Presentation of the Final Report

Long-Term Uniform Corrosion of Passive Metals

Presented by

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Presented to

U.S. Department of Energy (DOE) Bechtel SAIC Company, LLC (BSC)

> March 18-19, 2002 Las Vegas, NV

> > March 18, 2002

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General corrosion of Drip Shield and Waste Package is caused by 1. Dry Oxidation (RH<RH_{crit})

Thin, adherent, protective oxide (9.3 nm/yr)

2. Humid Air (RH>RH_{crit} and No Dripping)

Corrosion rate in humid air = corrosion rate in aqueous phase

3. Aqueous Phase (RH>RH_{crit} and Dripping)

Mean corrosion rate for Waste Package = 113 nm/yr = 1.13mm/10⁴yr Mean corrosion rate for Drip Shield = 25 nm/yr = 0.25 mm/10⁴yr General corrosion will not cause failure of WP provided passive films remain unchanged

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Technical Issues Structure and Composition of Passive Film

Uniform Corrosion In the Passive State In the Transpassive State Measurement of the Uniform Corrosion Rate

Modeling the Passive Film and Uniform Corrosion

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Technical Issues Structure and Composition of Passive Film Influence of Alloy Composition

Mechanism of Formation of Layered Passive Film

Air-Formed Oxide Film

Technical Issues Structure and Composition of Passive Film Influence of Alloy Composition Ni in acidic and neutral pH Ni-Cr in mildly alkaline Ni-Cr-Fe in neutral pH and mildly alkaline Ni-Cr-Mo in acidic and neutral pH

Technical Issues Structure and Composition of Passive Film

Influence of Alloy Composition

<u>Alloy</u>	<u>Alkaline</u>	<u>Neutral</u>	<u>Acidic</u>	
Ni		NiOª/Ni(OH) ^b 2	Ni ₃ O ^a 4	

Ni-Cr Outer: NiO/Ni(OH) $^{c}_{2}$ small Cr₂O₃ Inner: Cr₂O₃

Technical Issues Structure and Composition of Passive Film Influence of Alloy Composition <u>Alloy</u> <u>Alkaline</u> <u>Neutral</u> <u>Acidic</u> Ni-Cr-Fe^d Outer: NiO/Ni(OH)₂ small Cr_2O_3 Mid: Fe_xO_y Inner: Cr_2O_3

Technical Issues Structure and Composition of Passive Film

Influence of Alloy Composition

<u>Alloy</u>	<u>Alkaline</u>	<u>Neutral</u>	<u>Acidic</u>
Ni-Cr-Mo		Outer: Ni-rich ^e	
		Inner [.] Cr-rich	

Outer:Cr-,Mo-rich,Ni^f Inner: Cr-rich, Ni

Technical Issues Structure and Composition of Passive Film

Influence of Alloy Composition (Cr>15a/o)

<u>Alloy</u>	<u>Alkaline</u>	<u>Acidic</u>
Ni-Cr	Outer: Ni-rich	
	Inner: Cr-rich	
Ni-Cr-Fe	Outer: Ni-rich	
	Mid: Fe-rich	
	Inner: Cr-rich	
Ni-Cr-Mo	Outer: Ni-rich	Outer:
	Inner: Cr-rich	Inner:

Outer: Cr-,Mo-rich Inner: Cr-rich

Technical Issues Structure and Composition of Passive Film

Mechanism(s) of Formation of Layered Passive Film

1. Bi-layered PF on Fe and Stainless Steel in 288°C Water

Outer layer forms by oxidation of inner layer

- 2. Bi-layered PF on Ni-Cr
- 3. Tri-layered PF on Ni-Cr-Fe
- 4. Bi-layered PF on Ni-Cr-Mo

Results => Multi-layered films on Ni-Cr alloys are a consequence of relative affinities of elements for oxygen and diffusivities of cations in Cr_2O_3 .

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Technical Issues Structure and Composition of Passive Film

Air-formed Oxide Films

24 / High-Temperature Cornelon of Engineering Alleys



Oxidation resistance at 980°C of Fe-Ni-Cr with 15-25% Cr is dramatically increased when Ni > 32%. Oxidation resistance is due to Cr_2O_3 . Results => Cr_2O_3 is expected to form on Alloy 22 at high temperatures in air.

Technical Issues Structure and Composition of Passive Film

Air-formed Oxide Films

At T>1000°C, $Cr_2O_3 \rightarrow Volatile CrO_3$

- Inconel 600 good resistance up to 1090°C/80 hrs.
 - 1204°C: significant corrosion; subsurface oxidation and void formation within

 $50 \ \mu m$ of surface

- Ni-20Cr $\sim 1 \mu m/hr$ at $1100^{\circ}C$
- Results => Alloy 22 has good oxidation resistance at $T < \sim 1100^{\circ}$ C.

Technical Issues Structure and Composition of Passive Film

<u>Air-formed Oxide Films</u>^f

RT, air-formed oxide on Alloy 22 is

-as protective against corrosion in acidic chloride as is the passive film.

-unchanged by immersion in acidic chloride at 200mV vs. Ag/AgCl

-uniform oxidation rate remained acceptably low as T was raised every 10-12 h in increments of 10°C to a max. of 85°C

=> uniform corrosion of Alloy 22 unaffected by RT oxide

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Long-Term Uniform Corrosion of Passive Metals

Technical Issues Structure and Composition of Passive Film

Project's Approach

- 1. Grow passive films in (1) LTCTF, (2) autoclaves (T,t) and (3) under electrochemical control
- 2. Characterize Films

Composition Raman Spectroscopy **XPS/Sputtering** Glav Discharge Spec SIMS/Sputtering Cross sectional TEM Auger Electron Spectr. X-ray Diffraction

Thickness

Tunneling AFM XPS/Sputtering SIMS/Sputtering

TGA

AFM/Patterning

AC Impedance Spectr.

Cross sectional TEM

Ellipsometry

(XANES, Low Angle)

March 18, 2002

Crystal Structure

Raman Spectroscopy X-ray Diffraction Cross sectional TEM

Technical Issues Structure and Composition of Passive Film

Project's Approach

UWO^g

Solutions: SCW (pH neutral) and BSW (pH13)

Samples: Pre-conditioned:

Air/2 wks. Air@200°C/4 wks. Water Sat'd Air@100°C/4 wks.

TOF-SIMS and XPS

Technical Issues Structure and Composition of Passive Film

Project's Approach - UWO^{f,g}

Solution: $1M \text{ NaCl} + 0.1M \text{ H}_2\text{SO}_4$

TOF-SIMS and XPS => Bi-layered Passive Film (PF)

Inner layer = Cr/Ni rich

Outer layer = Cr/Mo rich

Potential	Thickness	<u>Film</u>
Air-formed	18Å	29%Cr ₂ O ₃ -60NiO-11MoO ₃
200 mV	20Å	43%Cr ₂ O ₃ -47NiO-10Mo
500 mV	23Å	56%Cr ₂ O ₃ -32NiO-12MoO ₃
700 mV	28Å	63%Cr ₂ O ₃ -25NiO-12MoO ₃

Technical Issues Structure and Composition of Passive Film Project's Approach - GE CRD^h

Solution: 2800xJ-13 (pH=12.2) for 2 months

XPS => Passive Film (PF) covered by silicate deposit Layered? Enriched in Cr and Mo w.r.t. Ni

Technical Issues Structure and Composition of Passive Film Project's Approach - LLNLⁱ

Environment: Dry oxidation in air at 550°C/10,000 hrs. SCW (pH8) at 90°C Cross-sectional TEM, EDS, XPS

Dry oxidation in air at 550°C/10,000 hrs. Tri-layered: Cr=inner/Fe=Mid/Ni=outer 500Å thick

Technical Issues Structure and Composition of Passive Film

Panel's Recommendations

1. Coordination of analytical work at different laboratories.

Techniques; chemistry of test solutions

2. Identify possible critical values of temperature, potential, and solution pH at which structure/composition of passive film changes. This recommendation seeks to resolve two discrepancies: (1) between the results of the LTCTF, which indicate uniform corrosion rate is independent of test temperature (60°-90°C), and results of short-term electrochemical tests, which indicate uniform corrosion increases with increasing temperature, and (2) between prediction of the Point defect Model, which indicates steady-state uniform corrosion is not a function of potential, and results of short-term electrochemical tests, which indicates with increasing temperature uniform corrosion is not a function of potential, and results of short-term electrochemical tests, which indicate uniform

Technical Issues Structure and Composition of Passive Film Panel's Recommendations (continued)

- 3. Investigate changes in structure/composition of high temperature oxide films in solutions relevant to repository as a function of potential and temperature.
- 4. Investigate influence of surface segregation of sulfur and high applied potentials potentials on structure and composition of passive film. This recommendation is based on the view that surface segregation of sulfur and high corrosion potentials are the most likely cause of high uniform corrosion rates.

Technical Issues Uniform Corrosion of Alloy C22 in the Passive State

Lloyd et al^f (pH1) and Bellanger and Rameau^j (pH3) =>

- oxidation rate decreases rapidly with time
- decrease in corr rate with time in pH3 is due to film thickening
- decrease in corr rate with time in pH1 is due to changes in film's composition and/or structure

Lloyd et al => non steady-state oxidation rate in 1N NaCl + $0.1M H_2SO_4$ increases with high potentials (= +300 mV vs. Ag/AgCl) and high temperatures (85°C).

Technical Issues Uniform Corrosion of Alloy 22 in the Passive State

High potentials and high temperatures cause high uniform corrosion, at least in the short term, and high potentials and high temperatures might occur in the repository:

> T of WP decreases from 100°C to 85°C over 900 yrs. (Mon, 2002)

High potentials

- ennoblement of corrosion potential in SAW at 90°C
- radiation
- Fe⁺³ corrosion products

Technical Issues Uniform Corrosion of Alloy 22 in the Passive State Two mechanisms of surface segregation of sulfur

Equilibrium surface segregation

Ni-23Co-20Cr-12Al^k (Briant and Luthra)

1100°C/5-60min. -> 10% S

900°C/6 h -> 13 % S

 $800^{\circ}C/30 h$ -> no sulfur segregation

Anodic segregation

preferential dissolution leaves surface enriched in S



Technical Issues Uniform Corrosion in the Passive State

Anodic segregation of Sulfur

With 400 ppm bulk sulfur concen., uniform corrosion of 1 μ m of Alloy 22 can produce a monolayer of S.

At a uniform corrosion rate of 0.01 μ A/cm² (=0.7mm/10,000 y), one monolayer of S can be formed at alloy's surface in ~ 10 y.

Technical Issues Uniform Corrosion in the Passive State

Equilibrium surface segregation of Sulfur

S segregates to free surfaces of Ni and Ni-base alloys but not to metal/oxide interface.

S segregation to voids formed during high temperature heat treatments?

To prevent void formation, may need to limit anneal temp. to $\sim 1100^{\circ}$ C.

Technical Issues Uniform Corrosion in the Passive State

Surface segregation of Sulfur

Anodic segregation of sulfur poses a greater risk to uniform corrosion resistance than equilibrium segregation. Anodic segregation and equilibrium segregation of sulfur can be minimized by decreasing the alloy's bulk sulfur concentration.

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Technical Issues Uniform Corrosion in the Passive State
Project's Approach
Measurements of Corrosion Rate of Alloy 22
Test
Corrosion Rate
Wt. Loss in LTCTF
Mean of the time-average corrosion rate

Of 144 samples over 2 yr. = 113 nm/y = $1.13 \text{ mm}/10^4 \text{y}$ Maximum of the time-average corrosion Rate of 144 samples over 2 yr. = 794 nm/y = $7.94 \text{ mm}/10^4 \text{y}$

* AMRGeneral Corrosion Localized Corrosion Waste Package Outer Barrier(Jan. 2000)

March 18, 2002

Technical Issues Uniform Corrosion in the Passive State

Project's Approach

Test LPR in 10xJ-13` At 25°C for 5 mos.

Potentiostatic polarization 100 mV above corrosion potential for 300 hrs. in 0.028M NaCl at 95°C Corrosion Rate 11 nm/y = 0.11mm/ 10^4 y

 $8 \,\mu m/y = 14 \, mm/10^4 y$

Waste Package Degradation Process Model Report (Dec. 2000) $80 \text{ nm/y} = 0.80 \text{mm}/10^4 \text{y}$

Potentiostatic polarization 100 mV above corrosion potential for 300 hrs. in SCW at 90°C

"Summary of Recent information Relevant to Waste Package and Drip Shield Degradation Process Model," p.E-19, Nov. 2001.

March 18, 2002

Technical Issues Uniform Corrosion in the Passive State

Project's Approach^f

TestCorrosion Rate1M NaCl + 0.1M H2SO4 $19x10^{-9}$ A/cm2 = 1.33 mm/104y200 mV/48 hrs. at 75°C $19x10^{-9}$ A/cm2 = 1.33 mm/104y500 mV/48 hrs. at 75°C $2x10^{-7}$ A/cm2 = 14 mm/104y500 mV/48 hrs. at 75°C $2x10^{-7}$ A/cm2 = 14 mm/104ySAW at 90°C, 167 hrs. $4x10^{-8}$ A/cm2 = 2.8 mm/104y400 mV vs Ag/AgClLian et al.i

Technical Issues Uniform Corrosion in the Passive State

Project's Approach Effect of Temperature

LTCTF

No T dependence On avg. corr rate At 60°C and 90°C Short Term(non steady-state)

Electrochemical Tests

Corr rate increases with increasing T

and increasing potential.

pH 3 sulfate 20°C-70°C (Bellanger 1996) pH 1 chloride/sulfate 25°C-85°C

(Lloyd et al^f)

Technical Issues Uniform Corrosion in the Passive State Project's Approach Influence of potential





Passive Dissolution and Corrosion potential

Technical Issues Uniform Corrosion in the Passive State					
Project's Approach Influence of potential					
 Characterization of the Passive Films of Alloy 22 as a Function of Time of Immersion in 90°C SAW. 					
	XPS and AES Depth Profiling				
		Ecorr			
Samp	le Solution	(vs Ag/AgCl)	Time	Thickness	Structure
C22	SAW/LTCTI	F +390 mV	4.5 yrs.	2000Å	Fe strong
					Nidepletion Cr/Ni>>1
C22	SAW	-120 mV	10 days	100Å	No Fe
C22	SAW/LTCTF	+50mV	4.5yrs.	400Å	Silicate
					Ni depletion
T.Lian o	et al (2002)				Cr/Ni>>1

March 18, 2002

Technical Issues Uniform Corrosion in the Passive State

Project's Approach Influence of potential

- Characterization of the Passive Films of Alloy 22 as a Function of Time of Immersion in 90°C SAW.
- Measurements of corrosion potential vs. time, corrosion rate vs. time, and composition of passive film vs. time suggest that ennoblement of corrosion potential of Alloy 22 in SAW at 90°C results in a decrease in corrosion rate and might be caused by an increase in chromium concentration of the passive film.

T.Lian et al (2002)ⁱ

Long-Term Uniform Corrosion of Passive Metals

Technical Issues Uniform Corrosion in the Passive State Panel's Recommendations

- 1. Complete investigation of cause of ennoblement of corrosion potential in SAW at 90°C.
- 2. Acquire mechanistic understanding of the increases in uniform corrosion caused by TCP, LRO and MIC.
- 3. Include tests at T>90°C in the LTCTF.
- 4. Measure uniform corrosion for long periods of time at high applied anodic potentials, especially in combination with high temperatures.
- 5. Measure effect of surface segregation of sulfur on uniform corrosion

Long-Term Uniform Corrosion of Passive Metals

- Technical Issue Uniform Corrosion in the Transpassive State
- Transpassive corrosion of Alloy 22 in 0.05M HCl with 0.48M O_2 at 360°C initiates locally at Cr and/or Mo rich phases and broadens out to uniform transpassive corrosion.^j
- Transpassive corrosion of Ni, Alloy 625 (22 Cr- 9 Mo) and Cr initiates at grain boundaries (gb segregation?) and broadens out to uniform transpassive corrosion.^m
- A combination of oxidizers from radiolysis of water, Fe⁺³ from corrosion of steel, low solution pH, and the presence of Cr-rich precipitates or grain boundary segregation might result in localized transpassive dissolution of Alloy 22

Long-Term Uniform Corrosion of Passive Metals

Technical Issue Uniform Corrosion in the Transpassive State

Project's Approach Values of Key Electrochemical Parameters of Alloy 22 Immersed in SAW at 90°C for 24hⁿ

State of Aeration	Transpassive		
	Vs. Ag/AgCl	at 500 mVvs. Ag/AgCl	Potential*
Aerated	-26 mV	3.9x10 ⁻⁶ A/cm ²	+672 mV
Unaerated	-98 mV	4.5x10 ⁻⁶ A/cm ²	+665 mV
Deaerated	-301 mV	14.3x10 ⁻⁶ A/cm ²	+647 mV
Potential for oxygen evolution = 800-1200 mV vs Ag/AgCl			
*solution color turned from clear to yellow-green			

- Technical Issue Uniform Corrosion in the Transpassive State
- Project's Approach
- Results of investigation of ennoblement of corrosion potential
- => corrosion potential arrests at ~ 400mV vs Ag/AgCl
- => transpassive corrosion will not occur without a combination of Fe⁺³ contamination of the water and radiolysis of water.

Technical Issue Uniform Corrosion in the Transpassive State

Panel's Recommends

- Determination of the likelihood of radiolysis of water causing transpassive corrosion of homogeneous Alloy 22.
- 2. Determine synergisms of radiolysis of water, composition of water (esp., solution pH and Fe⁺³), and metallurgical factors (e.g., grain boundary segregation, second phases rich in Cr and/or Mo) that will cause transpassive corrosion of Alloy 22.

Long-Term Uniform Corrosion of Passive Metals

Technical Issue Modeling Passivity and Uniform Corrosion Project's Approach

- 1. Point Defect Model (PDM) + Mixed Potential Model= General Corrosion Model.
- PDM=> Inner layer of PF forms by generation of $V_{O=}$ at the film/metal (f/m) interface. At steady state, film growth into the metal at the f/m interface = dissolution of inner layer at the interface between the inner and outer layers. High Cr of inner layer is due to preferential oxidation of Ni, rapid formation of Cr₂O₃, and high rate of transport of Ni through the Cr₂O₃ inner layer.

Technical Issue Modeling Passivity and Uniform Corrosion Project's Approach

2. General Corrosion Model.

Uses MPM to combine steady-state PF growth rate (from PDM) with rates of H⁺ and O reduction (Butler-Volmer equations).

Using kinetics of H⁺ and O reduction on 304 SS in water at 288°C, indicates uniform corrosion = 1.8mm/10,000 yr.

3. Calculation of Pourbaix Diagrams for Alloy 22 in solutions and temperatures relevant to repository.

Long-Term Uniform Corrosion of Passive Metals

Technical Issue Modeling Passivity and Uniform Corrosion Panel's Recommendations

- 1. Measurement of kinetic parameters of H+ and O reduction on Alloy 22 in solutions and at temperatures relevant to the repository.
- 2. Measurement of steady state passive corrosion rates of Alloy 22 to determine if the rates are independent of potential as predicted by PDM.
- 3. Further development of PDM or a new model of passivity that is capable of predicting non-steady state behavior, esp. effects of potential and temperature on uniform corrosion.

Conclusion and Major Recommendations

- The Panel has concluded that failure of the waste packages by uniform corrosion is unlikely.
- The resistance of Alloy 22 to uniform corrosion is the result of the protective nature of its passive film. Further work is needed to characterize the structures and compositions of the air-formed oxide films and passive films of Alloy 22.
- Surface segregation of sulfur and transpassivity are the two most likely phenomena that would cause relatively high rates of uniform corrosion. Changes in the structure and composition of the passive film as a function of the surface segregation of sulfur and as a consequence of highly oxidizing potentials should be investigated.
- High temperatures might cause higher rates of uniform corrosion. The effect of test temperatures > 90°C on the uniform corrosion rate should be investigated in the LTCTF.
- Short term electrochemical tests indicate higher rates of uniform corrosion at high potentials. The effect of high potentials, especially in combination with high temperatures, on the uniform corrosion rate should be investigated.

March 18, 2002

Long-Term Uniform Corrosion of Passive Metals

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Long-Term Uniform Corrosion of Passive Metals

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