

## INHIBITING LOCALIZED CORROSION DURING STORAGE OF DILUTE SRP WASTES

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### ABSTRACT

High-level radioactive waste will be incorporated in borosilicate glass in the Defense Waste Processing Facility (DWPF) at the Savannah River Plant (SRP). As part of this process, large volumes of inorganic salt wastes will be decontaminated for disposal as low-level waste. The principal contaminants,  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ , are removed by treatment with sodium tetraphenylborate and sodium titanate. The resulting solids will be slurried with a dilute salt solution and stored in existing carbon steel tanks for several years prior to processing and disposal. Initial tests indicated a tendency for localized corrosion of the tanks. An investigation, using nonradioactive simulants for the expected solution compositions, identified inhibitors which would protect the steel. Changes in solution compositions over time, due to radiolytic effects, were also accounted for by the simulants. Six inhibitors were identified which would protect the steel tanks. The effects these inhibitors would have on later processing steps in the DWPF were then evaluated. After this process, only sodium nitrite remained as an inhibitor that was both effective and compatible with the DWPF. The use of this inhibitor has been demonstrated on a real waste slurry.

### INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Plant (SRP) will immobilize high-level radioactive wastes in a borosilicate glass matrix(1). As part of this process, salt wastes, containing  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  as the primary radionuclides will be decontaminated(2) prior to disposal as a low-level waste in a cement-based wasteform (saltstone)(3). The radionuclides, once separated from the salts, will be incorporated into the glass matrix. This decontamination process will take place outside of, but in support of, the DWPF facility.

The decontamination process, which is to take place in existing carbon steel storage tanks, removes  $^{137}\text{Cs}$  and potassium by precipitation as cesium and potassium tetraphenylborate salts, and removes  $^{90}\text{Sr}$  and Pu by sorption on sodium titanate solids(2). The solids in the resulting slurry, are then concentrated by filtration, with the clear supernate serving as the feed to saltstone. The solids are then washed to reduce the concentration of soluble salts in the slurry. This washed precipitate slurry is then stored in one of the 4900 cubic meter carbon-steel processing tanks.

The washed precipitate slurry will later be transferred to the DWPF where it will undergo acid hydrolysis to decompose the tetraphenylborate (TPB) solids(4). This step must eliminate at least 90% of the aromatic carbon from the stream going to the glass melter. This is required to keep the organics in the feed to the melter low enough to avoid reducing conditions in the melter, which would have an adverse impact on the process.

The average residence time for the washed precipitate slurry in the carbon steel tanks will be two years. With the much lower concentrations of soluble salts in this slurry than in typical wastes which have been stored at SRP, localized corrosion was a concern.

Preliminary tests indicated that an inhibitor would be required to protect the tank from pitting. The inhibitor must protect the tank both at the initial conditions, as well as after changes due to storage in a strong radiation field. This field is the result of concentrating the  $^{137}\text{Cs}$  in the slurry. A further constraint was that the inhibitor must be compatible with both the acid hydrolysis and glass making processes.

The approach used for this study was to investigate the mechanism of pitting and to identify inhibitors independent of their impacts on the rest of the processes. After effective inhibitors had been identified, the effects on the subsequent process and the necessary changes that would be required were evaluated.

### TEST METHODS

The majority of the corrosion testing was performed using cyclic polarization scans or partial immersion coupon tests in simulated waste solutions. In all tests the metal specimen was Type A-537 carbon steel, the same materials used to construct the tanks. The concentrations of the major species in the simulated waste solutions are given in Table I. These represent the nominal composition of the waste. Variations in the concentrations were used to represent extreme cases expected during waste processing, and to simulate changes which occur during storage, such as the radiolytic conversion of nitrate to nitrite. The solutions were filtered to remove TPB and other solids prior to use for the polarization scans.

Coupon tests involved suspending a 0.3 x 1.9 x 7.6 cm carbon steel coupon by a Teflon string so that it was partially immersed in a waste solution in a one liter Teflon bottle. The temperature was maintained at 40°C and the liquid level was kept constant throughout the four month test period. A water-saturated air flow was provided to approximate the volumetric flow per surface area of solution that will be present in the

actual tank. Both polished (600 grit finish) and mill-scale coupons were used. Upon completion of the tests, the coupons were cleaned with Clarke's solution(5) and examined for corrosion.

## CORROSION MECHANISM

Early coupon tests showed more frequent pitting just above the waterline, with only occasional pitting below the waterline. The pits were generally less than 0.01 cm deep, but have been observed as deep as 0.13 cm after 4 months of exposure. A wetted film has been observed up to 15 cm above the waterline. The hypothesis for the corrosion mechanism is that the composition of the wetted film is the same as that of the bulk solution with two exceptions. First is that there is no tetraphenylborate (TPB) film on the metal beneath the wetted film like there is on the metal in contact with the bulk solution. This is based on evidence from reflectance infrared spectroscopy. The second difference is that the pH of the film solution is lower than in the bulk solution due to uptake of carbon dioxide. This depletion of hydroxide results in a solution buffered at a pH of approximately 9.5. The wetted film reaches a steady state condition at this pH rapidly, while the bulk solution requires considerable time to reach the same pH, depending on the ratio of surface area to volume of the solution.

The cyclic polarization scans have demonstrated that TPB forms a weakly passive film on the metal, which in this model will help protect the area beneath the waterline. The scans were run in solutions adjusted to the pH and carbonate concentrations expected in the film, and without any TPB present. A good correlation was noted between the scans under these conditions and coupon tests which used the standard simulant and allowed the wetted film to reach steady-state conditions.

The polarization scans indicate that the nitrate concentration controls the amount of inhibitor required to eliminate the pitting. Relatively large increases in sulfate, chloride, or fluoride concentrations also increase the amount of inhibitor needed, and all four ions are considered aggressive species. Microprobe analyses of the corrosion products indicate the presence of chloride which had been concentrated in the pits. This indicates that the pitting is probably induced by chloride at sulfide inclusions(7).

Upon storage of the washed precipitate slurry in the strong radiation field, the nitrate is reduced to nitrite by radiolysis, yielding a less corrosive solution. However, the relative concentrations of aggressive anions are such that the sulfate concentration soon determines the amount of inhibitor required to eliminate pitting. The data indicate that as long as sufficient inhibitor is added to protect the wetted film above a fresh waste solution, the aged solutions will also be protected.

## EFFECTIVE INHIBITORS

The screening of inhibitors to eliminate pitting of carbon steel was carried out without consideration of the effects of the inhibitors on the processes which the slurry would undergo after storage. Both organic and inorganic materials were tested, based on the material having been reported as an inhibitor for localized attack. Questions of inhibitor stability in the high radiation fields present in the waste slurry were not used to eliminate an inhibitor during the screening period. Polarization scans were used to test the materials at a number of concentrations, often greatly exceeding the reported effective levels.

TABLE I

Simulated Washed Precipitate  
Solution Composition

Species	Concentration (M)
nitrite	0.026
nitrate	0.084
sulfate	0.0059
chloride	0.0012
fluoride	0.0007
sodium	0.23
hydroxide	0.072
carbonate	0.007
aluminate	0.013
TPB solids	0.22

Cyclic polarization scans were used as a more rapid test to determine the tendency for pitting(6). These were performed using 600 grit surface A-537 carbon steel disks in aerated solutions. The test is a controlled potential scan beginning just below the corrosion potential, scanning to slightly beyond the breakdown or pitting potential, and reversing the scan back to the corrosion potential. A plot of the current as a function of voltage is recorded, as shown in Fig. 1. Negative hysteresis indicates that the steel would be expected to pit if left in the solution for a sufficient length of time. The disks were examined under a stereomicroscope for evidence of pitting or crevice attack after the scans.

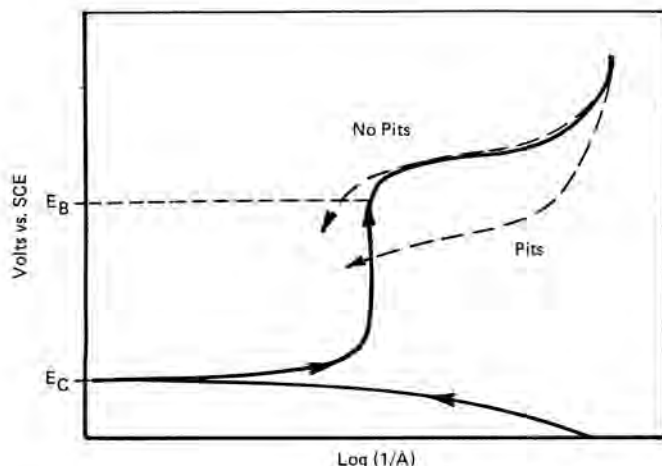


Fig. 1. Cyclic Polarization Scan.  $E_C$  IS the Corrosion Potential and  $E_B$  is the Breakdown Potential.

The six inhibitors which were found to be effective, and the minimum effective level for each are given in Table II. The minimum effective inhibitor concentrations are those determined using polarization scans. For most of these species, the minimum effective level has been verified in more time consuming coupon tests. The actual amount used to protect the storage tank would be greater than this minimum effective level to insure that adequate protection is provided. This will ensure that the solution does not fall below the critical inhibitor level and result in a few, very severe pits.

TABLE II

Effective Corrosion Inhibitors

Inhibitor	Minimum Effective Concentration (M)	Minimum Acceptable Concentration (M)
NaNO <sub>2</sub>	0.065	0.20
Na <sub>2</sub> CO <sub>3</sub>	0.20	0.10
Na <sub>2</sub> MoO <sub>4</sub>	0.01	0.002
Na <sub>2</sub> CrO <sub>4</sub> -H <sub>2</sub> O	0.02	0.01
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> -10H <sub>2</sub> O	0.08	0.08
NH <sub>4</sub> TcO <sub>4</sub>	0.0005	-

A number of inhibitors were determined to be not effective. These include water soluble organic species, commercial proprietary inhibitor formulations, and several inorganic salts. Aluminate and silicate salts were not effective at any concentration in this waste solution. Phosphates reduced the rate of pitting attack, but no concentration could be found at which it completely eliminated the tendency to pit. Sodium hydroxide additions to maintain a higher pH were not effective in coupon tests. The wetted film apparently still drops to a pH low enough to allow pitting to occur.

Only sodium salts of the inhibitors were found to be effective. Potassium salts were undesirable as they would precipitate additional TPB solids, requiring additional volumes of an expensive reagent during salt processing. Alkaline earth salts of the inhibiting anions precipitated carbonates, chromates, and phosphates from the solution and resulted in a more corrosive solution.

COMPATIBILITY WITH DWPF

After the effective inhibitors had been determined, each was evaluated for compatibility with the precipitate hydrolysis process and the glass making processes in the DWPF. The maximum acceptable concentrations for the inhibitors, based on these evaluations, are listed in Table II. The evaluation indicates that only sodium nitrite is acceptable for inhibition of the pitting in this system.

The sodium carbonate is unacceptable to the glass making process as it introduces too much sodium in the waste streams, and would require a frit for the glass making process that would not melt at an adequate rate. Both chromates and molybdates add sufficient amounts of the metal that they would exceed the solubility of the metal in the glass at the expected waste loadings.

Sodium tetraborate, at the minimum effective concentration, does not add more sodium or boron than can be handled by adjustments in the frit. However, it cannot be added above this level without too great a

sodium addition. Furthermore, it is a caustic species, and at the concentrations required, buffers the solution strongly at a pH of approximately 9. The precipitate hydrolysis step requires making the solution slightly acidic with formic acid. The additional formate which this introduces into the glass melt causes very reducing melter conditions, and gives unacceptable glass properties.

The ammonium pertechnetate was an attractive inhibitor, as the technetium would be available if removed from the feed to saltstone. The amounts required for inhibition with an adequate safety margin were in excess of what can be obtained for this use, and it is therefore unacceptable.

The effectiveness of sodium nitrite in eliminating pitting in A-537 steel immersed in these solutions has been demonstrated in coupon tests with all varieties of the simulant used in this study. In addition, an in-tank demonstration of the decontamination process on real waste resulted in a real washed precipitate slurry which has been stored under actual conditions. Nitrite has successfully kept the storage tank from showing any visible localized corrosion.

CONCLUSIONS

TPB precipitate slurry which will be generated during in-tank decontamination of the SRP salt wastes is corrosive to the carbon steel storage tanks. Chloride induced pitting corrosion is expected, with sulfate, nitrate, and fluoride acting as aggressive anions. Six inhibitors were determined to be effective at eliminating the tendency for the carbon steel to pit. Of these, only sodium nitrite was effective and compatible with the other constraints placed on the system by the rest of the DWPF processes. Sodium nitrite has been demonstrated to be effective on a real waste solution that was produced during an in-tank demonstration of the salt decontamination process.

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REFERENCES

1. R. G. Baxter, R. Maher, J. B. Mellon, L. F. Shafranek, and W. R. Stevens, III, "The Defense Waste Processing Facility Project at the Savannah River Plant," Proceedings, Waste Management 84, Tucson, Arizona, March 11-15, 1984, Vol. 1, p. 275 (1984).
2. H. D. Martin, M. A. Schmitz, M. A. Ebra, D. D. Walker, and L. L. Kilpatrick, "In-Tank Precipitation Process for Decontamination of Water Soluble Radioactive Waste," Proceedings, Waste Management 84, Tucson, Arizona, March 11-15, 1984, Vol. 1, p. 291 (1984).
3. C. A. Langton and M. W. Dukes, "Defense Waste Salt Disposal at the Savannah River Plant," Proceedings, Waste Management 84, Tucson, Arizona, March 11-15, 1984, Vol. 1, p. 297 (1984).
4. J. P. Doherty, R. E. Eibling, and J. C. Marek, "Defense Waste Processing Facility Precipitate Hydrolysis Process," Proceedings, Waste Management 86, Tucson, Arizona, March 2-6, 1986, Vol. 2, p. 475 (1986).

5. ASTM Standard: G1-81, "Standard Practices for Preparing, Cleaning, and Evaluating Corrosion Test Specimens," American Society for Testing of Materials, Philadelphia, PA, 1981.
6. ASTM Standard; G61-78, "Standard Practice for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion," American Society for Testing of Materials, Philadelphia, PA, 1981.
7. G. Wranglen, "Pitting and Sulphide Inclusions in Steel," Corrosion Science, 14, 331, 1974.