

Project ID: **60401**

Project Title: **Mechanism of Pitting Corrosion Prevention by Nitrite in Carbon Steel Exposed to Dilute Salt Solutions**

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Research Award Summary

June 15, 1999

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Research Objective

The overall goal of this project is to develop a fundamental understanding of the role of nitrite in preventing the breakdown of protective oxide(s) on carbon steel and the onset of pitting. Pitting corrosion of carbon steel exposed to dilute alkaline salt solutions can be induced by nitrate, sulfate, and chloride ions and is prevented by sufficient concentration of nitrite. A significant example of this material/electrolyte system is the storage and processing of DOE's high-level radioactive liquid waste in carbon steel tanks. Added nitrite in the waste has a considerable downstream impact on the immobilization of the waste in a stable glass form. Waste tank integrity and glass production efficiency may benefit from the fundamental understanding of nitrite's role in preventing pitting.

Research Progress and Implications

Summary

This report summarizes progress for the last 12 months. It accounts for approximately eighteen months of effort in this three-year EMSP project. This report adds to the report submitted last year (June 1998) which described progress after approximately six months of the project. The planned activities of the project are listed at the end of the report. We have updated the completion dates and projections to reflect the current status of the project. During the last year we experienced a four-month delay on the spectroscopic studies task when the circuit board on the FT-IR instrument overheated and required repair and re-calibration. At this time we expect to complete all of the tasks of the project on time despite this instrument failure.

The experimental and theoretical work has continued to focus on the electrochemical behavior of carbon steel in simplified non-radioactive solutions that simulate complex dilute radioactive waste solutions. These solutions contain corrosion-inducing species such as nitrate and chloride and the corrosion-inhibiting nitrite at moderately alkaline pHs. We are interested in three critical aspects of the electrochemical behavior. One aspect is that of the open-circuit potential of the steel specimen at equilibrium and we are interested in how it changes as a function of inhibitors in the experimental electrolyte. The other two aspects include measures of the steel's passivity and passivity breakdown.

We have published two refereed papers in conference proceedings (1,2) that describe measurements of these aspects as a function of inhibitor concentration and electrolyte concentration. We have completed the design of combined spectroscopic-electrochemical cells for the purpose of studying the surface species as a function of applied potential and electrolyte concentration. We have begun the FT-IR and FT-Raman experiments. We have developed a model to describe the data on the open-circuit potential and the current-potential relationship prior to pit formation (3). This model will be presented in November and a paper will be submitted prior to that conference. We have started a second model to describe the electrochemistry that occurs in a pit as a function of electrolyte composition and concentration.

Electrochemical Studies

The electrochemical behavior is evaluated by the cyclic potentiodynamic polarization (CPP) technique. The technique involves the measurement of the electric current (i.e., the electrochemical reaction rate) in response to a voltage, or potential, applied to the test specimen. The technique can reveal the susceptibility

of an alloy to pitting corrosion, which initiates upon breakdown of a passive film on the metal specimen. In a CPP scan, passivity manifests itself through a range of applied potential in which the resulting passive current (density) is unvarying. Passivity breakdown is expressed experimentally as the potential at which the current increases abruptly from a relatively low, potential-*independent* value.

Cyclic potentiodynamic polarization scans were conducted on specimens of ASTM A537 carbon steel, the waste tank material of construction. In the present experiments, the potential was scanned from near the open-circuit potential to about +1 volt with respect to a saturated calomel reference electrode (1V SCE) and then returned to near the open-circuit value. The scan rate was 0.5 mV/sec, which is a reasonable balance between approximating steady-state conditions and acquiring data efficiently. Test solutions were mixed from reagent grade chemicals and distilled water. The solutions contained various nitrate and chloride concentrations. The initial pH of the solutions was 9.7 (established by a bicarbonate-carbonate equilibrium), and the test temperature was 40°C.

Initial experiments demonstrate significant differences in the steel's behavior in nitrate versus chloride solutions. Chloride is the classic initiating ion of pitting corrosion. With increasing chloride concentration in the range 0.01 to 0.3 M, the breakdown potential decreases from a value above the transpassive transition (~ 750 mV SCE) to a value below the open-circuit potential (open-circuit potentials range from -500 to -100 mV SCE). Chloride-induced breakdown is mitigated by nitrite; and nitrite drives the breakdown potential higher. Nitrate has been shown to induce pits in carbon steel, and such pitting can also be mitigated by nitrite. In fact the action of nitrite is empirically the same for nitrate and chloride. However, in the present experiments increasing nitrate concentrations do not result in the observation of a breakdown potential. CPP scans in solutions with a nitrate concentration of as high as 2.2 M continue to show a transpassive transition at about 750 mV SCE. The corrosivity of nitrate toward carbon steel *is revealed* in an increase in the passive current density. These results have been presented as shown in Refs. 1 and 2. We expect to perform additional experiments to verify and test hypotheses formulated during the development of the models and during the analysis of the spectroscopic studies.

Spectroscopic Studies

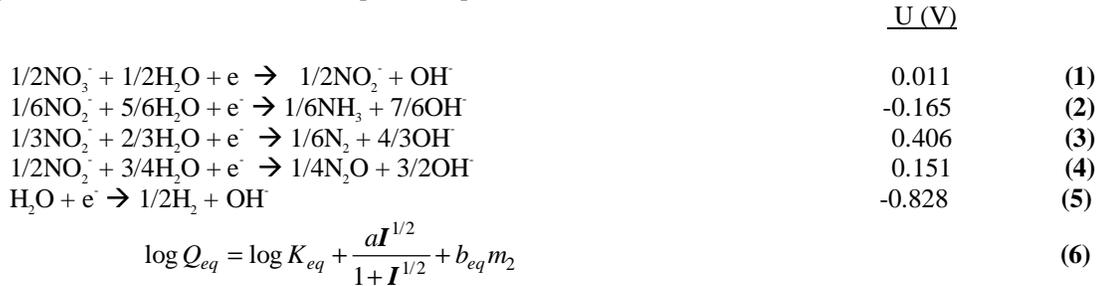
In addition to the potentiodynamic polarization scans, spectroscopic studies have been started. The goal of these studies is to investigate the oxide film and its response to changes in the concentration of corrosive and protective species with *in-situ* vibrational spectroscopy. A specially designed cell has been constructed to allow for combined Electrochemical Impedance Spectroscopy and FTIR or FT Raman measurements. These EIS/FTIR and EIS/FT Raman cells will be used to determine if surface enhanced signals can be observed. Raman/EIS cells are being tested using a number of optical configurations.

One of these designs will be used to test the cell optics and Raman sensitivities and it will incorporate two glass plates. A thin metallic film will be deposited on the inner surface of one plate. The space between the plates will contain the test solution. Counter and reference electrodes have been installed. The cell can then be positioned in the Raman spectrometer in two orientations: (1) the exciting beam passes through the unmetallized plate and solution before striking the metal film; and (2) the beam enters through the back of the metallized plate and strikes the film from the rear. The evanescent Raman from this orientation will minimize optical sampling of the solution.

Another design studied this year includes the use of ASTM A537 carbon steel as the back plate with one of the glass plates as the front plate. We are working on minimizing the signal loss through the solution with this configuration. The advantage to this design is the ability to polish the surface of the cell to the same roughness as the coupons in the electrochemical studies. We will be studying techniques to initiate the pit at a specific point to facilitate the observations in a pit. Results of these studies were delayed during the last year due to a failure of a circuit board and a tuning laser on the FT-IR portion of the FT-Raman. The instrument has been repaired and re-calibrated and preliminary data has been obtained. The spectroscopic studies will be a major focus of the work during the next year.

Analysis and Modeling

The analysis of the passivation/activation phenomena has been aided by a fundamental understanding of the solution chemistry. Studies of the interaction of nitrate and nitrite seem to indicate that the redox reactions shown by reactions 1-5 below are involved. As a first step in the analysis of the solution effects, the effect of ionic strength on the equilibrium and solubility products for the Pourbaix diagram has been calculated using equation 6. Here the dilute solution equilibrium constant, K_{eq} , and the actual equilibrium constant Q_{eq} are related to the ionic strength, I , the molality of the dominant species. Reference 1 presents the effects of ionic strength on the Pourbaix diagram and showed that the regions of film formation and dissolution changed significantly with concentration of simulant the at the pH of the experiments. Future work will involve the effect of temperature on the equilibrium solubility products, the hydrolysis reactions, and the exchange current densities for film breakdown. We plan to study theoretically the adsorption characteristics of chloride, nitrate, and nitrite as a function of temperature and ionic strength and to compare these with the data from the spectroscopic studies.



We have also developed a model to describe the data on the open-circuit potential and the current-potential relationship prior to pit formation (3). The model for the initiation of a pit in iron is developed by using [Figure 1](#). The mass fluxes include diffusion, migration, and convection in the two-region, three-boundary condition problem. Six species plus the potential are used as dependent variables and two electrode reactions were considered to take place on steel surface. One is iron electrode reaction; the other is reversible reduction of nitrate to nitrite.

The competition of nitrite oxidation and iron oxidation can partially explain the inhibition of nitrite to iron corrosion. Predictions have been prepared for the concentration profiles through the passive film and diffusion layer, for the solution potential distribution, and for the relationship between the steel's potential and the overall current density. The model results are being used to test hypotheses and to suggest reaction mechanisms for the passivation behavior by comparing the V-I predictions with experimental data for different ratios of $\text{NO}_2^-/\text{NO}_3^-$ concentrations as shown in [Figures 2](#) and [3](#). This model will be presented in November and a paper will be submitted prior to that conference. We have started a second model to describe the electrochemistry that occurs in a pit as a function of electrolyte composition and concentration according to the schematic of [Figure 4](#).

Planned Activities

<i>Activity</i>	<i>Completion</i>
1. Perform potentiodynamic and potentiostatic scans to evaluate the differences in the chloride and nitrate effects on the breakdown potential and passive current density.	12/98
2. Spectroscopic studies to design & fabricate EIS/FTIR and EIS/FT Raman cells	12/98
3. Perform measurements to check for surface enhancement and study the effect of the exciting beam passing through the solution before striking the metal film and the effect of the exciting beam passing through the back of the metallized plate and striking the film from the rear.	5/00
4. Mathematical model of pitting phenomena	9/00

References

1. P. E. Zapp, L. Chen, and J.W. Van Zee, "Studies on the Mechanism of Pitting Corrosion Prevention by Nitrite in Carbon Steel Exposed to Dilute Salt Solutions," *Proceedings of the Symposia on Interfacial Corrosion*, R.G. Kelley Ed., The Electrochemical Society, Pennington, NJ, PV 98-27, pp. 551-563 (1998).
2. P. E. Zapp and John W. Van Zee, "Electrochemical Studies of Nitrate Pitting in Carbon Steel," Paper No. 471 in *Corrosion 99*, National Association for Corrosion Engineers, Spring Meeting, April 1999.
3. P. E. Zapp, L. Chen, and J.W. Van Zee, "A Model for the Effect of Nitrate and Nitrite on the Behavior of Carbon Steel Prior to Pitting," to be presented in the Symposium 1e02, "Tutorials in Corrosion Science and Engineering II", 1999 AIChE Annual Meeting, Dallas, TX, Nov. 1999

Figures

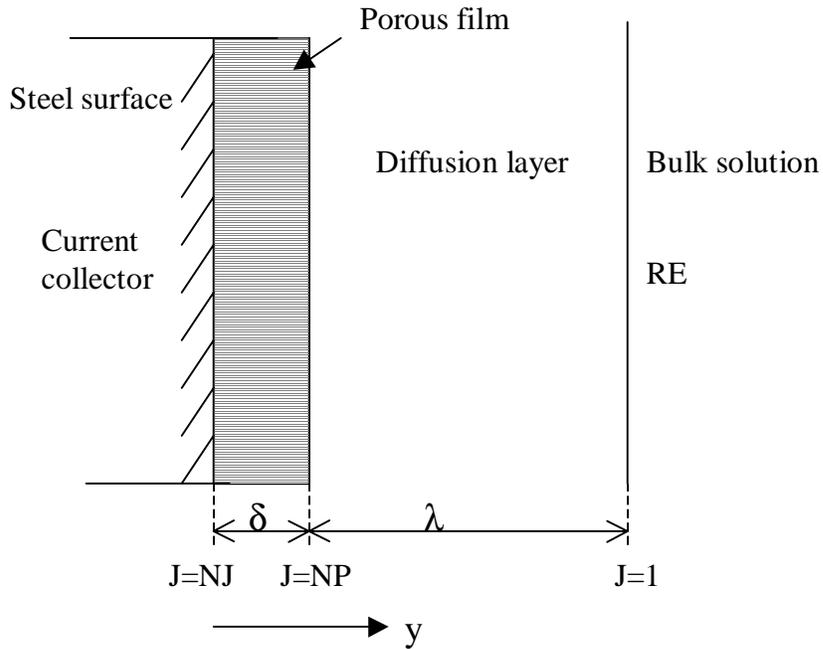


Figure 1. Schematic diagram for the first model.

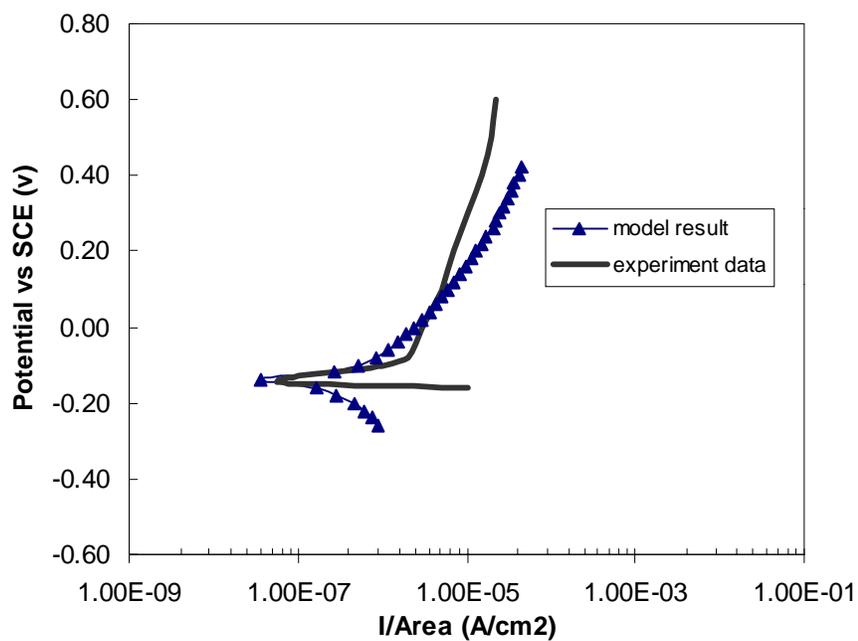


Figure 2. Comparison of experiment data and model predictions. The experiment data comes from cyclic potentiodynamic polarization scans at 0.02M nitrate and 0.11M nitrite as shown in Ref. 2.

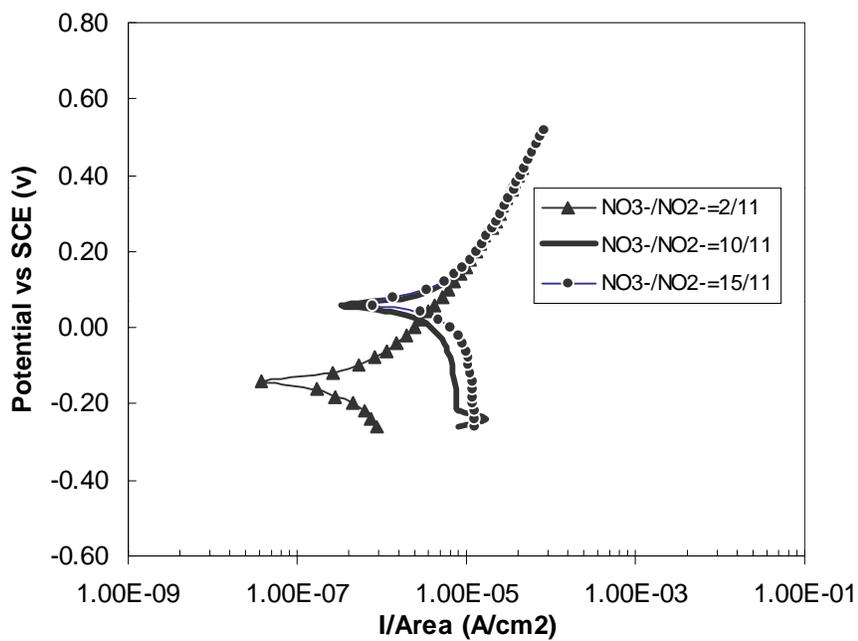


Figure 3. Predictions of the effect of the nitrate/nitrite ratio on the potential-current relationship.

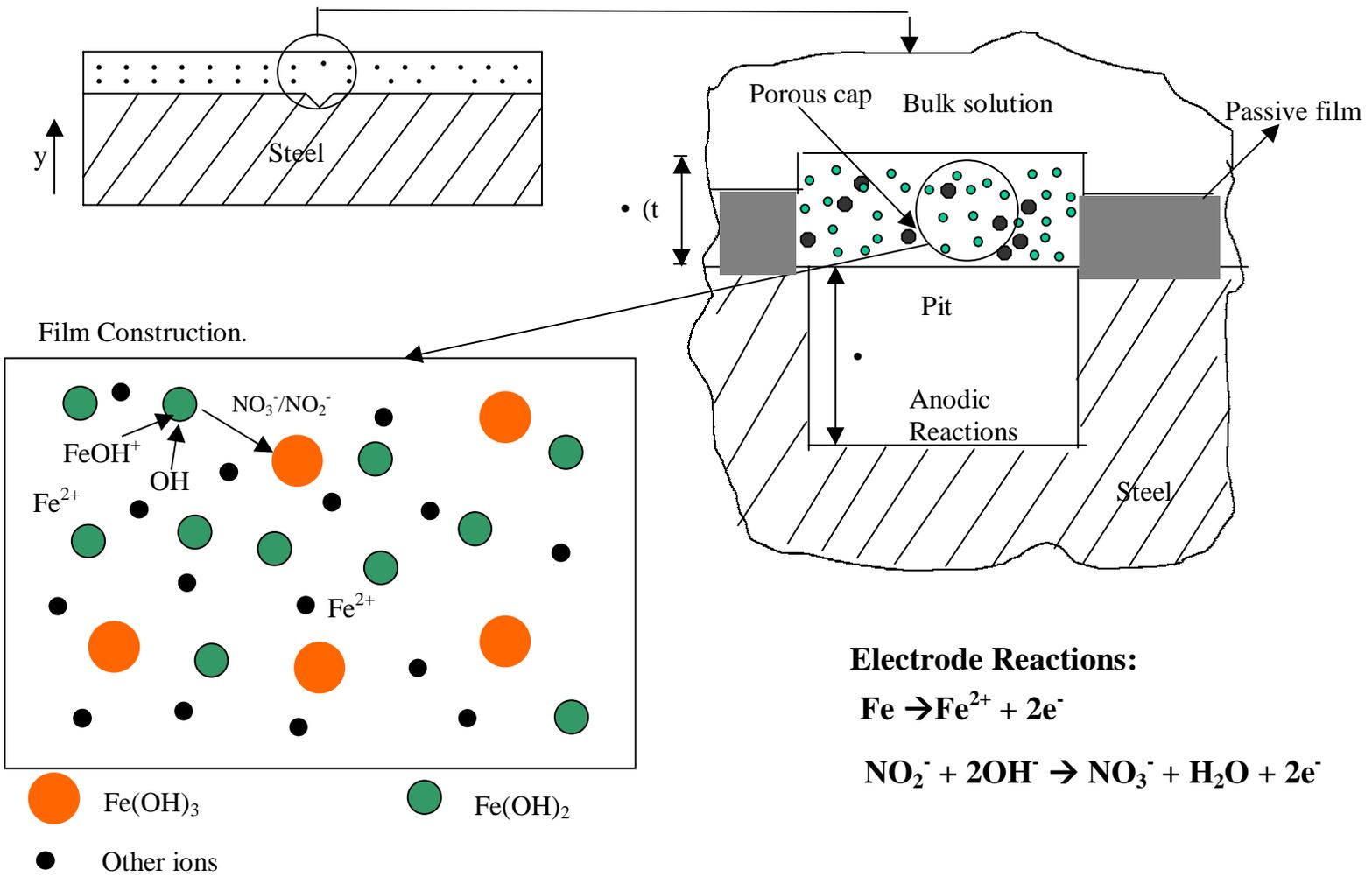


Figure 4. Schematic for Pit Model.