

Conf-920458-9

WSRC-MS--91-519

DE92 015334

# INHIBITING PITTING CORROSION IN CARBON STEEL EXPOSED TO DILUTE RADIOACTIVE WASTE SLURRIES (U)

by

P. E. Zapp and D. T. Hobbs

Westinghouse Savannah River Company  
Savannah River Site  
Aiken, SC 29808

AC09-89SR18035

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

A paper proposed for presentation at the  
*National Association of Corrosion Engineers Annual Conference 1992*  
Nashville, Tennessee  
April 27 - May 1, 1992

and for publication in the proceedings

Received by USG  
JUN 11 1992

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

JMP MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**INHIBITING PITTING CORROSION IN CARBON STEEL  
EXPOSED TO DILUTE RADIOACTIVE WASTE SLURRIES**

Philip E. Zapp and David T. Hobbs  
Westinghouse Savannah River Co.  
Savannah River Laboratory  
Aiken SC 29808

**ABSTRACT**

Dilute caustic high-level radioactive waste slurries can induce pitting corrosion in carbon steel. Cyclic potentiodynamic polarization tests were conducted in simulated and actual waste solutions to determine minimum concentrations of sodium nitrite which inhibit pitting in ASTM A537 class 1 steel exposed to these solutions. Susceptibility to pitting was assessed through microscopic inspection of specimens and inspection of polarization scans. Long-term coupon immersion tests were conducted to verify the nitrite concentrations established by the cyclic potentiodynamic polarization tests. The minimum effective nitrite concentration is expressed as a function of the waste nitrate concentration and temperature.

Keywords: High-level radioactive waste, nitrite, hydroxide

**INTRODUCTION**

High-level radioactive wastes are stored in large underground carbon steel tanks at the U.S. Department of Energy's Savannah River Site near Aiken, SC. The wastes result from the nitric acid dissolution of nuclear fuel and target components performed in the course of nuclear materials production for national defense and space programs. All waste is neutralized with sodium hydroxide prior to transfer to the tanks. Because of the high pH, the waste consists of two phases: a liquid phase or supernatant liquid, comprised of water soluble salts, and a solid phase or sludge, comprised of hydrous oxides of various metal ions. The sludge, which is suspended in a salt solution, contains most of the radioactivity; radioactive cesium and strontium are water soluble and thus reside in the supernatant liquid. The supernatant liquid and the liquid phase of the sludge suspension contain high concentrations of nitrate.<sup>1</sup> The high free hydroxide concentration in the liquid inhibits both nitrate stress corrosion cracking and general corrosion of the carbon steel.

**Publication Right**

Copyright by NACE. NACE has been given first rights of publication of this manuscript. Request for permission to publish this manuscript in any form in part or in whole, must be made in writing to NACE, Products Division, P.O. Box 218340, Houston, Texas 77218. The manuscript has not yet been reviewed by NACE, and accordingly, the material presented and the views expressed are solely those of the author(s) and are not necessarily endorsed by the Association. Printed in the U.S.A.

Tank storage is not considered a permanent disposal method for high-level waste. Permanent disposal will be achieved by concentrating and incorporating the radioactive species into a borosilicate glass. The borosilicate glass will be solidified in stainless steel canisters, which will be transferred to a federal waste repository. To concentrate the water soluble radionuclides, the supernatant liquid will be treated with sodium tetraphenylborate to precipitate radio-caesium and monosodium titanate to adsorb radio-strontium. This process will be carried out in a waste tank identical in construction to those used for waste storage, but which has been equipped for chemical processing.

Glass quality and minimization of glass volume require that the concentrations of soluble salts in the supernatant liquid and in the sludge liquid be reduced. The soluble salt concentrations will be reduced by washing the solids. Washing will also be carried out in waste tanks. Since washing necessarily lowers the concentration of hydroxide, the solutions may no longer contain the level of inhibitor required to protect the steel.

While the temperature of the washed solutions will be low enough to eliminate stress corrosion cracking as a concern, localized corrosion in the form of pitting may occur in inadequately inhibited solutions. Previous work demonstrated that the reduced hydroxide concentration in the washed precipitate solution rendered the steel vulnerable to pitting corrosion.<sup>2</sup> In particular, pitting occurred immediately above the liquid level on laboratory coupons which were partially immersed in a non-radioactive simulant of washed precipitate slurry.

It has been postulated that the aqueous film on the steel above the liquid level becomes rapidly depleted in hydroxide through the reaction of hydroxide with absorbed atmospheric carbon dioxide to form bicarbonate and carbonate. The hydroxide concentration in the aqueous film is calculated to decline by a factor of about  $10^4$  through the combined effects of washing and reacting with  $\text{CO}_2$  (that is, a reduction of pH from 14 to 10).

The maximum alkali content in the borosilicate glass waste form prohibits the use hydroxide alone to inhibit pitting corrosion during washing operations. Maintaining the integrity of the steel therefore requires that another inhibitor be added to the waste streams to supplement or replace hydroxide. Five corrosion inhibitors were identified that would protect carbon steel from pitting when exposed to washed precipitate solutions. Of the five only sodium nitrite was deemed compatible with the vitrification process and product. Minimum nitrite concentrations were established for inhibiting pitting corrosion in carbon steel exposed to the washed precipitate slurry.

Nitrate, sulfate, chloride, and fluoride were shown to be independently acting aggressive anions capable of inducing pitting. The composition of the liquid phase of the slurry is such that nitrate is the controlling anion; that is, the level of nitrite inhibitor is a function solely of the nitrate ion concentration and temperature. Only at concentrations higher than those expected for washed precipitate do sulfate, chloride, and fluoride become inhibitor controlling.

Washed precipitate slurries are complex solutions which contain inorganic and organic compounds. Washed sludge slurries share many of the inorganic species, including the four corrosion-inducing anions, but they do not contain organic compounds. This difference, coupled with the different washing method (discussed below), provided the incentive to investigate the suitability of nitrite as a corrosion inhibitor for this system and to determine the particular concentrations of nitrite required to inhibit pitting.

In the proposed scheme for sludge washing, sludge waste will be transferred from waste storage tanks to dedicated processing tanks. Washing will consist of 1) addition of inhibited wash water to a sludge batch, 2) thorough mixing of the tank contents, 3) settling of the solids, and 4) decanting of the supernate. These steps will be repeated until the soluble salt concentration has been diluted by a factor of 70. On average, a total of 13 washing steps will be required to completely wash a sludge batch. One washed sludge batch will be stored and transferred over a two-year period to the waste vitrification facility. Experience with washed precipitate slurries indicates that, in the absence of added inhibitors, pitting may initiate during the

washing phase as well as during the storage and transfer period. Therefore, the corrosivity of the entire range of compositions was investigated.

## EXPERIMENTAL

Electrochemical and coupon immersion tests were performed to determine the concentrations of sodium nitrite needed to inhibit pitting corrosion in steel exposed to a given wash step. The electrochemical test technique was cyclic potentiodynamic polarization, which provided a relatively rapid determination of 1) the susceptibility of the steel to pitting in a given waste composition and 2) the minimum level of sodium nitrite needed to inhibit pitting. Long-term coupon tests provided verification of the minimum effective nitrite levels revealed in the electrochemical tests. The tests were conducted at temperatures in the range of 23°C to 60°C; actual tank contents are expected to range from about 30°C to 50°C.

Tests were conducted with both actual waste and non-radioactive simulants of sludge slurries. The compositions of the simulants for the electrochemical tests are given in Table 1. The table shows the concentrations of soluble species in an calculated average unwashed sludge slurry and in the 13 dilutions expected to be produced in washing to the desired endpoint. All fourteen compositions were tested at a temperature of 40°C. Simulants of the 4th, 7th, 10th, and 13th wash steps were also tested at 23, 30, 50, and 60°C.

The concentrations of one wash step differ uniformly from the adjacent steps by a factor of 1.39. The nitrate level in the simulants ranged from 1.44 M in the unwashed or initial condition (referred to as the 0th wash step) to 0.0205 M in the final (or 13th) wash. The nitrite concentration in the test solution was varied at each wash step. The pH of the solutions used in the electrochemical tests was adjusted to steady-state levels calculated according to the model of absorption of and reaction with atmospheric carbon dioxide. These values are also shown in Table 1.

The coupon immersion tests with simulated sludge slurries were of similar composition to those used for electrochemical tests on equivalently washed (diluted) solutions, with the two exceptions. The nitrate ion was supplied entirely through transition metal salts (copper, iron, mercury, and nickel) rather than through the sodium nitrate used in electrochemical test solutions, where it was desirable to limit the amount of precipitated transition metal hydroxides; and the pH was set at the anticipated value of the bulk solution, rather than the steady-state value of the hydroxide-depleted aqueous film. Nitrite concentrations in the coupon test solutions were set to bracket the minimum effective nitrite concentrations determined in the cyclic potentiodynamic polarization tests.

The analysis of the actual sludge supernate is given in Table 2. The sludge supernate nitrate concentration was 0.73 M, a level equivalent to the 2nd wash in the ideal scheme. Cyclic potentiodynamic polarization tests were run in this solution, with the pH buffered to a value calculated from the hydroxide depletion model. Coupon immersion tests were run in the as-received sludge supernate and in solutions made from diluting the filtered sludge supernate with distilled water. A 5X dilution produced a solution equivalent to the 7th wash simulant, and a 25X dilution produced a solution equivalent to the 12th wash simulant. Nitrite was added to one sample of each dilution.

Specimens used in this study were fabricated from ASTM A537 Class 1 steel, the material of construction of the waste tanks. Disc specimens 1.58 cm in diameter were used in the electrochemical tests, and coupons 7.6 cm long by 1.9 cm wide by 0.32 cm thick were used in the immersion tests. All specimens were polished to a 600 grit finish and were cleaned in acetone and distilled water immediately before use.

A Princeton Applied Research (PAR) Model 351 Corrosion Measurement System<sup>(1)</sup> (incorporating a

---

<sup>(1)</sup>EG&G Princeton Applied Research, Electrochemical Instruments Division, CN 5205, Princeton NJ 08543

PAR Model 273 potentiostat) was used to run the cyclic potentiodynamic polarization tests with simulant waste slurries. A PAR Model 173 potentiostat was used in the tests run with sludge supernate. Standard test cells with graphite counter electrodes were used.<sup>3</sup> The disc specimens were mounted in a standard PAR specimen holder, presenting a 1-cm<sup>2</sup> exposed area to the solution. Polytetrafluoroethylene knife-edge gaskets were used to seal the specimen in the holder.<sup>3</sup> In the tests, specimens were placed in the electrolyte and initially held at open circuit potential ( $E_{\text{CORR}}$ ) for 1800 s, after which they were anodically polarized at a rate of 0.166 mV/s from a potential of -50 mV versus  $E_{\text{CORR}}$  to a vertex potential of about 900 mV. The potential scan was then reversed to end the scan at  $E_{\text{CORR}}$ . Scans in simulant solutions were run in duplicate. The test solutions were sparged with air which had been scrubbed of carbon dioxide in order to maintain the pH constant during the scan. The pH changed typically by less than  $\pm 0.1$  over the course of the scan. Temperature of the test solution was maintained within  $\pm 1^\circ\text{C}$  with a Thermowatch<sup>(2)</sup>-controlled heating mantle.

Coupon immersion tests were conducted in simulated sludge slurries with the compositions of the fourth, seventh, tenth, and thirteenth wash steps and in actual sludge supernate at the same dilutions used in the electrochemical tests (i.e., undiluted, 5X diluted, and 25X diluted). Four coupons were suspended with polytetrafluoroethylene string in each 1 L polyethylene or polytetrafluoroethylene test bottle, which was filled with 500 mL of sludge solution, so that the coupons were immersed half way into the solution. Air was flowed into the bottles at a rate of about 1.6 mL/s to simulate the airflow maintained in the waste tanks.

The tests were run for about 120 days at temperatures of 30, 40, 50, and 60°C. Both air ovens and a water bath were used to maintain the elevated temperatures. Temperature control was within  $\pm 2^\circ\text{C}$  in the ovens and  $\pm 1^\circ\text{C}$  in the water bath. Test solutions were replenished periodically with distilled water to compensate for evaporation loss.

Specimens which were exposed to sludge simulants were cleaned in Clarke's solution<sup>5</sup> at room temperature for about 30 seconds after testing to remove corrosion products. Specimens exposed to actual sludge supernate were cleaned for longer times in order to remove radioactive contamination as well as corrosion products so that those specimens could be removed from the shielded cells for examination.

## RESULTS

Cyclic potentiodynamic polarization scans were run at 40°C in simulants of all wash steps and in the actual sludge supernate. An additional sludge simulant, representing a 2X dilution of the 13th wash step, was also tested. Duplicate scans were also run at temperatures of 23, 30, 50, and 60°C in simulants of the 4th, 7th, 10th, and 13th wash steps to reveal the effect of temperature on pitting inhibition. All simulant scans were run in duplicate. The sodium nitrite concentration for a given wash step simulant was varied to reveal the minimum concentration necessary to inhibit pitting at that step. Nitrite concentrations ranged from 0.0025 M to 1.20 M. Three levels were usually run at each wash step to establish the minimum level, which was defined as the lowest tested nitrite concentration at which the pair of duplicate specimens was free of pitting corrosion.

The disc specimens were examined microscopically after the scans for the presence of pits. The test solution was deemed corrosive if pits were visible at magnifications of 70X or less. The pits that were observed were elliptical in profile<sup>6</sup> and had rough surfaces. There often was superficial crevice attack of the specimens under the knife-edge gasket, but this attack usually did not interfere with the assessment of pitting. Etch pits from sulfide inclusions exposed to Clarke's solution were often seen on the specimens, but these appeared on both test solution-exposed and unexposed surfaces equally, and thus could be readily distinguished from sludge-induced pitting.

---

(2) Instruments for Research and Industry, 108 Franklin Ave., Cheltenham PA 19102

There was excellent correlation between the presence of large pits visible at magnifications of the order or 10X and the presence of "negative hysteresis" in the scan plots. Negative hysteresis is said to exist in scans whose plots showed a higher current density during the reverse potential scan than in the forward scan. Conversely positive hysteresis occurs when the reverse scan current density was smaller than the forward scan current density. Examples of negative and positive hysteresis are given in Figures 1a and 1b. The hysteresis can be characterized by the difference between forward and reverse scan current densities at a potential just anodic to the active-passive transition seen on the forward scan. In very aggressive solutions the reverse scan current density exceeded the forward scan density by one half to one order of magnitude. In well inhibited solutions the forward scan current density exceeded the reverse by at least one order of magnitude. These observations were used to suggest subsequent levels of nitrite which should be tested to converge on the minimum level necessary to inhibit pitting.

The results of cyclic potentiodynamic polarization scans in sludge simulants at 40°C are shown in Figure 2. Nitrate is the dominant aggressive anion in this system; its concentration, plotted on the ordinate in Figure 2, is used to represent the wash step in test. The presence or absence of pitting in a wash step with a given nitrite concentration, which is plotted on the abscissa, is indicated by the appropriate symbol. "Not pitted" and "Pitted" mean that both specimens in a pair of duplicate scans were in the indicated condition. "Occasionally pitted" indicates that one specimen in a pair was not pitted and that one was pitted. The minimum nitrite concentrations at which pitting was inhibited in duplicate scans are plotted against their respective nitrate concentrations in Figure 3.

Coupon immersion tests were run to verify the minimum effective nitrite levels revealed with the cyclic potentiodynamic polarization scans. Nitrite levels in the sludge simulants ranged from about 0.3 times to about 3 times the minimum levels to ensure that solutions would range from the highly aggressive to the highly protective. Solutions containing insufficient nitrite produced substantial general corrosion on the coupon above the liquid level (Figure 4a), while the surfaces of coupons exposed to a well-inhibited solution were virtually free of any corrosion (Figure 4b).

As with the electrochemical test specimens, the coupons were examined under low power optical microscopy for pitting. Corrosion features were identified as pits when the depths exceeded about 40  $\mu\text{m}$  and when the features were isolated and not clearly associated with a patch of general corrosion. When associated with general corrosion pits were so identified if the depths exceeded the adjacent generally corroded steel by about 80  $\mu\text{m}$ . The identification of a feature as a pit became subjective as these limits were approached. Pitting in isolation is shown in Figure 5. An example of pitting associated with general corrosion is shown in Figure 6. Pitting was observed on coupon surfaces both above and below the liquid level. The deepest pits were seen above liquid level and were about 100  $\mu\text{m}$  (.004 in.) deep.

The results from coupon tests conducted in simulants and in actual sludge supernate at 40°C are plotted in Figure 3 along with the minimum effective nitrite concentrations determined from the cyclic potentiodynamic polarization tests. There is excellent agreement between the results of the two test methods, and excellent agreement between the results obtained with simulants and with actual sludge supernate.

Minimum effective nitrite concentrations to inhibit pitting were also determined at 23, 30, 50, and 60°C using cyclic potentiodynamic polarization scans. Coupon immersion tests were run at 30, 50, and 60°C to verify the inhibitor requirements determined with the scans. In general there was again good agreement between the electrochemical and immersion tests. However the results at 50 and 60°C showed greater scatter than had been seen in the 40°C data. This in part due to the conservative interpretation of the results, whereby the minimum effective nitrite level to inhibit pitting was taken as nitrite concentration which produced inhibition in both test methods. Figure 7 shows a plot of minimum nitrite concentrations for all the temperatures tested.

The pH of the actual sludge solutions in which coupon tests were run was measured periodically throughout the 4-month exposures. A plot of the pH for each solution (undiluted supernate, and the two dilutions with and without added nitrite) is shown in Figure 8. As expected, the pH of solutions decreased as a result of the absorption and reaction of atmospheric carbon dioxide. Steady-state conditions were reached

with the 25X diluted solutions as evidenced by the constant pH approximately one month into the test. The 5X diluted solutions were nearly at steady-state conditions by the end of the test. The concentrated solution had just entered the region of rapid pH change as a result of depletion of >99% of the free OH<sup>-</sup> in solution.

## DISCUSSION

The minimum effective nitrite concentration was related to temperature and nitrate concentration in a multiple regression analysis. The fitting procedure of least squares with equal weights was applied to the logarithms of the nitrate and nitrite concentrations. Logarithms of the concentrations were used in order to provide equal weight to all concentration values. The temperature was not transformed and was expressed in °C. The data for nitrate concentrations above 1.0 M was excluded since plans are to use hydroxide to inhibit at nitrate concentrations greater than 1.0 M. The statistical analysis yielded this equation:

$$[\text{NO}_2^-] = 0.038 [\text{NO}_3^-]^{0.98} 10^{0.041 T} \quad (1)$$

where [NO<sub>2</sub><sup>-</sup>] and [NO<sub>3</sub><sup>-</sup>] are the molar concentrations of the nitrite and nitrate ions, respectively, and T is the temperature in °C. The standard error in the nitrate concentration exponent is 0.099, so that there is no statistical significance in changing that exponent to 1. The standard error in the coefficient for temperature is only 0.0043; therefore the value of 0.041 has not been adjusted. Solutions to Equation (1) are plotted at 23, 30, 40, 50, and 60°C in Figure 7.

Other forms of fitting equation were examined and found to yield poorer fits than did Equation (1) or to yield insignificant improvement. Higher order terms in nitrate concentration and temperature and nitrate-temperature cross-terms did not offer a significantly better fit. A polynomial expression relating [NO<sub>2</sub><sup>-</sup>] to [NO<sub>3</sub><sup>-</sup>] and temperature did not produce as good a fit as Equation (1).

## SUMMARY AND CONCLUSIONS

Pitting corrosion in carbon steel exposed to dilute high-level radioactive waste can be inhibited with additions of sodium nitrite. Cyclic potentiodynamic polarization scans provided a rapid and reliable means of assessing the corrosivity of waste solutions and establishing the minimum effective nitrite concentration to inhibit pitting. The results of these scans were corroborated by coupon immersion tests. The minimum effective nitrite level was empirically related to the nitrate ion concentration and temperature. Partially immersed coupons showed pitting attack above the liquid level after exposure to solutions with insufficient nitrite.

## ACKNOWLEDGEMENTS

The statistical analysis of the data was performed by C. P. Reeve. Helpful discussions with D. F. Bickford are gratefully acknowledged. This paper was prepared in connection with work done under contract No. DE-AC09-80SR18035 with the United States Department of Energy.

## REFERENCES

1. R. S. Ondrejcin, "Chemical Compositions of Supernates Stored in SRP High Level Waste Tanks," Report No. DP-1347, E. I. duPont de Nemours & Co., Savannah River Laboratory, Aiken SC (1984).

2. J. W. Congdon, "Inhibition of Nuclear Waste Solutions Containing Multiple Aggressive Anions," *Materials Performance* vol. 27, 34 (1988).
3. ASTM Standard G5-87, "Standard Reference Method of Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements," *Annual Book of ASTM Standards*, vol. 3.02, ASTM, Philadelphia, PA, 1987.
4. ASTM Standard G61-86, "Standard Test Method of Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys," *Annual Book of ASTM Standards*, vol. 3.02, ASTM, Philadelphia, PA, 1987.
5. ASTM Standard G1-90, "Standard Practice of Preparing, Cleaning, and Evaluating Corrosion Test Specimens," *Annual Book of ASTM Standards*, vol. 3.02, ASTM, Philadelphia, PA, 1990.
6. ASTM Standard G46-76 (Reapproved 1986), "Standard Practice of Examination and Evaluation of Pitting Corrosion," *Annual Book of ASTM Standards*, vol. 3.02, ASTM, Philadelphia, PA, 1990.



**Table 1**  
**Molar Concentrations of Constituents**  
**of Simulated Sludge Solutions at Indicated Wash Step**

Salt	13th	12th	11th	10th	9th	8th	7th
Sodium Carbonate	4.55E-03	7.25E-03	1.12E-02	1.73E-02	2.63E-02	3.93E-02	5.82E-02
Sodium Bicarbonate	2.17E-02	2.78E-02	3.53E-02	4.46E-02	5.64E-02	7.07E-02	8.88E-02
Sodium Oxalate	7.26E-05	1.01E-04	1.40E-04	1.94E-04	2.68E-04	3.72E-04	5.16E-04
Sodium Chromate	2.98E-05	4.13E-05	5.73E-05	7.94E-05	1.10E-04	1.53E-04	2.12E-04
Sodium Molybdate	3.87E-06	5.37E-06	7.44E-06	1.03E-05	1.43E-05	1.98E-05	2.75E-05
Sodium metasilicate	2.95E-05	4.09E-05	5.67E-05	7.86E-05	1.09E-04	1.51E-04	2.10E-04
Sodium Phosphate	8.35E-05	1.16E-04	1.61E-04	2.23E-04	3.09E-04	4.28E-04	5.93E-04
Sodium Chloride*	3.10E-04	4.30E-04	5.96E-04	8.26E-04	1.15E-03	1.59E-03	2.20E-03
Sodium Fluoride	1.55E-04	2.15E-04	2.98E-04	4.13E-04	5.73E-04	7.94E-04	1.10E-03
Sodium Sulfate	1.36E-03	1.89E-03	2.61E-03	3.63E-03	5.03E-03	6.97E-03	9.66E-03
Sodium Nitrate*	2.05E-02	2.84E-02	3.94E-02	5.46E-02	7.58E-02	1.05E-01	1.46E-01
<b>Steady State pH</b>	9.51	9.59	9.66	9.73	9.79	9.85	9.91
Salt	6th	5th	4th	3rd	2nd	1st	0th
Sodium Carbonate	8.65E-02	1.27E-01	1.87E-01	2.72E-01	3.98E-01	5.75E-01	8.31E-01
Sodium Bicarbonate	1.11E-01	1.39E-01	1.73E-01	2.16E-01	2.68E-01	3.32E-01	4.09E-01
Sodium Oxalate	7.15E-04	9.92E-04	1.38E-03	1.91E-03	2.64E-03	3.67E-03	5.08E-03
Sodium Chromate	2.94E-04	4.07E-04	5.64E-04	7.83E-04	1.09E-03	1.50E-03	2.09E-03
Sodium Molybdate	3.81E-05	5.29E-05	7.33E-05	1.02E-04	1.41E-04	1.95E-04	2.71E-04
Sodium metasilicate	2.91E-04	4.03E-04	5.59E-04	7.75E-04	1.07E-03	1.49E-03	2.07E-03
Sodium Phosphate	8.23E-04	1.14E-03	1.58E-03	2.19E-03	3.04E-03	4.22E-03	5.85E-03
Sodium Chloride*	3.05E-03	4.23E-03	5.87E-03	8.14E-03	1.13E-02	1.57E-02	2.17E-02
Sodium Fluoride	1.53E-03	2.12E-03	2.94E-03	4.07E-03	5.64E-03	7.83E-03	1.09E-02
Sodium Sulfate	1.34E-02	1.86E-02	2.58E-02	3.57E-02	4.95E-02	6.87E-02	9.52E-02
Sodium Nitrate*	2.02E-01	2.80E-01	3.88E-01	5.38E-01	7.46E-01	1.03E+00	1.44E+00
<b>Steady State pH</b>	9.96	10.01	10.06	10.12	10.17	10.22	10.28

**Salts Added at Constant Concentration at Every Step**

Sodium Metaaluminate	4.50E-04
Cobalt (II) Nitrate	3.00E-05
Nickel (II) Nitrate	1.50E-03
Iron (III) Nitrate	2.48E-04
Mercury (II) Nitrate	2.50E-04
Copper (II) Nitrate	4.30E-05
Chromium (III) Chloride	3.75E-05
Manganese Dioxide**	5.75E-03

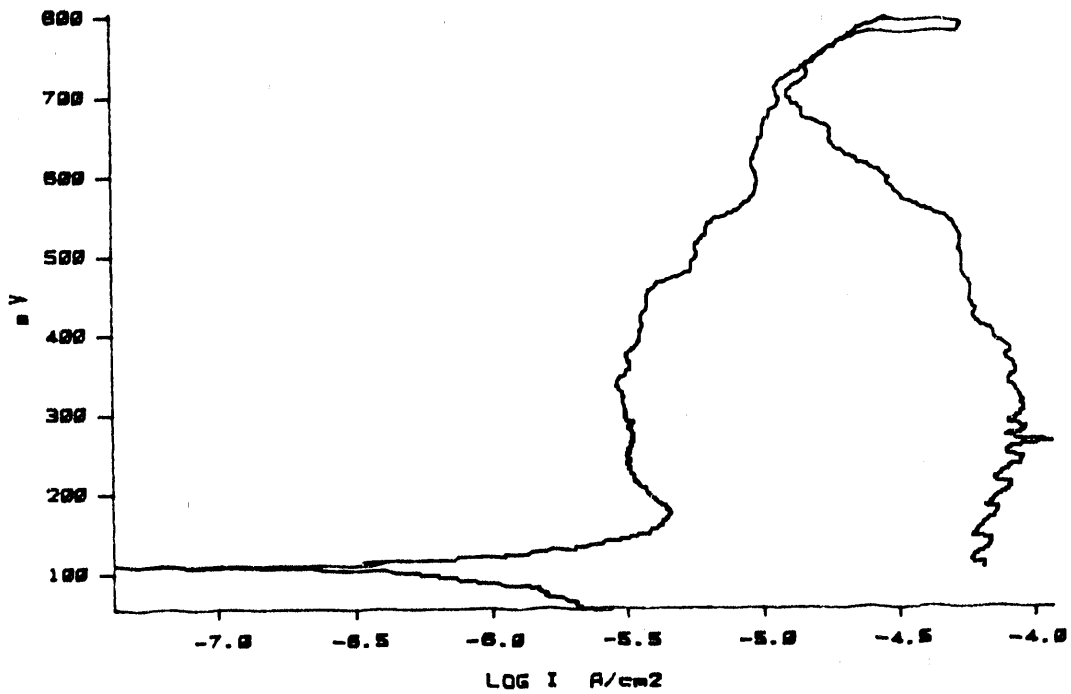
\* Entry represents the total anionic concentration. The weight of this salt used to make the simulant is reduced to account for the contributions from the transition metals.

\*\* Insoluble. One gram added per 2-liter batch of simulant.

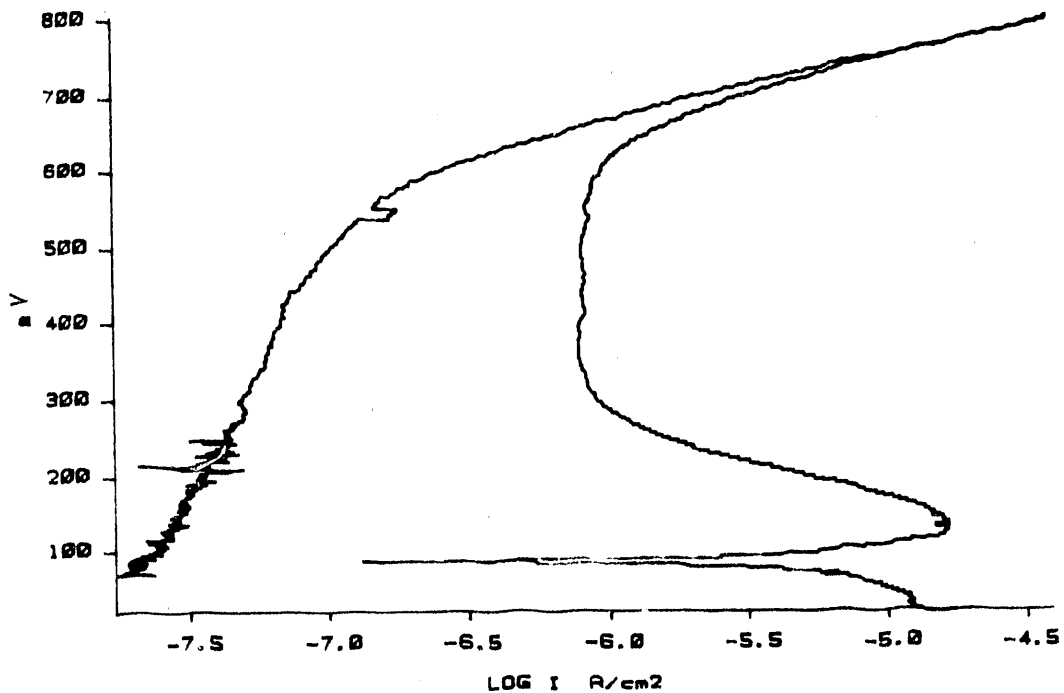
**Table 2**

**Composition of Actual Supernate Test Solution**

<u>Species</u>	<u>Molar Concentration</u>
Nitrate	0.76
Nitrite	0.63
Sulfate	0.071
Fluoride	0.025
Chloride	<0.0056
Free Hydroxide	0.50
Total Hydroxide	0.69
Aluminate	0.10
Total Carbonate	0.039
Adjusted pH	10.11



(a)



(b)

Figure 1. Typical cyclic potentiodynamic polarization scans. (a) Negative hysteresis in a scan recorded in a wash sludge simulant with 0.03 M nitrite. (b) Positive hysteresis in a scan recorded in a 9th wash simulant with 0.075 M nitrite.

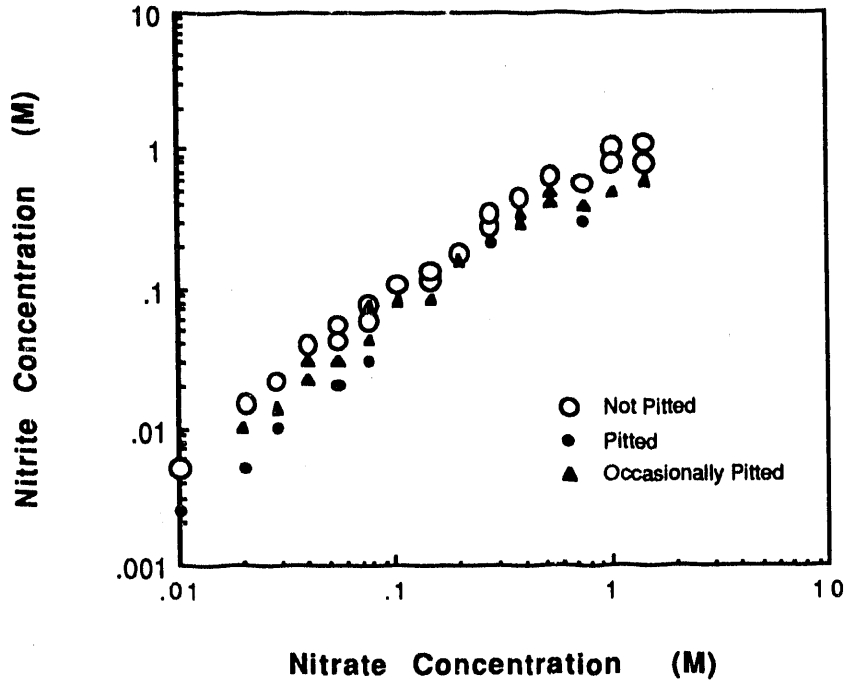


Figure 2. Cyclic potentiodynamic polarization scan results from sludge simulants at 40°C.

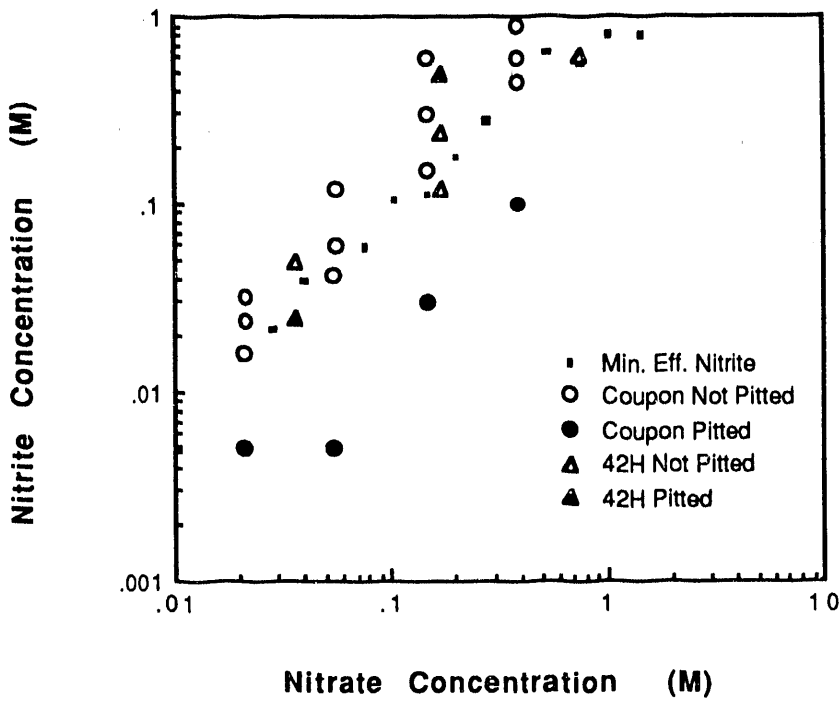
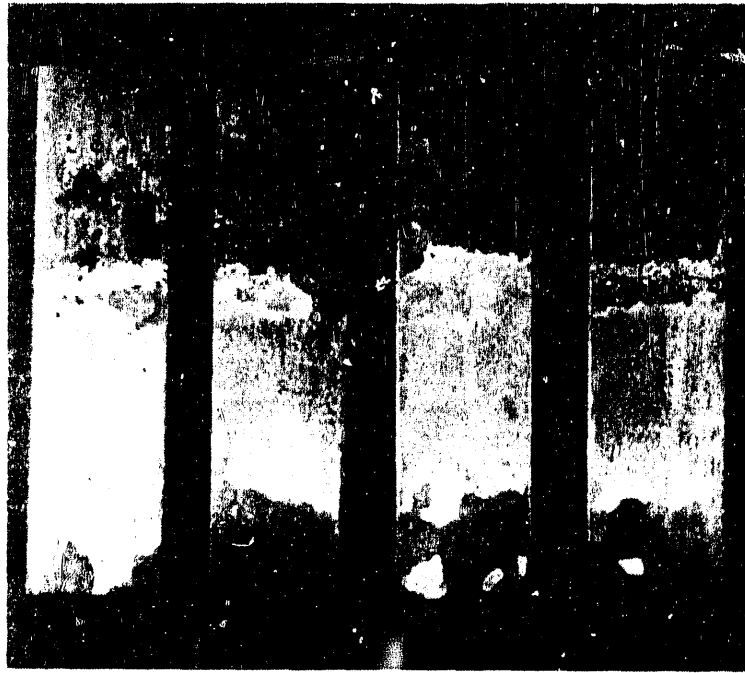


Figure 3. Minimum nitrite concentrations to inhibit pitting in washed sludge slurries at 40°C, with results of coupon immersion tests in simulants ('Coupon' in the legend) and in actual sludge supernate ('42H' in the legend).



(a)



(b)

Figure 4. Typical appearances of ASTM A537 Class 1 coupons exposed for four months to a waste simulant (a) without sufficient inhibitor and (b) with a high level of inhibitor.



Figure 5. Isolated pits above the liquid level on an ASTM A537 Class 1 coupon at 13X magnification.



Figure 6. Pits associated with general corrosion above the liquid level on an ASTM A537 Class 1 coupon at 23 X magnification.

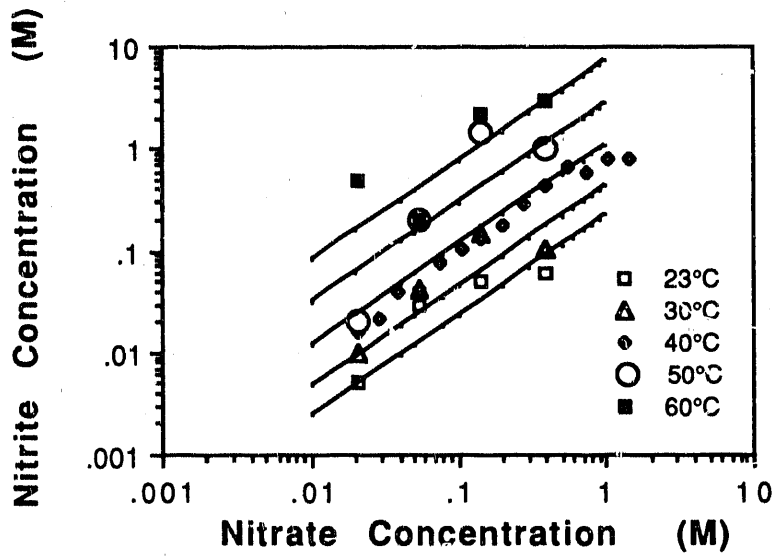


Figure 7. Minimum nitrite concentrations to inhibit pitting at indicated temperatures. The straight lines are solutions to Equation (1).

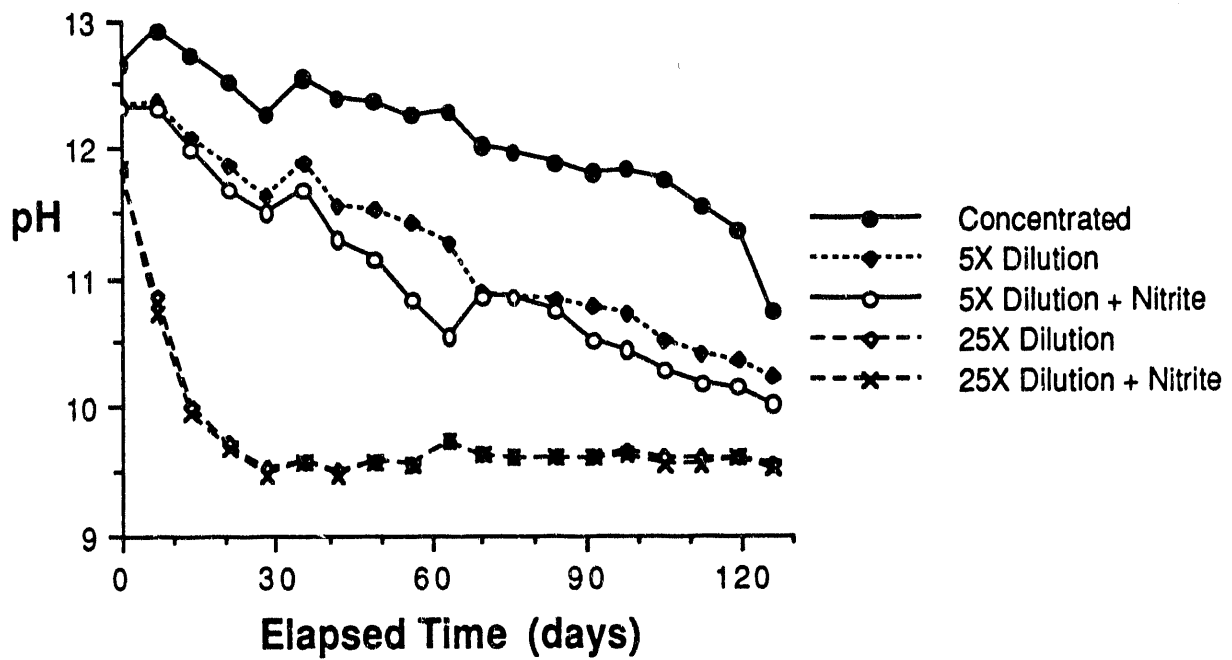


Figure 8. pH change during coupon immersion tests in actual sludge supernate.

**END**

**DATE  
FILMED**

**7 / 22 / 92**



