Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-87-379

Key Words: Waste Tank
Corrosion
Pitting
Nitrite
Inhibitors
Washed Sludge

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April 7, 1987

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INHIBITION OF WASHED SLUDGE WITH SODIUM NITRITE

INTRODUCTION

Washed sludge is an aqueous slurry consisting of a relatively dilute salt solution in equilibrium with several transition metal oxides and hydroxides. This slurry will be produced by in-tank washing of sludge and each batch will be stored for approximately two years in existing carbon steel (ASTM A-537) tanks. Batches of washed sludge will be removed periodically and sent to the DWPF for processing into glass. Washed sludge contains several species (nitrate, sulfate, chloride, and fluoride) which are known to act as pit inducing (aggressive) anions.[1]

Pitting of the waste tanks has been identified as a corrosion concern for washed precipitate[2] which has a composition similar to washed sludge. This prompted concern about the corrosivity of washed sludge. Pitting is most likely to occur in the region just above (0 to 6") the waterline based on the corrosion mechanism described for washed precipitate.[3]

This report describes the results of electrochemical tests used to determine the relationship between the concentration of the aggressive anions in washed sludge and the minimum effective inhibitor concentration. Sodium nitrite was added as the inhibitor because of its compatibility with the DWPF process.[4]

SUMMARY

A minimum of 0.05M nitrite is required to inhibit the washed sludge simulant solution used in this study. When the worst case compositions and safety margins are considered, it is expected that a minimum operating limit of nearly 0.1M nitrite will be specified. The validity of this limit is dependent on the accuracy of the concentrations and solubility splits reported in BDR-90.[5] Sodium nitrite additions to obtain 0.1M nitrite concentrations in washed sludge will necessitate the additional washing of washed precipitate in order to decrease its sodium nitrite inhibitor requirements sufficiently to remain below the sodium limits[4] in the feed to the DWPF.

Nitrate will be the controlling anion in "fresh" washed sludge unless the soluble chloride concentration is about ten times higher than predicted by the solubility splits in BDR-90. Inhibition of "aged" washed sludge will not be a problem unless significant chloride dissolution occurs during storage. It will be very important to monitor the composition of washed sludge during processing and storage.

EXPERIMENTAL

Cyclic potentiodynamic polarization tests were used to determine the pitting behavior of ASTM A-537 carbon steel in various compositions of synthetic washed sludge. The experimental procedure and equipment have been described previously.[6]

The composition of washed sludge simulant was based on data reported in BDR-90. Imbedded in BDR-90 are solubility splits for various species. These splits (Table 1) can have a significant effect on the soluble concentration of several species in washed sludge. For the simulant recipe, it was assumed that nitrate, sulfate, and fluoride were fully soluble. This is 3, 2, and 20 times the respective BDR-90 soluble values, and should adequately represent worst-case for these ions. The BDR-90 solubility value of 2% was used for chloride. All other species were added at the soluble concentrations reported in BDR-90. Several electrochemically important transition metals were added with precipitation allowed to occur in situ.

The various compositions of the test solutions (i.e. nitrite/aggressive anion ratios) were selected by a best guess approach based on the results of previous tests rather than a fixed matrix of compositions. Since the soluble fluoride concentration in washed sludge is very low, the effects of variations in the fluoride concentration were not evaluated in this study, however, it was always present at the maximum expected level. The compositions of the simulant solutions were adjusted by the addition or removal of the appropriate sodium salts.

After each scan was completed, the specimens were cleaned with Clarke's solution[7] and examined with an optical microscope for evidence of pitting and crevice corrosion. Pitting was defined as the presence of corrosion on the exposed portion of the specimen.

RESULTS and DISCUSSION

The effects of the concentration of the primary aggressive anions (nitrate, chloride, and sulfate) in washed sludge on the minimum nitrite concentration required for inhibition are shown in Figures 1, 2, and 3. All species were present at the concentrations specified above, except for the one being varied. The line in each of the plots represents the minimum nitrite concentration required to inhibit pitting as a function of the aggressive anion concentration. A minimum of 0.05M nitrite is required to inhibit the washed sludge simulant used in this study.

All three log-log plots show a region in which the minimum nitrite concentration is independent of the aggressive anion concentration. This behavior has also been reported for washed precipitate[1] and indicates that there are no interaction effects between the aggressive anions.

These results also indicate that nitrate controls the inhibitor requirement in "fresh" washed sludge. If the soluble concentration of chloride increases to >0.002M (which is 10x the concentration predicted in BDR-90), the nitrite requirements will be controlled by the soluble chloride concentration. If chloride concentrations are this high, the required sodium nitrite additions could be sufficiently high to necessitate rewashing of the slurry to lower the total sodium to concentrations acceptable to the DWPF process.[4] At present, there is no information on the dissolution of chloride into washed sludge during storage. Chloride levels in washed sludge will be monitored very closely during processing and storage.

Radiolysis effects during the storage of washed sludge make the slurry less corrosive as nitrate is converted to nitrite. Since there is no tetraphenylborate anion (TPB) in washed sludge, nitrite depletion is not a problem. Nitrite depletion in washed precipitate is apparently related to the volatile decomposition products of TPB.[8]

The results presented in Figure 3 indicate that nearly a ten fold increase in the sulfate concentration is necessary before the nitrite requirements for washed sludge begin to increase. This is important since the concentration of soluble sulfate is difficult to predict for the various stages of sludge washing because of the presence of insoluble calcium sulfate. The sulfate concentration determines the critical nitrite concentration (0.009M) on the nitrite/nitrate plot (Figure 1) based on an extrapolation of the slope of nitrite/sulfate plot to the BDR-90 sulfate concentration (0.00258M). Therefore, the inhibitor requirements for "aged" BDR-90 washed sludge (i.e. nitrate depleted) will be controlled by the sulfate concentration if the sulfate is fully soluble. The data indicates that, if the solubility splits in Table 1 are correct, the inhibitor requirements for the soluble chloride and sulfate in "aged" washed sludge are both ~0.005M nitrite. Hence, an increase in the soluble concentration of either species would increase the inhibitor requirements for the aged slurry. As discussed earlier, the nitrite concentration resulting from the radiolytic conversion of nitrate to nitrite will be more than sufficient to inhibit "aged" washed if the solubility split for chloride is correct in BDR-90.

PROGRAM

Four month coupon tests to demonstrate the effectiveness of nitrite inhibition at selected washed sludge compositions are in progress. Electrochemical tests are in progess to establish the nitrite requirements for partially washed sludge at each stage of processing. Electrochemical tests to establish the nitrite requirements in a worst case composition of washed sludge are planned, if the conservative assumptions in this report do not adequately represent a worst-case solution composition.

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Table 1. Total Concentration and the Percentage Soluble of Selected Species in Washed Sludge

Species	Total Concentration M	% Soluble
NaOH	0.152	20
Na_2CO_3	0.00148	100
$NaNO_2$	0.0158	100
Total NO_3	0.0630	36
Total Cl	0.0245	1.3
NaF	0.00341	4.5
Na_2SO_4	0.00258	53
$Na_2C_2O_4$	0.0000726	100
Na_2CrO_4	0.0000298	100
Na_2MoO_4	0.00000387	100
Na_2SiO_3	0.0000368	80
Na_3PO_4	0.000188	44

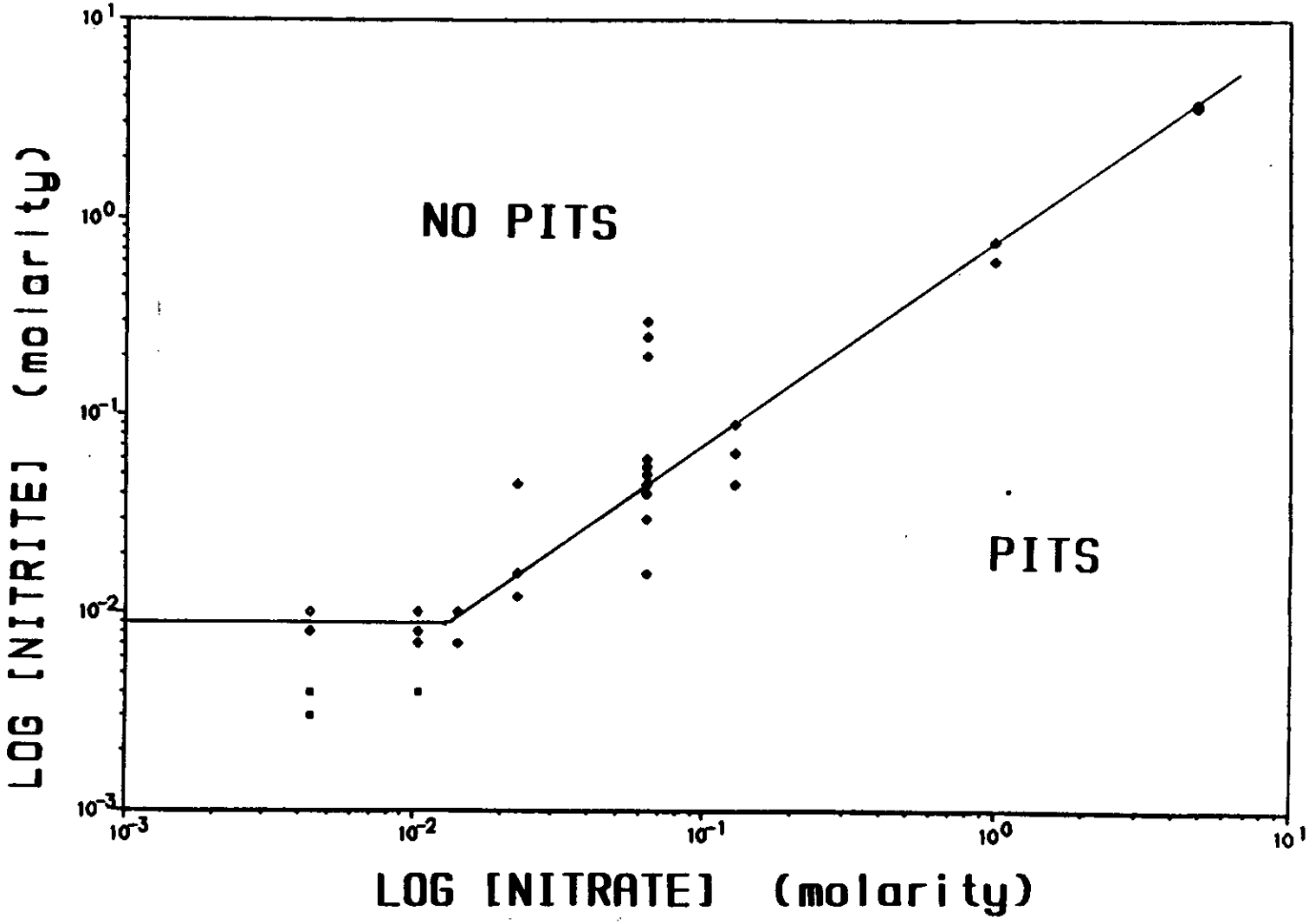

Figure 1: **Effect of Nitrate Concentration on the Minimum Nitrite Concentration Required to Prevent Localized Corrosion of A-537 Carbon Steel in Washed Sludge.**

Key: ◇ No Pits

Occasional Pitting

Pits

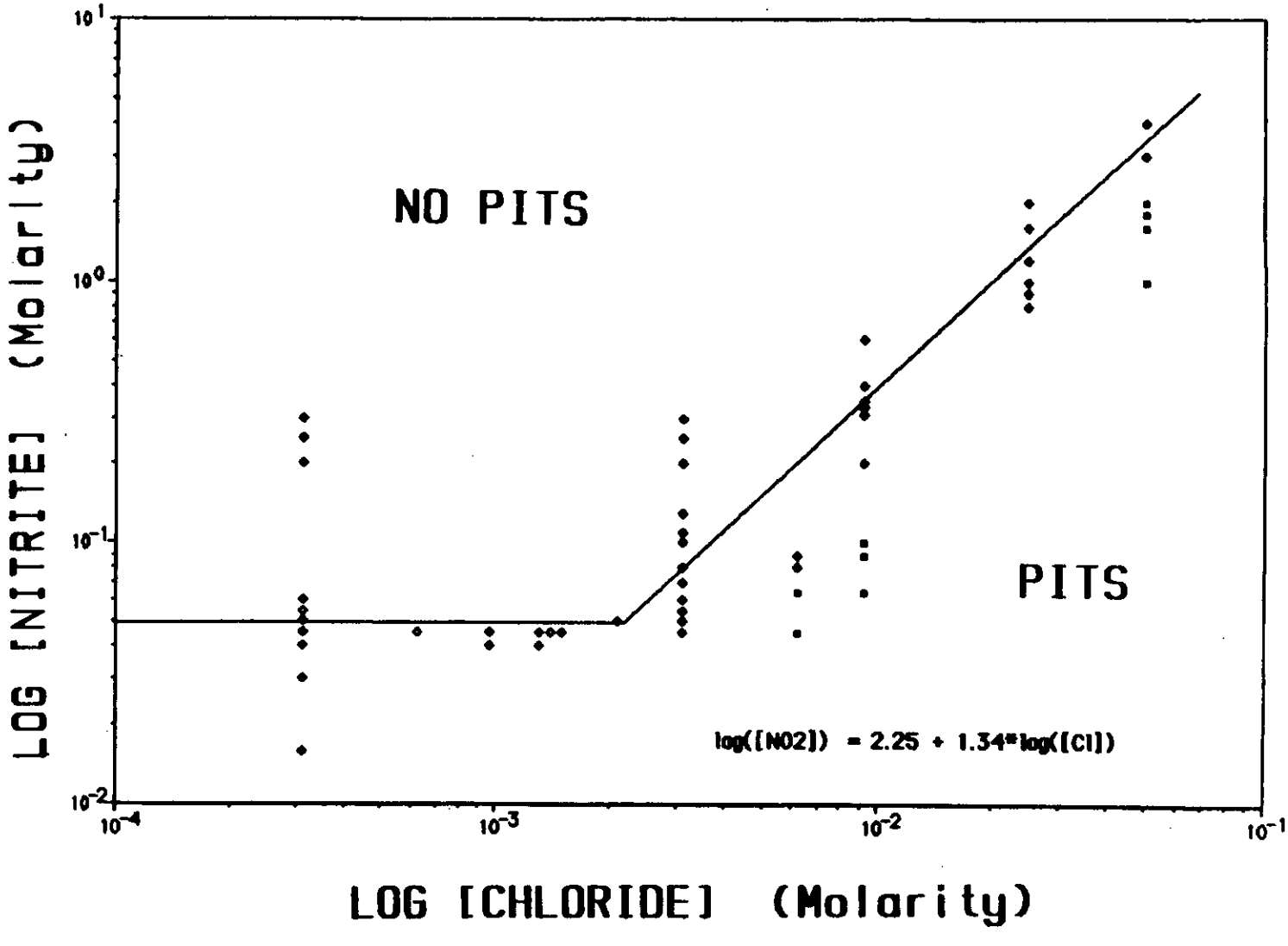

Figure 2: **Effect of Chloride Concentration on the Minimum Nitrite Concentration Required to Prevent Localized Corrosion of A-537 Carbon Steel in Washed Sludge.**

Key: ◇ No Pits
Occasional Pitting
Pits

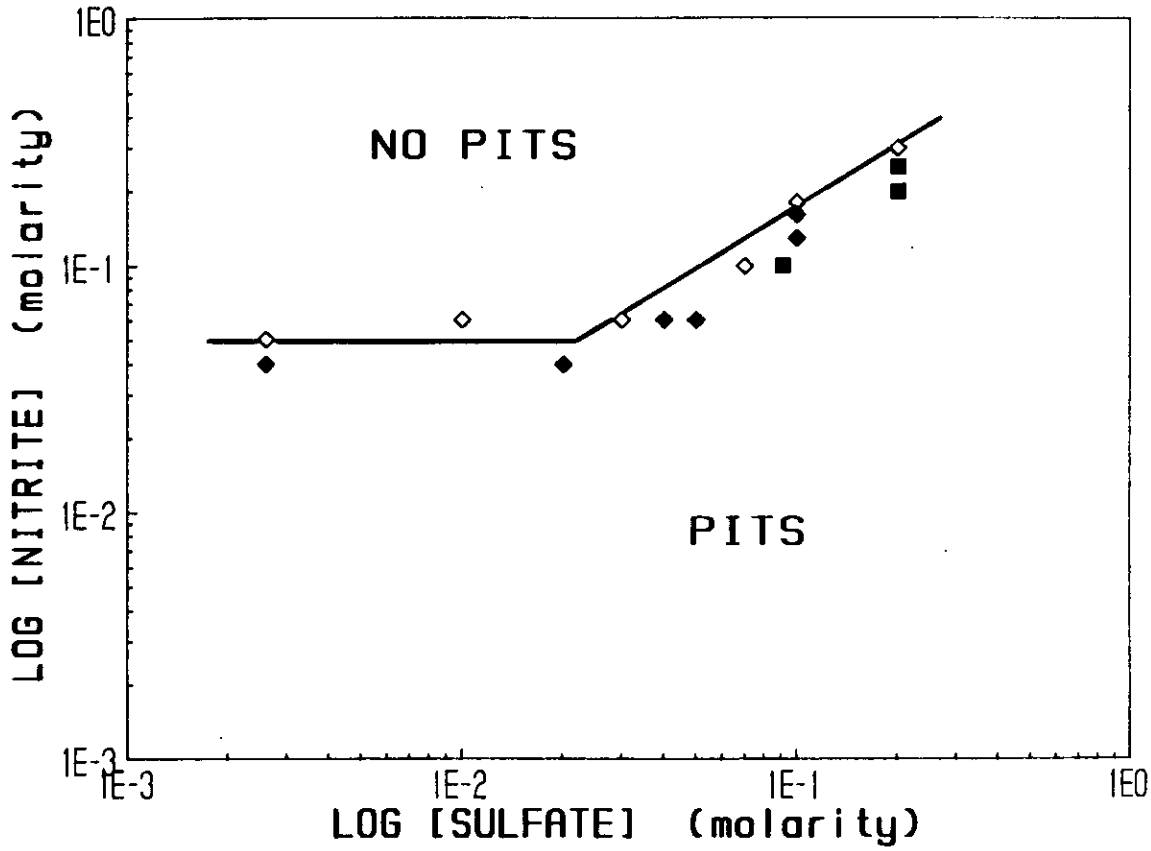

Figure 3: **Effect of Sulfate Concentration on the Minimum Nitrite Concentration Required to Prevent Localized Corrosion of A-537 Carbon Steel in Washed Sludge.**

Key: ◇ No Pits
◆ Occasional Pitting
■ Pits