OCRWM Office of Science and Technology and International

CASE WESTERN RESERVE UNIVERSITY

Materials Performance Targeted Thrust

Presented to:
NWTRB Informal Fact Finding Meeting

Presented by:
Joe H. Payer
Thrust Lead
Case Western Reserve University

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Las Vegas, NV

This presentation has been funded in whole or in part by the U.S. Department of Energy

Technical Scope and Directions

- Good Science
  - Materials Performance; Corrosion; Electrochemistry; Materials Science; Physical Chemistry; Geochemistry
  - Responsive to Office of Science and Technology and International(OST&I) Mission and distinction between Science and Technology(S&T) and Project Baseline & License matters
- Addresses State-of-Science Issues
  - Enhance the understanding of materials corrosion performance
  - Explore technical enhancements

Technical Scope and Directions

- **Sources of Information on Corrosion Related Issues**
  - **DOE OCRWM**
  - **DOE Basic Energy Sciences/OCRWM Corrosion Workshop**
  - **DOE Peer Reviews and International Peer Reviews**
  - **NRC, NWTRB and ACNW Comments**
  - **External Comments**

Programmatic Structure

- Focus is on process of corrosion, materials science, electrochemistry, physical chemistry, geochemistry
- Coordinated, Multi-Investigator Approach
  - Critical mass for targeted topics
- Engage leading scientists/engineers from universities and national laboratories
- Coordination projects with Natural Barriers Thrust and Source Term Thrust

Programmatic Structure

- **Transition science to advanced technologies and Yucca Mountain Project**
  - **High Performance Corrosion Resistant Metals Project co-funded by DOE/OST&I and Defense Advanced Research Project Agency (DARPA) to Advanced Technologies Program**
- **Communicate and coordinate with Yucca Mountain Project and others**
- **Disseminate findings through publications and presentations with technical associations and professional societies**

Participants in Materials Performance Targeted Thrust - Universities

- **DOE/OST&I Multi-University Corrosion Cooperative (CorrCoOp)**

  Comprised of some 14 Principle 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)

OST&I Materials Performance Thrust Participants and Management

Universities

- Arizona State
- Case Western Reserve
- Ohio State
- Penn State
- Univ of Cal Berkley
- Univ of Minnesota
- Univ of Toronto
- Univ of Western Ontario
- Univ of Virginia

National Labs

- ANL
- LBNL
- LNLL
- ORNL
- PNNL
- AECL - Canada

Director OST&I: John Wengle
Materials Performance Thrust Lead: Joe Payer

Executive Committee
Joe Payer-Case; Jerry Frankel-Ohio State; Rob Kelly-U Va; Digby Macdonald-Penn State; John Scully-U Va

Technology/Research Committee
All University and National Lab PI's

Advisory Committee
R. Baboian, R. Frankenthal and A. J. Sedriks

International Affiliates
Martin Straatman-Max-Plank Institute, Duesseldorf
Christopher Leygraf-Royal Institute of Technology, Stockholm

Materials Performance Targeted Thrust

Dr. Joe H. Payer-Thrust Lead of Materials Performance Targeted Thrust of the Science and Technology Program of OST&I

- Dr. Payer is an internationally recognized expert in corrosion science and engineering, and has intimate knowledge and understanding of corrosion issues.

Yucca Mountain Experience:

- Chairman of the Waste Package Materials Performance Peer Review Panel (Final Report, February 2002)
- Member of the Total System Performance Assessment (Viability Assessment) Peer Review Panel (Final Report, February 1998)
- Invited presentations on corrosion issues on the NWTRB and ACNW

Management Experience:

- Director of the Yeager Center for Electrochemical Sciences at Case
- Department Chairman of Materials Science and Engineering at Case
- Manager Corrosion Section at Battelle Columbus Laboratories
- Manager of Materials Technology at Battelle Houston Operations

Materials Performance Targeted Thrust External Review Panel

Robert Baboian, Ph. D., P.E. – Retired from Texas Instruments, Principal Fellow, Head and Founder of TI Electrochemical and Corrosion Lab, past president of ASTM

Expertise – Corrosion and reliability of electronic materials and devices; corrosion; passivation; physical and analytical electrochemistry.

Awards – The Speller award of NACE, the Cavanaugh award from ASTM, the Vittorio de Nora from the Electrochemical Society, the National Materials Advancement award. Holder of 15 US patents, editor of 13 books, and author of over 175 technical publications.

Robert Frankenthal, Ph.D. – Retired as a Distinguished Member of Technical Staff from Bell Laboritories, Lucent Technologies; research assistant at US Steel Corp.

Expertise – Marine corrosion, stress-corrosion cracking, high-temperature corrosion, stainless steel, nickel base alloys, coatings, corrosion sensors, titanium alloys, and aluminum alloys.

Awards – Frank Newman Speller award of NACE, Fellow of ASM International, and Fellow of NACE International

A. JOHN SEDRIKS, Ph.D. – Retired Program Officer in the Materials Science and Technology Division at the Office of Naval Research (ONR); former head of the Metallurgy Dept at Martin-Marietta's Research Institute; Manager of Research at International Nickel Company's LaQue Center for Corrosion Technology.

Expertise –marine corrosion, stress-corrosion cracking, high-temperature corrosion, stainless steels, nickel-base alloys, coatings, corrosion sensors, titanium alloys, and aluminum alloys.

Awards – Frank Newman Speller award of NACE, Fellow of ASM International, and Fellow of NACE International.

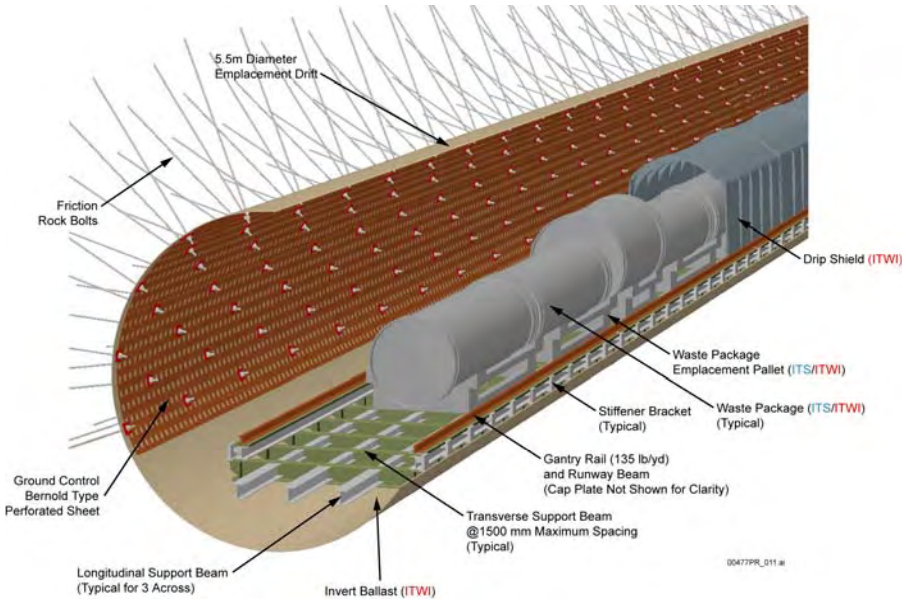
Excerpts from External Review Panel Report

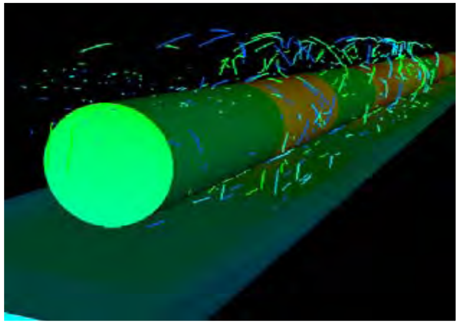
- It was the unanimous opinion of the members of the External Review Panel that the programs within the Materials Performance Targeted Thrust are of the highest quality.
- While the programs themselves are in their infancy, their logical layout and some preliminary data already available promise major advances in the understanding, and hence long-term predictability, in this area of corrosion science.
  - …subject of great importance with regards to corrosion behavior.
  - …focused interest on bold new corrosion science topics that have not been addressed before in any systematic way.
  - The development of new methods to investigate this area will advance the science and technology
  - …not aimed at achieving incremental improvements in understanding of known corrosion phenomena but represent development of new knowledge
  - The work will enhance the understanding of the science and technology…and lead to new technologies…
  - New and innovative technological approaches have been described by many of the workers.
  - The overall project is unique in that it seeks a basic, fundamental understanding of the rates and mechanisms of complex real-world reactions by simultaneously studying both model systems and the real complex ones.
  - …have been designed to obtain fundamental data and understanding from highly complex, real world systems …
  - Many opportunities exist for cross-fertilization and synergism among the projects.
  - Major significant advances are likely to be made in furthering our understanding of the kinetics and mechanisms of fundamental corrosion processes.

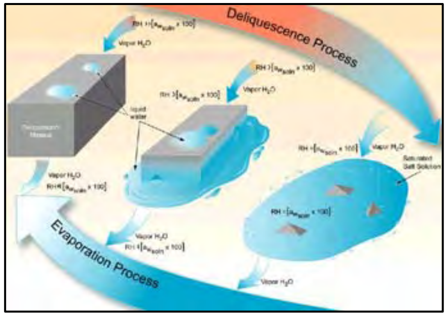
Scope: Major Technical Thrusts

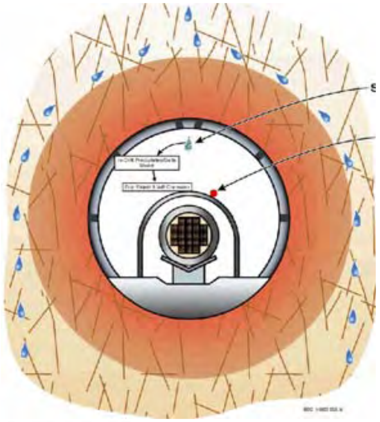
- To enhance the understanding of materials corrosion performance and to explore technical enhancements
- Corrosion processes metal surfaces covered with particulate and deposits
  - Effects of moisture on corrosion performance of metals
- Evolution of corrosion damage by localized corrosion
  - Initiation,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

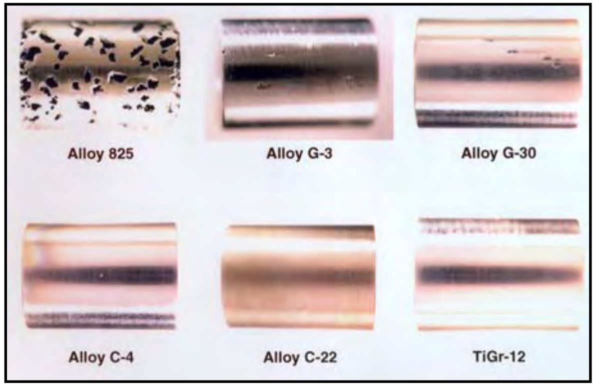
Corrosion and Materials Performance

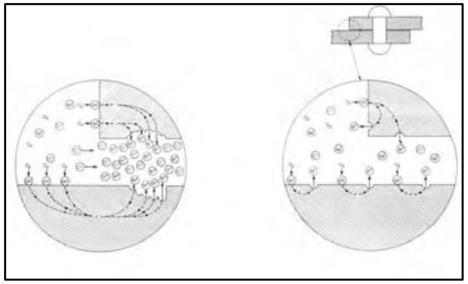












Corrosion Resistance is Crucial to Waste Package Performance

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

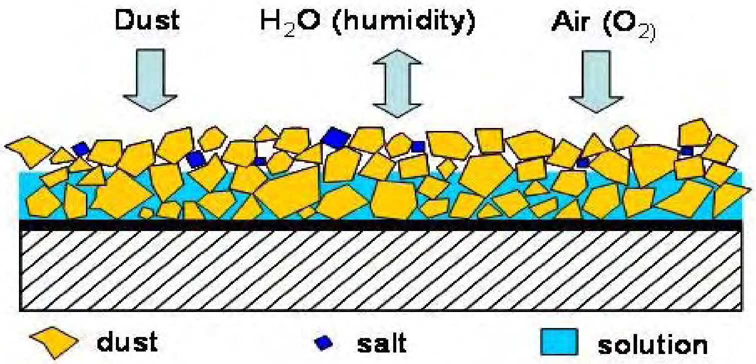
16,000 to 160,000 years to penetrate the thickness of one U.S. Quarter for a corrosion rate of 0.1 to 0.01 µm/yr.

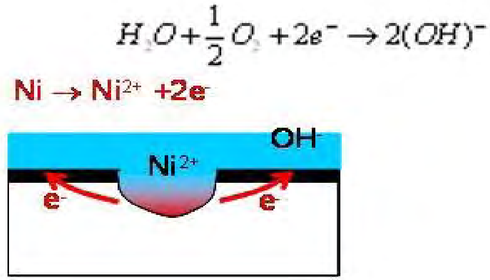
Corrosion rates of approximately 0.01 µm/year are measured in exposures of over 5-years at LLNL Long Term Test Facility.

Corrosion processes metal surfaces covered with particulate and deposits

- <u>Kinetics of the Cathodic Reduction of Oxygen on Passive Metals</u>
  - David W. Shoesmith and Jamie Noel; University of Western Ontario
- <u>Oxygen Electro-reduction on Passive Metals in Particulate and Deposited Layers</u>
  - Dominic Gervasio; Arizona State University
- <u>Corrosion Cells beneath Thin Films, Particulate and Deposited Layers</u>
  - Joe H. Payer; Case Western Reserve University
- <u>Kelvin Probe Measurements of Corrosion under Thin Deliquescence Brine Layers</u>
  - Gerald S. Frankel and Rudy G. Buchheit; The Ohio State University
- <u>Mechanism of Mixed-Ion Effects on Corrosion in Thin Films</u>
  - Roger C. Newman; University of Toronto
- <u>Durability of Passive Films-Effects of Sulfur and Thermal Treatment</u>
  - Russ Jones and Chuck Windich; Pacific Northwest National Laboratory
- <u>Effect of Environmental Variables on the Structure and Composition of Passive Films</u>
  - Thomas M. Devine; University of California, Berkeley

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: $Ni \rightarrow Ni^{2+} + 2e^-$
- Cathode: $H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$

Evolution of Environment

Evolution of Solution Layer Chemistry in the Presence of Particulate

Robert G. Kelly; University of Virginia

Modeling and Measurement of Current Distribution in Particulate and Deposited Layers

Uziel Landau and Joe H. Payer; Case Western Reserve University

High-Temperature, Multi-Species Solution Properties and Behavior

Don Palmer; Oak Ridge National Laboratory

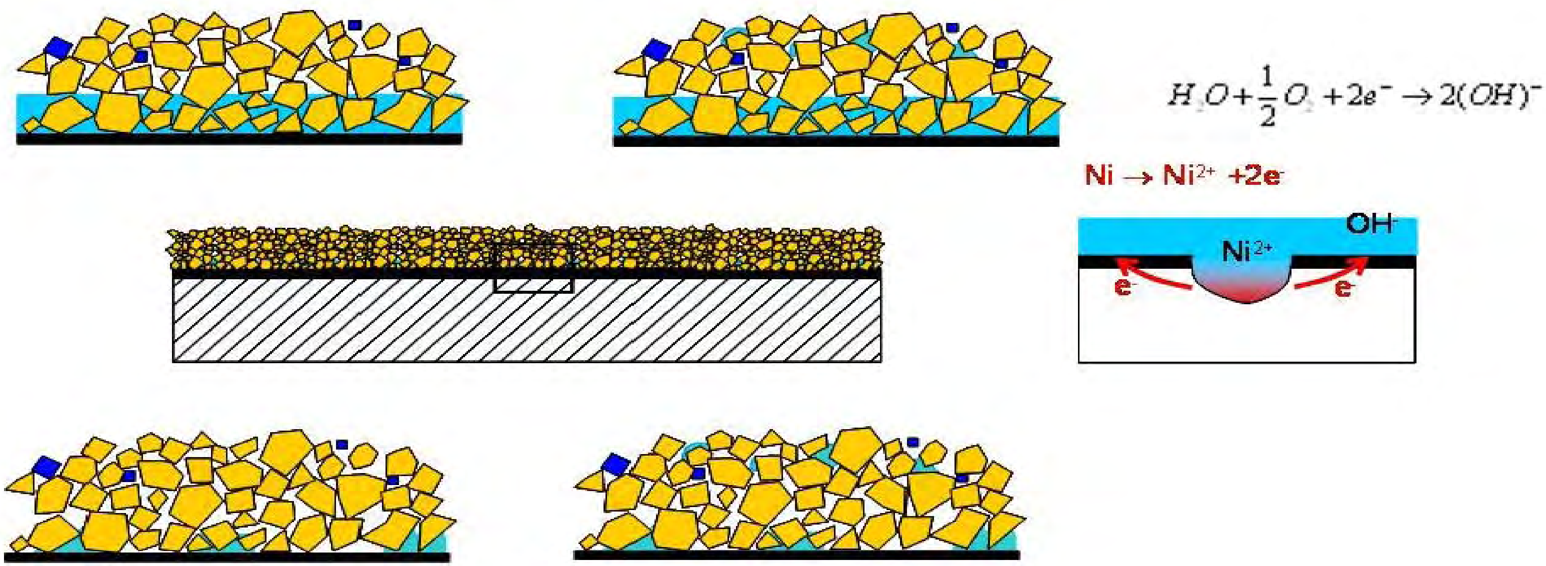
Microelectronic and MEMS Devices to Support Combinatorial Methods for Corrosion Evaluations

C.C. Liu and Joe H. Payer; Case Western Reserve University

Optical Probes and Sensors to Determine Concentration Distributions in Thin Films on Reactive Surfaces

William H. Smyrl; University of Minnesota

Scenarios of Moisture in Particulate



Evolution of Corrosion Damage

Crevice Corrosion Electrochemistry

John R. Scully; University of Virginia

Modeling of Critical Chemistry for Crevice Corrosion

Robert G. Kelly; University of Virginia

Experimental Determination of the Evolution of Crevice Corrosion Damage

David W. Shoesmith and Jamie Noel; University of Western Ontario

Coupled Crevice Tests for Initiation, Propagation and Arrest of Crevice Corrosion

Brian Ikeda; Atomic Energy of Canada Limited

Localized Corrosion Stability in the Presence of Non-Chloride Anions

Roger C. Newman; University of Toronto

Microstructural Effects on Localized Corrosion of Ni-Cr-Mo Alloys

Gerald S. Frankel and Rudolph G. Buchheit; The Ohio State University

Combinatorial Chemistry Approaches for Alloy Composition and Corrosion Behavior

Rudolph G. Buchheit and Gerald S. Frankel; The Ohio State University

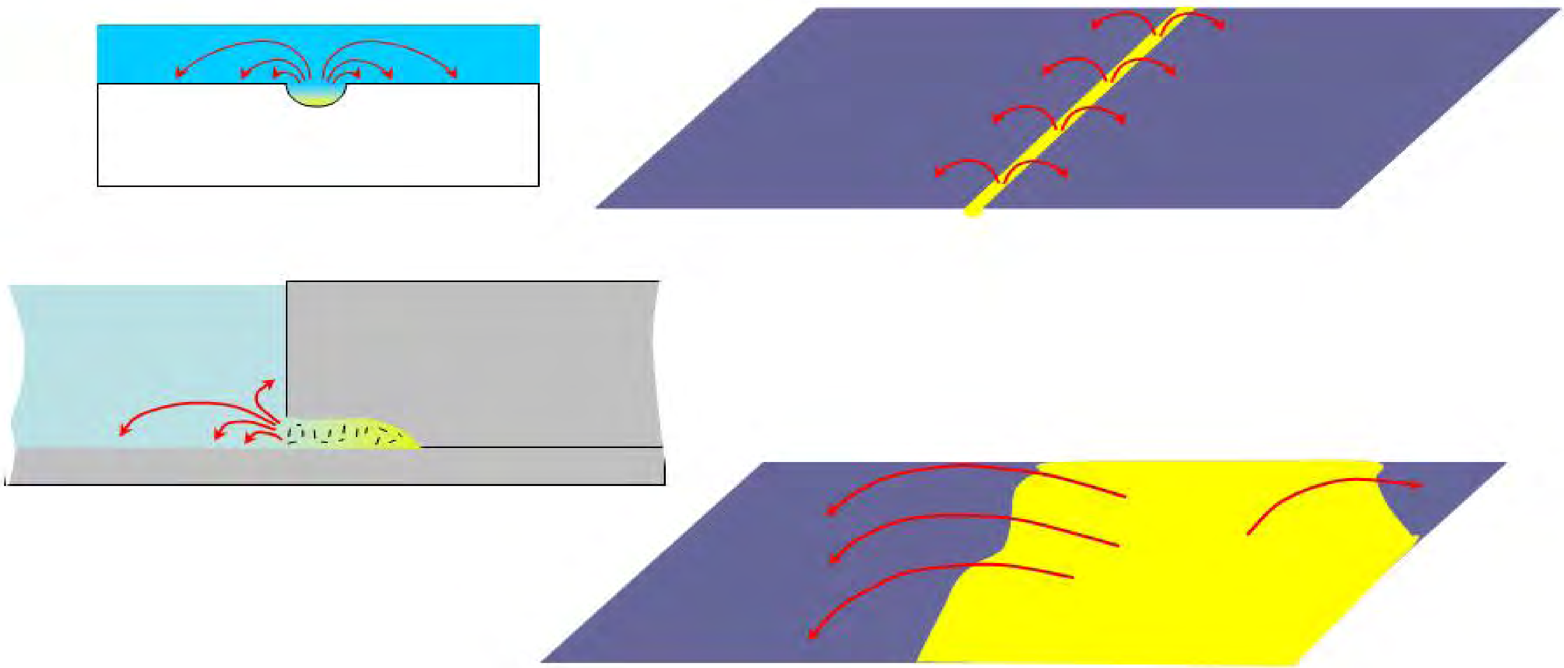
Prediction of the Time Evolution of Localized Corrosion Damage

Digby D. Macdonald; Pennsylvania State University

Data Mining of Experimental Localized Corrosion Data

Mirna Urquidi-Macdonald; Penn State University

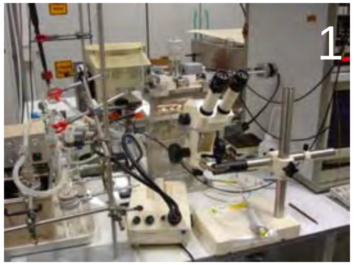
Scenarios of Corrosion Cells

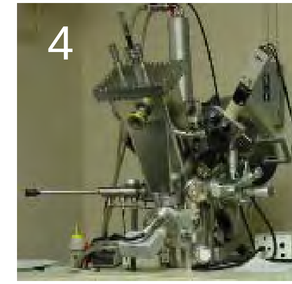


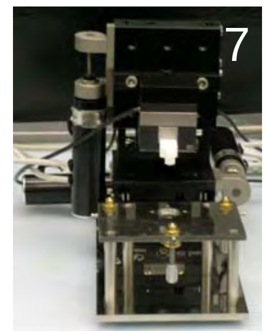
Specialized Capabilities and Facilities

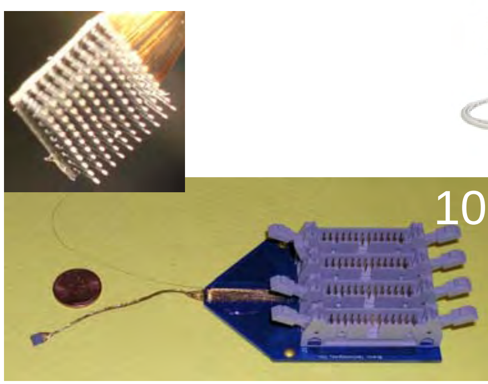
- **World-class, specialized facilities and equipment**
- **Synergistic, complementary experiments and analysis**
- **Cross fertilization and sharing of technique development and application**

Specialized Capabilities and Facilities



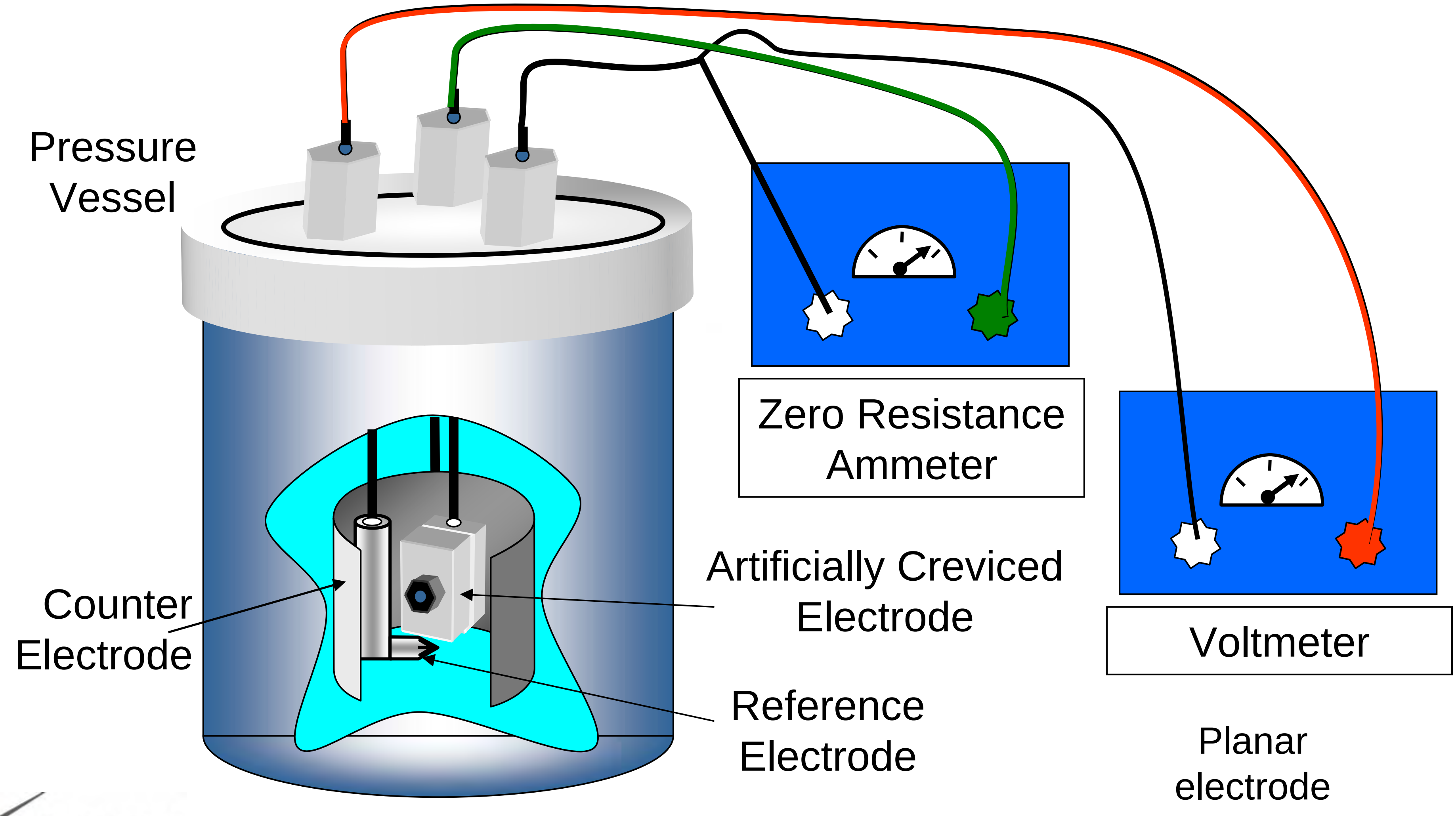




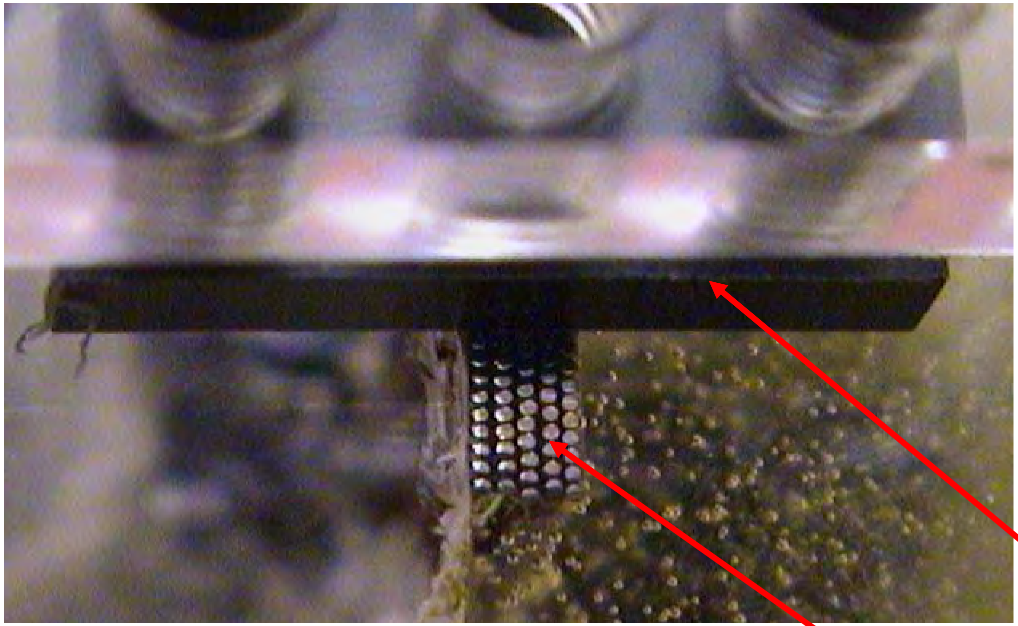


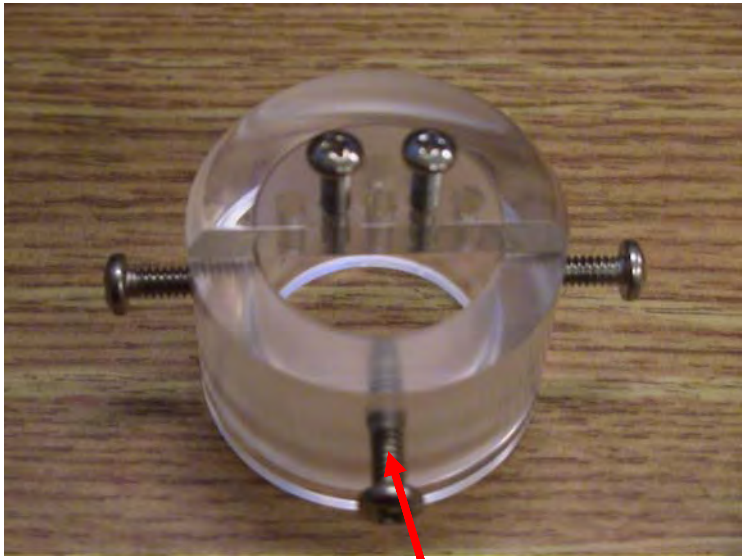
1. Kelvin Probe and Scanning Kelvin Probe
2. Laser-directed powder deposition for graded Ni-Cr-Mo compositions
3. Experimental apparatus for thin-layer electrochemical studies of stability of corrosion sites
4. X-ray Photo-Electron Spectrometry
5. 200KV Transmission Electron Microscope
6. Salt Particle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

Coupled Crevice Experiment



Multi-Electrode Rescaled Crevice

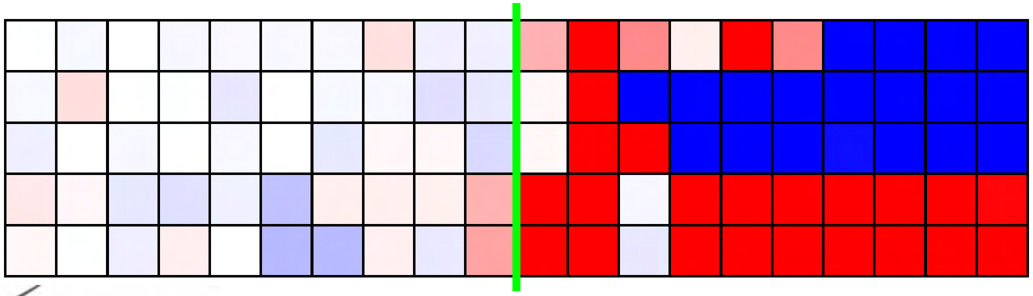




Crevice Former Line

Multi-Electrode Array (MEA)

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



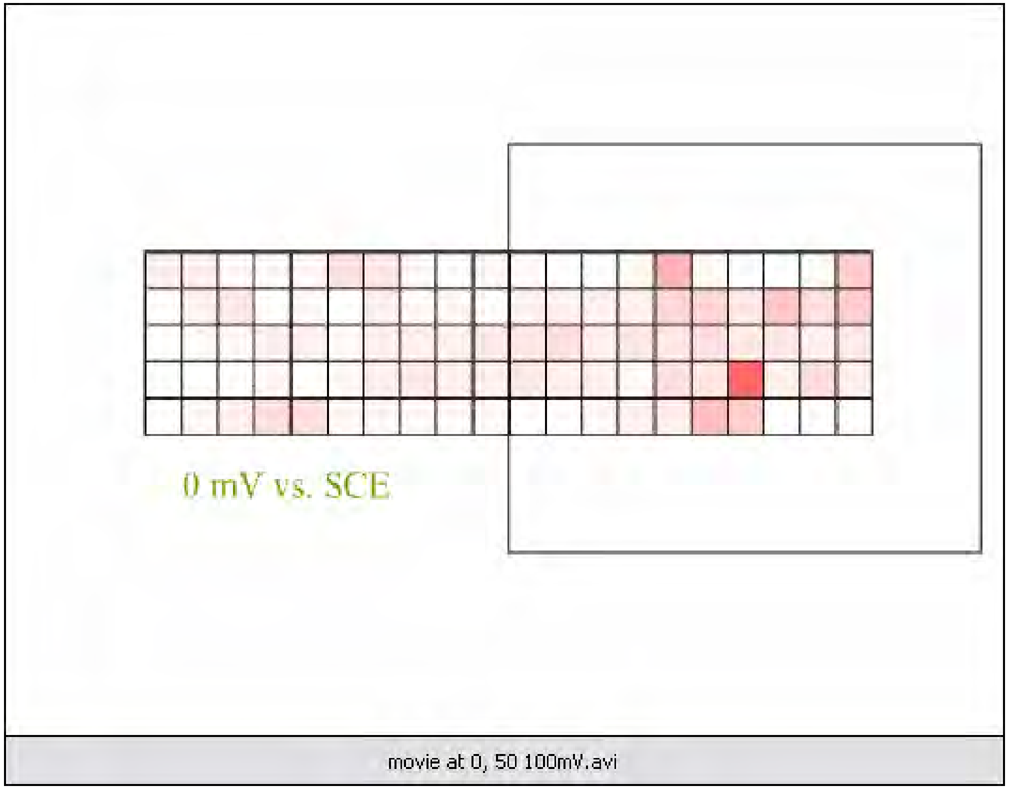
Crevice Former Holder

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

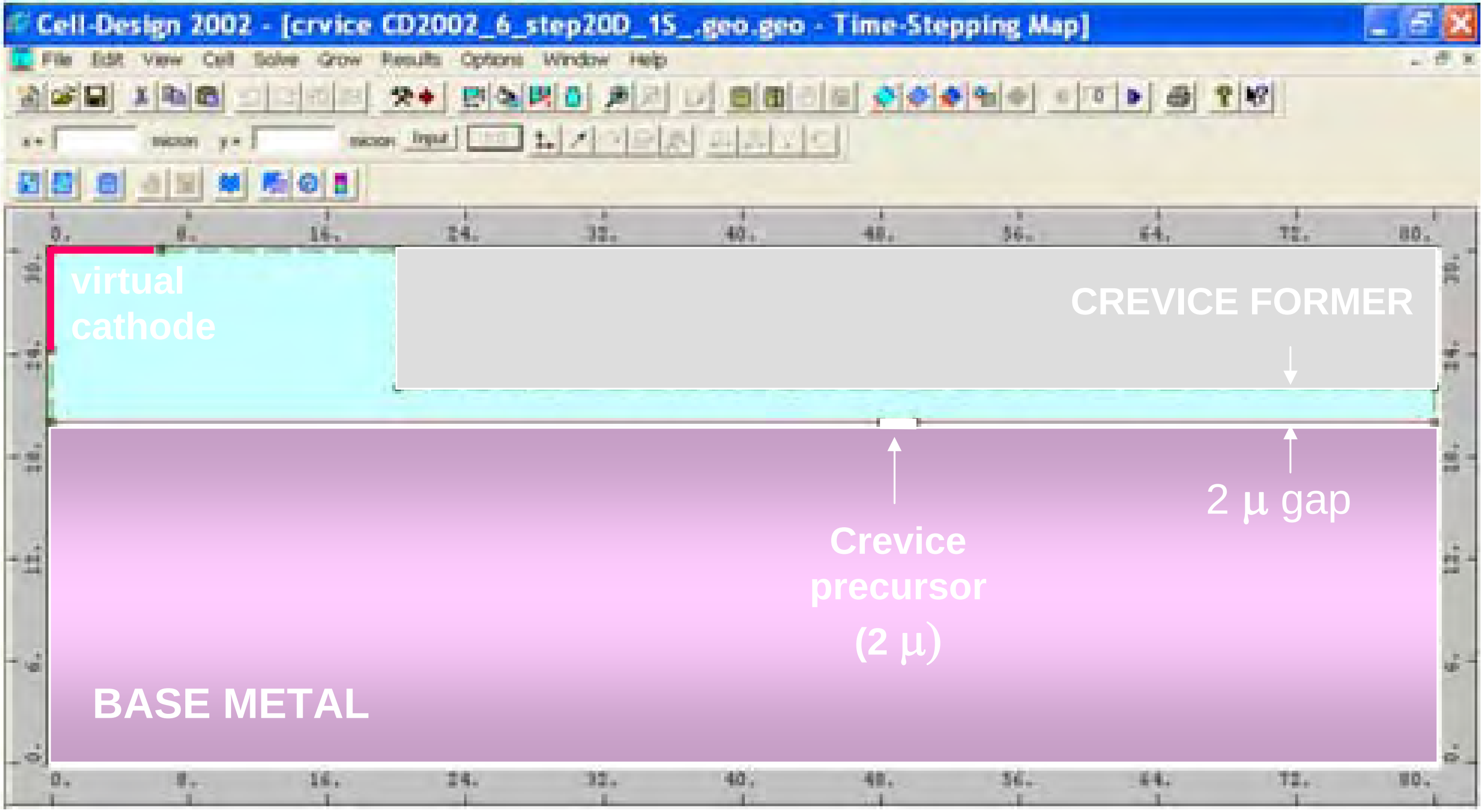
•AISI 316 SS in 0.25 M Fe_3Cl

Crevice Corrosion Damage Evolution

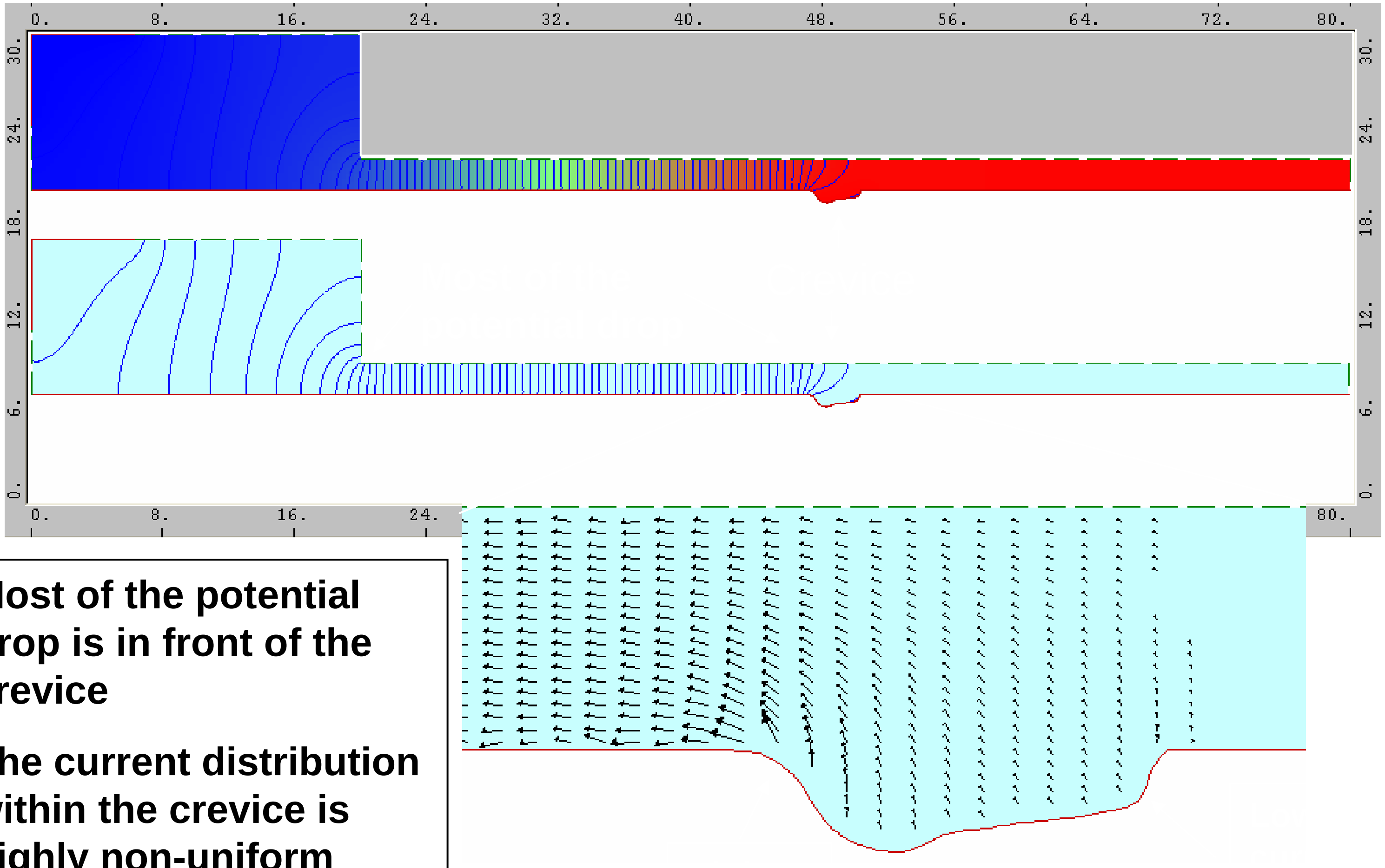
•*316 SS at 47 °C, 1M NaCl, 1 hr at 0 V vs. SCE, 1 hr at 0.05 V vs. SCE and 1 hr at 0.1 V vs. SCE, aerated. SCE is a Saturated Calomel Reference Electrode.*



Simulation of Crevice Propagation

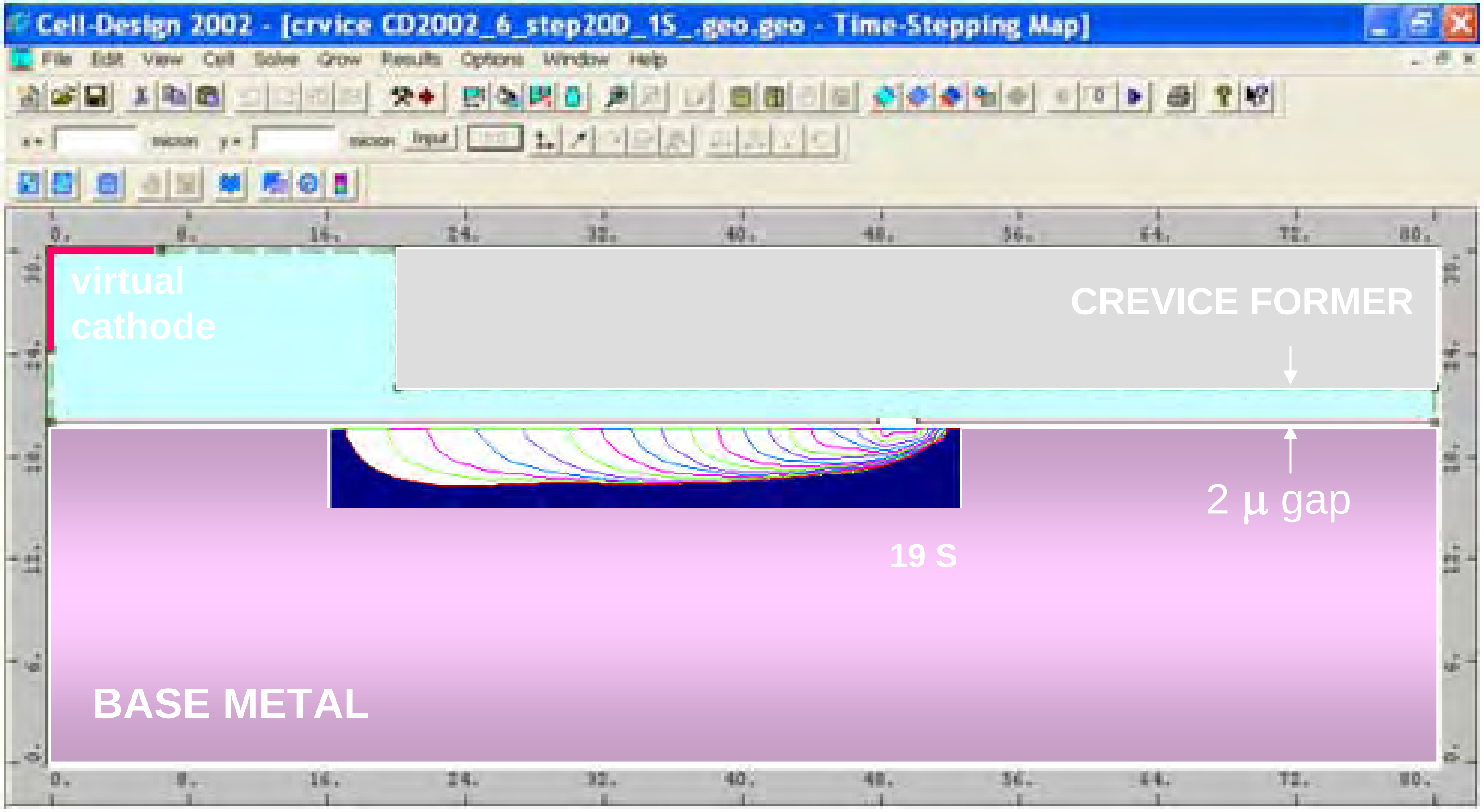


Potential and Current map in a Crevice



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

Simulation of Crevice Population



OST&I Materials and Performance Thrust

- **Programmatic Milestones**
  - **Materials Performance (Corrosion) Thrust Start-up Projects; projects in the S&T project portfolio identified and grouped to form the Targeted Thrust area; FY04**
  - **DARPA/DOE High Performance Corrosion Resistant Metals project transitioned from Materials Performance Thrust to Advanced Technologies, FY05**
  - **Corrosion Cooperative established, June 1, 2004**

Summary

- **Collaborative technical thrusts focused on important topics**
  - **Long-term behavior of protective, passive films**
  - **Composition and properties of moisture in contact with metal surfaces**
  - **Rate of penetration and extent of corrosion damage over extremely long times**
- **Each technical thrust has a set of coordinated projects**