

Technical Basis for a Minimum Hydroxide Concentration in Tanks Containing Dilute Waste (U)

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**TECHNICAL BASIS FOR A MINIMUM HYDROXIDE
CONCENTRATION IN TANKS CONTAINING DILUTE WASTE (U)**

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TECHNICAL BASIS FOR A MINIMUM HYDROXIDE CONCENTRATION IN TANKS CONTAINING DILUTE WASTE (U)

SUMMARY

Laboratory tests were performed to address the protection of waste tank steel from corrosion in situations of elevated temperatures up to 75 °C (hot spots) in the sludge layer of Extended Sludge Processing (ESP) tanks. Coupon immersion tests were conducted at 75 °C in two ESP simulants at four hydroxide (or pH) levels. The nitrite concentrations of the simulants were calculated from the ESP technical standards based on a temperature of 40 °C. The results showed that a hydroxide concentration of at least 0.01 M prevented significant corrosion of the steel at the elevated temperature. This conclusion provides the technical basis for the revised minimum hydroxide concentration of 0.01 M in the draft WSRC 241-82H Control Room Process Requirements.

INTRODUCTION

Pitting corrosion in dilute high-level radioactive waste solutions can be prevented by maintaining sufficient concentrations of hydroxide and nitrite. The required nitrite concentration to prevent pitting in Extended Sludge Processing (ESP) tanks is given in the ESP technical standards, in which the nitrite level is a function of the nitrate concentration and the temperature of the waste, for temperatures between 20 °C and 60 °C.[1] The dependence on temperature is strong, with a temperature increase from 40 °C to 60 °C yielding a factor of 6.6 increase in the required nitrite concentration. Nitrite is added to waste tanks as a concentrated sodium nitrite solution. In addition to the increased expense of supplying the inhibitor, higher nitrite also means higher sodium levels, which require further washing to meet alkali limits in the feed to the Defense Waste Processing Facility. High temperatures are, therefore, undesirable because they demand high nitrite concentrations.

The protective nitrite limit is based on the supernate temperature because carbon steel is first vulnerable to pitting at the supernate-air interface. Atmospheric carbon dioxide quickly dissolves into the liquid film at the interface and depletes hydroxide by reacting with it to form bicarbonate and carbonate.[2] Carbon steel becomes susceptible to pitting at pHs below the 10-to-12 range, depending on aggressive ion content. The steady-state pH in the film falls to between 9.5 and 10.4, depending on the bulk waste composition and partial pressure of carbon dioxide in the atmosphere. This susceptibility is offset by added nitrite, which acts with the remaining hydroxide to prevent the breakdown of the passive oxide layer on the steel. Hydroxide depletion is fast in the liquid film at the interface, with steady state being achieved in a few hours. However, the time to reach steady state throughout the bulk waste volume is of the order of years. Therefore, the steel that is initially susceptible to pitting lies under the interfacial film.

Operating experience has shown that a dilute high-level waste tank may have non-uniform temperatures. There have been instances when the temperature in the sludge layer of ESP tanks exceeds the supernate temperature. The higher temperature can

arise from the operation of slurry pumps and the distribution of heat-generating radionuclides in the sludge layer. With the nitrite inhibitor level set by the lower supernate temperature, the higher temperature readings raised the question of the susceptibility of nearby steel to corrosive attack. Specifically in early June, 1994, a hot spot or region of high temperature was observed near the H slurry pump in tank 42H. A thermocouple attached to the outside of the tank bottom near this location registered 57 °C; at the same time the supernate temperatures in tank 42H were of the order of 35 °C.[3] After the slurry pumps were shut down, the temperature at the hot spot decreased to < 50 °C. Throughout this time, the nitrite concentration exceeded the minimum required by the technical standards, which is based on the supernate temperature. The nitrite level was sufficient to prevent pitting at supernate temperatures up to 49°C for the existing tank nitrate concentration.

The Waste Tank Corrosion Working Group determined that the hot spot did not render the tank bottom vulnerable to corrosion because the chemical conditions in the sludge are less aggressive than those at the liquid-vapor interface. The hydroxide concentration in tank 42H was 0.02 M (pH of ~ 12.3) at the time of the hot spot occurrence. The bulk hydroxide concentration is much greater than the hydroxide level in the aqueous film at the liquid-vapor interface, which is the level that drives the nitrite requirement. The concentration of nitrate is likely to be lower in the sludge, because more nitrate is destroyed by radiolysis in the radionuclide-rich sludge than in the supernate.[4] Thus, the higher hydroxide and lower nitrate in the sludge hot spot should offset the effects of higher temperature and render the steel immune to corrosion.

The present work was undertaken to confirm experimentally the immunity of carbon steel to corrosion under conditions similar to those of the tank 42H hot spot: a temperature well above the supernate temperature and a free hydroxide concentration of at least 0.01 M. Specifically, experimental verification was sought for the protection of carbon steel at 75 °C with ESP simulants containing 0.01 M hydroxide and nitrite at a concentration appropriate for 40 °C. The 40 °C temperature was chosen as a typical supernate temperature in ESP tanks.

EXPERIMENTAL PROCEDURE

Long-term coupon immersion tests were conducted at 75 °C in non-radioactive simulants of two intermediate dilutions or washes of an average ESP slurry. The simulants were based on the calculated average washed sludge composition reported in the Defense Waste Processing Facility Basic Data Report.[5] The particular washes were chosen as representatives of dilute ESP solutions in which pitting is prevented with nitrite additions. They will be referred to as "5th wash" and "10th wash". The 5th wash composition represented approximately 19% of the unwashed sludge composition, and the 10th wash approximately 3.8%. The calculated nitrate concentration in unwashed sludge solution is 1.44 M. Thus, the nitrate concentrations were 0.280 M for the 5th wash and 0.0546 M for the 10th wash. The composition of the 5th wash simulant is shown in Table 1; 10th wash concentrations were a factor of 5.12 lower. Four one-liter volumes of each composition were prepared from reagent grade chemicals and distilled water. The nitrite concentration in each simulant was that specified by the technical standards to prevent pitting at 40 °C. Sodium hydroxide and sodium carbonate were added to each volume to produce a series of buffered pHs: for the 5th wash, 10, 10.4, 12.0, and 12.6; and for the 10th wash, 10.0, 11.0, 11.9, and 12.5.[6] The

sodium hydroxide additions accounted for the consumption of hydroxide in the precipitation of transition metal hydroxides (e.g., ferric hydroxide) and in the conversion of the Al^{+3} ion to $\text{Al}(\text{OH})_4^-$.

The coupons used in this study were fabricated from ASTM A537 class 1 carbon steel and supplied by Metal Samples, Inc., Munford, Ala. Their size was 0.75 in. by 3 in. by 0.12 in., and they were used in the as-received condition with 600 grit surface finish. The coupons were cleaned in acetone, rinsed in distilled water, dried, and weighed. Four coupons were suspended in one-liter polyethylene bottles with TeflonTM-coated wire. The bottles were filled with one liter of test solution, sealed, and placed in a convection oven set at 75 °C. The coupons were maintained at temperature for 142 days.

Upon removal from the test solutions, the coupons were cleaned in either inhibited hydrochloric acid or a sodium hydroxide solution - zinc mixture, weighed, and examined with optical microscopy. Uniform corrosion rates were calculated from the weight loss, and depths of corrosive attack were measured with a digital-micrometer-equipped microscope.

RESULTS AND DISCUSSION

In general the coupons had patches of light uniform corrosion of somewhat irregular depth. Distinct pitting separate from the patches of uniform corrosion was not observed. In the course of the test, sufficient evaporation occurred to drop the liquid level below the tops of some coupons, thus exposing the steel to the more aggressive conditions of differential oxygenation at the water line. Consistent with these conditions, the light corrosion patches were located mainly on the upper half of the coupons, with the deepest points of attack coinciding with the water line.

Table 2 shows the average corrosion rate in mils per year calculated from the weight losses of the four coupons in each test. The table also includes the make-up, or initial pH and the post-test pH of each test solution. As expected, the corrosion rates were low. In 5th wash simulants the corrosion rate varied from 1.1 mils/yr for a make-up pH of 10.0 to 0.14 mils/yr for a make-up pH of 12.6. Among the 10th wash simulants the corrosion rates were 1.3 mils/yr for a pH of 10.0 and 0.32 for a pH of 12.5. Post-test measurements showed that the pH of the solutions tended to decrease especially in instances of a make-up pH of about 12 or higher. As can be seen in Table 2, the post-test pH was about 10.5 for the 5th wash solutions and about 10.0 for the 10th wash solutions. These pHs are low enough to induce corrosion in the absence of sufficient inhibitor. The test conditions were, therefore, more aggressive than they would have been if the pH had been maintained at a constant value.

The data indicated that carbon steel exposed to 75 °C ESP solutions containing hydroxide at a pH of 12 and nitrite at a value appropriate for only 40 °C was not subject to significant corrosion. The highest measured corrosion rate was only 1.3 mils/yr at a make-up pH of 10.0. This rate falls in the range categorized as "ideal" in the Corrosion Data Survey, which applies that label to rates less than 2 mils/yr.[7] The measured rate is less than 4 mils/yr, which places it in the range defined as "resistant" in the DECHHEMA Corrosion Handbook. Actual ESP tank conditions should result in a corrosion rate less than 1.3 mils/yr, because of the lower temperatures and limited duration of hot spots. In Tank 42H, for example, a hot spot was observed in 1988 with a maximum temperature in the 50 to 60 °C range.[9] The 75 °C test temperature

represents a high value for a hot spot. Under the typical hot spot temperatures of < 60 °C, the actual corrosion rate is expected to be < 1 mil/yr because chemical reactions decrease in general by a factor of 2 for each 10 °C drop in temperature.[10] The limited duration of hot spots means that the waste tanks will be exposed to such rates only infrequently. The potential metal loss as a result of hot spots is, therefore, insignificant when the hydroxide concentration is maintained at a minimum of 0.01 M and the nitrite concentration is maintained at a value calculated for 40 °C.

CONCLUSIONS

Laboratory tests were performed to investigate the protection of waste tank steel from corrosion in situations of elevated temperature up to 75 °C (hot spots) in the sludge layer of Extended Sludge Processing (ESP) tanks. Coupon immersion tests were conducted at 75 °C in two ESP simulants at four hydroxide (or pH) levels and nitrite concentrations based on 40 °C. The results show that a hydroxide concentration of at least 0.01 M prevents significant corrosion of the steel at the elevated temperature.

This conclusion provides the technical basis for the revised minimum hydroxide concentration of 0.01 M in the draft WSRC 241-82H Control Room Process Requirements for the ESP tanks. This limit applies under conditions of a tank bottom or sludge temperature exceeding the supernate temperature when the nitrate concentration is < 1.0 M. The nitrite inhibitor level continues to be based on the ESP supernate temperature and the nitrate, chloride, or sulfate concentration.

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Table 1
Composition of 5th Wash ESP Simulant

Compound	Concentration, M
Sodium Nitrate	1.24E-01
Sodium Oxalate	4.07E-04
Sodium Sulfate	1.86E-02
Ferric Nitrate	1.25E-02
Aluminum Nitrate	3.41E-02
Cupric Nitrate	2.40E-03
Mercuric Nitrate	3.78E-04
Nickel Nitrate	5.06E-03
Chromic Chloride	2.77E-04
Sodium Chloride	3.40E-03
Sodium Fluoride	2.12E-03
Sodium meta-Silicate	4.03E-04
Sodium Phosphate	1.14E-03
Sodium Molybdate	5.29E-05
Sodium Chromate	4.07E-04
Sodium Nitrite	3.09E-01

Table 2
pH Values and Average Corrosion Rates

Solution	Make-Up pH	Final pH	Corrosion Rate, mils/yr
5th Wash	10.0	10.43	1.1
	10.4	10.43	0.15
	12.0	10.65	0.92
	12.6	10.49	0.14
10th Wash	10.0	9.97	1.3
	11.0	9.64	0.93
	11.9	9.99	1.2
	12.5	10.05	0.32

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