U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
EBS PANEL MEETING

SUBJECT: CURRENT AND PLANNED MATERIALS RESEARCH

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Current and Planned Materials Research

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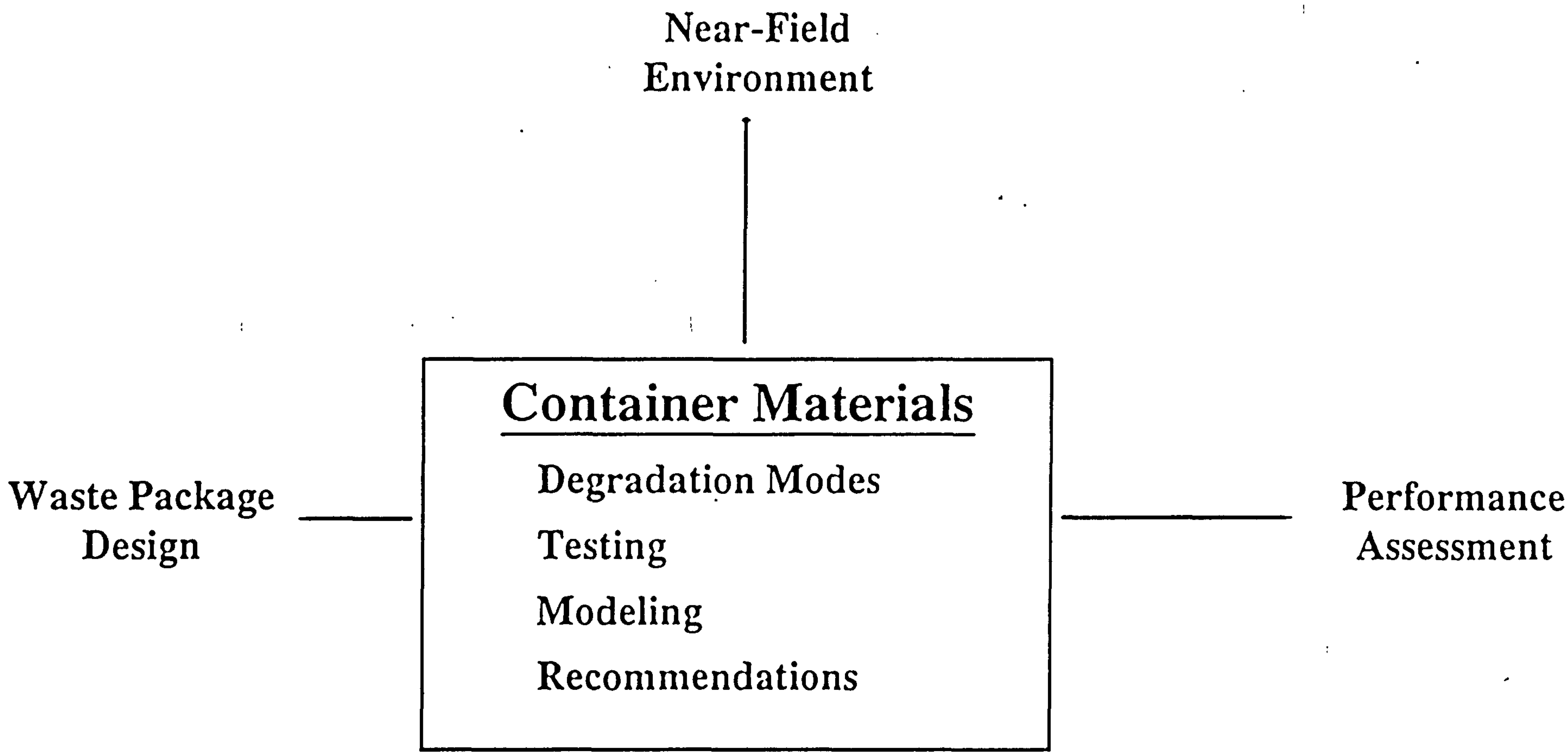
2/22/94-1

Reason for Container Materials Research

- Information basis for container material selection
  - Available technology
- Information basis for long-term behavior predictions
  - Containment
  - Controlled release
  - Emplacement environment


Near-Field
Environment
Container Materials
Degradation Modes
Testing
Modeling
Recommendations
Waste Package
Design
Performance
Assessment

Container Materials Considered in Advanced Conceptual Design Multiple-Barrier Waste Packages

Inner Barrier (Corrosion Resistant)

Nickel-Base Alloys

- Incoloy 825
- Inconel 690
- Hastelloy C-4
- Hastelloy C-22
- Hastelloy C-276

Titanium-Base Dilute Alloys

- Grade 12
- Grade 16

Copper and Nickel Alloys

- 70/30 Copper-Nickel
- Monel 400

Outer Barrier (Corrosion Allowance)

Ferrous Materials

- Carbon Steels
- Low Alloy Steels (Cr-Mo, "weathering")
- Ductile Cast Irons
- Silicon Cast Irons

Copper-Base Materials

- Unalloyed Coppers
- Aluminum Bronzes

Examples of Combinations of Materials

- Carbon Steel outer — Incoloy 825 inner
- Carbon Steel outer — Ti Grade 12 inner
- Ductile Cast Iron outer — Hastelloy C–4 inner
- Unalloyed Copper outer — 70/30 Copper-Nickel and Monel 400 inner
- Carbon Steel and Unalloyed Copper outer — Hastelloy C-22 inner

Many other combinations possible

Multiple Barrier Approach

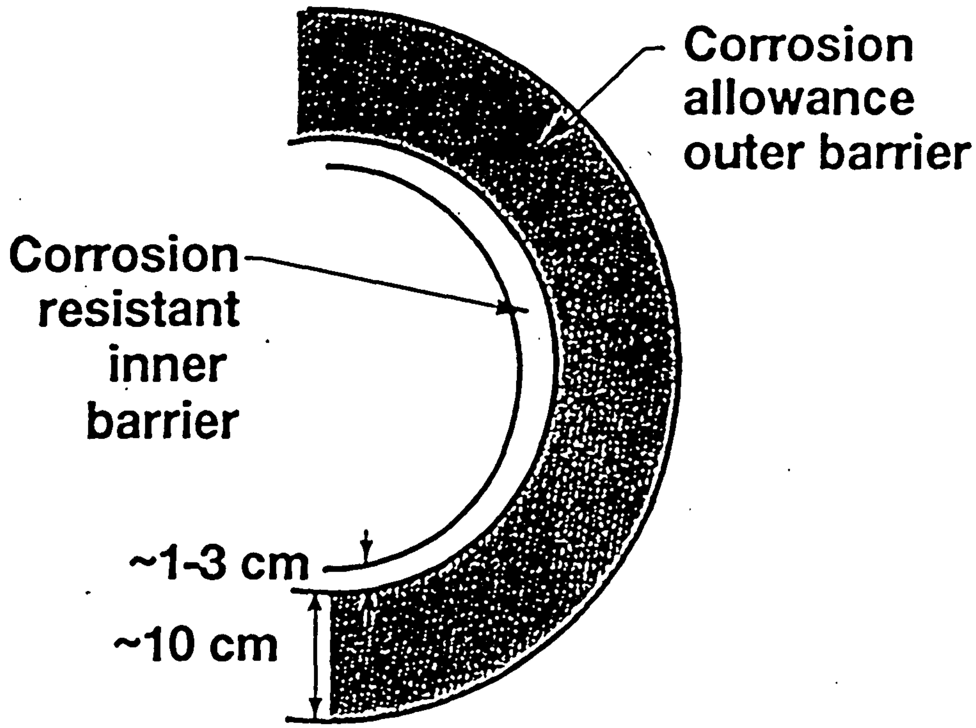
- Defense in-depth strategy
- Synergism between barriers
- Example: Corrosion allowance outer barrier
  Corrosion resistant inner barrier
- Principle: Outer barrier slowly oxidizes and, if wet, corrodes to protect inner barrier.

  As long as some outer barrier remains, inner barrier is galvanically protected in a wet environment.

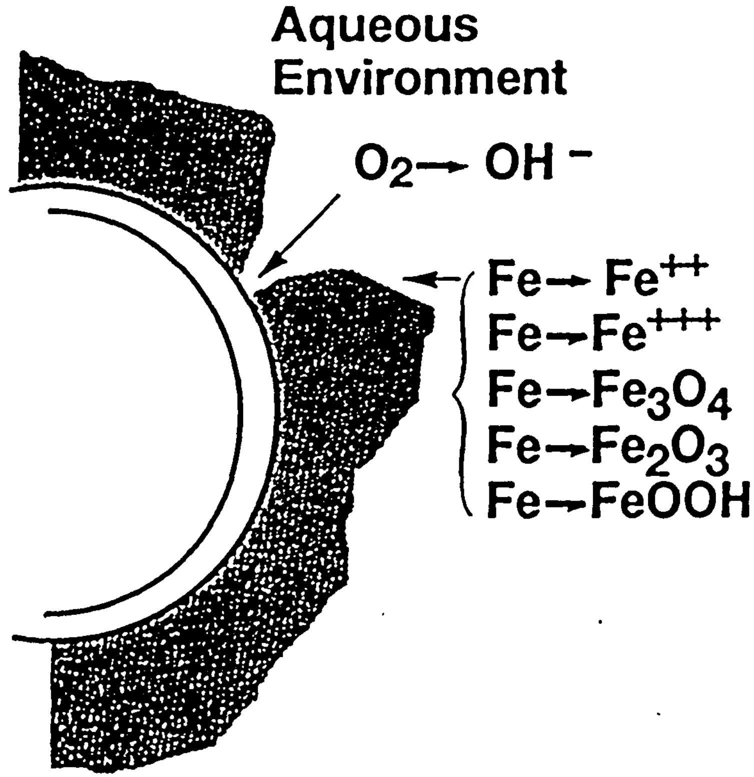
  Corroding outer barrier protects against localized corrosion and stress corrosion of inner barrier

  Eventually, inner barrier "stands on its own" when outer barrier is consumed.

As long as some of the Outer Barrier remains, the Inner Barrier is protected from the environment



Intact surfaces

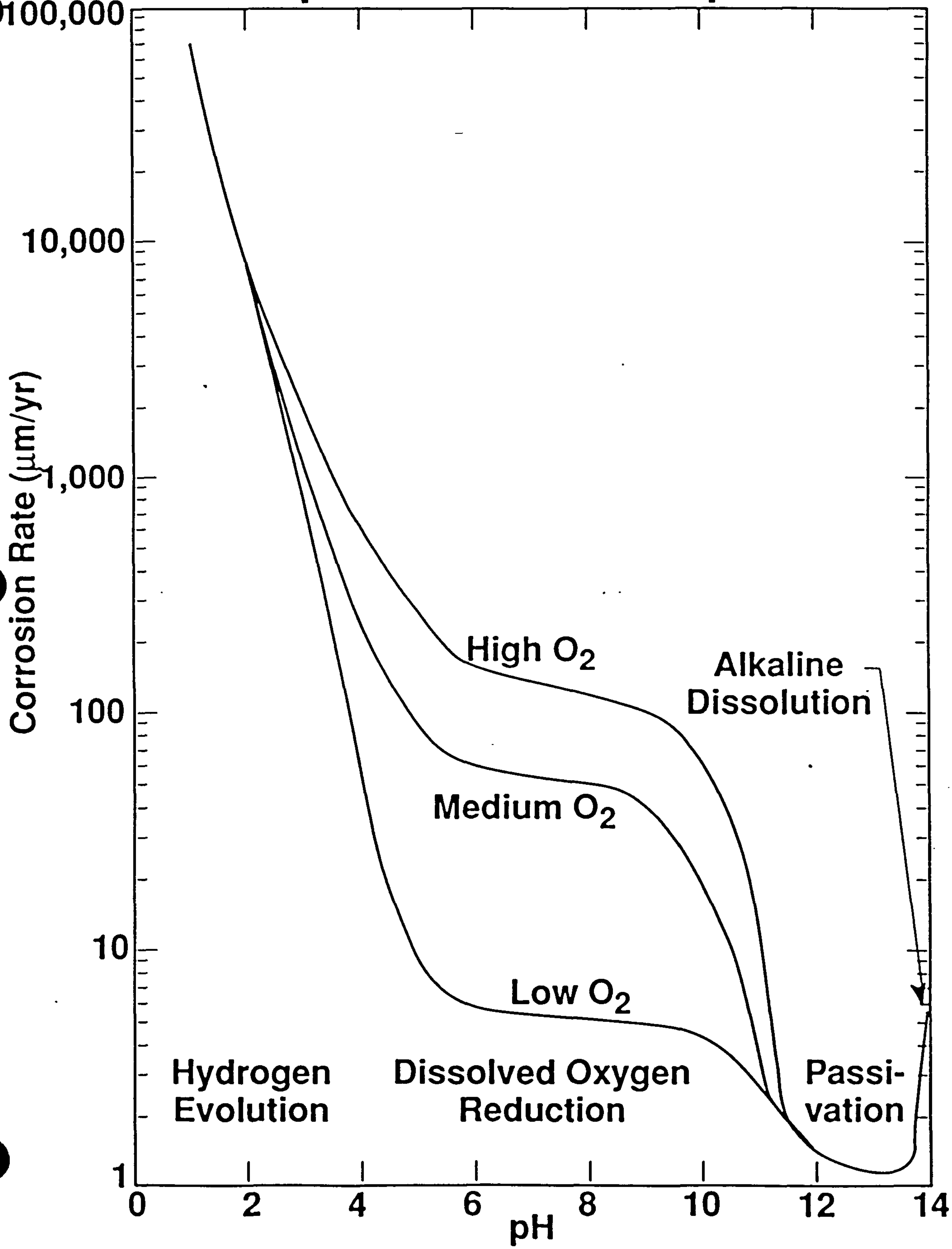


Corroded surfaces

However, There are Caveats to the Galvanic Protection Principle

- Demonstration of "critical potentials" for pitting, stress corrosion, etc., for long-term performance.
- Unwanted cathodic reaction on inner barrier (e.g. hydrogen embrittlement)
- Influence of corrosion products (Fe^{+3}, Cu^{+2}) on eventual corrosion of inner barrier.

Corrosion rate of carbon steel depends on solution pH



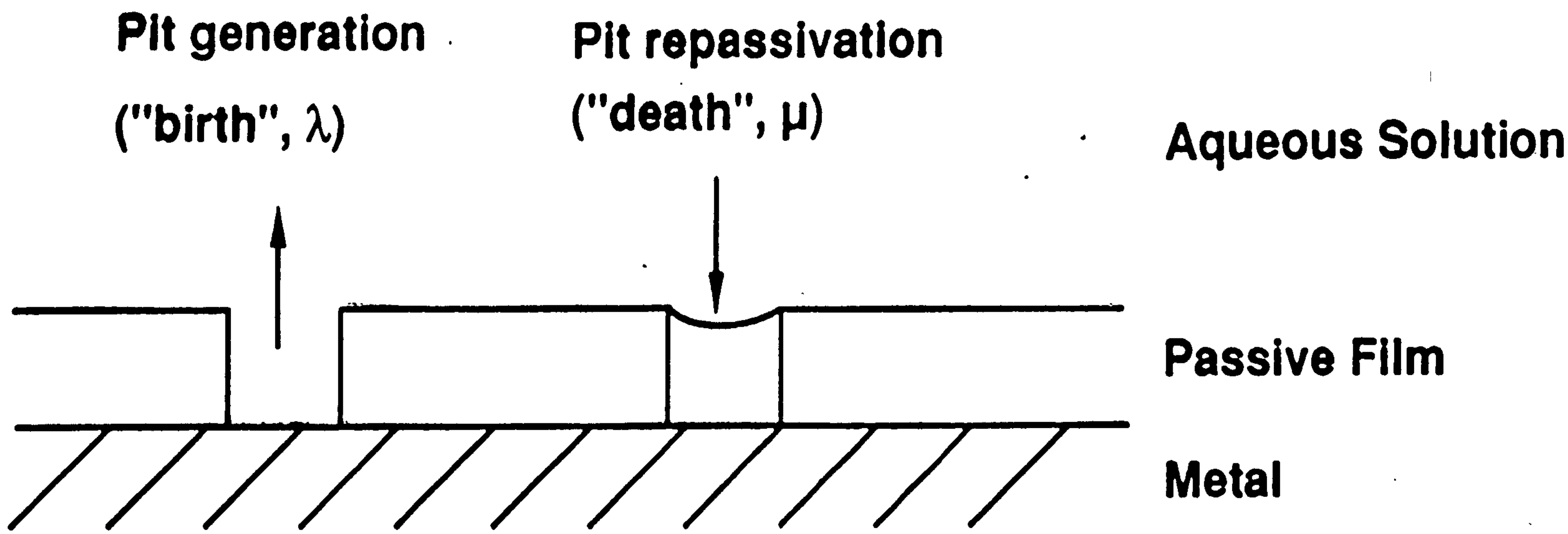
Degradation Mode Surveys on Ferrous Materials

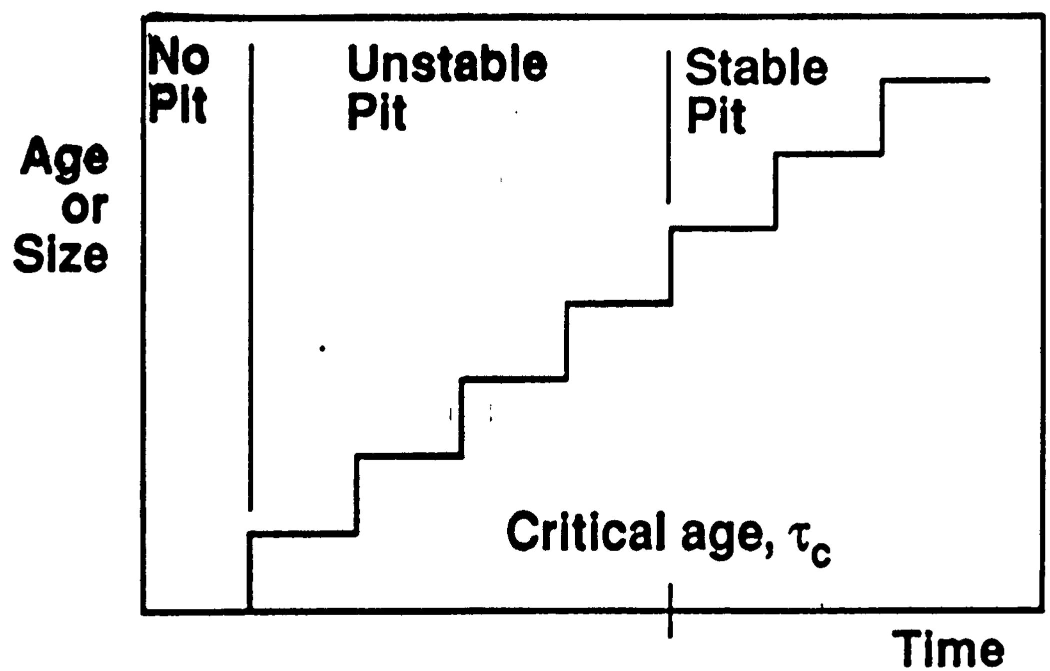
Tentative Conclusions:

- Dry oxidation results in negligible wastage
- Aqueous corrosion in neutral pH is dependent on oxygen availability
- Therefore, all the ferrous materials show about same corrosion rate in static, neutral pH waters
- "Weathering" steels show low corrosion rates under alternate wet/dry cycles, but show no improvement in corrosion rate (over plain carbon steel) under immersion conditions
- Cr/Mo alloy steels show some improvement in oxidation and corrosion in aggressive waters, but weldability is issue.
- High silicon cast irons show remarkable improvement in aggressive waters, but are brittle
- Therefore, selection among ferrous materials depends on factors other than corrosion

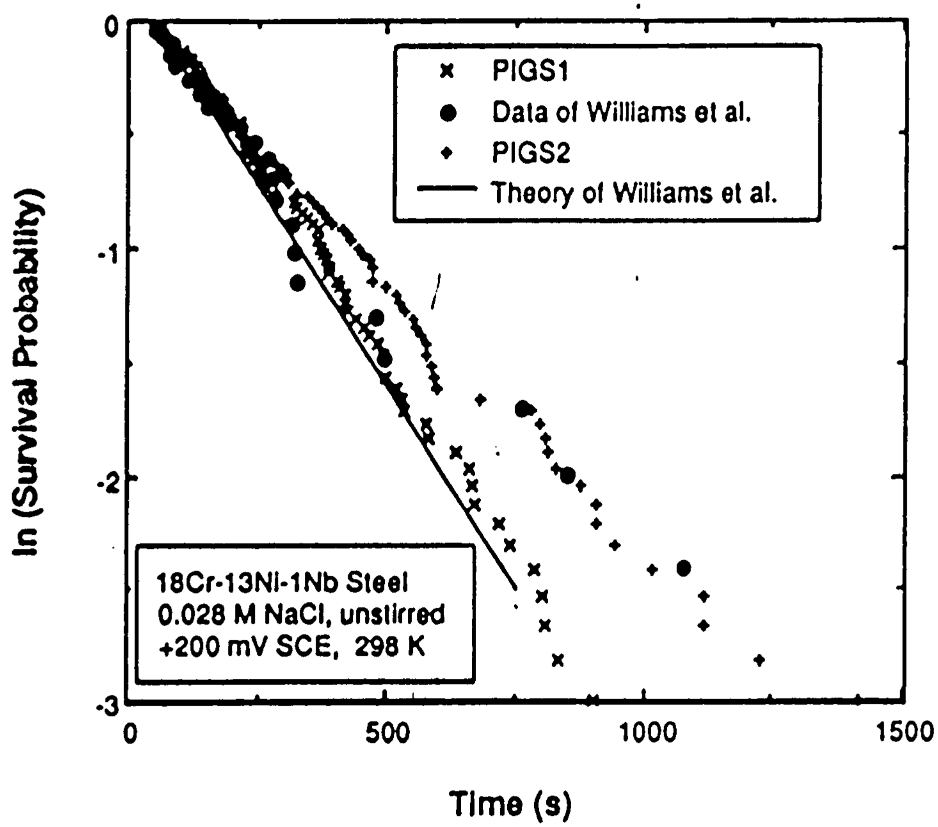
- Principal Investigator — D. Bullen (Iowa State University)

Stochastic Pit Nucleation





Simulation of Survival Probability: Enhanced Model



However, Experimental Work is Needed to Confirm Computer Simulations of Pitting

- Conduct experiments with controlled electrochemical potential
- Develop surface imaging and electrochemical noise techniques to quantify pitting attack
- Determine "pit generation", "pit repassivation", and "critical age" parameters for alloy/environment combinations
- Establish validity of "critical potential" threshold to predicting long-term behavior
- Principal Investigator — G. Henshall

Current Testing Activities

- Oxidation/corrosion transition in humid environments (corrosion allowance materials — iron-base and copper-base) — TGA
  - Principal Investigator — G. Gdowski
- Slow crack growth of corrosion resistant materials using reversing DC technique (fracture mechanics test)
  - Principal Investigators — J. Y. Park and D. Diercks (ANL)
- These are the subjects of the next two presentations.

Near–Future Testing Activities

- Electrochemically–based pitting parameter tests
- Additional fracture mechanics stress corrosion tests
- Field exposure in support of "large block test"

Materials Testing Evaluations (Welds and Base Metals)*

		Test Duration	Barrier
• Dry to Aqueous Transition (TGA)		Short	Outer
• Dry Oxidation (Weight Gain)		Long	Outer
• Aqueous/Corrosion (Immersion + Humidity)		Long	Outer
• Pitting	[Electrochemical Potential (ECP) Scanning]	Short	Inner, (Outer)
	(ECP Control)	Short/Long	Inner, (Outer)
• Crevice	(ECP Scanning)	Short	Inner
	(ECP Control)	Short/Long	Inner
	(Geometry Effects)	Long	Inner
• Intergranular Corrosion		Long	Inner
• Other Localized (As Needed)		Short/Long	Inner
• Environmentally Assisted Cracking			
– Stress Corrosion Cracking		Short/Long	Inner, Outer
– Fracture Mechanics		Long	Inner, Outer
– Hydrogen Effects		Long	Inner, Outer

Materials Testing Evaluations (Welds and Base Metals)* (Continued)

	Test Duration	Barrier
• Materials Compatibility (Galvanic Effects)	Short/Long	Inner, Outer
• Microbiologically Influenced Corrosion (MIC)	Short/Long	Inner, Outer

(*) Testing Matrix

- Temperature
- Water Chemistry
  - Vadose (J-13)
  - Altered Water Composition
  - Concentrated
- Man-Made Materials and Human Intrusion
- Irradiation Effects
- Stress and Strain
- Multiple Specimens
- Material Variability
- Cyclic Immersion

Design Experiments for Long-Term Testing

- Plan for more than one year of exposure (want 5 – 10 years)
- Identify approximately 6 environments that are meaningful with respect to (1) anticipated container thermal/chemical environments; (2) unanticipated but credible "upset" thermal/ chemical environments
- Accommodate several materials (in same or separate cells)
- Accommodate several types of specimens (flat coupons, creviced samples, self-loaded stress corrosion specimens, galvanically coupled specimens, etc.)
- Minimal surveillance; back-up power supply
- Facility to add and withdraw specimens
- Conduct as Quality Assurance Affecting activity

Non-Metallic Barrier Offers Conservative Alternative to All-Metal Multiple Barrier Approach

- Major advantage – resistance to aggressive water chemistry
- Non-metal barrier would be used in conjunction with metal barrier
- Possible candidates – alumina-based ceramics, titania-based ceramics, graphite
- How used – shell inside metal barrier; flame spray on metal barrier
- Technical issues:
  - how to fabricate ceramic material to dimension
  - how to join and seal
  - porosity
  - quality control
  - long-term slow crack propagation
  - compatibility with other barriers (graphite, metallic)
  - environment
- Survey in preparation
  - assess state of technology
  - identify likely candidate materials
  - identify degradation modes and testing needs
- Plans to make prototype
- Principal Investigator — K. Wilfinger

Container Materials Research — Summary Status

- Candidate materials identified for Advanced Conceptual Design multiple barrier configurations
- Degradation mode survey on ferrous materials nearing completion; previous volumes prepared for other materials
- Modeling of localized corrosion underway; plan to conduct experiments to provide input parameters
- Current testing activities directed toward (1) oxidation/ corrosion transition in humid environments; (2) slow crack growth studies
- Testing needs outlined for the short term and long term
- Survey initiated on non-metallic alternatives/supplements to metal barrier containment