

Environmental Management Science Program

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Mechanism of Pitting Corrosion Prevention by Nitrite in Carbon Steel Exposed to Dilute Salt Solutions

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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

This report summarizes progress after approximately six months of effort in this three-year EMSP project. Initial experimental and theoretical work has focused 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. The electrochemical behavior of interest here is that of the open-circuit potential of the steel specimen at equilibrium in the experimental electrolyte and the measures of the steel's passivity and passivity breakdown.

This 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.

Electrochemical Studies

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;

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.

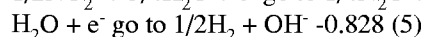
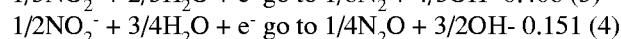
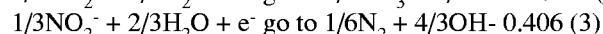
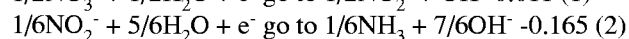
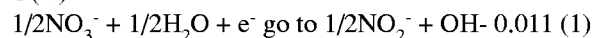
Spectroscopic Studies

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.

Analysis and Modeling

The analysis of the passivation/activation phenomena will be aided by a fundamental understanding of the solution chemistry and the adsorption characteristics of chloride, nitrate, and nitrite as a function of temperature and ionic strength. Studies of the interaction of nitrate and nitrite may involve the redox reactions shown by reactions 1-5 below. 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. We believe that the effect of temperature will be reflected in the equilibrium solubility products, the hydrolysis reactions, and the exchange current densities for film breakdown.

U(V)



$$\log Q = \log K a \cdot \sqrt{I} / (1 + \sqrt{I}) + b \cdot m \text{ (6)}$$

Planned Activities

Activity Completion

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 9/98.
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 9/99.
4. Mathematical model of pitting phenomena 9/00.