses of both the maximum rate and the stability of localized corrosion.



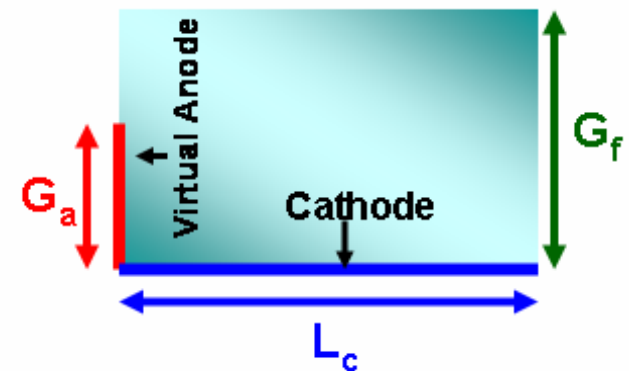
Computational Studies of Cathode Capacity

Cathodic region is decoupled from the localized corrosion region

SCHEMATIC DIAGRAM OF A CREVICE



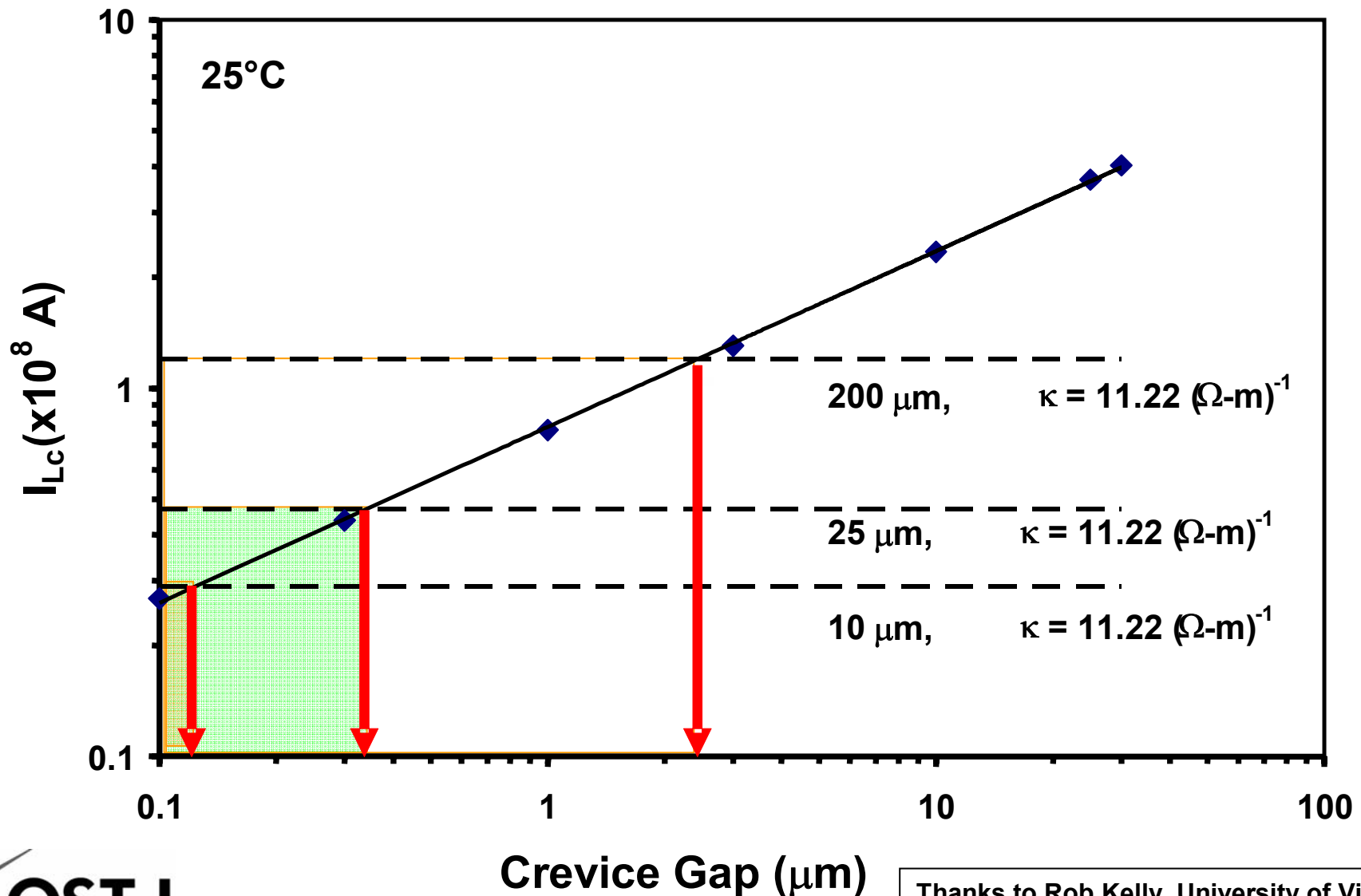
DECOUPLED CATHODE MODEL



Consider the effects of:

- Size of Wetted Area
- Water Layer Thickness
- Electrolyte Conductivity
- Particulates
- Temperature

Crevice Corrosion Can be Sustained When Anode Demand is Less Than or Equal to Cathode Capacity



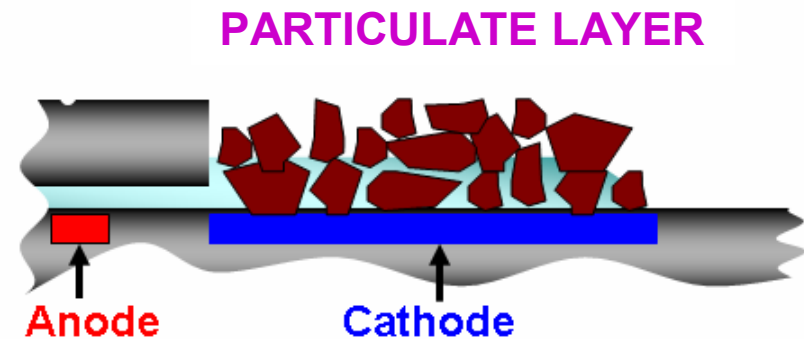
Effects of Particulates

PARAMETERS (of particulate layer)

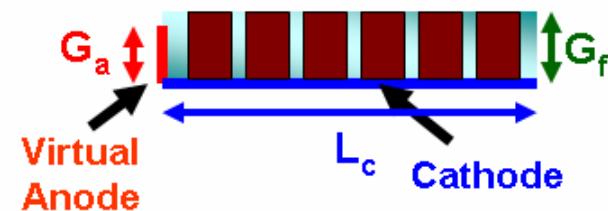
- Particle size
- Particle arrangement
- Particle shape
- Electrode area coverage ($A_{\text{exposed}}/A_{\text{total}}$)
- Volume fraction blockage ($V_{\text{solution}}/V_{\text{total}}$)

MODELING CONSTRAINTS

- Uniform particle distribution
- Steady state
- Monolayer of particles (height_{particle} = thickness_{electrolyte})
- No chemical changes



MODEL GEOMETRY



Durability of Passive Films

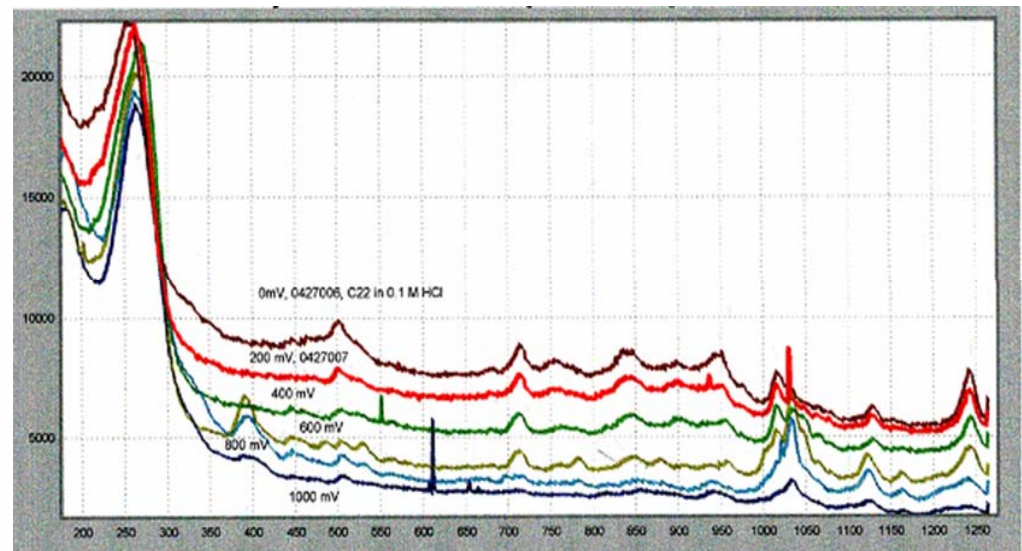
- **Structure and Composition of Passive Films on Ni-Cr-Mo Alloys**
 - **Tom Devine, University of California - Berkeley**
- **Kinetics of Cathodic Reduction of Oxygen on Passive Metals**
 - **David Shoesmith, University of Western Ontario**
- **Electrochemical Measurements in Thin Films of Electrolyte**
 - **Gerald Frankel, Ohio State University**
- **Mechanism of Mixed-Ion Effects on Corrosion in Thin Films and Anodic Dissolution of Ni-Cr-Mo Alloys**
 - **Roger Newman, University of Toronto**
- **Passive Film Properties and Behavior**
 - **University of Western Ontario**
 - **University of California - Berkeley**
 - **Case Western Reserve University**
- **Computational Model for Passivity: Point Defect Model**
 - **Digby Macdonald, Pennsylvania State**

Effect of Environmental Variables on the Structure and Composition of Passive Films

- In-situ surface analysis and characterization
- To determine structure, composition, electrochemical and electronic properties of passive films on Ni-Cr-Mo alloys in hot, chloride solutions



Surface Enhanced Raman Spectroscopy (SERS) – The electrochemical cell containing the sample under investigation (e.g. Alloy 22) by SERS.

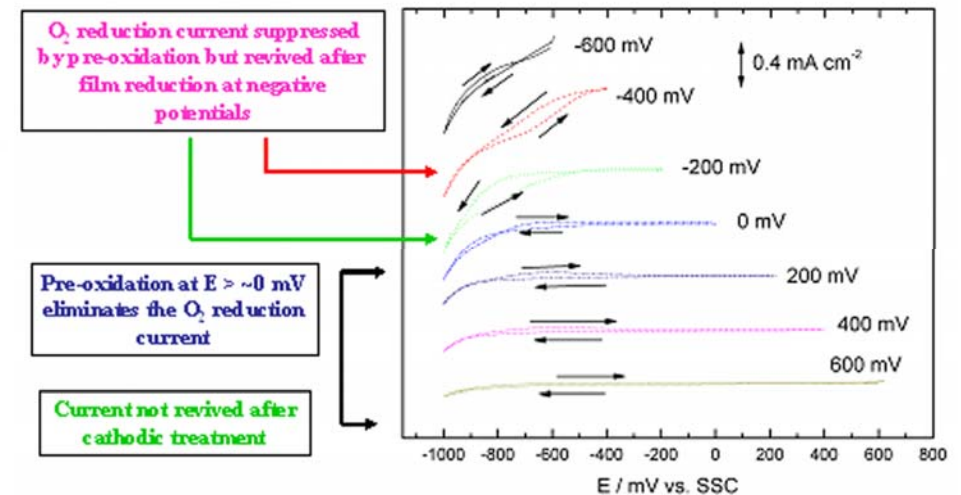
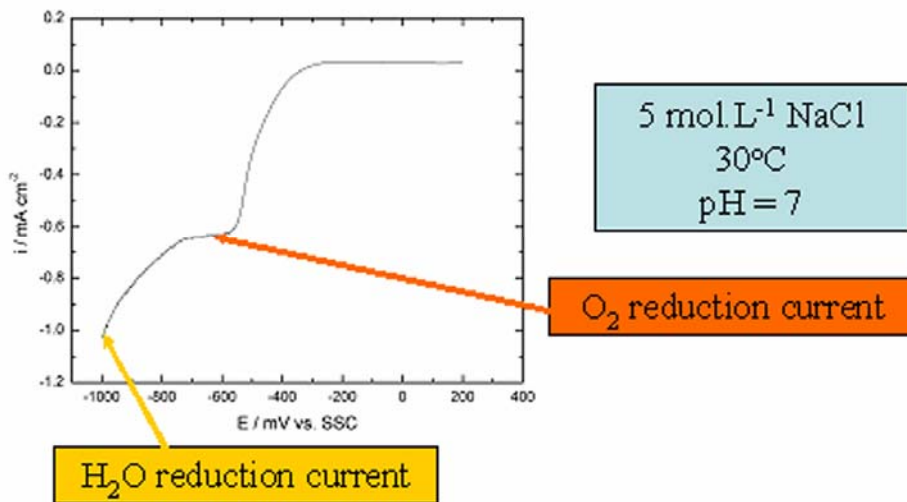


SERS of passive film formed on Alloy 22 in 0.1M HCl at potentials of 0V, 0.2V, 0.4V, 0.6V, 0.8V, 1.0V vs. SCE.

Thanks to Thomas M. Devine, University of California - Berkeley

Kinetics of the Cathodic Reduction of Oxygen on Passive Metals

- Elucidation of the mechanism and kinetics of the cathodic reduction of oxygen on Ni-Cr-Mo (W) alloy
- Investigate the influence of the composition and electrical properties of thin film layer on the electrochemical currents for oxygen reduction reaction
- Examine the effects of pre-soaking on passive film



Polarization scan for Alloy 22 showing a limiting oxygen reduction current on a rotating disk electrode at 23.5Hz

Influence of 60 minutes oxidation of Alloy 22 at various potentials on the O_2 reduction current at 30°C

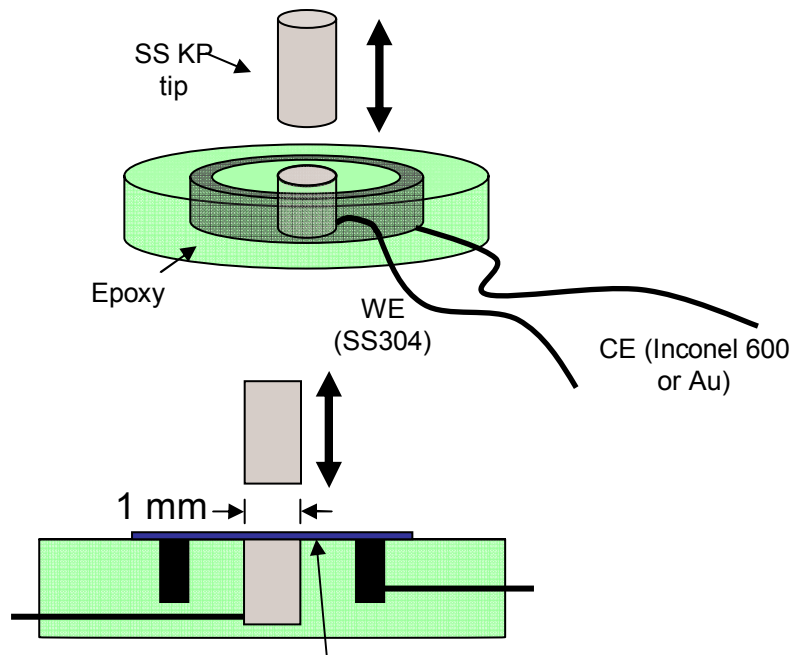
Thanks to David W. Shoesmith, University of Western Ontario

Electrochemical Measurements and Pitting Under Thin Films

- Problem is getting reference electrode into thin layer – solved by Kelvin Probe

Electrochemical Kelvin Probe sample

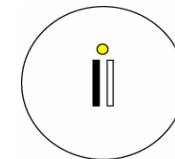
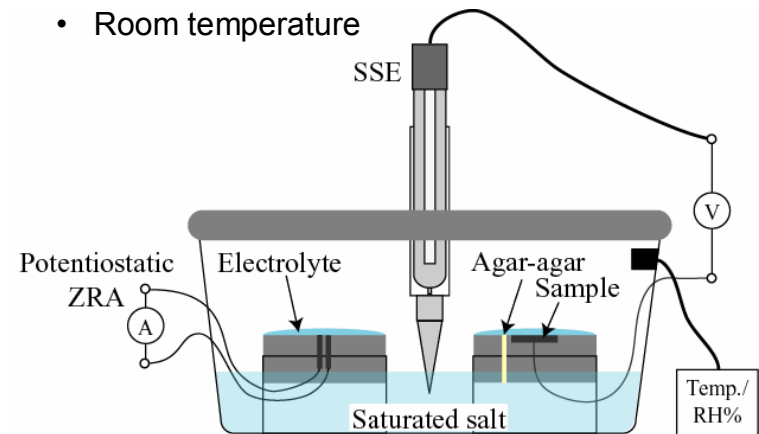
Similar to rotating disc electrode



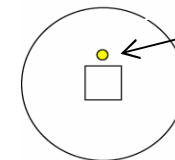
Thin electrolyte layer

- 5 μm – 1 mm Cl^-
- equilibrated with 95% RH
- ~1 M Cl^-

- Sample: Silica-coated 304SS
- Electrolyte: 0.5 M NaCl or 0.5 M MgCl_2
- Electrolyte thickness: 500 μm
- Relative humidity controlled by saturated LiCl or MgCl_2
- Room temperature



Cell for measurements of galvanic currents



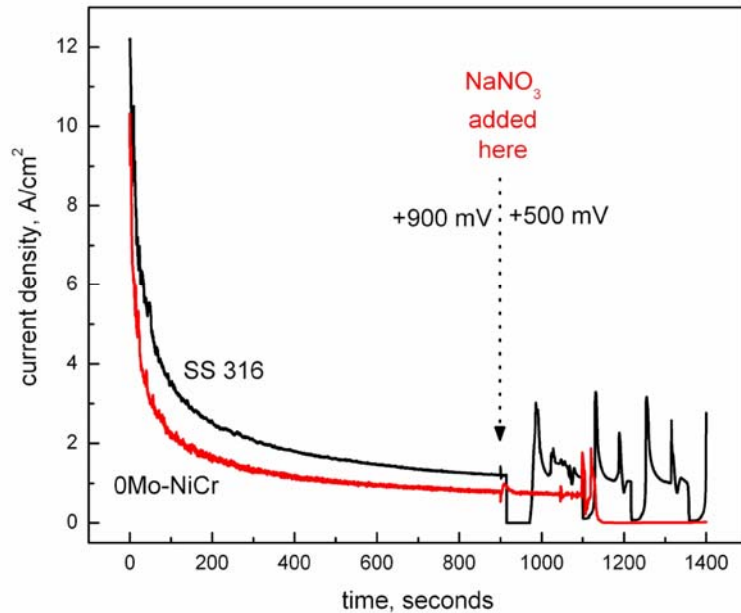
Agar-agar

Cell for measurements of OCP transients

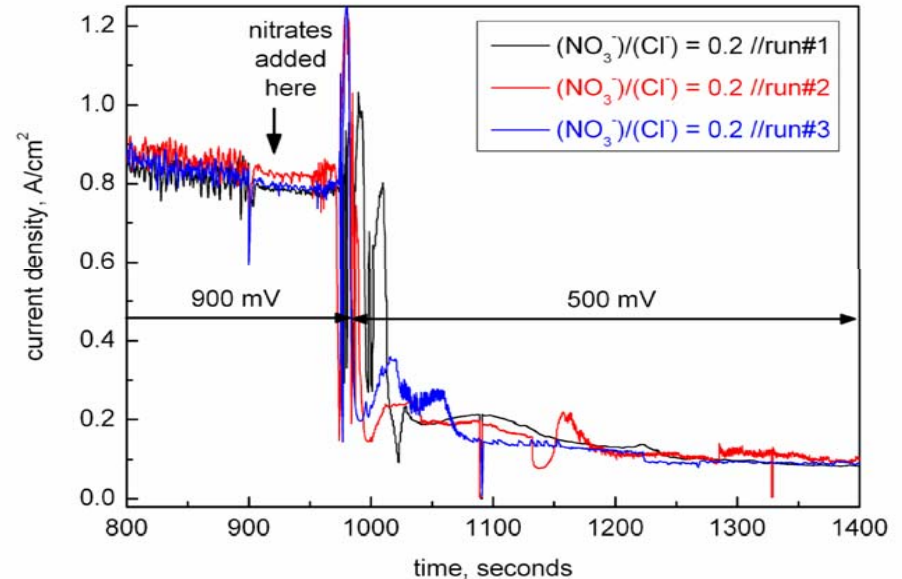
Thanks to Gerald S. Frankel, Ohio State University

Mechanism of Mixed-Ion Effects on Localized Corrosion and Thin Films

- To generate fundamental data and scientific understanding for the localized corrosion kinetics of Ni-Cr-Mo alloys in presence on non-chloride ions, e.g. nitrate
- To measure and to understand how the thickness of a moist particulate layer, containing mixed aggressive and inhibiting salts, affects localized corrosion kinetics



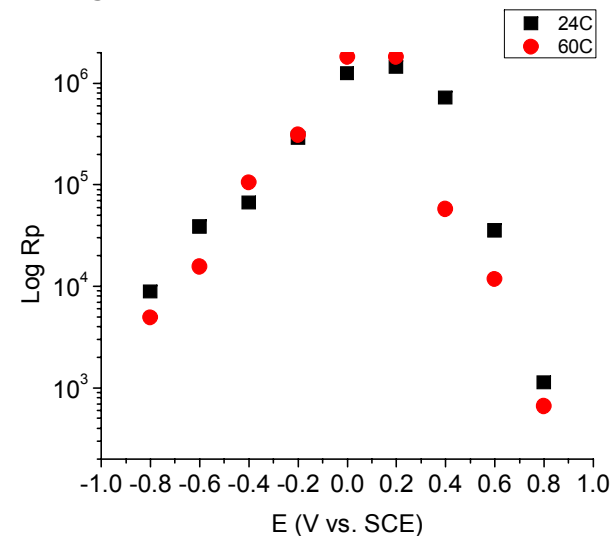
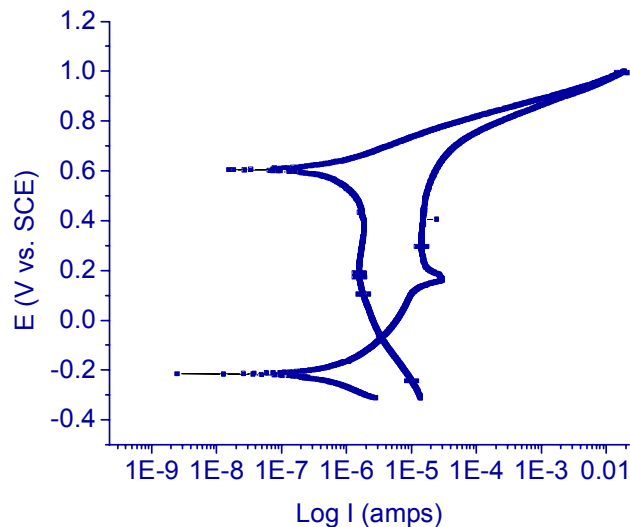
Growth of artificial pits on 316 SS and Mo-free Ni-22Cr(0Mo-NiCr) in 1M NaCl with 0.05M NaNO₃ injected just after the vertical line, showing oscillation and repassivation



Cyclic polarization curves on Ni-22Cr in 250um thick layers of SiO₂/NaCl mixture with different silica-to-salt ratios at 60°C and 75%RH (scan rate of 3mV/s)

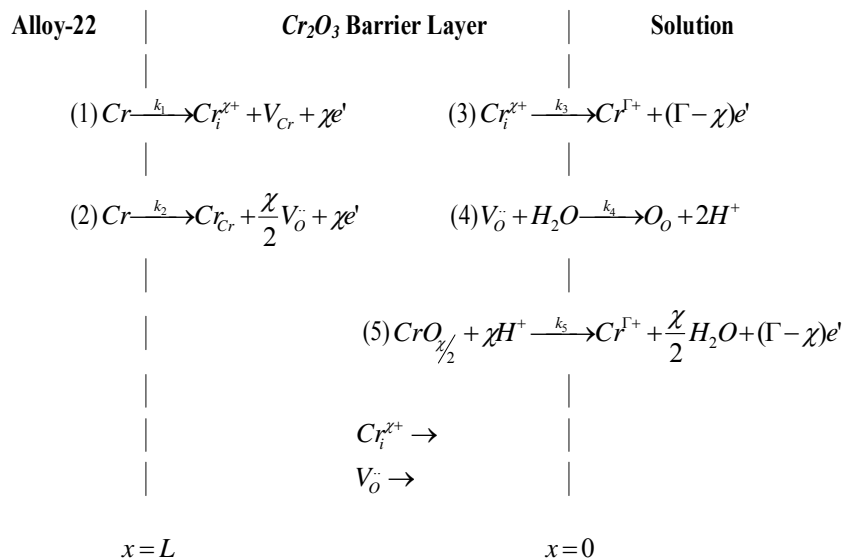
Passive Film Properties and Behavior

- Cathodic Reduction for cleaning the surface
- Holding at Open Circuit Potential (OCP) for potential to stabilize
- Perform a Reverse-Forward Scan for determining the suitable potentials
- Electrochemical Spectroscopy
- Holding at potential of interest
- Performing Electrochemical Impedance Spectroscopy
- Performing Mott-Schottky Analysis



Variation of total impedance (polarization resistance) with potential (-0.8 V to 0.8V SCE and temperature (24 & 60°C)

Computational Model for Passivity: Point Defect Model



| Reaction | a_i (V^{-1}) | b_i (cm^{-1}) | Units of k_i^0 |
|-------------------------------------------------------------------------------------------------------------------|---------------------------------------|------------------------|--------------------------------|
| (1) $Cr \xrightarrow{k_1} Cr_i^{\chi+} + V_{Cr} + \chi e'$ | $\alpha_1(1-\alpha)\chi\gamma$ | $\alpha_1\chi K$ | $\frac{mol}{cm^2 s}$ |
| (2) $Cr \xrightarrow{k_2} Cr_{Cr} + \frac{\chi}{2} V_O + \chi e'$ | $\alpha_2(1-\alpha)\chi\gamma$ | $\alpha_2\chi K$ | $\frac{mol}{cm^2 s}$ |
| (3) $Cr_i^{\chi+} \xrightarrow{k_3} Cr^{\Gamma+} + (\Gamma - \chi)e'$ | $\alpha_3\alpha\Gamma\gamma$ | 0 | $\frac{cm}{s}$ |
| (4) $V_O + H_2O \xrightarrow{k_4} O_O + 2H^+$ | $2\alpha_4\alpha\gamma$ | 0 | $\frac{cm}{s}$ |
| (5) $CrO_{\frac{\chi}{2}} + \chi H^+ \xrightarrow{k_5} Cr^{\Gamma+} + \frac{\chi}{2} H_2O + (\Gamma - \chi)e'$ | $\alpha_5\alpha(\Gamma - \chi)\gamma$ | 0 | $\frac{mol^{0.4}}{cm^{0.2} s}$ |

Schematic of physicochemical processes that are envisioned to occur within the barrier oxide (Cr_2O_3) layer on passive Alloy-22, according to the truncated Point Defect Model.

Rate constants $k_i = k_i^0 e^{a_i V} e^{-b_i L}$ for five interfacial reactions in terms of Point Defect Model

According to PDM, Steady state thickness of the barrier oxide layer is given by

$$L_{ss} = \frac{1}{\varepsilon} \left[1 - \alpha - \frac{\alpha\alpha_5}{\alpha_2} \left(\frac{\Gamma}{\chi} - 1 \right) \right] V + \frac{1}{\varepsilon} \left[\frac{2.303n}{\alpha_2\chi\gamma} - \beta - \frac{\alpha_5\beta(\Gamma - \chi)}{\alpha_2\chi} \right] pH + \frac{1}{\alpha_2\chi K} \ln \left(\frac{k_2^0}{k_5^0} \right)$$

J. of Electroanal. Chem. 575 (2004) 421-431, "An electrochemical impedance study of Alloy 22 in NaCl brine at elevated temperature. II. Reaction mechanism analysis", Digby D. Macdonald, Adan Sun, Namal Priyantha, Palitha Jayaweera

Thanks to Digby Macdonald, Pennsylvania State University

Summary of Long-Term Corrosion Behavior

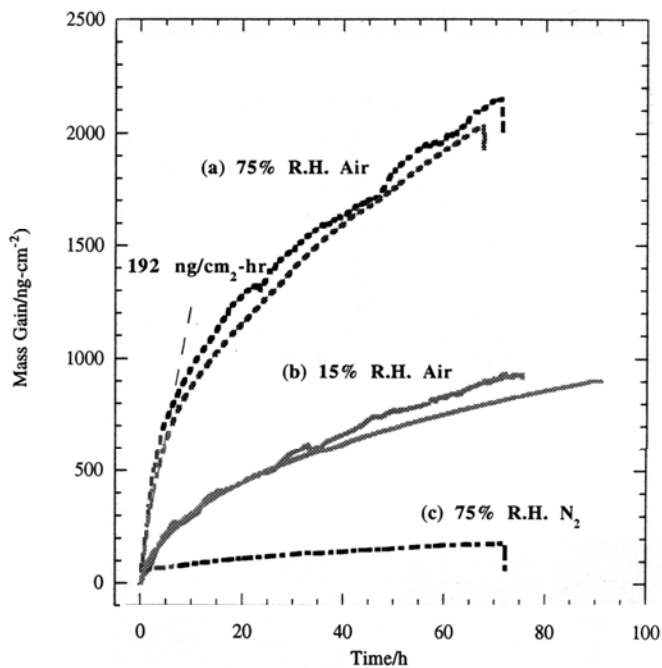
- **Corrosion is a primary determinant of waste package performance**
 - **Controls the delay time for radionuclide transport from the waste package**
- **Two major aspects**
 - **Evolution of corrosion damage by localized corrosion**
 - **Durability of passive films**
- **Analysis of the potential for damage by corrosion is crucial and a major effort has been undertaken to enhance the technical basis for long-term behavior**
 - **Can corrosive environments form and persist?**
 - **Will localized corrosion start and persist?**
 - **What damage would result?**

Reliability of Microelectronics, Computers and Communications

- **Ubiquitous use of microelectronic systems and devices**
 - › No longer in air conditioned control rooms
 - › Under car hoods, on shop floors, other hostile environments
- **Industry has no corrosion, but they sure can have “reliability” issues due to environmental stresses**
- **Environment is thin layers of condensed moisture with absorbed corrosive gases at ppb levels (H_2S , SO_2 , NO_x , Cl's)**
- **Corrosion science has led to advances in life prediction and accelerated testing**
 - › From the early work of Vernon to identify the “critical relative humidity” for atmospheric corrosion to the development of advanced models, e.g. GILDES

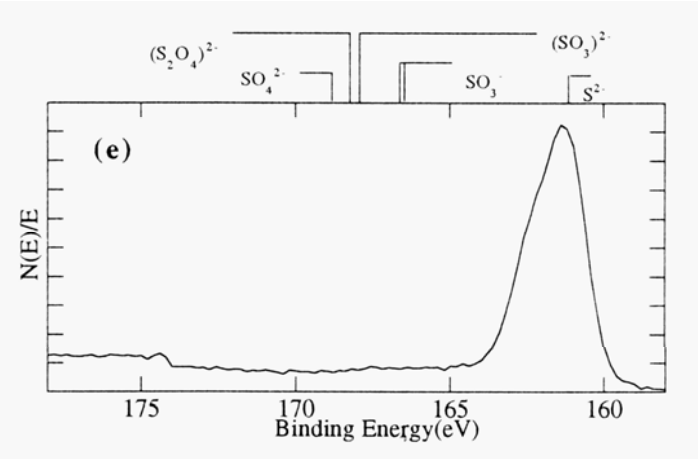
Application of Multiple-Techniques to Examine Tarnishing of Silver

Silver exposed to 100 ppb H₂S in flowing-mixed-gas cell

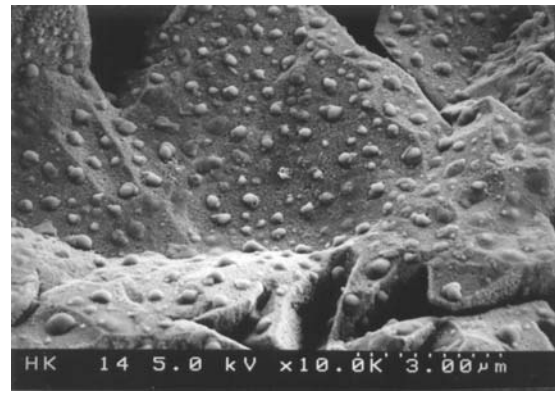


Quartz crystal microbalance measures weight gain vs time; can distinguish moisture gain from corrosion products

S-2p

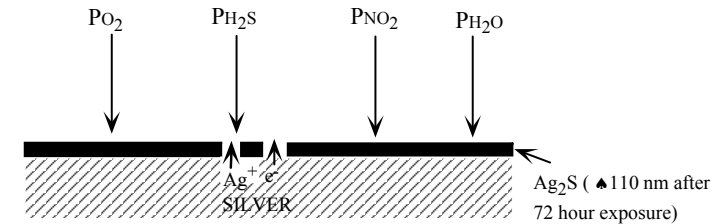
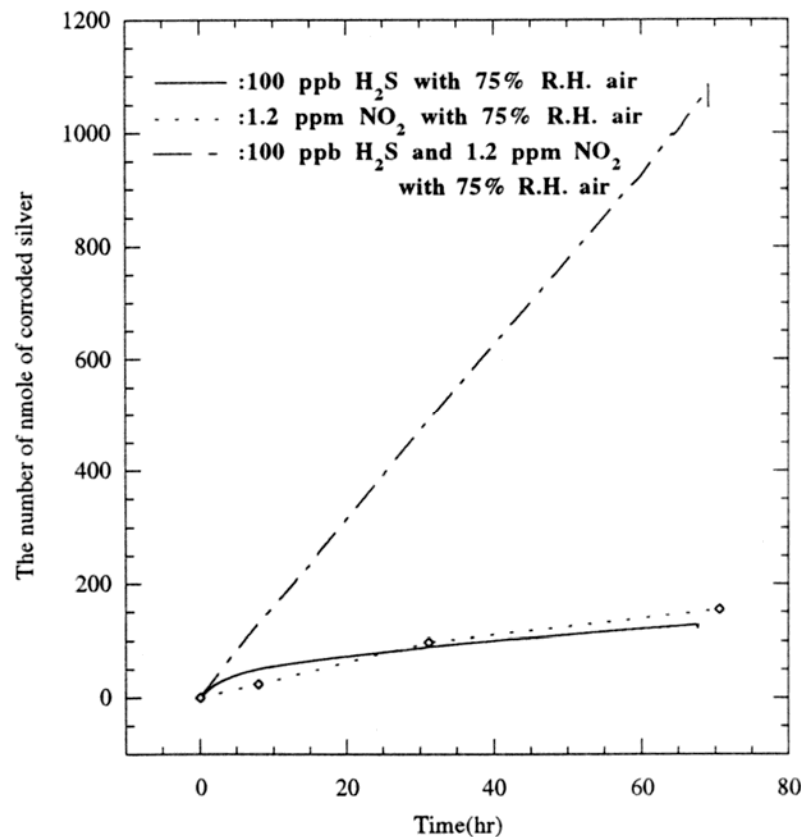


XPS analysis: S-2p detects sulfur as sulfide with no indication of sulfite or sulfate.

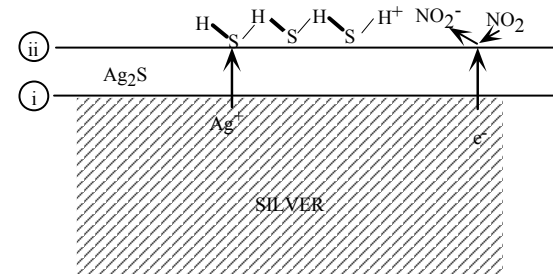


FESEM determines structure and morphology

Synergism of H₂S (corrodant) and NO₂ (oxidant) for Silver Corrosion



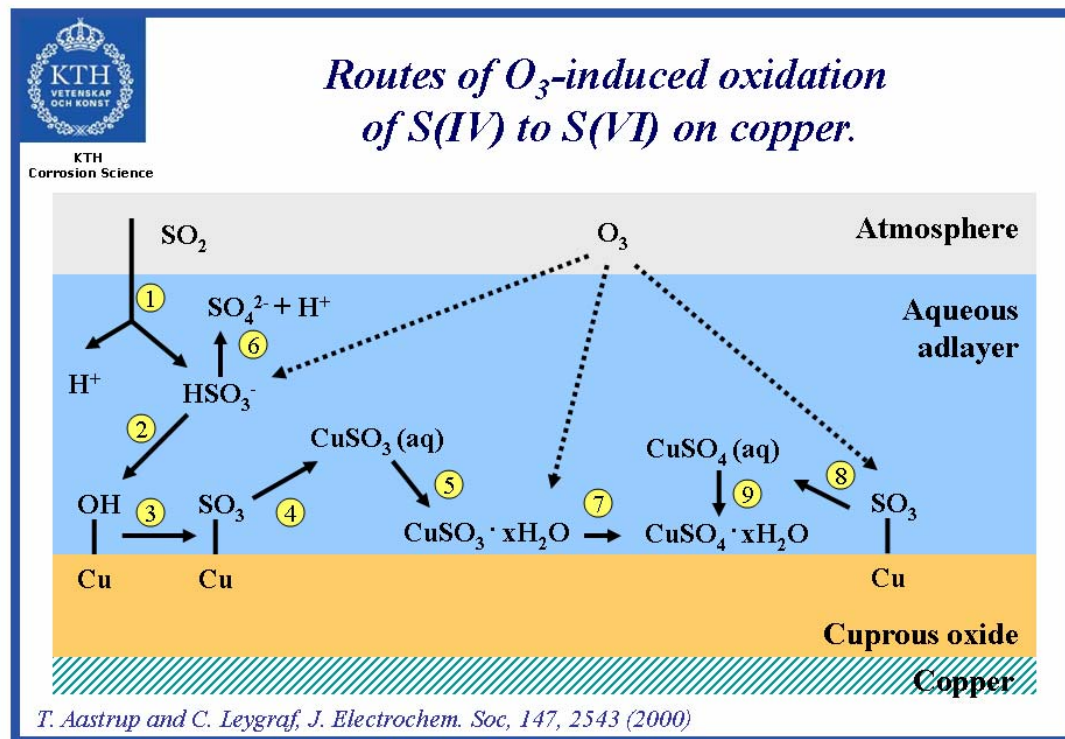
- oxidation of silver at (i) : $\text{Ag} \rightarrow \text{Ag}^+ + e^-$
- reduction of oxidizing species at (ii) : $\text{NO}_2 + e^- \rightarrow \text{NO}_2^-$
- formation of Ag₂S at (ii) : $2\text{Ag}^+ + \text{H}_2\text{S} + 2\text{NO}_2 \rightarrow \text{Ag}_2\text{S} + 2\text{HNO}_2 \uparrow$



- oxidation of silver at (i) : $\text{Ag} \rightarrow \text{Ag}^+ + e^-$
- reduction of oxidizing species at (ii) : $\text{NO}_2 + e^- \rightarrow \text{NO}_2^-$
- formation of Ag₂S at (ii) : $2\text{Ag} + 2\text{NO}_2 + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + 2\text{HNO}_2 \uparrow$

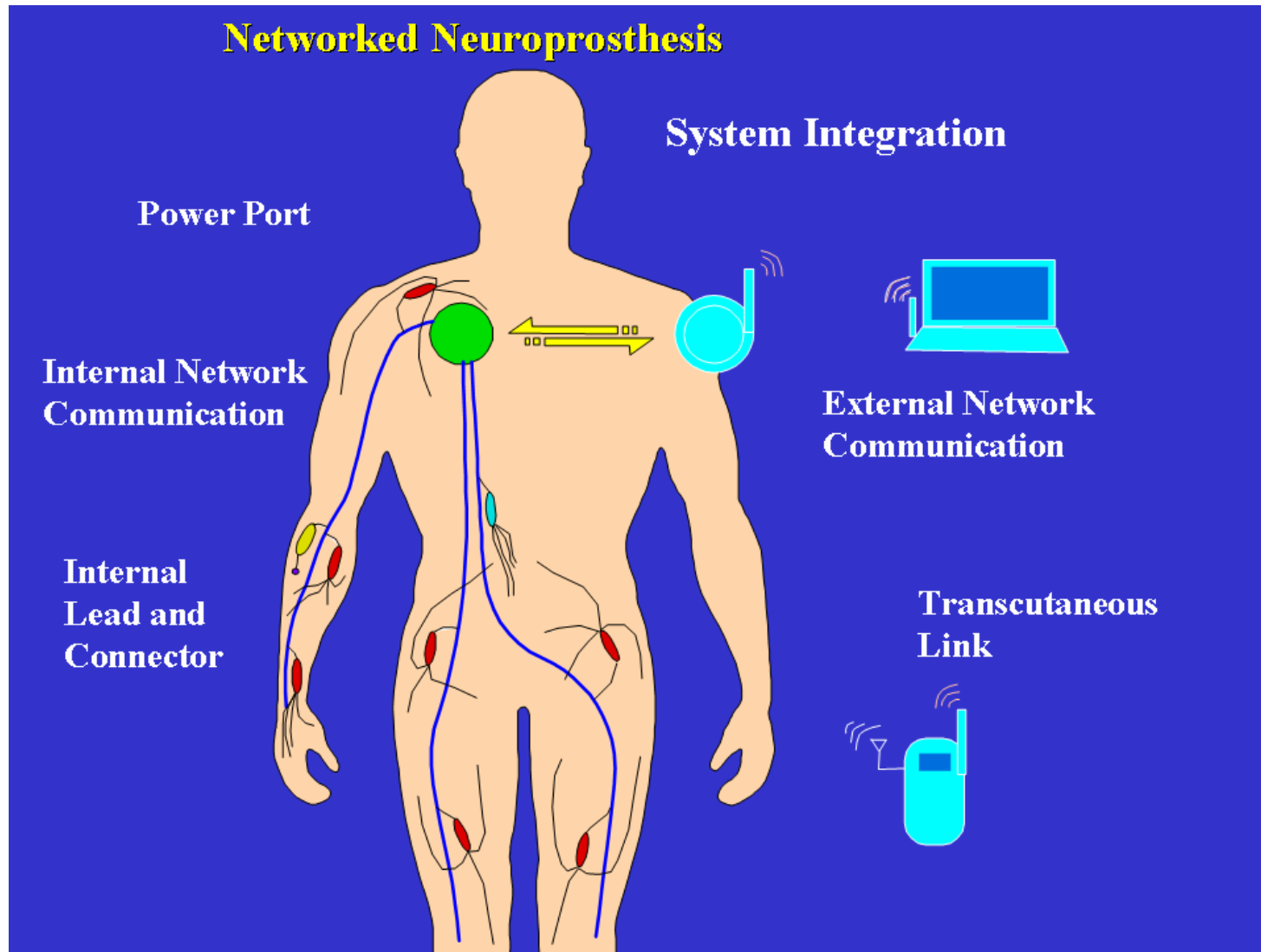
Computational Model for Atmospheric Corrosion: GILDES

Gas Interface Liquid Deposition Electrode Surface




Thanks to Christofer Leygraf; KTH-Division Corrosion Science; Stockholm, Sweden


Implantable Neuroprosthesis Systems




Implantable Neuroprosthesis Systems







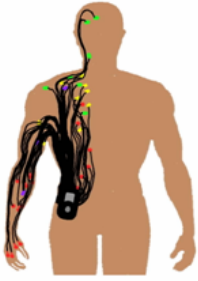

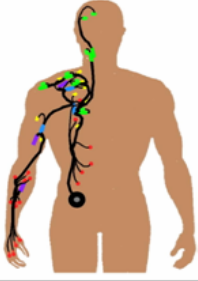

- * Grasping and Reaching
- * Standing and Stepping
- * Bladder and Bowel Function






Networked Neuroprosthesis

Case Western Reserve University
PI: Hunter Peckham, Ph.D.
Co-PI: Kevin Kilgore, Ph.D.

| | Central Device System | Micro-Injectable System | Distributed Neuroprosthetic System | |
|---------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| External Components |  |  |  |  |
| Internal Components |  |  |  |  |

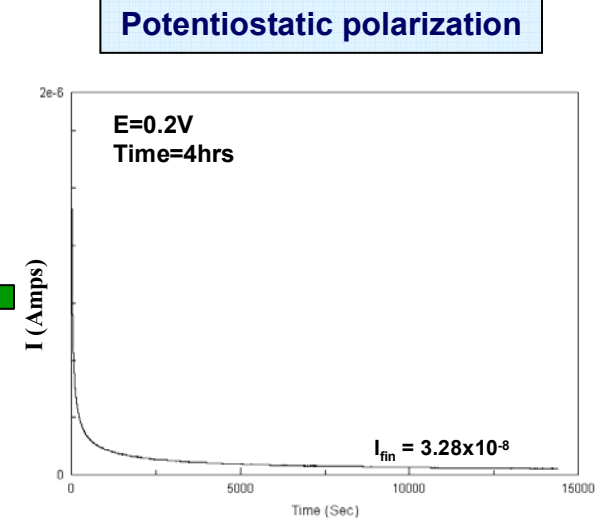
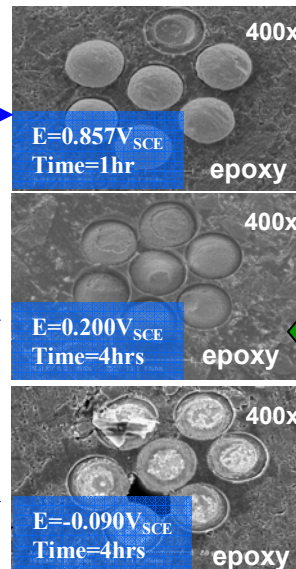
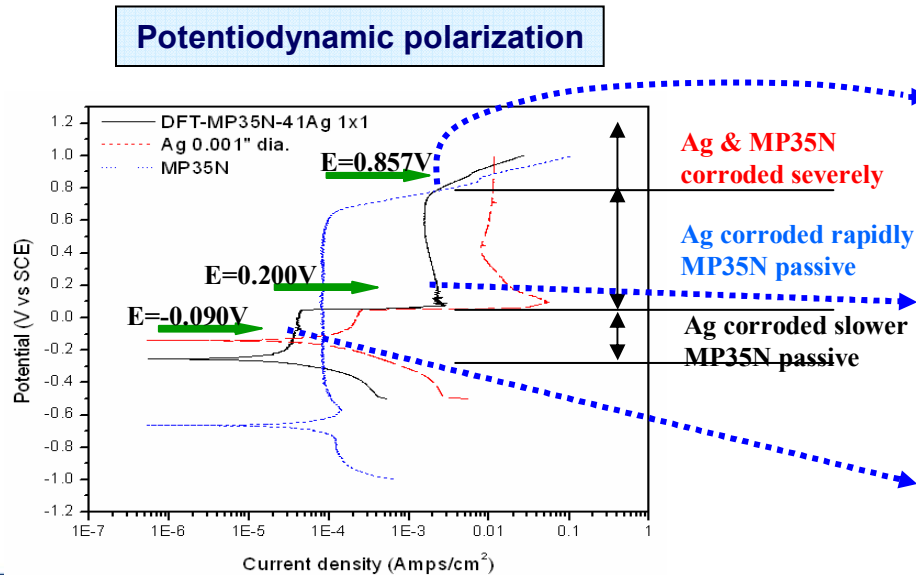
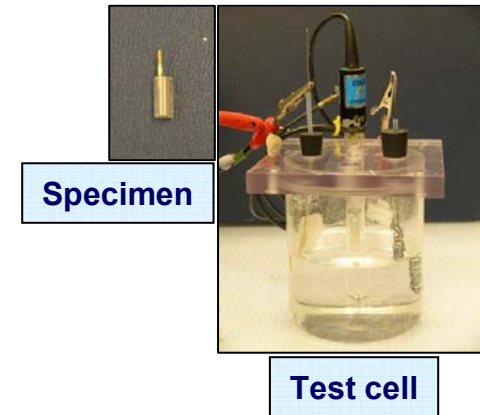
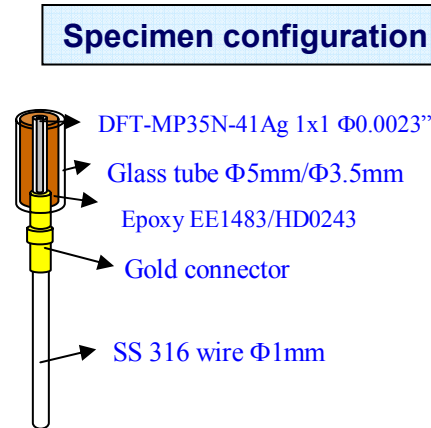
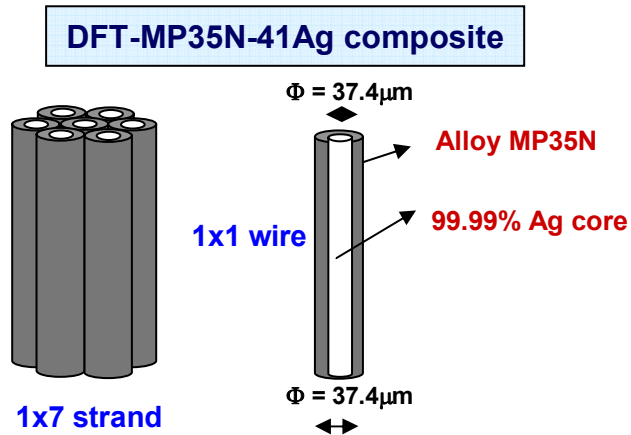


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J Payer-Plenary Lecture, Corrosion NACExpo 2006, San Diego, CA, March 13, 2006

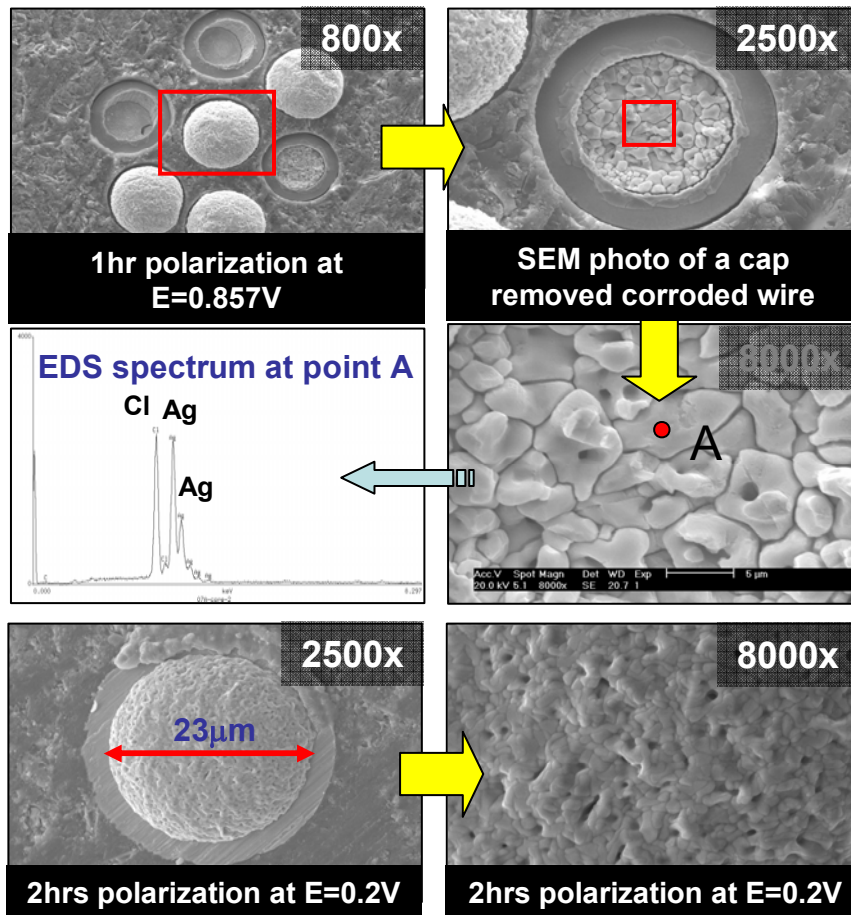
62

Anodic Polarization of Drawn Filled Tube DFT-MP35N-41AG

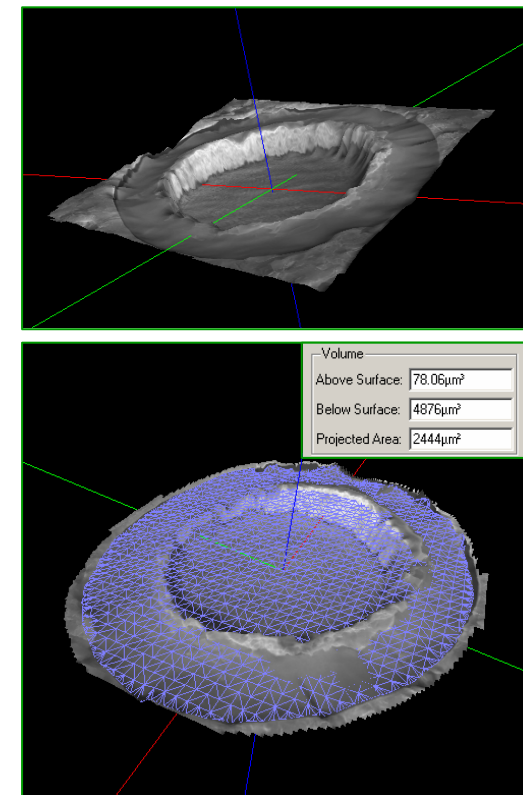


Examination of DFT-MP35N-41Ag Wires After Anodic Polarization

SEM/EDS Analysis



3D reconstruction



Opportunities for the Corrosion Community and NACE International

- **Major opportunities are at hand**
 - › **To promote, develop and implement enhanced understanding of material performance**
 - › **To probe technical enhancements**
 - » **Optimized performance**
 - » **Increased reliability**
 - » **Greater cost effectiveness**
- **Progress is realized through**
 - › **Increased scientific understanding**
 - › **Enhanced process models and**
 - › **Advanced technologies for corrosion control**

Key Drivers to Advances

- **Improved specifications and technical bases for performance**
 - › **Design/materials/construction**
 - › **Defined service conditions**
 - › **Performance specifications over service life**
- **Enhanced process models**
 - › **Integrated models/assessment tools**
 - › **Understanding at the molecular level**
- **Analytical/diagnostic tools, e.g. damage evolution, electrochemical, chemistry and structure**
- **Computational methods for complex and coupled processes**

Keys to Success

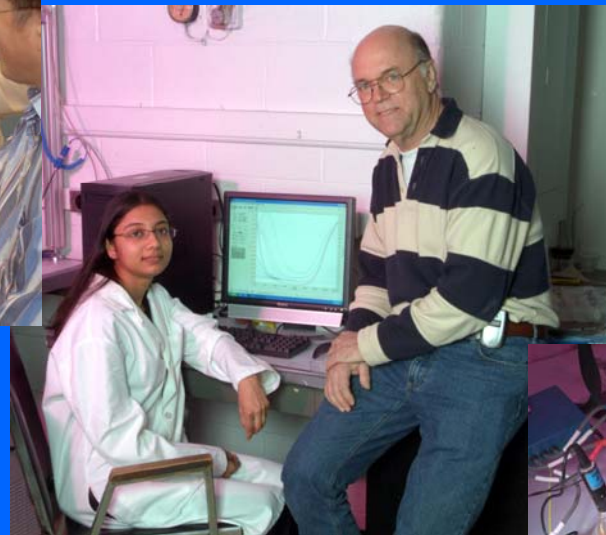
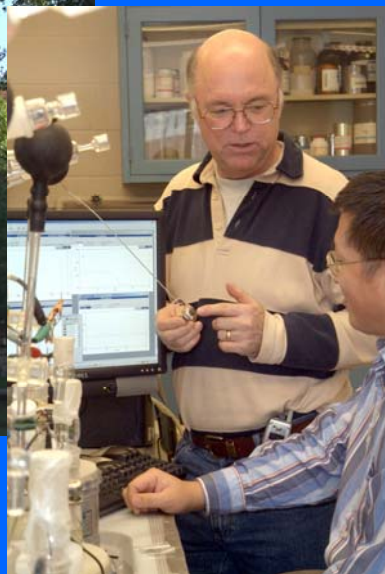
- **Well defined needs and applications**
 - › **Awareness and recognition by policy and decision makers**
 - › **Focused and measurable targets**
- **Coordinated and sustained programs**
 - › **Regular and effective communication among providers and users**
 - › **Multi-investigator, collaborative projects**
 - › **Focused technical thrusts**
 - › **Critical mass of resources**
- **Synergism of experimental and computational efforts**
- **Executable plan for transition to practice and implementation**
- **Take action—Make good things happen**



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Thank You



SCHOOL OF ENGINEERING