WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER
Inter-Office Memorandum

WSRC-TR-93-437

Key Words: Corrosion, Pitting, Carbon Steel, Nitrite, Extended Sludge Processing. Permanent Retention

August 26, 1993

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TECHNICAL BASIS FOR WASH WATER INHIBITOR LEVELS (U)

Summary

A review was conducted of waste tank operating experience, relevant SRTC laboratory testing, and corrosion literature data to determine safe concentrations of corrosion inhibitors for ITP and ESP wash water. Based on this review, it is concluded that hydroxide alone at pH 12 is not sufficient to inhibit the wash water and prevent pitting. Nitrite is required for adequate protection. Wash water must contain at least 0.01 M (0.17 g/L or 170 ppm) hydroxide and 0.011 M (0.5 g/L or 500 ppm) nitrite to ensure that the tank wall and cooling coils will be protected from pitting corrosion. Operational Safety Requirements for ITP and future Process Requirements for ESP should incorporate these minimum hydroxide and nitrite concentrations.

Introduction

Washing of In-Tank Precipitation (ITP) and Extended Sludge Processing (ESP) slurries is necessary to reduce their soluble salt concentrations. In the system of carbon steel tanks exposed to the dilute salt solutions produced by washing, there is the potential for the loss of service of the tank through pitting corrosion. Nitrite and hydroxide limits are specified in the Operational Safety Requirements (OSRs)and Waste Tank Farm Technical Standard for the contents of ITP and ESP tanks, respectively, to ensure the prevention of pitting. In the early stages of washing, dilute waste solutions which contain the specified inhibitor levels may be used as the washing liquid. At later stages, however, large volumes of raw water may be added to Tank 48 and the ESP tanks. This "wash water" is presently specified in the OSRs and ESP Technical Standard only to contain hydroxide at a pH ≥ 7.

Wash water is assumed to lie unmixed on top of the tank contents for some period of time, due in part to differences in specific gravity and the absence of mechanical mixing. It is also assumed that aggressive anions will diffuse into the wash water from the bulk tank solution, and that inhibiting anions will not diffuse at sufficient concentrations to prevent pitting. Under these assumptions, wash water must contain sufficient inhibitors to protect the tank. A review of the available data indicated that wash water containing only hydroxide at pH 12 may induce pitting in waste tank steel (walls and cooling coils) beneath the wet film that extends above the liquid level.[1] This conclusion is based on (1) the literature data that pure water of pH < 10 may induce pitting in carbon steel, (2) the experience of cooling coil failures in Type I and Type II waste tanks and the experiments to reproduce the corrosion rates indicated by those failures, and (3) carbon steel corrosion experiments in dilute waste slurries. Including nitrite in the pH-12 wash water inhibits pitting.

This memorandum provides the technical basis for the requirement that the large wash water additions be inhibited with 500 ppm nitrite along with 0.01 M hydroxide. A waste tank corrosion issue related to wash water additions is that of inhibition of small water additions, such as water used to flush transfer lines. These are analyzed differently from wash water additions, because the small water additions can attain, in a short enough time, the necessary inhibitor concentrations by diffusion from the bulk waste. The maximum allowable volumes of small water additions for these conditions are calculated in another memorandum.[2]

Discussion

Pitting Corrosion in Carbon Steel

Pitting in carbon steel exposed to ITP and ESP slurries is a random process initiated by nitrate and sulfate ions under conditions of relatively low hydroxide concentration (i.e., low pH). The low hydroxide concentrations arise from washing and from reaction with absorbed atmospheric carbon dioxide. This reaction proceeds until a low, steady-state hydroxide concentration is reached.[1] Table 1 shows some initial hydroxide concentrations and pHs, and the resulting steady-state pHs.[3] During the washing steps of ITP and ESP slurries the bulk hydroxide concentration ranges from 1.0 M down to about 0.015 M. The hydroxide depletion reaction reaches steady state in a period of hours in the wet film, and pitting is therefore of first concern in the steel under the film. For ITP and ESP steps of a few weeks' or months' duration, the focus of corrosion protection is the steel at the liquid-air interface. A full tank of washed ITP or ESP slurry will reach steady state in about two years, after which all wetted tank steel becomes vulnerable.

Corrosive species which are capable of inducing pitting in carbon steel include chloride and fluoride as well as nitrate and sulfate. These anions contribute to the break down of the protective passive film on the steel in high alkaline solutions. However, carbon steel pitting may also occur without an aggressive species present, in water whose pH is reduced below 10.[4] The pitting increases in severity qualitatively with decreasing pH. Pitting is absent if the pH is > 10. Inhibition by hydroxide concentrations that yield a pH > 10 is consistent with SRS experience. Table 1 indicates that inhibition in alkaline water which can absorb CO_2 requires that the bulk solution pH be >13.8 to maintain a steady-state pH > 10. In SRS waste tanks, pitting has never been detected while the bulk pH has remained high (> 13.8). This indicates that the corrosion inhibition observed in water with pH ≥ 10 extends to water which contains corrosive anions.

Pitting in Waste Tank Cooling Coils

SRS waste tank operating experience includes pitting corrosion during sludge removal operations in the 1960s.[5] Carbon steel cooling coils (of about 0.15-in. wall thickness) in Type 1 and II tanks began failing rapidly after the start of sludge removal, which used pressurized water to suspend the sludge. Through-wall pitting was confirmed as the mode of failure by metallographic analysis of one coil. The pitting probably resulted from dilution of the hydroxide and nitrite concentrations, caused by the pressurized water. The earliest failure occurred at one month following the start of sludge removal, indicating a very high corrosion rate, approximately 0.15 in./month (1.8 in./year).

Laboratory experiments were conducted to reproduce this corrosion rate. Steel coupons were immersed in 100-, 1,000-, and 10,000-fold dilutions of a simulant of Tank 11H supernate. The 100-fold dilution contained 400 ppm nitrite and had a pH of 11.9; the 1,000-fold dilution, 40 ppm nitrite and pH 10.9; and the 10,000-fold dilution, 4 ppm nitrite and pH 9.9. The coupons had pitting rates <0.003 in./month, which was too low to account for the perforation of the cooling coils.

A general corrosion rate of 0.05 in./ month, however, was measured in a 10,000-fold dilute solution which contained sulfate at 0.03 M. Sulfate may have increased during waste removal operations by dissolution of calcium sulfate from the sludge. The general corrosion rate of 0.05 in./month could account for the cooling coil failures if the corrosion were localized as for pitting. Pitting was not seen on coupons immersed in a 100-fold dilute solution (pH 11.9 and 0.40 g/L nitrite) which contained 0.03 M sulfate. Thus, a highly diluted waste supernate was shown to be very corrosive if it contained an increased concentration of sulfate, and the combination of pH 11.9 and 0.40 g/L nitrite prevented pitting induced by 0.03 M sulfate. These results suggest that pH 12 wash water without added nitrite, which may be viewed as a highly dilute salt solution, could be corrosive if an aggressive anion were present.

ESP Pitting Experiments in Dilute Solutions

Extensive electrochemical and coupon immersion tests have been conducted to establish minimum effective nitrite levels to prevent pitting attack in waste tank steel exposed to ESP slurries of various concentration. The electrochemical tests (cyclic potentiodynamic polarization scans) were performed in solutions whose pH values were in the range of 9.35 to 10.3. Nitrite concentration limits required to inhibit were determined from these tests.[6,7] The nitrite limits were incorporated into the Operational Safety Requirements[8] and Waste Tank Farm Technical Standard,[9] which specify minimum hydroxide and nitrite inhibitor levels for the contents of ITP and ESP tanks, respectively.

Tests with a 100-fold dilution of the expected feed to ESP are most relevant to wash water inhibitor levels. The principal aggressive anion in this solution (as in all ESP solutions) was nitrate, at 0.01 M concentration. The pH, representing steady state in the waste tank, was 9.35. This pH is equivalent to an initial, bulk pH of 12.1 (Table 1). The test results showed that pitting was inhibited by 0.005 M (0.23 g/L or 230 ppm) nitrite. Therefore, wash water at a pH of 12 and a concentration of 230 ppm nitrite provides adequate corrosion protection in solutions which contain up to 0.01 M nitrate.

Conclusions

The inhibitor requirements were analyzed for wash water to be added to ITP and ESP tanks. Several conservative assumptions were made for this analysis. First, the wash water forms an unmixed layer on top of the tank contents. Second, aggressive anions diffuse into the wash water from the bulk tank solutions. Third, inhibiting anions do not diffuse into the wash water at levels sufficient for inhibition.

The literature and experimental data showed: (1) Carbon steel may experience pitting when exposed to water with a pH < 10. This pH range is attainable in a short time in a wet film on the steel surfaces immediately above the wash water-air interface through absorption of atmospheric carbon dioxide if the wash water pH is not $>$ about 13.8. Pitting in this case is not dependent on the presence of an aggressive anion. (2) The failures of cooling coils during sludge removal and the experiments to produce the pitting rates of some cooling coils showed that dilute aqueous solutions with pH < 10 and a relatively high aggressive anion concentration greatly accelerated pitting. Inhibition was achieved if solution pH was 11.9 and the nitrite concentration was 400 ppm. (3) Finally, electrochemical tests demonstrated inhibition in a very dilute ESP test solution whose equivalent bulk pH was about 12.1 and whose nitrite concentration was 230 ppm.

Based on these data, wash water will be safely inhibited if it contains 0.50 g/L (500 ppm) nitrite and has a pH$\geq$12 (hydroxide concentration ≥ 0.01 M). Operational Safety Requirements for ITP and ESP should be changed to reflect these minimum hydroxide and nitrite concentrations.

References

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9. Technical Standard Waste Tank Farms, DPSTS-241-5.03, Rev. 1, December 19, 1990.

Table 1
Results of Carbon Dioxide Absorption

Initial [OH^-] M	Initial pH	Steady-State pH
1.0	13.8	10.2
0.1	12.9	9.8
0.015	12.1	9.3
0.01	12.0	9.2
0.001	11.0	8.3
0.0001	10.0	7.3
0.00001	9.0	6.3

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