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

#### NUCLEAR WASTE TECHNICAL REVIEW BOARD FULL BOARD MEETING

#### SUBJECT: CORROSION RESEARCH AND MODELING UPDATE

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PRESENTER'S TITLE AND ORGANIZATION:

TION: TECHNICAL AREA LEADER, ENGINEERED BARRIER MATERIALS CHARACTERIZATION MANAGEMENT AND OPERATING CONTRACTOR LAS VEGAS, NEVADA

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### **Outline of Presentation**

- Revised Scientific Investigation Plan (SIP)
  - Candidate Materials
  - Bounding Environments
- Status of Experimental Work
  - Types of Corrosion Tests
- Status of Performance Modeling
  - General Corrosion and Oxidation
  - Pitting Corrosion
- Brief Status of Other Activities
- Summary and Outlook

# Container Materials Work Governed by a Scientific Investigation Plan (SIP)

- SIP is formal description of work to be performed
- Individual activities are 'graded' for determining quality assurance levels
- Most recent SIP (January 1995) covers work planned for next five years
- Activities grouped into four areas:
  - Degradation mode surveys and information bases
  - Corrosion testing and physical properties evaluation
  - Model development of performance behavior
  - Materials recommendations

# Commentary on Planned Activities in the Metallic Barriers SIP

- Degradation mode surveys and information bases
  - Compile existing information as it applies to Yucca Mountain
  - Determine test needs
  - Engineered Materials Characterization Report and updates
- Corrosion testing and physical properties evaluation
  - Mostly laboratory-based in this design phase
  - "Anticipated" environments, "accelerated" test environments, and credible "what-if" scenarios
  - Abiotic and microbial testing environments
  - Base metal and weld metal tested and evaluated
  - Frequent dialogue with model development
  - May support some field tests

# Commentary on Planned Activities in the Metallic Barriers SIP (cont'd)

- Model development for performance behavior
  - Organized by degradation mode
  - Determine important chemical, physical, metallurgical, mechanical parameters (Deterministic Models)
  - Evaluate stochastic factors (esp. forms of localized corrosion and stress corrosion - Deterministic and Probabilistic Models)
  - Describe performance as a "damage function"
- Materials recommendations
  - Establish selection criteria, weighting factors, ranking (conducted with other elements in the Project)
  - Provide additional specifications on selected materials (as needed)
  - Likely seek outside review of selection process

### Sequence of Major Container Materials Activities



Corrosion Testing and Physical Evaluation





م License Application

### Interfaces Between Engineered Barrier Materials Work and Other Efforts



### Candidate Materials for Multiple Barrier Waste Package Containers

- Require several candidate materials
   because :
  - Different candidate materials for the different barriers (inner and outer barriers)
  - Possibly use different candidate materials for different waste package designs consistent with the expected "thermal load strategies"

#### CANDIDATE CORROSION RESISTANT MATERIALS

UNS Number	<b>Commercial Name</b>	ASTM Number	Composition
	Ni-Fe-Cr-Mo		
	Alloys		
N08825	Alloy 825, Incoloy 825	B 424 (plate)	42% Ni, 21% Cr, 32% Fe, 3% Mo, 2% Cu, 1% Ti
N06985	Alloy G-3, Hastelloy G-3	B 581 (plate)	49% Ni, 22% Cr, 19 % Fe, 7% Mo, 1% W
	Ni-Cr-Mo Alloys		
N06022	Alloy C-22, Hastelloy C-22	B 575 (plate)	58% Ni, 21% Cr, 13% Mo, 4% Fe, 3% W
N06455	Alloy C-4, Hastelloy C-4 Titanium	B 575 (plate)	62% Ni, 16% Cr, 16% Mo, 3% Fe, 1% Ti
			<i></i>
R53400	Titanium Grade 12	B 265 Grade 12 (plate)	"Lean alloy" containing 0.7% Ni, 0.3% Mo
new alloy	Titanium Grade 16	B 265 Grade 16 (plate)	"Lean alloy" with 0.05% Pd

#### CANDIDATE CORROSION ALLOWANCE MATERIALS Carbon and Alloy Steels

UNS No.	<b>Commercial Name</b>	ASTM No.	Composition
<b>G10200</b>	1020 wrought carbon steel	A 516 (grade 55)	0.22 max C, 0.6- 1.2 Mn, 0.15-0.40 Si
J02501	centrifugally cast carbon steel	A 27 (grade 70-40)	0.20 max C, 1.40 max Mn, 0.8 max Si
K21590	2-1/4 Cr - 1 Mo alloy steel	A 387 (grade 22)	2.0-2.5 Cr, 0.9-1.1 Mo, 0.15 max C, 0.3-0.6 Mn, 0.5 max Si

#### CANDIDATE "INTERMEDIATE" OR MODERATELY CORROSION RESISTANT MATERIALS Copper and Nickel Alloys

UNS Number	<b>Commercial Name</b>	ASTM Number	Composition
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N04400	Alloy 400, Monel 400	B 127 (plate)	Ni-Cu alloy containing 67% Ni, 32% Cu, 1% Fe
C71500	70/30 Copper- Nickel, CDA 715	B 171 (plate)	Cu-Ni alloy containing 67% Cu, 31% Ni, 1% Fe

### Interaction of Container Corrosion and Man-Made Materials Test Activities

- "Man-made", or "introduced" materials, may significantly influence chemistry of water contacting waste package container
- "Bounding" environments selected to account for changes in water chemistry due to:
  - Diesel fuels and other organics
  - Microbial metabolism
  - Concretes and grouts

#### "Bounding Environments" Proposed for 5-Year Corrosion Tests

#### Dilute Groundwater

• like J-13

• base case

Acidified Concentrated Groundwater	Concentrated Groundwater	Alkalized Concentra Groundwater
•pH as low as 2	• 20-100x J-13 ionic cencentation	•pH as high as 12
<ul> <li>simulates extreme case of "man made" materials conditioning environment (diesel fuels, organics, sulfur containing comp'ds)</li> </ul>	<ul> <li>simulates dry-out and resaturation of ionic species as temperature increases and decreases</li> </ul>	•simulates water conditioning by concretes, grouts
<ul> <li>chemically simulates microbial metabolism</li> </ul>		
• Test • Test some	at 60° and 90°C in liquid phase, in vapor phase over liquid (p specimens at water line)	oossible

### **Outline of Presentation**

- Revised Scientific Investigation Plan (SIP)
  - Candidate Materials
  - Bounding Environments

### ⇒Status of Experimental Work

### $\Rightarrow$ Types of Corrosion Tests

- Status of Performance Modeling
  - General Corrosion and Oxidation
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### Corrosion Testing Underway or Proposed for Near Future

- "Long term" (5-yr) "comprehensive" corrosion test
- Critical pitting and crevice corrosion potential determinations
- Corrosion tests under electrochemical control
- Thermogravimetric analysis (TGA) studies
- Fracture mechanics crack growth studies
- Microbiologically influenced corrosion (MIC) scoping studies
- Radiolytic effects on corrosion of container materials
- Studies on "basket" materials

### INITIATION OF A 5-YEAR COMPREHENSIVE CORROSION TEST IS A HIGH PRIORITY



#### **"MULTITUDE" OF SPECIMENS REQUIRED**

- Candidate Materials
- Specimen Types
- Replicates
- Water Chemistries
- Temperatures
- Exposure Regions (Water, Vapor, Water-Line)
- Metallurgical Conditions (Base Metal, Weld)
- Evaluation Intervals

#### EACH PARAMETER IS MULTIPLICATIVE

### Features of 5-year Comprehensive Corrosion Test

- Expose multitude of specimens of different materials and different geometries
  - flat coupons for weight loss, pitting, intergranular observation
  - creviced specimens
  - self-loaded specimens with and without welds for stress corrosion, hydrogen embrittlement
  - galvanically coupled sandwich specimens
- Withdraw specimens at periodic intervals
  - examine for attack pattern
  - quantify degradation
  - destructively examine some specimens
  - archive or replace specimens back in test cell for additional exposure
  - expose for 5 years or longer

### Features of 5-year Comprehensive Corrosion Test (cont'd)

- Results will indicate
  - general corrosion rates
  - pitting corrosion attack (number pits, depth of attack, distribution of pits)
  - crevice corrosion attack (depth of attack, distribution of attack)
  - intergranular/selective attack (depth, pattern)
  - stress corrosion or hydrogen embrittlement (stress level, pattern, distribution)
  - galvanic attack or galvanic protection

### Status of 5-Year Comprehensive Corrosion Test

#### Experimental Design

- 44 separate test cells, 800 liters each, required volume
- 50% complete, internal design review on April 25, 1995

#### Laboratory Refurbishment

- Large dedicated laboratory required
- Carpentry and painting completed
- Major electrical and plumbing work begun

#### Procurements

- Order for 12,000 corrosion test specimens (weight loss, crevice, Ubends being competitively bid)
- Order for galvanic corrosion specimens being assembled

#### • Near-Term Future Plans

- Complete design by May 15
- Release all procurements by May 31

### Measurements of "Critical" Potentials Indicate Localized Corrosion Susceptibility

- "Passive Film Breakdown Potential" and the "Repassivation Potential" determined by electrochemical techniques
- Position of these two critical potentials relative to corrosion potential indicates susceptibility to pitting corrosion and crevice corrosion
- Individual determinations performed in 1-2 days; supplements results of "5-yr" comprehensive corrosion test
- Large number of responses obtained for alloy/environment combinations
- Tests performed over wide range of chemical and metallurgical parameters, e.g., pH, T, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, "heat to heat" variations in the alloy, and so on -- Determine single and combined effects of variables

### **Corrosion Testing Under Electrochemical Control**

- Conduct tests maintained at constant applied potentials for longer term check of "critical potential" determinations
  - Provides important input parameters to model development
  - Experimental validation of model predictions
- Conduct companion tests to 5-yr comprehensive corrosion test to determine any changes of corrosion potentials with time
- Most electrochemical tests will run for a few
  weeks, but selected number will run much longer

#### **Thermogravimetric Analyzer Apparatus**



#### **Thermogravimetric Analysis Studies**

- Determine the temperature-humidity regions where there is susceptibility to thin-film aqueous (electrochemical) corrosion
- Results of studies will be used to select conditions for longer-term testing
- Thin-film aqueous corrosion is also dependent on:
  - susceptibility of metal
  - gaseous species (O<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, NO<sub>x</sub>, others)
  - surface condition (roughness, corrosion product)
  - hygroscopic species on surface (e.g., NaCl, CaCO<sub>3</sub>)
- Thermogravimetric analyzer
  - 50 110°C (custom designed temperature control)
  - in-situ humidity & temperature measurement
  - 50 µg resolution
  - computer control / data acquisition

#### **Thermogravimetric Analysis Studies (cont'd)**

- Previous studies of thin film water corrosion
  - ambient conditions
  - periodic wet / dry conditions (accelerates corrosion)
- Elevated temperature studies (50 110°C)
  - not extensively studied
  - reaction rate acceleration with temperature
  - effect of temperature on corrosiveness of gases
  - oxygen solubility decrease with temperature
  - stability of corrosion product form (change in microstructure with temperature of formation)
- Initial studies will emphasize carbon steel and copper-base materials

1020 Steel in Water Vapor at 65 C





### Results from Fracture Mechanics Stress Corrosion Crack Growth Measurements

- Currently testing Alloys 825, C-4, C-22, Ti Grade 12 in 93°C simulated J-13 water,  $K_{max}$  = 26 41 MPa•m <sup>-3/2</sup> , R = 0.5 and 0.7
- Crack growth rates < 10 <sup>-11</sup> m/sec
- Crack growth rates indicative of highly stress corrosion resistant material
- Will continue these tests, change K<sub>max</sub> and R to generate full crack velocity vs. stress intensity curve
- Will add other environments and temperatures (especially toward more aggressive conditions)
- Considering additional kinds of stress corrosion tests to supplement these tests

#### Impact of Microbiologically Influenced Corrosion (MIC)

Candidate Material	Susceptibility*
Carbon Steel	Many kinds of bacteria, both aerobic and anaerobic, attack steels, resulting in enhanced general corrosion, pitting, and hydrogen embrittlement (many studies)
70/30 Copper Nickel	Sulfate reducing bacteria caused pitting. Acid Polysaccharides increased corrosion (several studies)
Monel 400	Sulfate reducing bacteria caused deep pitting, intergranular attack (several studies)

\* Summarized from G. Geesey, "A review of the potential for microbially influenced corrosion of high -level nuclear waste containers" CNWRA 93-014 (June, 1993)

## Impact of Microbiologically Influenced Corrosion (MIC) (cont.)

Candidate Material	Susceptibility*
Incoloy 825	Sulfate reducing bacteria caused pitting and crevice attack in lake water and sea water (2 studies)
Hastelloy C-4, C-22	Appears to be immune, but pure Ni is attacked
Titanium	Appears to be immune

\* Summarized from G. Geesey, "A review of the potential for microbially influenced corrosion of high -level nuclear waste containers" CNWRA 93-014 (June, 1993)

### Plans for MIC Evaluation and Testing

- Workshop on Microbial Activity at Yucca Mountain (YM) held April 1995
- Plan to evaluate YM repository site for presence of microbial species known to enhance corrosion of candidate container materials
  - native microbial populations
  - microbes associated with introduction of "man made" materials into repository
  - consotriums of microbial populations
  - moisture films initiating aqueous corrosion also act as biofilms
- Plan to conduct experimental measurements of corrosion in controlled environments, as suggested from above evaluations
  - Compare results with those obtained under "abiotic" but chemically simulated conditions

### **Radiolytic Effects on Corrosion**

- Penetration of gamma radiation through container wall causes chemical changes (radiolysis) in environment that may enhance corrosion (e. g. O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>)
- Readily calculate gamma field attenuation through metal
- Need to determine radiolytic-induced corrosion changes as function of gamma dose rate to determine threshold
  - Limit of discernible corrosion attack
  - Changes in corrosion potential
  - Analytical determination of radiolysis products
- Plan to start late FY-95, early FY-96; emphasis on carbon steel and Cu/Ni alloys

### Corrosion Studies on "Basket" Materials

- SIP on Basket Materials completed and approved
- Experiments planned to evaluate expected long-term chemical environments
- Experiments planned to study short-term corrosion behavior to screen candidate materials
  - Structural candidates: Al, Cu, Stainless Steel, 702 Zr, ceramics
  - Neutron absorbers: B (in AI, Cu, SS), Hf in 702 Zr, Gd and other lanthanides in the ceramics
- Long-term corrosion testing of promising candidates will follow

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- ⇒Status of Performance Modeling ⇒General Corrosion and Oxidation

### ⇒Pitting Corrosion

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### Types of Models Depend on Degradation Phenomenon

#### **PHENOMENON**

Low Temperature Oxidation General Aqueous Corrosion Intergranular Corrosion Pitting Corrosion Crevice Corrosion Stress Corrosion Cracking Hydrogen Embrittlement Phase Instability

#### **MODEL TYPE**

Deterministic

Deterministic

Deterministic

Deterministic and Probabilistic Deterministic and Probabilistic Deterministic and Probabilistic Deterministic and Probabilistic Deterministic and Probabilistic

### Deterministic Models for Oxidation and General Corrosion of Steels

- Parametric correlation calculated from available literature data, where x = depth; t = time; T = temperature:
- Dry Oxidation: x = 1.79 x 10<sup>5</sup> t <sup>0.33</sup> exp[-6870/T]\*
  - derived from data obtained at somewhat higher temperature regime; implies a "cubic" growth law
- Aqueous Corrosion: x = 2.52 x 10<sup>6</sup> t <sup>0.47</sup> exp[-2850/T]\*
  - applies to near neutral pH, air saturated water, implies a "parabolic" oxide film growth
- Wastage of material heavily dependent on "thermal load" and projection of temperature decay

\* from D. Stahl, J.K. McCoy and R. D. McCright, *Impact of Thermal Loading on Waste Package Material Performance*, Proceedings of the Scientific Basis for Nuclear Waste Management, Kyoto Japan Conference, October 1995 to be published by MRS.

### Estimates of Wastage of Steel Containers

- Penetration due to dry oxidation is negligible regardless of thermal load (a few μm/10<sup>5</sup> yrs); therefore penetration for high thermal load case is quite small
- Transition from "dry" to "wet" conditions occurs at 60% relative humidity
- Penetration due to aqueous corrosion dependent on thermal load
- Estimate of 20 mm penetration in 5000 yrs., 40 mm penetration in 100,000 yrs. for low thermal load repository (somewhat higher rates at repository periphery)
- <u>However</u>, corrosion rates much higher if exponent on time increases (corrosion products spall off) or if water chemistry becomes more aggressive (e.g. microbial activity) -- experimental work to address these concerns

### Modeling Pitting Initiation and Growth

- Develop model that incorporates probabilities of initiation, growth, and death of pits for candidate corrosion resistant materials (Ni-base, Ti-base alloys)
- Confirm model with experimental data to be obtained from electrochemical tests and 5-year comprehensive corrosion test
- Work collaboratively with Performance Assessment to input model for container performance

• Microscopic fluctuations in local conditions cause local film breakdown.



### Definitions used in the Pitting Corrosion Model

- Embryo "birth" ( $\lambda$ ) corresponds to the localized breakdown of the passive film
- Embryo "death" ( $\mu$ ) corresponds to repassivation of the metal
- The critical age  $(\tau_c)$  required for stable pit formation is related to the ratio of the minimum stable pit depth to the velocity of embryo growth
- The pit growth probability (γ) may be related to a succession of death and renucleation events or that some pits grow at the expense of others

#### **Simulation of Induction Time Distribution**





#### **Pitting Corrosion "Damage Function"**



- Provides time to first penetration of container
- Provides number of pits penetrating container as a function of time





- Alcan 2S-O Aluminum
   20 °C Tap Water
   Data of Nathan and Dulaney
- Goal is to qualitatively simulate:
- (1) Number of small pits decreases with exposure time.
- (2) Peak at intermediate depths.
- (3) Peak moves to larger depths as exposure time increases.
- (4) Height of peak decreases as exposure time increases.
- (5) At long times, the distribution is skewed toward small pits.

- Exponential decay in pit "birth" probability with time
- Stochastic pit growth



### Modeling the Effects of Environment on Pitting

- Modeling environmental effects required for:
  - Extrapolating "accelerated" test data to longer times and less aggressive environments
  - Exploring various environmental scenarios
- For the stochastic model this means determining:
  - (1) birth probability, (2) death probability, (3) critical age, (4) pit growth probability
- A first attempt was made using simple phenomenological expressions that are physically reasonable
  - Included variables of (1) potential, (2) temperature, (3) chloride ion concentration and their assumed variation with time
  - These three variables interact on the four pitting model parameters in a fairly complex way
  - Illustrative model shown in next few viewgraphs







## Experimental Input to Support Pitting Model is Essential

- Combination of electrochemical and microscopic techniques to identify the "four" model parameters
- Conduct experiments over range of electrochemical potential (above and below the "critical potentials" for passive film breakdown and repassivation)
- Conduct experiments over range of physical, chemical, metallurgical parameters (temperature, electrolyte chemistry, pH, metal microstructure, and so on)
- Note that many of the same experiments are useful for alloy screening/selection

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### Degradation Mode Surveys (DMS) and Information Bases -- Brief Status

- Recently completed draft Engineering Materials Characterization Report (Dec. 1994) -- updates planned
- Recently completed DMS on Titanium and Ti-base alloys (Jan. 1995)
- DMS on remainder of Ni-base candidate materials; DMS on welding microstructures in progress
- DMS on galvanic effects planned

### Commentary on Materials Recommendations for Multiple Barrier Waste Package Containers

- Long material endurance is most important consideration
- Materials/fabrication processes limited to reasonably available technology
- Moderate strength materials are adequate
- Predictability of performance is important in selecting materials
- Uncertainty in environment changes over long time periods forces
   design/materials conservatism
- Revisit selection process used for SCP-CD materials
- Likely retain same selection criteria, but likely change weighting factors (different factors for inner and outer barriers, for "high" thermal load vs. "low" thermal load configurations)

### In Summary

- Scientific Investigation Plan (SIP) prepared, reviewed, and approved for Metallic Barriers work
- Candidate materials and bounding test environments described
- Experimental work is underway
  - Oxidation/corrosion transition
  - Fracture mechanics stress corrosion cracking
  - Construction of 5-year comprehensive corrosion test
- Experimental activity planned for near future
  - Electrochemical testing for localized corrosion
  - Microbiologically influenced corrosion scoping studies
  - Threshold for radiolytic corrosion

### In Summary (cont'd)

- Model development begun
  - Low temperature oxidation and general aqueous corrosion
  - Pitting corrosion initiation and growth (stochastic features)
- Additional modeling efforts planned for near future
  - Introduction of effects of experimental parameters into pitting corrosion model
  - Extension of pitting model to other corrosion modes with stochastic features (crevice corrosion, stress corrosion)
- Efforts continue on completing degradation mode surveys and updating Engineering Materials Characterization Report
- Progress made on developing methodology for materials selection

### Outlook

- High level of experimental activity forecast for next few years
  - Provides important basis for materials recommendations
  - Provides much input for performance models
- Expectation of greater effort in model development as test results become available
- Increasing interaction with other program elements essential for success
- Metallic Barriers SIP describes proposed work in considerable detail
  - "Plan your work; then, work your plan"