Solution Layer and Critical Crevice Chemistry Studies

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Project 1

Corrosion Co-op Thrust Area: Corrosion in Thin Layers of Moisture and Deposits
Project Title: Evolution of Solution Layer Chemistry in the Presence of Dust

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Introduction

Much of the expected corrosion that will occur in the repository will occur under atmospheric corrosion conditions, rather than full immersion. The waters that seep through the tuff will either drip or condense on the surface of the waste package with the conditions under which that occurs depending strongly on the final design and the environmental conditions assumed.

The corrosion modes that represent the most threat to waste package integrity are those that are localized (pitting, crevice corrosion, stress-corrosion cracking). There has been limited fundamental study of localized corrosion in thin electrolytes. Most atmospheric corrosion research has focused on the more uniform corrosion exhibited by nickel and copper when exposed to atmospheres of differing relative humidity (RH), temperature, and pollutant gas type and concentration [1-5].

In order to validate models of WP performance, the plausible extremes of the WP environment and subsequent corrosion need to be established. To accomplish that requires a combination of experimental and computational work that focuses on the controlling variables and establishes a scientific basis for the prediction of the stabilization of localized attack on the WP. This stabilization involves the connection between a stable, robust cathodic area and the localized corrosion site. The robustness of the cathodic area depends in large part on the chemistry, electrochemistry, and transport properties in the thin electrolyte that forms, which will include dust on the WP surface.

Understanding the atmospheric electrochemistry requires a determination of the extent to which cathodic and anodic sites under thin films and covered by deposits communicate with one another. The degree to which an anodic site (e.g., a pit) can interact with the surrounding cathodic sites will determine the maximum rate of localized corrosion, as rarely are the kinetics within the localized corrosion site the limiting factor, at least at early portions of a pitting cycle.

There has been limited fundamental study of localized corrosion in thin electrolytes. The environmental conditions of atmospheric corrosion are similar to crevice corrosion in the sense that there are geometric restrictions to the mass transport along the surface as well as homogeneous chemical reactions taking place that can alter the electrochemical kinetics. The main differences are that there is the delivery of additional cathodic reactants (oxygen) occurs across the entire surface, and atmospheric systems are by their nature under open circuit conditions (i.e., the surface is not externally polarized).

Proposed Work

Objective: Establish a scientific basis for the determination of the plausible extremes of environments on WP in the presence of submonolayer amounts of dust, and the extent to which the rates of localized corrosion can be supported by cathodic reactions within the dust layer.
Task 1: Modeling of steady state solution layer chemistry as a function of gas environment above surface, temperature, relative humidity, and dust composition.

Motivation
One of the primary challenges in life prediction under repository conditions is the need to develop models that link different processes. These processes occur over very different length and time scales, making computational linkages difficult. One linkage which impacts the corrosion of the WP is that between the in-drift chemistry and the environment of the waste package surface. The solution environment on the WP is determined by the interaction of the electrochemistry of the WP surface and the thin solution that forms, which may be affected by the presence of dust or deposits. There is a need to develop improved means of linking the in-drift chemical environment to the conditions on the waste package surface as affected by the important variables.

Approach
The work of Graedel [6-8] on developing a multi-regime model of atmospheric corrosion corrosion chemistry (GILDES) will serve as a framework for our modeling. The GILDES (Gas-Interface-Liquid-Deposition-Electrodic-Solid) model describes the six regions and their interactions with mathematical formulations based on a combination of fundamental principles and parameterization of data. As published, it provides a strong framework for the transport and reaction in the five of the six regimes (gas through deposition and solid). Given sufficient thermodynamic and kinetic data, these regimes can be handled. In the Electrodic regime, the model used is overly simplistic and do not represent the behavior of real systems well. For example, Tafel behavior is assumed in the Electrodic regime. Even for carbon steel exposed to an aggressive atmosphere, this representation is not realistic. For the corrosion-resistant alloys of interest, Tafel behavior is a particularly poor choice. We will adapt the GILDES framework to the relevant conditions at the repository, incorporating more realistic electrochemical kinetics.

The in-drift chemical environment will be used as the inputs for the Gas regime. The in-drift chemistry is determined by the amount of seepage water and its chemistry, which is controlled by its interactions with geology, and the thermohydraulic effects of the heat released from the WP. In addition, the extent of air exchange of the drift (e.g., due to forced ventilation) will affect the in-drift gaseous environment which is part of the in-drift environment. Our model will be exercised to determine the steady state solution layer chemistry as a function of gas environment above surface, temperature, relative humidity, and dust composition. The experimental data in Task 2 will be used to validate the model. Once validated, the model will be exercised to expand the domain of variable space over which plausible extremes of environment can be determined.

Interactions and Expected Outcomes
Electrochemical kinetics will be input from the localized corrosion tasks, whereas information on reduction reactions and water chemistry will be accepted from other tasks within the thin film and deposit tasks. Interactions with the task studying thicker deposits (Payer/Landau) will ensure for internal consistency and compatibility in addition to leveraging the programming efforts through the sharing of computer code. This task will result in steady state solution layer chemistry as a function of gas environment above surface, temperature,
relative humidity, and dust composition for comparison with the experimental results from Oak Ridge National Laboratory.

Task 2: Simulation of current and potential distributions in the presence of an active corrosion site (crevice, pit, stress-corrosion crack) as a function of thin layer thickness and current demand of active site.

Motivation
As discussed above, the mass transport conditions for atmospheric conditions are similar to those for crevice corrosion. Thus, the extension of models of crevice chemistry and electrochemistry represents an efficient approach to modeling of the interactions between the WP surface on which cathodic reactions dominate and the localized corrosion sites where anodic processes dominate. Unfortunately, most crevice corrosion models have several limitations with regards to the conditions of interest:
(a) difficulty handling the non-linear electrochemical boundary conditions characteristic of actual corroding interfaces,
(b) difficulties with inclusion of new physiochemical data without extension reprogramming,
(c) inability to consider open circuit conditions (i.e., the mouth of the crevice must be assumed by most models to be held at a constant potential),
(d) limited coupling to conditions outside the crevice, and none explicitly couple the crevice to a gaseous atmosphere.

Approach
We have recently adapted our crevice corrosion model, CREVICER [9-11], to atmospheric corrosion conditions, including the interactions between anodic sites and sacrificial metallic claddings [10] and to an organic coating that releases inhibitors at a rate dependent on pH [11]. The code can handle polarization curves that reflect the pitting-limited passivity exhibited by most corrosion-resistant alloys in bulk environments, as well local-chemistry-dependent active behavior known to occur within localized corrosion sites. The model maps the spatiotemporal chemical and potential fields within a crevice in two dimensions, taking into account diffusion, migration, and generation of species, including those by homogenous chemical reactions. Its object-oriented design breaks a program into discrete, independent units called objects, which can be reprogrammed and debugged separately. It is through these objects that information is passed into and out of the solving portion of the code. This encapsulation hides the internal functionality of the object away from other parts of the code.

The version of CREVICER adapted for atmospheric conditions [11] overcomes the limitations described above. We will further extend the code to consider the restricted mass transport conditions in a thin film or wet deposit that is coupled to an active corrosion site. It will also be linked to the corrosion chemistry model described in Task 3.

Interactions and Expected Outcomes
This task will have substantial interactions with the task establishing the kinetics of localized corrosion sites (Scully) as well as the task considering similar issues, but in thicker dust/deposit layers (Payer, Landau) and the task considering reduction reactions (Payer, Gervasio). This modeling will provide a scientific basis for determination of both the maximum
rate of localized corrosion and the conditions that must be maintained in order for propagation of the localized corrosion to become a structural integrity issue.

References
Project 2

Corrosion Co-op Thrust Area: Localized Corrosion
Project Title: Crevice Corrosion Critical Chemistry Modeling

Principal Investigator: R. G. Kelly
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Introduction

Crevice corrosion represents one of the primary modes of corrosion that threatens waste package performance. In addition to crevices that are part of the design (e.g., at the WP/support contact), additional crevices may form under deposits and scales. In order for crevice corrosion to represent a substantial challenge to WP performance, it must stabilize. Stabilization requires the maintenance of a highly acidic, highly concentrated solution composition within the crevice [1-3]. The balance between the anodic kinetics within the crevice, the cathodic kinetics outside the crevice, and the transport conditions between them determines the stability of the crevice. Thus, it is important to establish both the range of conditions under which crevice corrosion can propagate in Ni-Cr-Mo-Fe alloys under bulk atmospheric corrosion conditions, as well as the rate of that attack. The primary challenges to the maintenance of the crevice solution are the dilution power of diffusion and the evaporation of the solution outside the crevice. If either diffusion dilutes the crevice solution or the solution on the surface external to the crevice evaporates, then the crevice will stifle. Two classes of cases must be considered: (a) an isolated crevice (i.e., no external cathode), and (b) crevice with thin layer of solution outside the crevice on which cathodic reactions can be supported.

For a stable crevice, a surface solution exists on area outside the crevice, and the rate of crevice corrosion can be controlled by (i) the total cathodic current that the external surface can supply to the crevice, (ii) the rate of anodic dissolution within the crevice, or (iii) the potential drop between the dissolution position in the crevice and the external surface [4]. For stifled crevices, the rate of crevice corrosion will be controlled by the rate of the anodic and cathodic reactions within the isolated crevice [5].

The interactions amongst these factors are complex, and therefore difficult to control and understand based solely on experiments. In addition, the effects of the primary variables of interest (temperature, RH, external environment, alloy composition) add significantly to the dimensionality to the problem. Computational studies can aid in narrowing the domain space over which experimental studies should be concentrated. Such process models can also be abstracted for use by life prediction codes.

Proposed Work

Objective: Establish a scientific basis for the calculation of the stability of crevice corrosion propagation for Ni-Cr-Mo-Fe alloys as a function of temperature, alloy composition, RH, external solution layer composition, and cathodic kinetics on the outside surface.
Task 1: Adapt present UVa computational code for crevice chemistry for Ni-Cr-Mo-Fe alloys under conditions representing the repository. This adaptation will include the inclusion of relevant species, thermodynamic and physiochemical properties of all species at elevated temperature, and precipitation.

Motivation
A great deal of crevice corrosion modeling has been done [6-10]. Unfortunately, most crevice corrosion models have several limitations with regards to the conditions of interest:

(e) difficulty handling the non-linear electrochemical boundary conditions characteristic of actual corroding interfaces,
(f) difficulties with inclusion of new physiochemical data without extension reprogramming,
(g) inability to consider open circuit conditions (i.e., the mouth of the crevice must be assumed by most models to be held at a constant potential),
(h) limited coupling to conditions outside the crevice, and none explicitly couple the crevice to a gaseous atmosphere.

In addition, under some of the conditions of interest, precipitation will occur both within the crevice and in the outside, and will have important effects on transport. Developing a computational code that can overcome these limitations will serve as a basis for predictions of crevice stability and serve as an input to life prediction models.

Approach
At UVa, we have recently developed a computational code that overcomes most of these limitations [11-15]. It has been shown to handle non-linear electrochemical boundary conditions that depend on the local solution chemistry [5, 11, 13], the ability to consider surfaces exposed to atmospheric conditions at open circuit [14, 15]. Its object-oriented design not only allows new physiochemical data to be included without reprogramming, but also allows different degrees of information to be included about different species. For solutions as complex as those under consideration, this ability represents a major advantage as it prevents being limited in calculations to the level dictated by the species about which the least is known.

To date the code has been applied to stainless steels, pure Ni, and Al alloys. We will add the species relevant for Ni-Cr-Mo-Fe alloys as well as the species present in the solution layer outside the crevice. In addition, we will develop a means to handle precipitation in order to determine its effects on transport. We will couple into the elevated temperature thermodynamic and transport property database and calculation tools from OLI systems [16]. Coupling to the external surface will also be accomplished is a straightforward extension of our recent atmospheric corrosion work [14, 15].

Interactions and Expected Outcomes
There will be extensive interactions with the other modeling tasks in the cooperative. Primary links will be made to the tasks involved with modeling of the environment on the waste package, as well as to the damage evolution tasks. Input will be taken from the tasks involved with the anodic kinetics within the localized site and the cathodic kinetics on the boldly exposed surface. The outcome of the task will be a tool for calculating conditions within the crevice that will be available to others in the cooperative.
Task 2: Introduce appropriate electrochemical kinetics into code as a function of crevice chemistry and external cathodic kinetics into the code based on experimental results from other tasks.

Motivation
In order to assess crevice stability properly, the appropriate kinetics for both the crevice and the external surface must be included. These kinetics will vary as the chemistry within the crevice, the alloy composition, the external temperature, and the relative humidity. Accurate calculations of stability require that these kinetics be incorporated into the code.

Approach
The kinetics for the reactions external to the crevice will be available from tasks led by Kelly, Gervasio/Payer, and Landau/Payer. The kinetics for the reactions within the crevice will be available from the tasks led by Scully and Frankel. These kinetics will be incorporated in one of two ways: (a) abstracting their dependence on the external variables, then using these dependencies to construct the kinetics for a given local environment, or (b) using a look-up table containing the polynomial fits to the experimentally determined kinetics and a validated interpolation scheme to construct the kinetics [5, 11]. The two incorporation methods will be tested by comparison of kinetic predictions with actual measurements of kinetics over a range of conditions (to be performed by other tasks).

Interactions and Expected Outcomes
In addition to the interactions with the tasks providing descriptions of kinetics, there will be interactions with the tasks on damage evolution, in particular the task on geometric effects (Shoesmith) for which the two spatial dimensions available in the UVa crevice code will be of particular importance. The outcome of this task will be a tool that allows crevice stability to be calculated for conditions of interest in the repository.

Task 3: Calculate stability of crevice corrosion attack for the two types of cases considering the external variables of temperature, relative humidity, external solution layer chemistry (coupled to other task outputs).

Motivation
As described above, there are two types of cases of crevice stability that need to be considered: (a) an isolated crevice (i.e., no external cathode), and (b) crevice with thin layer of solution outside the crevice on which cathodic reactions can be supported. A scientific basis for establishing the repository and WP surface conditions that lead to rates of crevice corrosion that would compromise package integrity is needed.

Approach
We will consider the range of parameters (RH, temperature, external solution layer chemistry, thickness of dust/deposit layer, and alloy composition) on the stability of crevice corrosion. The parameters concerning the external surface solution layer will determine the size of the area that can interact with the crevice. The geometric parameters describing the crevice (gap, length) and the anodic kinetics (as determined by alloy composition, temperature, and local chemistry) will determine the anodic current present. In order for the crevice to be stable, the cathodic current available must be able to support the anodic current required to maintain the aggressive electrolyte within the crevice. This task will map the region of the domain space of
the variables in which crevice corrosion can stabilize as well as the rates of damage expected. In this way, the scientific basis for determining the effect of important external conditions on the stability of crevice corrosion can be developed.

Interactions and Expected Outcomes
The effects of geometry (length, gap), metallurgical condition, temperature, and relative humidity will be investigated. Results are important inputs to the determination of the extent of damage caused by crevice corrosion which will be used by the damage accumulation tasks (Shoesmith, Macdonald).

References