

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

Philip E. Zapp, Westinghouse Savannah River Co.
and John W. Van Zee, University of South Carolina

Introduction

Dilute alkaline radioactive waste solutions may induce pitting, a rapid localized form of corrosion, in carbon steel tanks when the solution pH falls below 12. Based on extensive laboratory testing in simulated waste solutions, nitrite ion additions prevent pitting. In waste solutions not containing organic species, the nitrite concentration that prevents pitting is related to the nitrate concentration and temperature by the empirical equation

$$[\text{NO}_2^-] = 0.025 [\text{NO}_3^-] 10^{0.041T}$$

where T is 23 - 60°C, and the pH is > 10.3.

This project seeks to develop a model that will account for the effective concentration of nitrite to prevent pitting. The research plan consists of four tasks. The first is the acquisition of the open circuit, pitting, and repassivation potentials in simple nitrate and chloride solutions, using the cyclic potentiodynamic polarization technique. The second is the design and fabrication of Fourier Transform Raman and Fourier Transform Infrared cells. The third task is the performance of combined electrochemical (including impedance) and vibrational spectroscopic studies with the cells. The fourth task is the mathematical modeling of pitting potentials based on nitrate and nitrite surface reactions on carbon steel.

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Project Goal

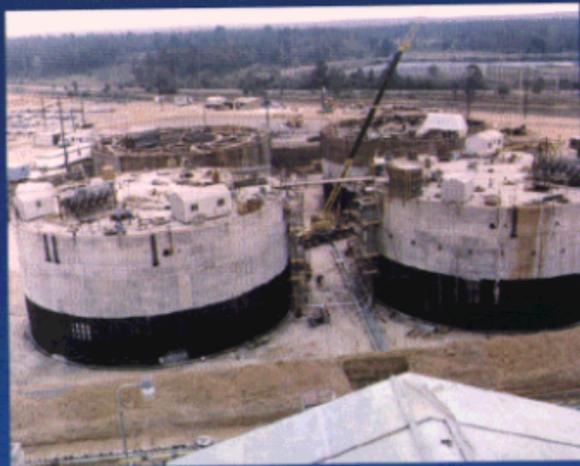
To develop a fundamental understanding of the role of nitrite in preventing the breakdown of the protective oxide on carbon steel and the onset of pitting.

Significance of Project to the EMSP

Permanent disposition of millions of gallons of defense high-level radioactive waste involves processing the waste as potentially corrosive dilute alkaline salt solutions in carbon steel tanks, prior to incorporating the waste into a borosilicate glass. Both waste tank integrity and glass production efficiency will benefit from a basic understanding of the role nitrite plays in preventing pitting corrosion.

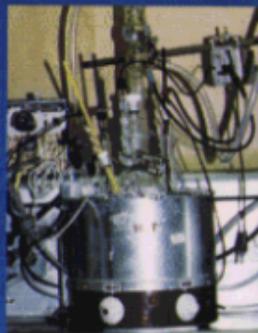
Defense High-Level Waste Storage and Processing

At the Department of Energy's Savannah River Site, defense high-level radioactive waste is being washed (diluted) in 1.3 Mgal double-wall tanks (ASTM A537 carbon steel) to prepare the waste for incorporation in borosilicate glass for permanent disposition at a federal repository. At a solution $\text{pH} < 12$ the nitrate, sulfate, and chloride may induce pitting corrosion in the tank primary wall and cooling pipes. Sodium nitrite additions prevent the initiation of pitting. Photograph shows Savannah River Site type III waste tanks under construction circa 1980.



Cyclic Potentiodynamic Polarization Experiments

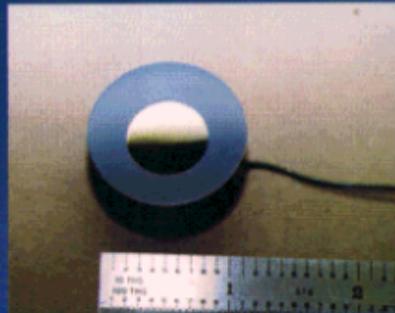
Cyclic potentiodynamic polarization (CPP) scans can reveal the breakdown or pitting potential and the repassivation potential of alloys exposed to corrosive solutions (ASTM Standard Test Method G 61). An applied potential is slowly swept (0.5 mV/s in the present tests) by the potentiostat from the open circuit potential to about 1 volt with respect to open circuit and then reversed. The resulting corrosion current is recorded. Current increases rapidly with potential upon passive film breakdown and pit initiation.



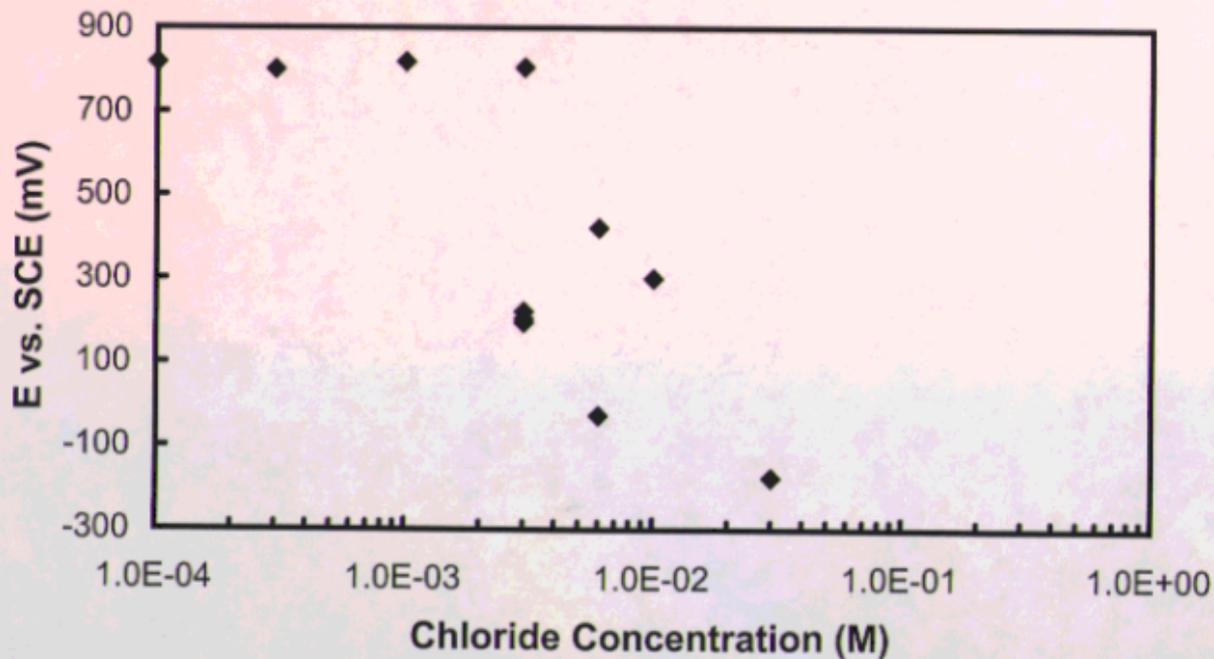
Electrochemical Testing with Mounted A537 Carbon Steel Specimens

A537 carbon steel discs are mounted in epoxy with copper conductor attached. Specimens are polished to a 1 micrometer finish. Upper photograph shows post-test specimen with small pit at left. Lower photograph shows heavily pitted specimen.

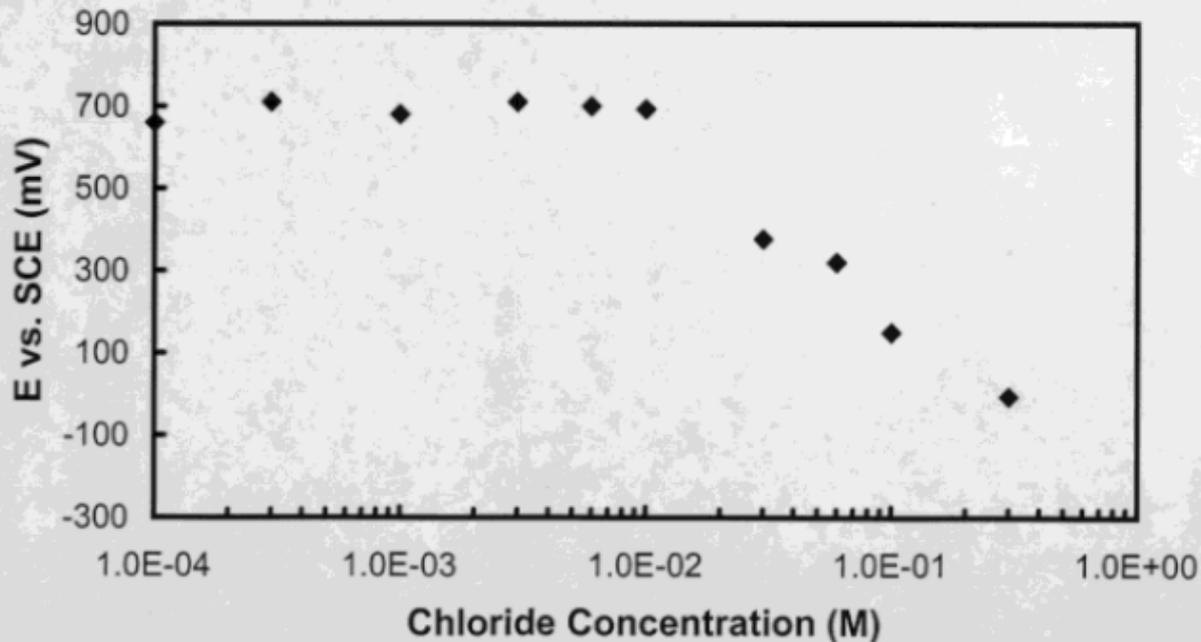
Tests have been performed in buffered bicarbonate-carbonate solutions, pH 9.73, at 40°C in the chloride-nitrite system and the nitrate-nitrite system. Pitting potentials have been measured as a function of chloride and nitrate concentration at 0 and 0.11 M nitrite.



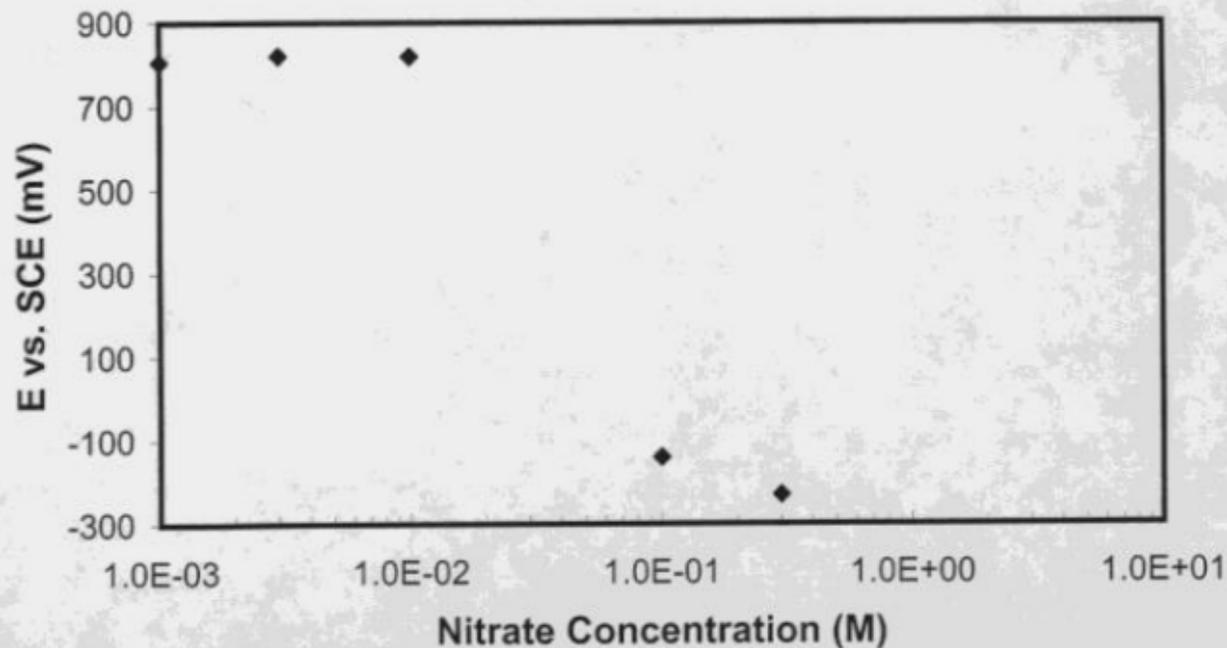
Pitting Potential vs. Chloride Concentration @ 0 M Nitrite



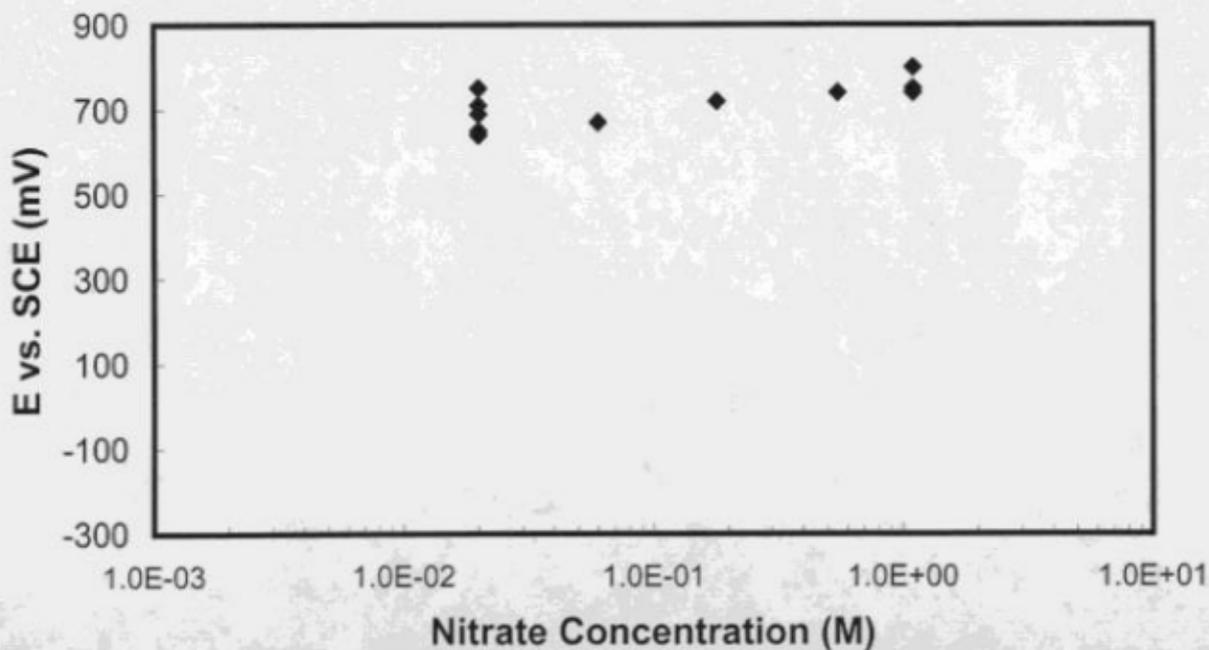
Pitting Potential vs. Chloride Concentration @ 0.11 M Nitrite



Pitting Potential vs. Nitrate Concentration @ 0 M Nitrite



Pitting Potential vs. Nitrate Concentration @ 0.11 M Nitrite



Status of Electrochemical Testing

Preliminary qualitative observations based on work to date in 1998:

1. In the absence of nitrite, nitrate, as well as chloride, a pitting potential can be measured. The nitrate concentration required to reveal a pitting potential is an order of magnitude greater than the chloride concentration.
2. At a 0.11 M nitrite concentration, no pitting potential is observed in the nitrate solution; only transpassive behavior is observed.
3. At a 0.11 M nitrite concentration, more than an order of magnitude greater chloride concentration is necessary to produce the chloride-induced pitting potentials seen in the absence of nitrite.
4. Passive current densities rise with increasing nitrate or chloride concentration.

Table 1 .Electrochemical and chemical reactions considered in the Pourbaix diagram for iron. (All values correspond to infinitely dilute concentrations at 25°C and standard conditions)

$\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$	$U^0 = -0.440 \text{ V}$	[1-1]
$\text{Fe} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$	$U^0 = -0.0470 \text{ V}$	[1-2]
$\text{Fe} + 2\text{H}_2\text{O} = \text{HFeO}_2^- + 3\text{H}^+ + 2\text{e}^-$	$U^0 = 0.493 \text{ V}$	[1-3]
$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$	$K_{\text{eq}} = 5.012 \times 10^{-14} \text{ mol/l}$	[1-4]
$\text{Fe}(\text{OH})_2 = \text{HFeO}_2^- + \text{H}^+$	$K_{\text{sp}} = 5.0119 \times 10^{-19} (\text{mol/l})^2$	[1-5]
$\text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+ + \text{e}^-$	$U^0 = 1.057 \text{ V}$	[1-6]
$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+$	$K_{\text{eq}} = 1.4488 \times 10^{-5} (\text{mol/l})^2$	[1-7]
$\text{HFeO}_2^- + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{e}^-$	$U^0 = -0.810 \text{ V}$	[1-8]
$\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + \text{H}^+ + \text{e}^-$	$U^0 = 0.271 \text{ V}$	[1-9]

Pourbaix diagram for iron

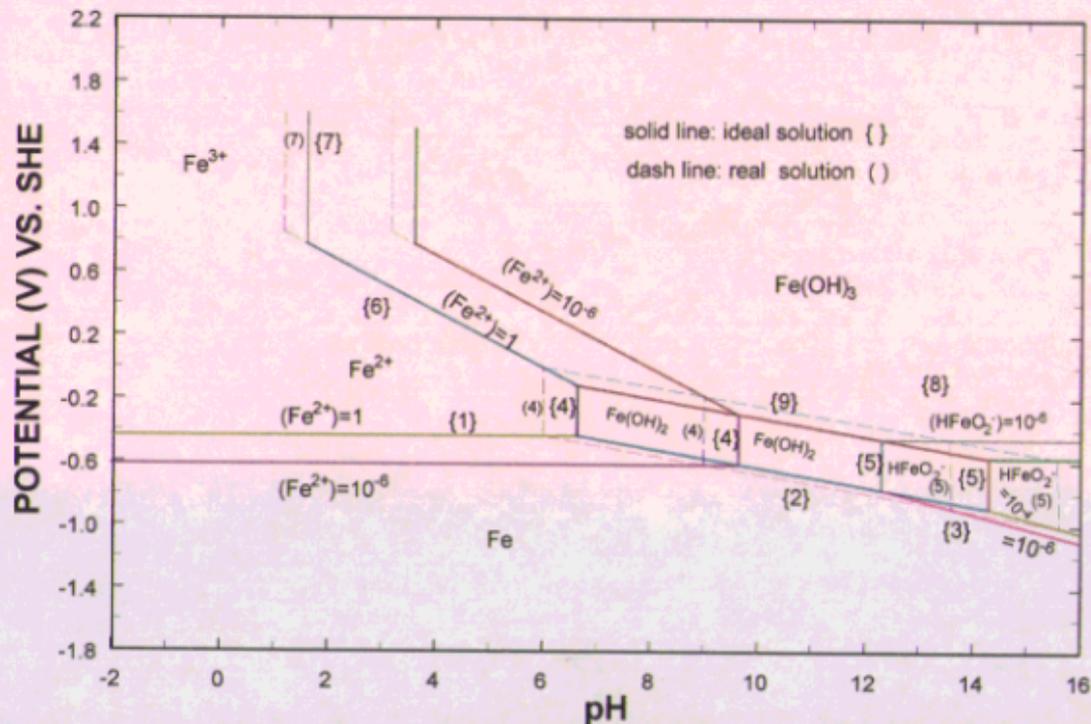
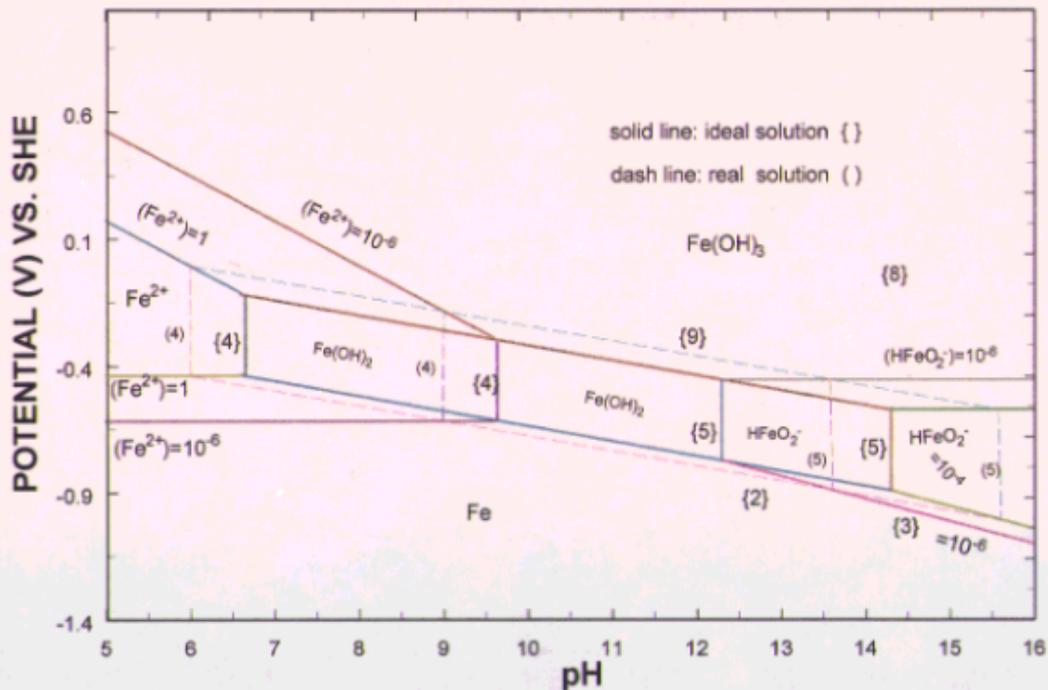


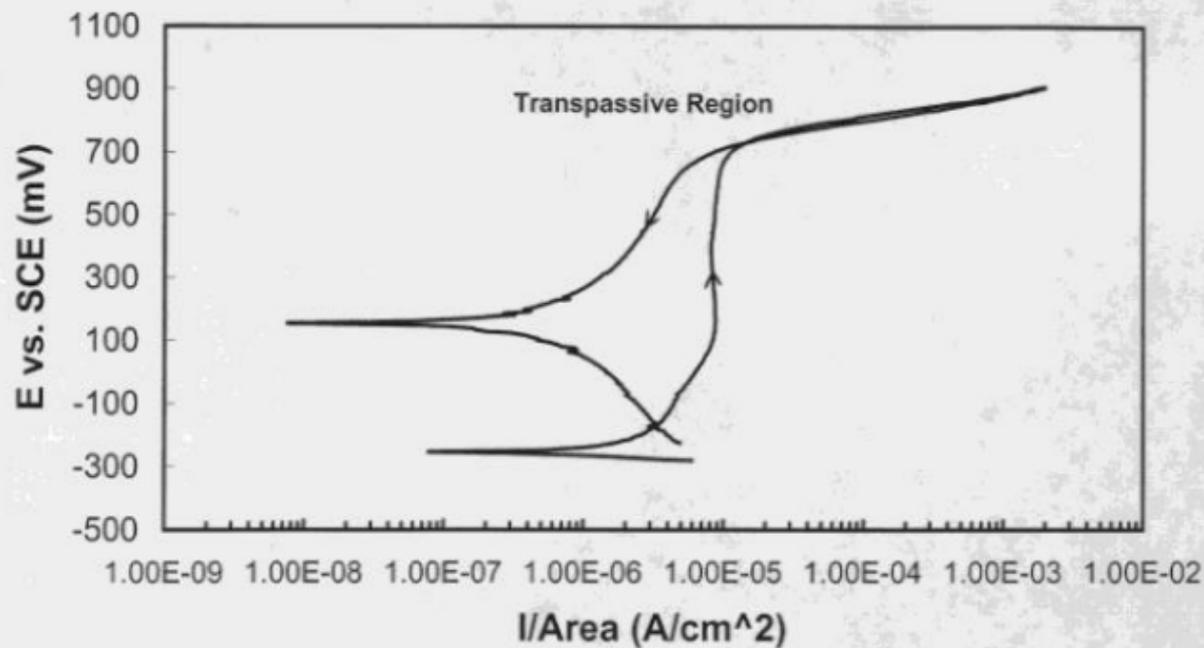
Table 2 Composition of Actual Supernate Test Solution¹¹¹ ;
Ionic Strength = 2.8506

Species	Molar Concentration
Nitrate (NaNO ₃)	0.760
Nitrite (NaNO ₂)	0.63
Sulfate (Na ₂ SO ₄)	0.071
Fluoride (NaF)	0.025
Chloride (NaCl)	<0.0056
Free Hydroxide (NaOH)	0.50
Total Hydroxide	0.69
Aluminate (Na ₃ AlO ₃)	0.10
Total Carbonate (Na ₂ CO ₃)	0.039
Sodium	2.4406

Pourbaix diagram for iron



Cyclic Potentiodynamic Polarization Scan 0.0001 M Chloride, 0.11 M Nitrite



Cyclic Potentiodynamic Polarization Scan 0.3 M Chloride, 0.11 M Nitrite

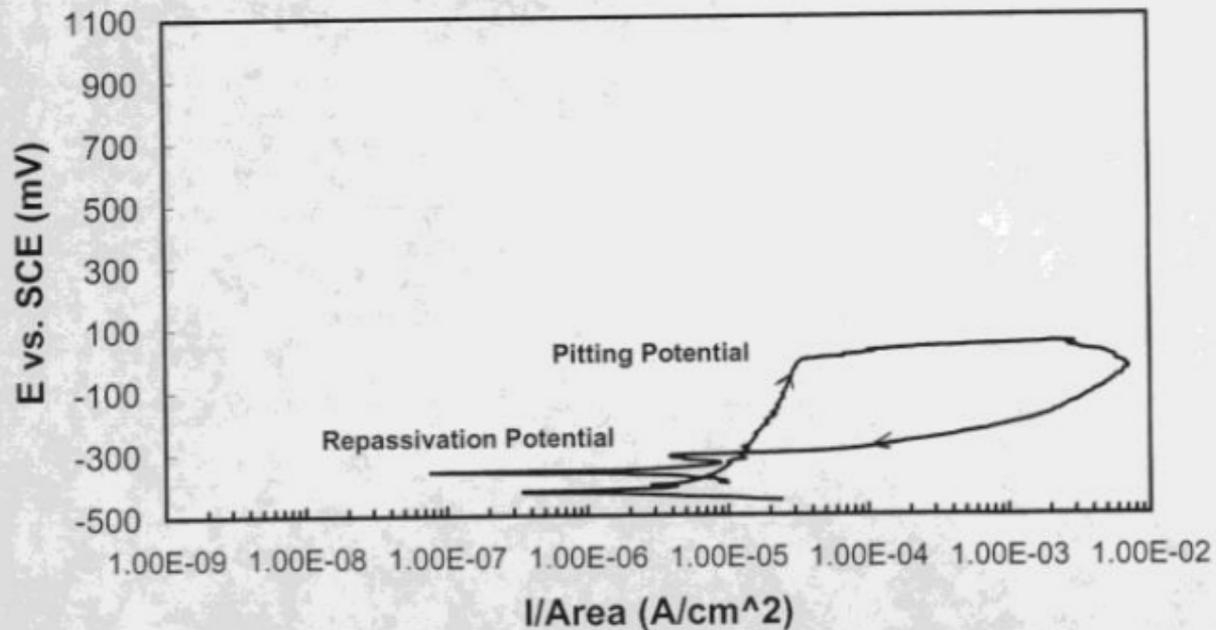
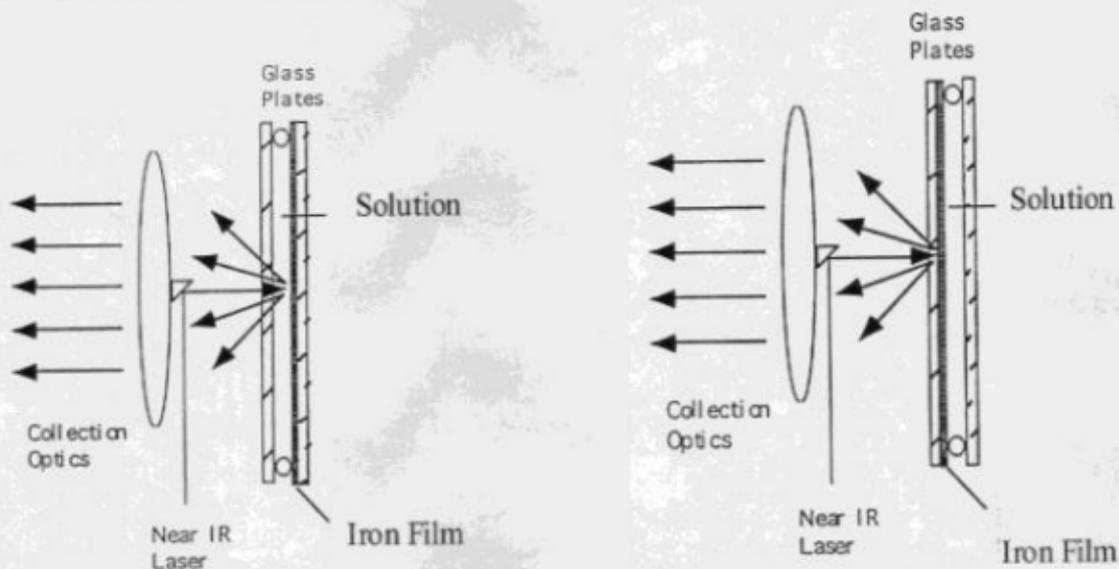


Table 3. Equations for Pourbaix Diagrams Including Ionic Strength

The Reaction	Equations (ideal solution)	Equations (real solution)
$\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$	$U_{\text{Fe}/\text{Fe}^{2+}} = -0.440 + 0.0295 \log(\text{Fe}^{2+})$	$U_{\text{Fe}/\text{Fe}^{2+}} = -0.440 + 0.0295 \log(\text{Fe}^{2+})$
$\text{Fe} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$	$U_{\text{Fe}/\text{Fe}(\text{OH})_2} = -0.047 - 0.0591 \text{pH}$	$U_{\text{Fe}/\text{Fe}(\text{OH})_2} = -0.085528 - 0.0591 \text{pH}$
$\text{Fe} + 2\text{H}_2\text{O} = \text{HFeO}_2^- + 3\text{H}^+ + 2\text{e}^-$	$U_{\text{Fe}/\text{HFeO}_2^-} = 0.493 - 0.0886 \text{pH} + 0.0295 \log(\text{HFeO}_2^-)$	$U_{\text{Fe}/\text{HFeO}_2^-} = 0.493 - 0.0886 \text{pH} + 0.0295 \log(\text{HFeO}_2^-)$
$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$	$\text{pH} = 6.65 - 0.5 \log(\text{Fe}^{2+})$	$\text{pH} = 6.008 - 0.5 \log(\text{Fe}^{2+})$
$\text{Fe}(\text{OH})_2 = \text{HFeO}_2^- + \text{H}^+$	$\text{pH} = 18.30 + \log(\text{HFeO}_2^-)$	$\text{pH} = 17.0167 + \log(\text{HFeO}_2^-)$
$\text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+ + \text{e}^-$	$U_{\text{Fe}^{2+}/\text{Fe}(\text{OH})_3} = 1.057 - 0.1773 \text{pH} - 0.0591 \log(\text{Fe}^{2+})$	$U_{\text{Fe}^{2+}/\text{Fe}(\text{OH})_3} = 1.057 - 0.1773 \text{pH} - 0.0591 \log(\text{Fe}^{2+})$
$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+$	$\text{pH} = 1.613 - (1/3) \log(\text{Fe}^{3+})$	$\text{pH} = 1.1851 - (1/3) \log(\text{Fe}^{3+})$
$\text{HFeO}_2^- + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{e}^-$	$U_{\text{HFeO}_2^-/\text{Fe}(\text{OH})_3} = -0.810 - 0.0591 \log(\text{HFeO}_2^-)$	$U_{\text{HFeO}_2^-/\text{Fe}(\text{OH})_3} = -0.810 - 0.0591 \log(\text{HFeO}_2^-)$
$\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + \text{H}^+ + \text{e}^-$	$U_{\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3} = 0.271 - 0.0591 \text{pH}$	$U_{\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3} = 0.346854 - 0.0591 \text{pH}$

Prototype FT-Raman Cell For Evaluation of Raman Scattering Characteristics of Sputtered Thin Films



Forward Scattering

Evanescent Scattering

FT-Raman/EIS Cell Schematic For Study of NO_3^- , NO_2^- , and Cl^- Species

