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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-86-604

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August 8, 1986

MEMORANDUM

TO: M. A. EBRA, 773-A

FROM: J. W. CONGDON, 773-A J. W. Congdon

EFFECT OF NITRITE/NITRATE CONCENTRATIONS ON CORROSIVITY OF WASHED PRECIPITATE

INTRODUCTION

Washed precipitate is an aqueous dilute salt solution containing insoluble tetraphenylborate (TPB) compounds. This slurry will be produced during in-tank processing of high-level radioactive waste for the DWPF and will be stored in existing carbon steel (Type A-537) waste tanks for long periods of time.

Corrosion problems are anticipated[1] and work has been performed to identify the corrosion mechanism[2] and evaluate corrosion inhibitors[3]. All of this previous work was done using simulated solutions based on average compositions of washed precipitate. However, it will be necessary to use a sufficient concentration of inhibitor to prevent corrosion in a worst-case composition of washed precipitate.

The purpose of this study was to determine the relationship of the nitrite and nitrate concentrations and the corrosivity of washed precipitate. This information was required to determine the worst case composition since large variations are expected in the concentrations of nitrite and nitrate.

First of all the initial concentrations of nitrite and nitrate in some batches of washed precipitate may vary from the average (based on BDR-90[4]) composition by as much as ± 30%.[5] Recent work[6] has shown that radiolysis effects will alter the nitrite and nitrate concentrations during storage. Nitrate will be converted to nitrite fairly rapidly. Also, nitrite will be depleted by reaction with organic species in the solution. The rates of these reactions have been measured in laboratory scale experiments and the preliminary results are shown in Figure 1.

Previous investigations[1,3] have demonstrated that nitrite is an effective inhibitor in washed precipitate. High concentrations of nitrate were ineffective as inhibitors and, moreover, tended to accelerate corrosion in coupon tests.[3]

Nitrite adsorbs on the steel and, at concentrations above a critical value, forms a protective iron oxide film which prevents corrosion.[7] This critical inhibitor concentration increases in the presence of chloride and sulfate ions.[8] A similar relationship between nitrite and nitrate was observed in coupon tests with carbon steel in neutral solutions.[9] In solutions containing aggressive anions (chloride, sulfate, or nitrate) a linear relation exists between the logarithm of the maximum concentration of aggressive anions and the logarithm of the nitrite concentration that will permit inhibition.

This report describes the results and implications of electrochemical tests in which the relationship between the corrosivity of washed precipitate and its nitrite and nitrate concentration were determined quantitatively.

Summary

Cyclic polarization scans were performed using A-537 carbon steel in simulated washed precipitate solutions of various nitrite and nitrate concentrations.

The results of this study indicate that nitrate is an aggressive anion in washed precipitate. Furthermore, a quantitative linear log-log relationship between the minimum effective nitrite concentration and the nitrate concentration was established for washed precipitate with other ions at their average (BDR-90)[4] compositions.

Radioloytic conversion of nitrate to nitrite will make washed precipitate non-corrosive in less than six months. Since nitrite depletion is relatively slow, it appears that nitrite could be used to inhibit washed precipitate. The worst case composition will be "fresh" batches with high nitrate and low nitrite concentrations.

Experimental

The equipment and experimental procedures used to produce the cyclic polarization scans were the same as those described in previous work[3]. The compositions of simulant solutions were based on the same recipe[10] used in previous work but with modifications to adjust the nitrite and nitrate concentrations. The nitrite concentration was altered by adjusting the sodium nitrite concentration. Nitrate was added as sodium nitrate. Low nitrate solutions were produced by eliminating sodium nitrate, aluminum nitrate, ferric nitrate, and sodium chloride and substituting sodium aluminate and ferric chloride. With these changes, the concentrations of soluble Cl^-, Fe^{3+}, and Al^{3+} species in solution were maintained.

Results and Discussion

Figure 2 is a compilation of the results of nearly fifty cyclic polarization scans. These results show the relationship between the ratio of log $[NO_2^-]$ to log $[NO_3^-]$ and the corrosivity of washed precipitate.

Nitrite obviously acts as a corrosion inhibitor in washed precipitate and nitrate acts as an aggressive anion. The role of nitrate in corrosion is probably limited to breaking down the protective film on the steel or preventing nitrite from forming a protective film rather than attacking the metal directly. The relative proportions of nitrite and nitrate adsorbed on the steel determine whether or not pitting can take place.

At nitrate concentrations < 0.027 M the critical nitrite concentration is 0.026 M and is independent of the nitrate concentration. This critical nitrite concentration can be attributed to the presence of other aggressive anions in washed precipitate. Chloride has been shown to be an aggressive anion in washed precipitate[2]. Work is in progress to determine if fluoride and sulfate are also aggressive anions in washed precipitate.

At nitrate concentrations greater than 0.027 M, the log of the critical nitrite concentration increases linearly with the log of the nitrate concentration. A critical ratio (C), defined as

$$C = a_{NO_2^-}/a_{NO_3^-}$$

where $a_{NO_2^-}$ = amount of nitrite adsorbed/unit area and $a_{NO_3^-}$ = amount of nitrate adsorbed/unit area, is required to form a passive film. Work is underway to better characterize these surface films.[11]

Matsuda and Uhlig[8] have offered an explanation for the linear log/log plot. These authors use the Freundlich adsorption isotherm to give a quantitative expression to describe competitive adsorption on the oxide film. Competition is postulated as being between aggressive anions that destroy the film and oxidizing anions that repair it. Other authors[9] have provided evidence to suggest that the primary function of the inhibitors anion is to keep the uptake of aggressive anions below a certain critical level. In both cases the following relationship is derived

$$\log [NO_2^-] = a + b \log [NO_3^-]$$

where: $[NO_2^-]$ = molarity of nitrite in solution

$[NO_3^-]$ = molarity of nitrate in solution

a and b = empirical constants

This relationship describes the critical ratio of nitrite to nitrate in solution which is required to achieve the critical ratio (C) of nitrite to nitrate adsorbed on the steel.

The empirical valves of a and b can be derived from the plot shown in Figure 2. Approximate values of a = -0.528 and b = 0.678 result in the empirical relation given by

$$\log [NO_2^-] = {}^-0.528 + 0.678 \log [NO_3^-]$$

for $[NO_3^-] > 0.027$ M.

These empirical parameters are for washed precipitate (BDR-90 composition) at 40°C. Deviations from these conditions may change the values of a and b.

The cross-hatches area in Figure 3 shows the range of nitrite and nitrate concentrations projected during the first three years of operation. The composition changes are due to radiolysis effects and tank farm batch additions.[6] For these tests and calculations it was assumed that the starting composition and batch additions were at the BDR-90[4] composition.

These results indicate that uninhibited BDR-90 washed precipitate will become non-corrosive after <6 months of storage. After three years of aging and batch additions, the slurry is still not corrosive despite some nitrite depletion. Gamma cell tests are not available to predict the composition after three years. The expected range of compositions is actually much larger than the cross-hatched area in Figure 3 since a ± 30% variation in the nitrite and nitrate compositions is predicted for batch additions.

Based on the corrosion data and the projected changes in composition due to radiolysis, washed precipitate will be most difficult to inhibit when it is first introduced into the tank. Furthermore, the worst case compositions will be batches with high nitrate and low nitrite concentrations. The maximum variation in the initial concentrations of these ions is expected to be ± 30% of their BDR-90 concentrations.

These results indicate that washed precipitate can be inhibited solely with nitrite additions. The nitrite depletion rates, as predicted by the gamma cell tests, are fairly low. It should be no problem to maintain a sufficient nitrite concentration to inhibit washed precipitate.

Also, it may be desirable to require higher nitrite concentrations during the first year of operation. After approximately one year the nitrate concentration decreases such that lower nitrite levels will inhibit the slurry.

PROGRAM

The recommended inhibitor requirements for storage of washed precipitate in carbon steel tanks will be based on tests using the worst-case composition. This worst-case recipe will include the maximum nitrate and minimum nitrite concentration anticipated for "fresh" washed precipitate.

The relationship between the critical inhibitor concentration and the concentration of other potentially aggressive anions (Cl^-, F^-, and $SO_4^=$) will also be investigated.

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JWC:khs

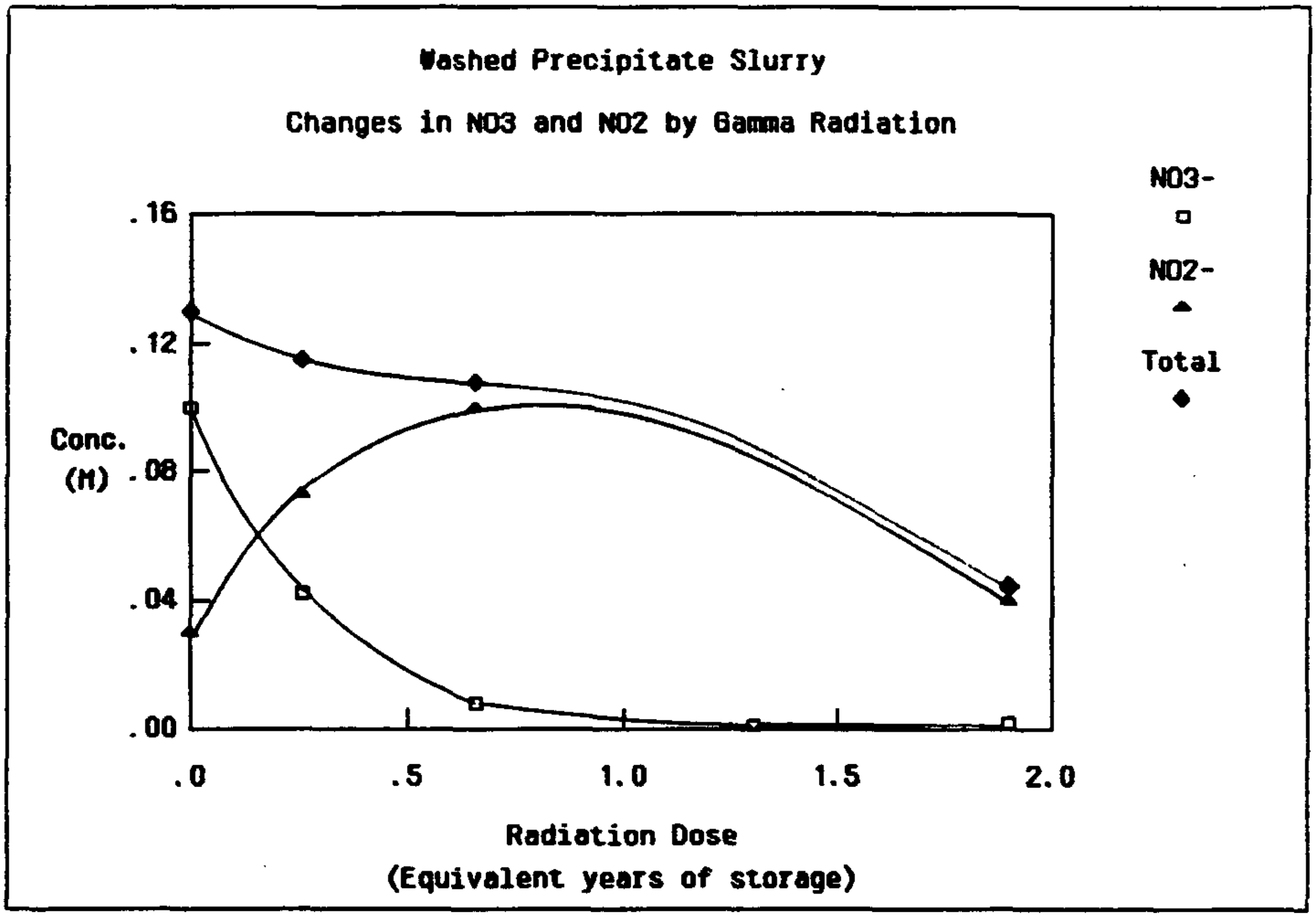

FIGURE 1. GAMMA CELL TESTS SHOW THE RADIOLYSIS EFFECTS ON THE NITRITE AND NITRATE CONCENTRATION OF WASHED PRECIPITATE DURING STORAGE. (FROM REFERENCE 6)

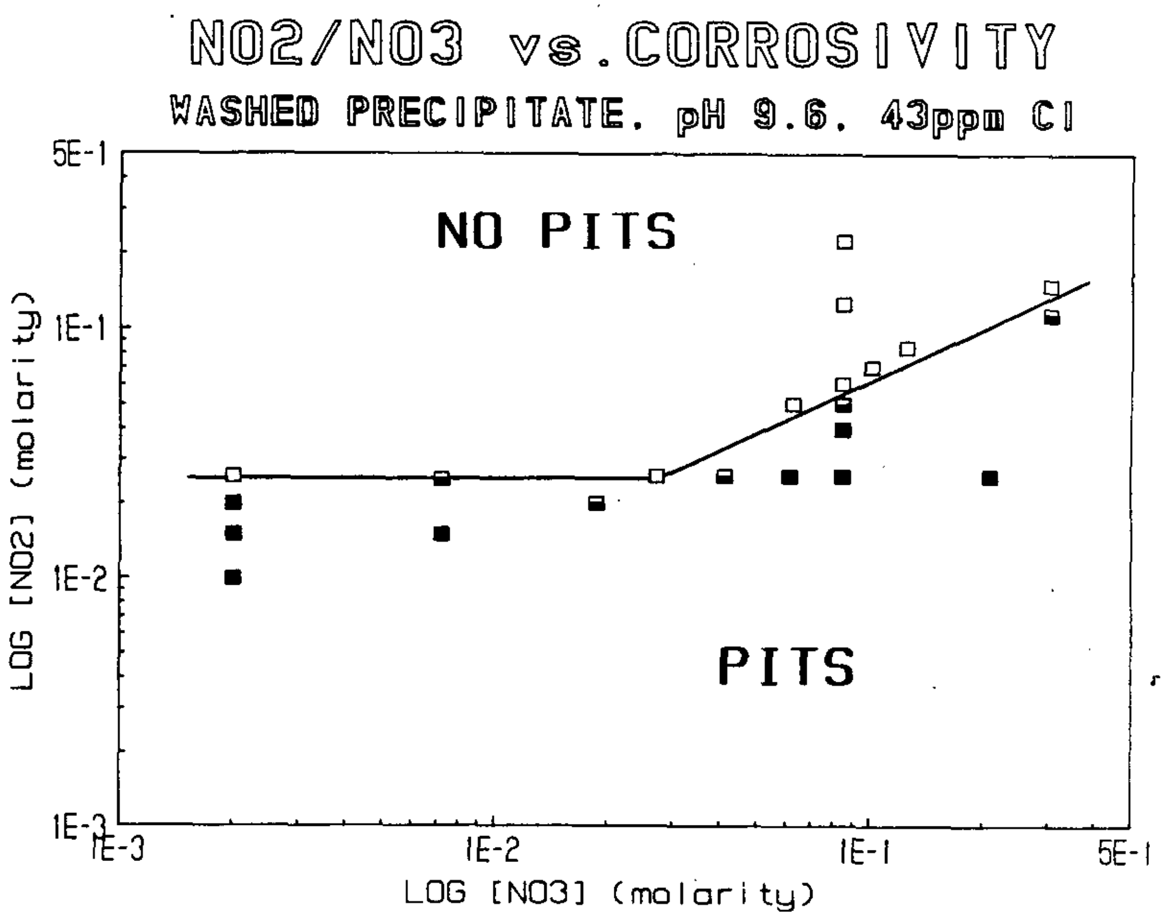

FIGURE 2: ELECTROCHEMICAL TEST RESULTS SHOW THE RELATIONSHIP BETWEEN THE NO_2^-/NO_3^- RATIO AND THE CORROSIVITY OF WASHED PRECIPITATE.

<u>KEY</u>

☐ NO PITS

⊟ *OCCASIONAL PITTING (ON 1 OF 2 OR 1 OF 3 TESTS)*

■ PITS

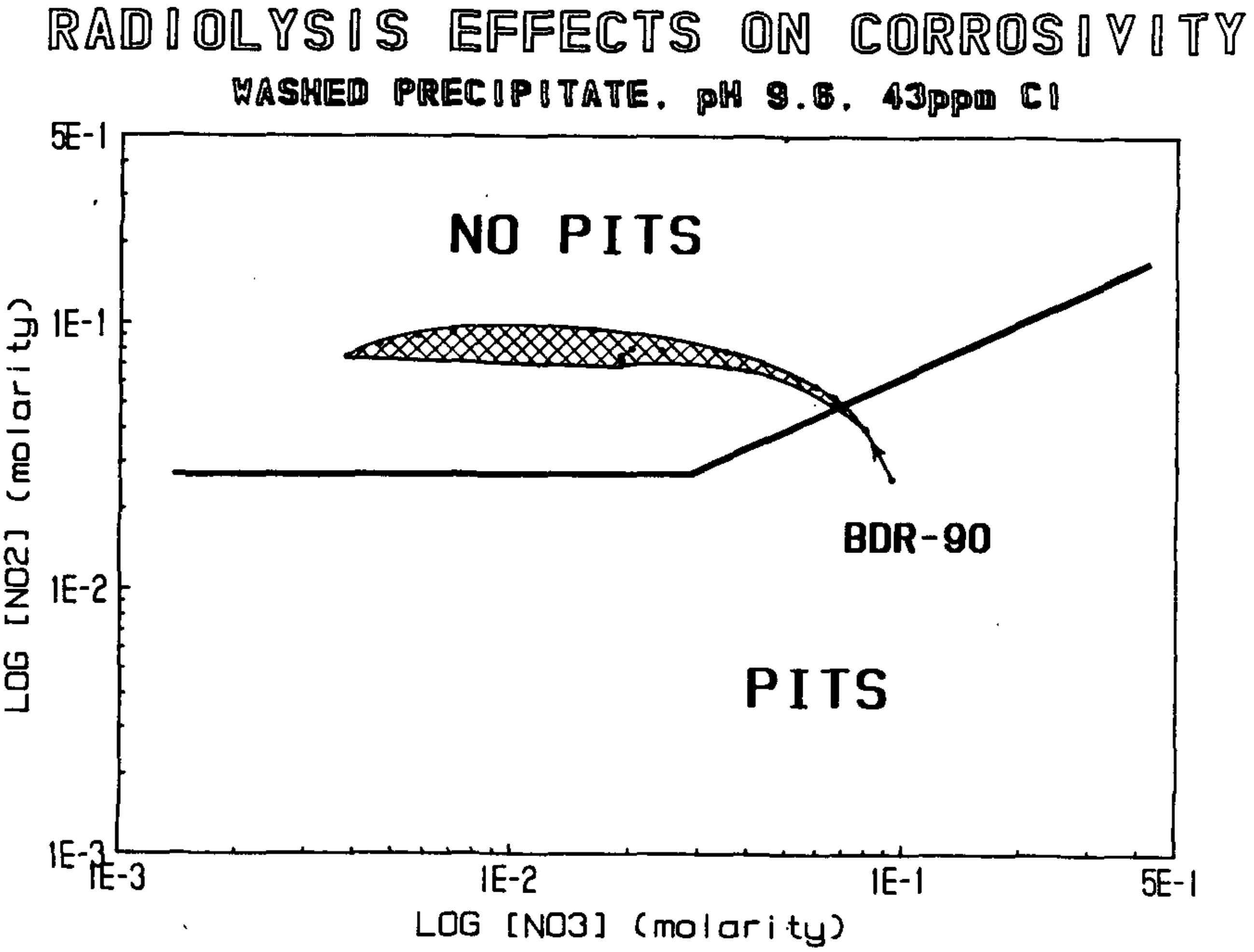

FIGURE 3: CROSS-HATCHED AREA SHOWS RANGE OF NITRITE AND NITRATE CONCENTRATIONS PROJECTED DURING THE FIRST THREE YEARS OF OPERATION. COMPOSITION CHANGES ARE DUE TO RADIOLYSIS EFFECTS AND TANK FARM BATCH ADDITIONS. (FROM REFERENCE 6)