

NUCLEAR ENERGY RESEARCH INITIATIVE (NERI) PROGRAM  
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TECHNICAL PROGRESS REPORT

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OSTI

First Quartile 2000  
(Period 1/1/00 – 3/31/00)

Status Summary of NERI Tasks – Phases 1-3:

**Phase 1:**

Milestone/Task Description	Plan Completion Date	Actual Completion Date
Definition of the Environment	4/30/2000	
Continued Model Development	1/31/2002	
Development of Theories of Repassivation	4/30/2002	
Measurements of Key Model Parameters	4/30/2002	

Narrative:

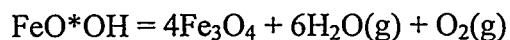
**Task: 1. Definition of the Environment**

1. Task status:

During the past quartile we continued to solve the problem of defining the critical temperature,  $T_{cr}$ , at which “wet” corrosion first becomes operable in the Yucca Mountain repository.

2. Issues/Concerns

Our previous consideration of the definition of the critical temperature,  $T_{cr}$ , (i.e. the temperature at which the oxide is in equilibrium with the oxyhydroxide or hydroxide and water vapor under the expected repository conditions of temperature and pressure) has been restricted by the case of simple oxides: FeO, Fe<sub>3</sub>O<sub>4</sub>, NiO, Cr<sub>2</sub>O<sub>3</sub>, and CrO<sub>2</sub>. In particular, it has been shown that iron (III) oxyhydroxide, FeO\*OH, can exist under the conditions of the Yucca Mountain repository due to the reaction:



at  $T < T_{cr} = 366\text{ }^{\circ}\text{C}$ . Accordingly, the possibility that corrosion initiates and propagates at temperatures significantly above the boiling temperature of water cannot be ignored.

## **DISCLAIMER**

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Because our aim is to define the maximum possible value of  $T_{cr}$ , we have extended our thermodynamic analysis to the mixed oxides:  $Fe_2NiO_4$ ,  $Cr_2FeO_4$ , and  $Cr_2NiO_4$  which are known to form on alloys. Our calculations show that the presence of the oxide  $Fe_2NiO_4$  does not increase the previously determined value of  $T_{cr}$ . Up to now, we have also not obtained an increased  $T_{cr}$  due to the presence of  $Cr_2FeO_4$  and  $Cr_2NiO_4$ . However, the last oxides have not been investigated for the all-possible hydroxide and oxyhydroxide dehydration reactions. These thermodynamic calculations will be carried out in the near future.

## **Task: 2. Continued Model Development:**

### **1. Task status:**

During the past quartile we continued to develop models for estimating pit and crevice growth rates and for calculating the corrosion potential under thin electrolyte film in the Yucca Mountain repository.

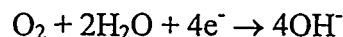
### **2. Issues/Concerns:**

We concentrated our efforts on the problem of enhancing the speed of computation of existing codes for describing potential and concentration distributions in the corrosion cavities. This issue is very important, because prediction of the path of evolution of corrosion damage may require hundreds or even thousands of individual rate calculations to properly capture the effect of changes in the system conditions (e.g., stress, temperature, dose rate) over an extended period.

Enhancing the speed of computation is being accomplished on the basis of analyzing the physical picture that exists inside and outside of a corrosion crevice. Thus, it has been shown that only those species that dominate in the crevice enclave need to be considered in determining the potential distribution down the crevice. In many cases, we can even regard the electrolyte in the crevice as being binary. It has been also shown that, in many cases, the anodic current that is produced at the crevice (pit) tip is consumed on the crevice sides near the tip. At larger distance from the crevice tip, a "balanced charge transport" region, with zero net current density in the solution and on the crevice sides occurs. Finally, near the crevice mouth, there exists a region of non-zero net current density that is compensated for outside of the cavity. Clear criteria for the existence of one, two, or three concentration and potential regions in the crack, along with the potential and concentration distributions have been obtained. The possibility of subdividing the corrosion crack into regions, within which simplified mathematical descriptions of the transport processes are possible, is very important from the point of view of enhancing the speed of computer codes for calculating the crevice propagation rate. In many cases, it is possible to obtain analytical expressions for the crack propagation rate, which enable very rapid calculations to be performed. This possibility is also very important for defining the minimum number of physical parameters that are necessary for quantitatively describing the corrosion process.

We have also continued the development of computer code for calculating the corrosion potential (on the basis of the Mixed Potential Model) for Alloy C22 when

covered by the thin electrolyte film. The experimentally determined values of the passive dissolution current density for Alloy C22 and the kinetic parameters for the cathodic reduction of oxygen



on the surface of Alloy C22 (see below) has been introduced into the model. We also have begun to expand the Mixed Potential Model to incorporate reactions involving nitrogen. This issue is important, because of the radiolytic formation of the oxyacids of nitrogen from  $\text{N}_2$  (air) or from the  $\text{O}^{16}(\text{n,p})\text{N}^{16}$  reaction. The effect of these reactions will be to acidify the interface, which could have a significant effect on the corrosion behavior. Although we expect the effects of radiolysis on corrosion to be minimal, the long exposure times preclude the exclusion of radiolytic effects.

### **Task 3: Development of Theories of Repassivation**

#### **1. Task status:**

During the past quartile we initiated the development of the theory of prompt repassivation.

#### **2. Issues/Concerns:**

The PDM postulates that the nucleation of metastable pits occurs, because of the formation of a cation vacancy condensate at the metal/film interface, followed by film thinning due to dissolution of the barrier layer. At some point, the "cap" over the condensate is perforated and solution leaks into the cavity. We propose to simulate prompt repassivation by solving the set of transport equations for the coupled internal and external environments. The objective of the simulation will be to determine those  $N_b$  nuclei out of a total population of  $N_p$  for which diffusion out of the cavity eventually exceeds the electromigration of electrolyte into the cavity through the perforation in the cap, as a function of the size of the perforation.

As a starting point we began to develop a computer code for calculating the concentration and potential distribution inside a closed pit (under the "cap") with the arbitrary axisymmetric geometry.

### **Task 4: Measurements of Key Model Parameters:**

#### **1. Task status:**

During the past quartile, the investigation of electrochemical and corrosion behavior of the Alloy C-22 alloy in NaCl solutions have been conducted by the methods of voltammetry and chronoammetry. Exchange current density and transfer coefficients for oxygen reduction on Alloy C-22 and carbon steel for the range of temperature 25 – 95

°C have been determined. These measurements are being performed under subcontract to SRI by the Frumkin Institute in Moscow, Russia.

## 2. Issues/Concerns:

Anodic voltammograms for Alloy 22 in NaCl solutions have three main segments at various temperatures (18-90°). (1) A short region near the open-circuit potential, where the current increases with the potential, which can be defined as the active dissolution region. The Tafel constant for this case is 120 mV (18°C). Assuming that the kinetics of active dissolution of the alloy is determined by its nickel matrix, the exchange current density for the dissolution reaction is estimated to be  $10^{-9}$  A/cm<sup>2</sup>. (2) The passivity region (the current depends slightly on the potential or is virtually independent of potential). (3) The transpassivity region (the current increases steeply with the potential).

According to the chronoammetric data, in the passivity region, the current decreases for a very long period of time. The experiments performed in this work did not allow us to determine the final value to which the current decreases with time. We can say with certainty that the alloy dissolution rate in the passivity region may correspond to a current density that is lower than  $10^{-7}$  A/cm<sup>2</sup>. The current transients were observed in the chronoammograms, which were significantly more intense at high temperatures. However, the transients did not lead to the formation of stable pits. The general trend of the current decreasing with time is retained.

In the transpassivity region, very high rates of alloy dissolution can be achieved; however, we can not envision any process that would result in such high potentials in the field, so that this region is of little interest.

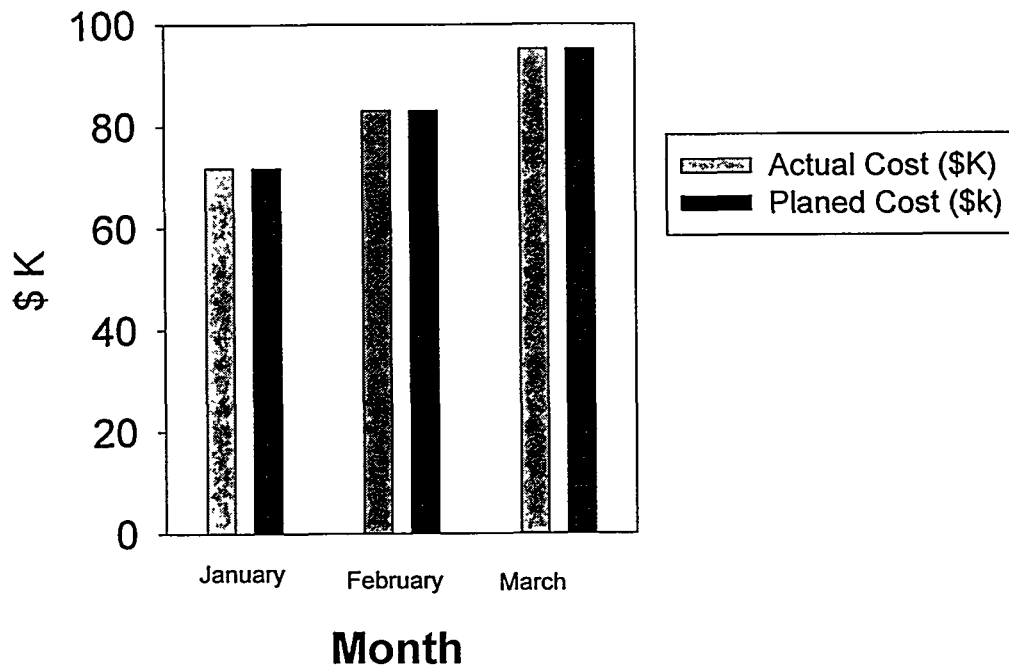
The region of active dissolution is not well understood. The experiments (140 h) showed localized alloy dissolution. This potential range is of great importance for the corrosion prediction, because, first, it lies in the immediate vicinity of the open-circuit potential and, second, in this potential range, the metal is not yet protected by the anodic passive film, which forms at higher potentials. It is worthwhile performing a further investigation over prolonged times, in order to determine whether local dissolution will gradually give way to uniform corrosion or whether the centers of initial dissolution will deepen.

A study of possible cathodic processes showed that, as expected, in the corrosion of Alloy 22, the most probable cathodic reaction is the reduction of oxygen dissolved in water. The exchange current of this reaction is of the order of  $10^{-10}$  A/cm<sup>2</sup> and the Tafel slope is 130 mV (18°C).

A study of electrochemical behavior of carbon steel, which was performed for comparison, showed considerably different results: the absence of the passivity region, intense pitting at potentials in the immediate vicinity of the open-circuit potential, an increase in the current with time at virtually all potentials more positive than the open-circuit potential.

The results of the comparative study showed that Alloy 22 has a unique resistance to pitting in NaCl solutions, including those at elevated temperatures (to 90°).

Cost Performance:



# Federal Assistance Milestone Plane

ID	Task Name	Durat	Start	Finish	1999				2000				2001				2002			
					Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4		
1	Definition of the Environment	9 m	8/1/99	4/3/00																
2	Continued Model Development	30 m	8/1/99	1/31/02																
2.1	Model of Pit Growth	9 m	8/1/99	4/30/00																
2.2	Model of Crevice Growth	9 m	11/1/99	7/31/00																
2.3	Thin Layer Mixed Potential Model	9 m	11/1/99	7/31/00																
2.4	Point Defect Model	12 m	8/1/00	7/31/01																
2.5	Damage Prediction Algorithm	18 m	8/1/00	1/31/02																
3	Development of Theories of Repassivation	30 m	2/1/00	4/30/02																
3.1	Prompt Repassivation	18 m	2/1/00	7/31/01																
3.2	Delayed Repassivation	18 m	10/1/00	4/30/02																
4	Definition of the Corr. Evolutionary Paths	12 m	1/8/01	7/31/02																
5	Measurements of Key Model Parameters	30 m	10/1/99	4/30/02																
5.1	Survival Probability Constant	9 m	11/1/99	4/30/00																
5.2	Damage Functions	30 m	11/1/99	4/30/02																
5.3	Exchange Current Densities	9 m	11/1/99	4/30/00																
5.4	Transfer Coefficients	9 m	11/1/99	4/30/00																
5.5	Breakdown Potentials	9 m	7/1/00	4/30/01																
5.6	Parameters for Point Defect Model	30 m	10/1/99	4/30/02																
6	Predicting of the Evolution of Corr. Damage	18 m	2/1/01	7/31/02																
Summary																				

Project: Deterministic Prediction of Corrosion Damage in High Level Nuclear Waste Containers	Task	Summary	Rolled Up Progress
	Progress	Rolled Up Task	
	Milestone	Rolled Up Milestone	
Date: 4/28/2000			