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WVNS Tank Farm Process Support

Corrosion Evaluation of Waste Storage Tank 8D-2 Under Simulated Sludge Washing Conditions

M. R. Elmore

January 1996

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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West Valley Nuclear Services
West Valley, New York
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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Radioactive liquid wastes resulting from spent fuel reprocessing operations at West Valley Nuclear Services (WVNS), West Valley, New York, have been stored in two carbon steel underground storage tanks for several years. Constructed in 1964, these tanks are designated as Tanks 8D-1 and 8D-2. Tank 8D-2 has contained the bulk of the radionuclide inventory, about 2120 kL of caustic waste slurry resulting from spent fuel reprocessing operations.

In preparing to vitrify the high-level wastes, WVNS recognized the need to pretreat the waste slurry to separate water-soluble salts, especially sulfate, from the high-level fraction. The sulfates were expected to cause processing problems during vitrification of the wastes, based on extensive testing with simulated wastes.

While the sludge washing would reduce sulfate concentration, it also would remove other soluble salts, including nitrite and hydroxide, which act to inhibit corrosion of the steel waste tanks. It was unknown, however, what concentrations of the soluble nitrite and hydroxide would be necessary to adequately protect the tanks from corrosion, or if planned sludge washing would also dilute the corrosion inhibitors below those threshold concentrations. More understanding was needed of the roles of nitrite and hydroxide as corrosion inhibitors for carbon steel in WVNS high-level wastes.

Corrosion testing was conducted at Pacific Northwest National Laboratory to gain this understanding. Steel specimens in nonradioactive simulated WVNS waste solutions were used to evaluate the potential for corrosion of the 8D-2 storage tank before, during, and after planned in-tank sludge washing operations. Specimens of various configurations [standard flat specimens for uniform corrosion, bolted pairs of flat specimens for crevice corrosion, and U-bend specimens for stress corrosion cracking (SCC)] were exposed to different simulated waste environments. Test conditions consisted of: 1) two solution temperatures (66°C and 88°C), 2) multiple simulated waste compositions (unwashed waste and 1st-, 2nd-, and 3rd-stage washed waste compositions), and 3) different specimen positions (vapor space, submerged in the solutions, and vapor/liquid interface). The various corrosion tests were conducted for durations ranging from 3 to 9 months.

In general, results of corrosion tests verified to the extent possible that conditions in Tank 8D-2 following each of the sludge washing steps would be acceptable. Corrosion rates were typically highest for specimens suspended in the vapor space of the test vessels. Calculated uniform corrosion rates for the vapor space specimens varied from less than 0.0025 mm/yr up to 0.064 mm/yr. Uniform corrosion rates for specimens submerged in the test solutions were generally less than 0.0025 mm/yr, and in most cases less than 0.00025 mm/yr. No significant difference was noted in corrosion rates between specimens at the two different test temperatures. Corrosion rates showed a tendency to decrease with time, as passivating layers of corrosion products accumulated on the surfaces of the specimens. The long-term corrosion rates calculated by the end of the tests are probably more indicative of actual conditions in the waste tanks.

Some pitting was observed on all the vapor space specimens from these tests. Pits ranging from 0.15 to 0.33 mm deep were noted on some of the vapor space specimens. No pitting was observed on any of the submerged specimens, except for specimens from the "original" 3rd-stage wash test. It is believed that under the conditions of the original 3rd-stage wash waste composition, the nitrite concentration was diluted below a threshold concentration necessary to prevent pitting corrosion. For those specimens, pits as deep as 0.15 mm were observed after the 9-month test. No SCC was noted on the U-bend specimens from any cycle of testing.

After conducting the 3rd-stage wash corrosion test, WVNS decided to alter the sludge washing process to include a transfer of a nitric acid-based THOREX waste into Tank 8D-2 from another tank prior to the 3rd sludge wash cycle. Therefore, the original 3rd-stage wash corrosion test was rerun using a "revised" 3rd-stage wash simulant composition. Results of both the original and revised 3rd-stage wash corrosion tests are included in this report.

Based on the positive results of this corrosion testing, WVNS decided to proceed concurrently with actual in-tank sludge washing. No apparent degradation of the tank has been detected, and, at this time, WVNS is proceeding with startup of their high-level waste vitrification process.

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1.0 Introduction

Radioactive waste solutions resulting from spent fuel reprocessing operations at West Valley Nuclear Services (WVNS), West Valley, New York, have been stored in two carbon steel underground storage tanks for several years. Constructed in 1964, these tanks are designated as Tanks 8D-1 and 8D-2. Tank 8D-1 has contained about 64,000 kg of cesium-loaded zeolite and about 380 kL of a relatively dilute solution of sodium nitrite and sodium hydroxide; Tank 8D-2 has contained about 2120 kL of waste slurry resulting from spent fuel reprocessing operations. Over the next few years, plans for permanent disposal of the tank contents will be implemented. Until the waste is removed, the integrity of the tanks must be maintained. A corrosion support program is being conducted at Pacific Northwest National Laboratory (PNNL)[a] to investigate internal and external corrosion of the tanks and to make recommendations accordingly. Tank 8D-1 was selected as the focus for an evaluation of external corrosion, and results of that investigation are provided in Mackey and Westerman (1995). Tank 8D-2 was investigated for internal corrosion. The results of the corrosion study for Tank 8D-2 are given in this report.

Planned waste disposal operations at WVNS call for the settled sludge in Tank 8D-2 to be retrieved, pretreated, and vitrified; but first, the sludge requires "washing" to reduce the concentration of soluble sulfates in the waste, which would interfere with the vitrification process. However, while the sludge washing would reduce sulfate concentration, it also would remove other soluble salts, including nitrite and hydroxide, which act to inhibit corrosion of the steel waste tanks. It was unknown, however, what concentrations of the soluble nitrite and hydroxide would be necessary to adequately protect the tanks from corrosion, or if planned sludge washing would also dilute the corrosion inhibitors below those threshold concentrations. More understanding was needed of the roles of nitrite and hydroxide as corrosion inhibitors for carbon steel in WVNS high-level wastes.

Although corrosion of carbon steel in aqueous environments has been studied extensively, in the particular environment of Tank 8D-2 little is known about specific corrosion mechanisms and corrosion rates as functions of various influencing parameters (e.g., system geometry, temperature, radiolysis, pH, $[NO_3^-]$, $[NO_2^-]$, etc.). The work reported here was conducted to simulate the waste compositions (excluding radionuclides) in the tank at each of the sludge washing steps. Sludge washing was conducted at WVNS in three separate operations; a 3- to 9-month corrosion test was conducted at PNNL preceding each sludge wash step to identify beforehand any unexpected and potentially unacceptable corrosion of the tank resulting from the changing chemistry of the washed waste.

The sludge washing process implemented by WVNS consisted of decanting the supernatant liquid from the settled solids, then adding a roughly equivalent volume of dilute sodium hydroxide and sodium nitrite solution to the tank. This mixture was stirred with multiple submerged-jet mixer pumps, thereby

(a) Operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

dissolving more of the soluble sulfate salts. The mixer pumps were shut off; the solids were allowed to settle; and the process was repeated, beginning with decanting the supernatant liquid.

1.1 Objectives

The overall objective of this work was to assess the effects of past, current, and future conditions in Tank 8D-2 (i.e., waste chemistry, temperature, etc.) on the internal corrosion of the tank. Specific objectives are listed below:

- Determine baseline corrosion rates for estimating the rate of metal degradation that has occurred in the tank under recent waste storage conditions prior to sludge washing. These data also helped to provide a means of evaluating information obtained from corrosion probes that had previously been inserted into Tank 8D-2.

- Assess the potential effects of sludge washing operations on corrosion of the tank at the different stages. As sludge washing proceeds, critical (low) concentrations of hydroxide and nitrite may be reached where pitting or crevice corrosion could occur and compromise the integrity of the tank.

1.2 Related Corrosion Studies

Investigations of carbon steel corrosion have been performed for related types of projects under somewhat similar conditions. Divine et al. (1985) studied the corrosion of A-516 and A-537 carbon steel in various simulated Hanford-type waste solutions (primarily nitrate/hydroxide sludges with additional hydroxide and nitrite added as corrosion inhibitors) under static conditions over a range of component concentrations and temperatures. In general, uniform corrosion rates of less than 0.0254 mm/yr and no significant localized corrosion were reported for most test conditions, which led to revised Hanford tank farm operating specifications. Excessive uniform corrosion rates (>0.0254 mm/yr) occurred only at high OH^- concentrations (pH >13) and usually at temperatures above 140°C. Pitting and stress corrosion cracking (SCC) were only observed for tests with dilute waste compositions.

Related studies have been conducted at the Savannah River Site (SRS) over the past several years. Wastes stored in underground tanks at the SRS are to be washed in the tanks prior to retrieval. These wastes are also nitrate-hydroxide types of sludges generated during fuel processing operations at the SRS. Corrosion testing has been conducted at the SRS with simulated waste solutions to identify conditions where localized corrosion, especially pitting, may occur during washing. Testing has shown pitting may occur near the vapor-solution interface, apparently because CO_2 from the air in the head space of the tank is absorbed and lowers the solution pH (Bickford et al. 1988; Congdon 1988; Zapp 1988). The ongoing SRS work suggests that testing under conditions specific to the waste storage and proposed sludge washing conditions at WVNS is necessary to identify potential problems before tank conditions are radically changed.

2.0 Experimental Work

A phased approach was adopted to assess the potential for corrosion in Tank 8D-2 using laboratory-scale nonradioactive corrosion tests on carbon steel specimens made of material comparable to the type of steel used to fabricate Tank 8D-2. This evaluation started with corrosion tests using simulated unwashed waste, followed by tests with simulated 1st-, 2nd-, and 3rd-stage sludge wash solutions.

The potentials for uniform corrosion and localized corrosion were assessed by immersing steel specimens in heated 66°C and 88°C simulated Tank 8D-2 waste solutions, suspending others in the vapor space above the simulated waste solutions, and suspending some half-submerged at the solution/ vapor interface. [These selected temperatures were expected to approximate the typical (66°C) and maximum (88°C) temperatures to be encountered during sludge washing.] The conditions of the specimens were observed; pit depths were measured with an optical micrometer; and uniform corrosion rates for the specimens were determined from weight loss measurements. Tank 8D-2 conditions that could cause pitting, crevice corrosion, and SCC were of particular concern. Therefore, crevice specimens and welded/stressed (U-bend) specimens were included in the tests, along with standard flat specimens. Metallographic and microscopic analyses were conducted as appropriate on selected specimens to further evaluate the mechanisms and extent of observed localized corrosion.

2.1 Test Materials

The test materials representing the tank carbon steel and the simulated waste solution are described below.

2.1.1 Corrosion Test Specimens

A small amount of archived tank steel from Tank 8D-2 was available for these tests. However, because it was in limited supply, only SCC specimens (U-bends) were fabricated from the archived material. Available information indicates that the ASTM designation for the type of steel used in fabricating Tank 8D-2 (ASTM A-201A) has since been replaced with the designation ASTM A-516 (Grade 55 for carbon <0.18%). Test specimens for uniform corrosion and crevice corrosion evaluations were procured to the A-516 specification. Microstructural and chemical analyses had previously been conducted to verify conformance of archived Tank 8D-2 material with the new ASTM designation. Table 2.1 compares the chemical compositions of the archived tank steel with the A-516 test specimens.

Each of the test specimens initially had a standard ~120-grit abraded or equivalent surface finish, and was stamped with a unique reference number to permit traceability of the specimen material from material origin through testing and final data analysis.

Table 2.1. Compositions of Archived Tank Steel and Procured A-516 Test Specimens (wt%)

Steel Type	C	Mn	P	S	Si	Fe
Archived Tank Steel	0.14	0.56	0.016	0.04	0.30	Balance
Procured A-516 Specimens	0.12	0.63	0.01	0.026	0.26	Balance

2.1.2 Test Solution

A stock volume of the simulated unwashed test solution was prepared according to a previously developed procedure based on both process knowledge and analytical results of subsequent actual tank waste sampling. A sample of the prepared simulated waste solution was then analyzed by ion chromatography (IC) for principal anions to verify its composition. The composition of the simulated unwashed Tank 8D-2 waste solution is shown in Table 2.2, along with compositions of the subsequent 1st-, 2nd-, and 3rd-stage wash (original and revised) simulants. The pH of the unwashed simulated waste solution was ~11. Unwashed waste corrosion testing was conducted using a portion of this stock solution.

Test solution simulating the first sludge wash was then prepared by adding an appropriate volume of caustic (NaOH) wash solution to the stock solution to simulate the planned sludge washing procedure, as defined by WVNS. The resulting pH of this solution was ~11.5. Test solution simulating the 2nd-stage sludge wash was then prepared by first decanting 1st-stage wash supernatant liquid, then refilling the tank with water and agitating for ~2 hr to simulate the sludge washing procedure. The resultant pH of the solution was still slightly higher than 11.5, per WVNS specification, so no caustic was added to the wash solution in simulating the 2nd-stage wash.

Table 2.2. Composition of Simulated Waste Solutions (μg/mL)

Component	Unwashed Waste	1st-Stage Wash	2nd-Stage Wash	Original 3rd-Stage Wash	Revised 3rd-Stage Wash[a]
NO_3^-	234,000	191,000	79,000	5,900	21,900
NO_2^-	96,300	76,600	30,000	4,700	14,250
$SO_4^=$	22,800	19,000	7,000	1,900	1,130
Cl^-	1,800	1,800	600	80	40
pH	~11	~11.5	~12	>12	>12

(a) Revised wash based on addition prior to wash of acidic nitrate waste from another storage tank, plus additions of hydroxide and nitrite for corrosion control. The original sludge wash flowsheet called for adding the nitric acid waste after the 3rd wash, and then performing a 4th wash if needed.

The composition of the simulants for the "original" and subsequently "revised" 3rd-stage wash was specified by WVNS before each of the corresponding tests. By the time of the 3rd-stage wash corrosion testing, WVNS was predicting a waste composition significantly different from the composition previously expected because of differences in planned vs. actual sludge wash operations. Therefore, the simulated waste from the 2nd-stage wash test was discarded, and the original 3rd-stage wash simulant was prepared by dissolving the appropriate sodium salts in deionized water. Similarly, the revised 3rd-stage wash simulant was also significantly different from the original 3rd-stage wash composition, and was prepared fresh at the beginning of that test.

2.2 Test Equipment and Procedures

Equipment used during the corrosion testing included 1) Teflon-lined corrosion test vessels (resin kettles) equipped with reflux condensers for vapor recovery, air spargers to keep the system oxygenated (to simulate air absorption and to some extent radiolysis occurring in the tank waste), and thermocouples for temperature control; 2) high-temperature oil baths for heating the test vessels; 3) an electronic balance and calipers for measuring the weights and dimensions of the specimens before and after each test; and 4) an optical micrometer for measuring pit depths on specimens after final cleaning. Test specimens were suspended on Teflon rods at appropriate heights in the vessels to expose the specimens to test environments of interest (vapor space, interface, and submerged).

After being removed from the test solutions, the specimens were rinsed, briefly examined, then cleaned for weight loss determinations. The cleaning procedure involved immersing the specimens in an inhibited HCl acid cleaning solution formulated to remove corrosion products from the surface while minimizing the amount of metal dissolved from the specimens. After cleaning, the specimens were rinsed in deionized water and alcohol, then dried, weighed, and stored in a desiccator. Weight losses were converted to uniform corrosion rates.

A calibrated optical micrometer was used to measure the depths of pits on the specimens. Some specimens were sectioned, and the cross sections were examined under a microscope to further assess the depths of pits formed on the surfaces of the specimens.

Multiple sets of test specimens were used in each test. Two sets of specimens were placed in the vessels at the start of each test. At a predetermined interval (usually 1 month), one of the two sets of specimens was withdrawn from each vessel for examination. This set of specimens was replaced with an identical set, and the test continued. At the end of each test, both remaining sets of specimens were removed for examination. This approach provided three sets of specimens exposed for different durations over the course of the test. Three of the five tests reported here used 1-, 3-, and 6-month exposures. However, the duration of each test was selected according to the schedule of the sludge washing operations being conducted at WVNS at that time.

3.0 Test Results and Discussion

Tables 3.1 and 3.2 summarize uniform corrosion and pitting results, respectively, for all the testing performed under this activity, including corrosion tests with unwashed simulant, and with 1st-stage wash, 2nd-stage wash, original 3rd-stage wash, and revised 3rd-stage wash simulants. In general, corrosion was highest on specimens in the vapor space, and pitting was observed on all the vapor space specimens. Calculated uniform corrosion rate tended to decrease with time over the course of each test for both vapor and submerged specimens, as would be expected with the accumulation of a protective oxide layer on the specimen surfaces.

Although pit depths were measured on all sets of specimens, no evidence was seen of significantly accelerating or diminishing pitting rates. Table 3.2 gives the pit depths for just the full-length exposure sets. In some of the tests, pits were as deep at the first inspection as at the end of the tests, indicating that the pits initiated, deepened to ~0.15 mm, then apparently stopped growing. In other tests, pitting appeared to increase slowly throughout the tests, and, as in the case of the original 3rd-stage wash test, were as deep as 0.33 mm by the end of the 9-month test. A pitting rate of a constant 0.3 to 0.5 mm/yr seems a reasonable estimate for pitting under these conditions.

3.1 Unwashed Waste Corrosion Testing

The highest corrosion rates were found after a 1-month exposure of specimens to the vapor-phase environment (~0.05 mm/yr), decreasing to ~0.025 mm/yr by the end of the 3-month test. Pitting was noted on both the standard specimens and on the crevice specimens taken from the vapor space. Most of the pits ranged in depth from 0.05 to 0.15 mm, as measured with an optical micrometer. Similar pits were observed after 3 months of exposure, although none were deeper than ~0.15 mm (Table 3.2). Conditions tested with the unwashed waste simulant were apparently not suitable to sustain the pitting corrosion reactions.

For the submerged specimens, calculated uniform corrosion rates ranged from near zero to less than 0.0025 mm/yr after 1 month of exposure. By the end of 3 months, submerged uniform corrosion rates were still very low, indicating long-term uniform corrosion rates significantly less than 0.0025 mm/yr (Figure 3.1). No pitting was observed on these specimens at the 1-, 2-, or 3-month intervals.

No crevice attack per se was observed on any of the crevice specimens, vapor space or submerged, although pitting was sometimes concentrated around Teflon washers and nuts supporting some of the vapor space specimens. Also, no SCC was observed on U-bend specimens submerged in the test solutions.

Table 3.1. Uniform Corrosion Results from Simulated Sludge Wash Tests

Simulated WVNS Tank 8D-2 Sludge Wash Corrosion Testing (mm/yr)				
Unwashed Waste Test				
	66°C		**88°C**	
Exposure	**Vapor**	**Submerged**	**Vapor**	**Submerged**
1 mo	0.0533	0.0010	0.0406	0.0005
2 mo	0.0508	0.0003	0.0406	0.0005
3 mo	0.0330	0.0005	0.0178	0.0003
1st-Stage Wash Test				
	66°C		**88°C**	
Exposure	**Vapor**	**Submerged**	**Vapor**	**Submerged**
1 mo	0.0660	0.0015	0.0660	0.0013
3 mo	0.0356	0.0003	0.0229	<0.0003
6 mo	0.0051	<0.0003	0.0152	<0.0003
2nd-Stage Wash Test				
	66°C		**88°C**	
Exposure	**Vapor**	**Submerged**	**Vapor**	**Submerged**
1 mo	0.0279	0.0010	0.0254	0.0010
3 mo	0.0076	<0.0003	0.0229	<0.0003
6 mo	0.0102	0.0003	0.0051	<0.0003
"Original" 3rd-Stage Wash Test				
	66°C		**88°C**	
Exposure	**Vapor**	**Submerged**	**Vapor**	**Submerged**
1 mo	0.0305	0.0003	0.0508	0.0008
3 mo	0.0254	0.0003	0.0152	<0.0003
6 mo	0.0178	0.0003	0.0127	0.0003
9 mo	0.0203	<0.0003	0.0076	0.0003
"Revised" 3rd-Stage Wash Test				
	66°C		**88°C**	
Exposure	**Vapor**	**Submerged**	**Vapor**	**Submerged**
1 mo	0.0533	0.0008	0.0203	0.0008
3 mo	0.0076	0.0005	0.0178	0.0005
6 mo	0.0127	<0.0003	0.0025	<0.0003

Table 3.2. Results of Pit Depth Measurements (Deepest Pits at End of Each Test)

Test	Duration	Max. Pit Depths (mm)	
		Vapor	Submerged
Unwashed Waste	3 mo	0.15	none
1st-Stage Wash	6 mo	0.15	none
2nd-Stage Wash	6 mo	0.23	none
Orig. 3rd-Stage Wash	9 mo	0.33	0.15
Rev. 3rd-Stage Wash	6 mo	0.15	none

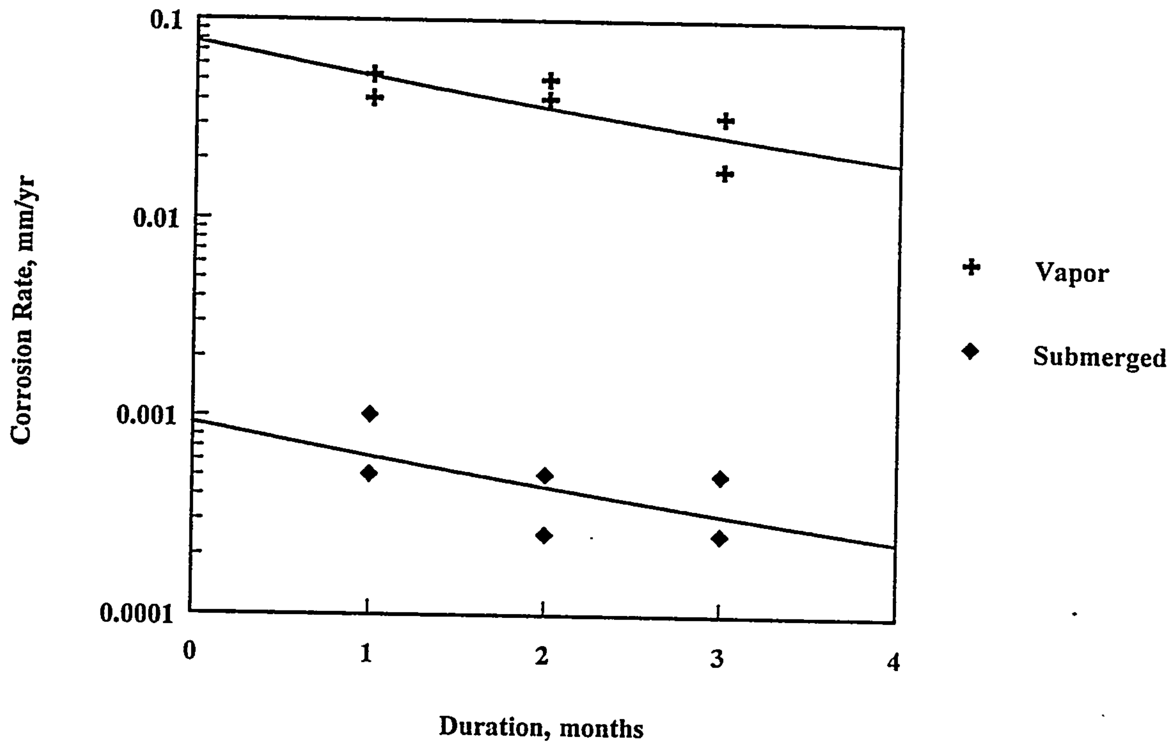

Figure 3.1. Plot of Corrosion Results from "Unwashed" Waste Test. The semi-log plot shows calculated uniform corrosion rates (determined after 1-, 2-, and 3-month exposures) for vapor space and submerged specimens.

3.2 First-Stage Wash Corrosion Testing

Results of the 1st-stage wash tests were similar to results of the unwashed waste test. The most severe corrosion (in terms of weight loss) occurred on the vapor space specimens (Figure 3.2). Pitting

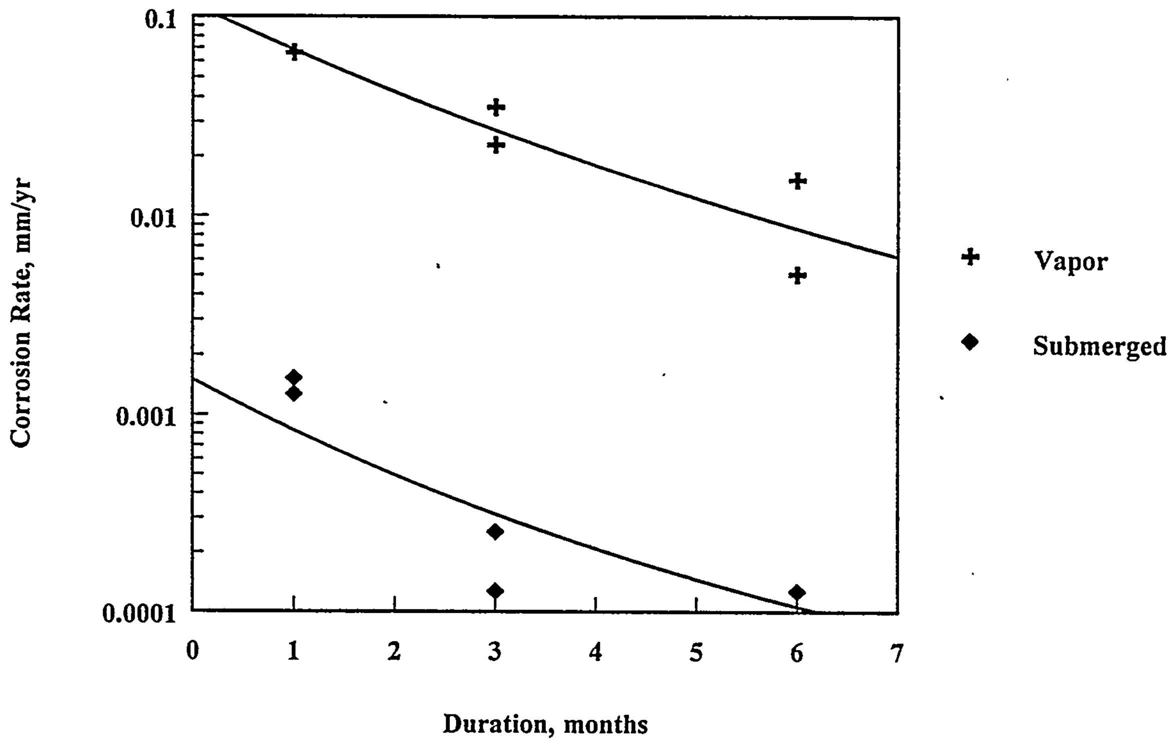

Figure 3.2. Plot of Corrosion Results from 1st-Stage Wash Test. The semi-log plot shows calculated uniform corrosion rates (determined after 1-, 3-, and 6-month exposures) for vapor space and submerged specimens.

was also observed on the vapor space specimens (Table 3.2) with pits ranging to ~ 0.15 mm deep after 6 months. No pitting was noted on submerged specimens at either test temperature, 66°C and 88°C. No SCC was observed on the submerged U-bend specimens. Long-term uniform corrosion rates for submerged specimens were low (<0.0025 mm/yr) by the end of the 6-month tests (Figure 3.2). No significant difference in calculated uniform corrosion rate for the submerged specimens was apparent between the 66°C and 88°C tests.

3.3 Second-Stage Wash Corrosion Testing

Second-stage sludge wash corrosion test specimens were inspected after 1-, 3-, and 6-month exposures to the test solutions. Again, the highest uniform corrosion rates were found on the specimens exposed for 1 month to the vapor-phase environment. Initial rates were much higher than rates after a few months when protective oxide layers were apparently more established on the specimen surfaces. Calculated uniform corrosion rates in the vapor space ranged from ~0.005 to 0.01 mm/yr, based on the 6-month specimens, which appear to approach a long-term steady-state rate.

Figure 3.3 shows a plot of uniform corrosion rate as a function of exposure time for the vapor space and submerged specimens. Data for 66°C and 88°C were combined on the same graph, since no significant difference was noted in corrosion rate between the two temperatures.

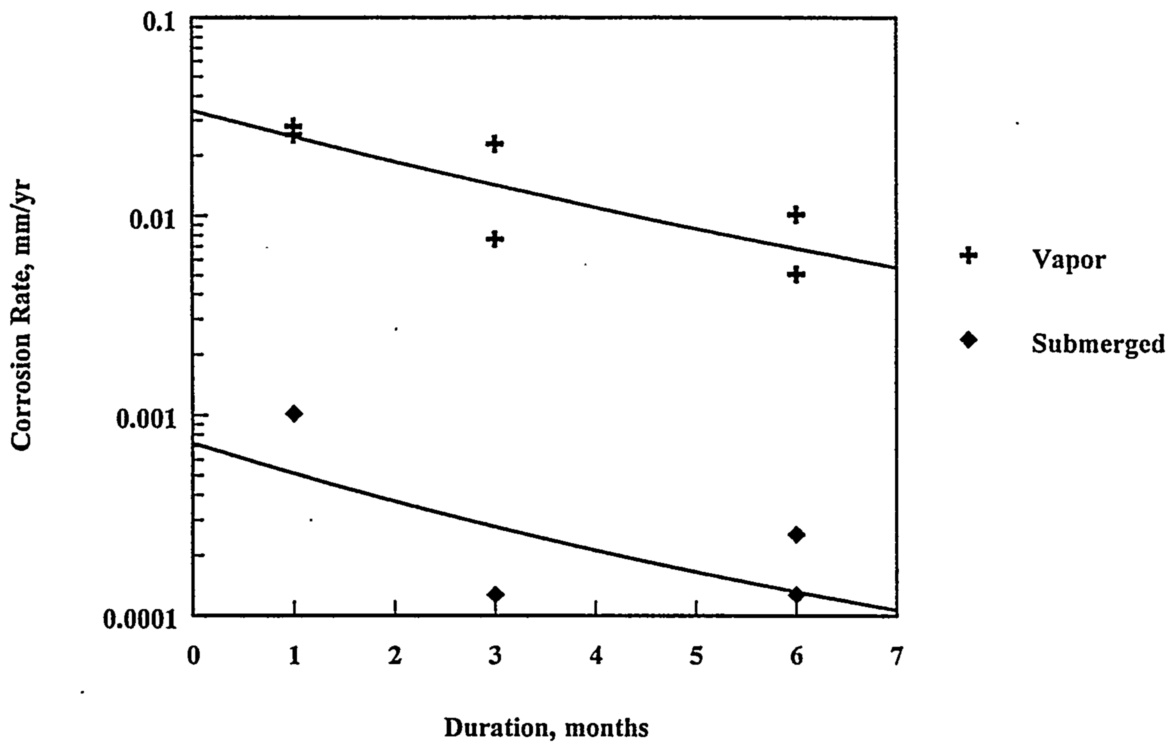

Figure 3.3. Plot of Corrosion Results from 2nd-Stage Wash Test. The semi-log plot shows calculated uniform corrosion rates (determined 1-, 3-, and 6-month exposures) for vapor space and submerged specimens.

Pitting was noted on both the standard specimens and on the crevice specimens taken from the vapor space. Depth of pits varied with exposure time. Most of the pits after 6 months of exposure ranged in depth from 0.08 to 0.13 mm, as measured with an optical micrometer. However, a few pits as deep as 0.23 mm were measured on two specimens (both from the 88°C tests) following the 6-month tests (Table 3.2).

For the submerged specimens, calculated uniform corrosion rates ranged from near zero to ~0.0003 mm/yr after the 6-month exposures (see Table 3.1 and Figure 3.3). No pitting was observed on the submerged specimens from the 1-, 3-, or 6-month durations.

Again, no significant crevice attack was observed on any of the crevice specimen pairs, vapor space or submerged, although pitting was sometimes concentrated around Teflon washers and nuts supporting some of the vapor space specimens where crevices may have been produced. Also, no SCC was observed on U-bend specimens.

On interface specimens (half submerged in the solution), no specific localized attack was noted at the waterline. The submerged portions of the specimens looked like the other submerged specimens (clean, no pitting). The vapor space portions, on the other hand, looked like the other vapor space specimens (more heavily corroded; some pitting but not worse than other vapor space specimens).

3.4 Third-Stage Wash Corrosion Testing

As before, the highest uniform corrosion rates were found on the specimens exposed to the vapor-phase environment. Calculated uniform corrosion rates in the vapor space ranged from 0.008 to 0.02 mm/yr, based on the 9-month specimens from the original 3rd-stage wash, and from 0.003 to 0.013 mm/yr, based on the 6-month specimens from the revised 3rd-stage wash. Corresponding rates for submerged specimens were less than 0.003 mm/yr.

Table 3.1 gives the calculated uniform corrosion rates for the 1-, 3-, 6-, and 9-month exposures for specimens from the original 3rd-stage wash test, and the 1-, 3-, and 6-month exposure specimens from the revised 3rd-stage wash test. Figure 3.4 shows a plot of uniform corrosion rate as a function of exposure time for the submerged and vapor specimens from the original 3rd-stage wash test. No significant difference was noted in corrosion rate between the 66°C and 88°C test temperatures. Figure 3.5 shows a plot of uniform corrosion rate for the submerged and vapor specimens from the revised 3rd-stage wash test. Again, no significant difference was noted in corrosion rate between the 66°C and 88°C test temperatures.

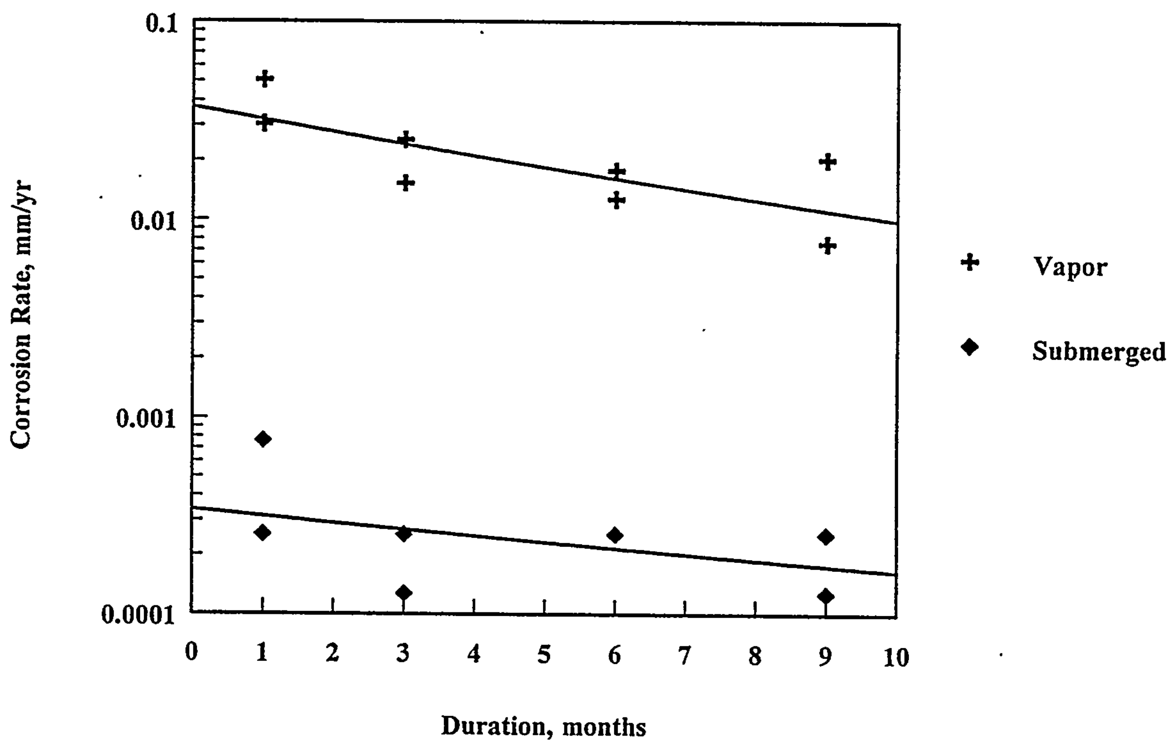

Figure 3.4. Plot of Corrosion Results from "Original" 3rd-Stage Wash Test. The semi-log plot shows calculated uniform corrosion rates (determined after 1-, 3-, 6-, and 9-month exposures) for vapor space and submerged specimens.

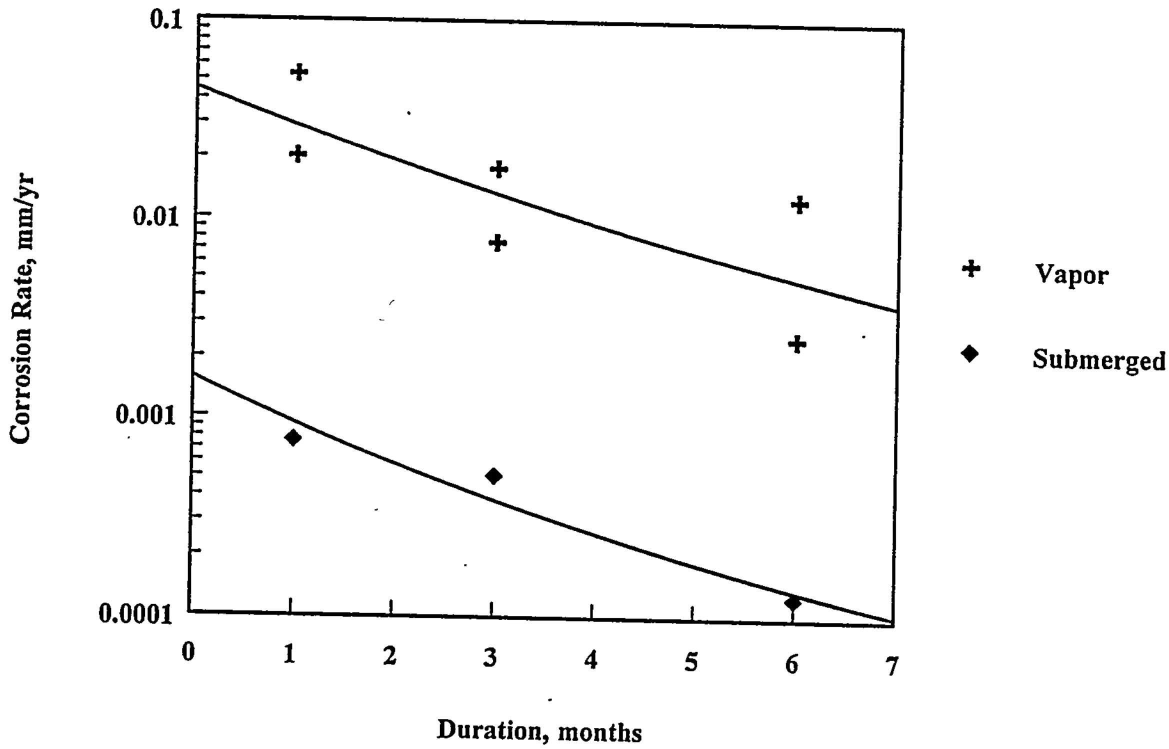

Figure 3.5. Plot of Corrosion Results from "Revised" 3rd-Stage Wash Test. The semi-log plot shows calculated uniform corrosion rates (determined after 1-, 3-, and 6-month exposures) for vapor space and submerged specimens.

Pitting was noted on both the standard specimens and on the crevice specimens taken from the vapor space. Depth of pits varied with exposure time. Most of the pits after 9 months (original 3rd-stage wash) and 6 months (revised 3rd-stage wash) of exposure ranged in depth up to 0.15 mm, as measured with an optical micrometer. However, a few pits as deep as 0.33 mm were measured on specimens taken from the 9-month tests. Table 3.2 summarizes the pit depths measured during the specimen examinations.

Minor but observable pitting was noted on some of the specimens from the 1-, 3-, 6-, and 9-month durations of the original 3rd-stage wash test. The depth of this localized attack was much less on the submerged specimens than the pitting attack on the vapor space specimens, and did not appear to become significantly worse between the 1-month and 6-month evaluations. [However, this was the first simulated sludge wash cycle where pitting was observed on the submerged specimens. One explanation is that the concentration of corrosion inhibitors (e.g., hydroxide and nitrite) had been diluted sufficiently that in this waste simulant pitting could initiate. Pitting on submerged specimens was not observed for the later revised 3rd-stage wash test, which contained higher concentrations of nitrite ion, simulating the addition of the nitric acid-based THOREX waste to Tank 8D-2.]

No significant crevice attack was observed on any of the crevice specimens, vapor space or submerged, although, as before, minor localized attack was sometimes concentrated around Teflon washers and nuts supporting some of the specimens where crevices may have been produced. Also, no SCC was observed on U-bend specimens. On some U-bend specimens exposed for 9 months (original 3rd-stage wash) and 6 months (revised 3rd-stage wash), minor localized attack was noted. On interface specimens (half submerged in the solution), no distinctive waterline attack was observed at the location of the solution interface.

4.0 Conclusions

Results of tests in simulated unwashed Tank 8D-2 waste corroborate reasonably well results of other corrosion tests in similar solutions. As a result of these tests, it was concluded that chemistry changes to Tank 8D-2 waste caused by the three cycles of sludge washing under conditions simulated in these tests would not adversely impact the tank integrity. Based on the outcome of these tests and the conclusion that impacts to the tank integrity should be negligible, WVNS staff proceeded with the sludge washing (and have since completed these operations) with no apparent problems to the tank. Specific conclusions based on the individual corrosion tests are given below.

- Uniform corrosion rates were low on submerged specimens in all tests. Long-term uniform corrosion rates were less than 0.003 mm/yr, which agreed well with results from corrosion probes located in Tank 8D-2.

- Localized corrosion was not evident on submerged specimens with one exception. In the 9-month original 3rd-stage wash test, pits as deep as 0.15 mm were observed. It is believed that the combined concentrations of nitrite and hydroxide were diluted below a threshold level necessary to inhibit pitting in the original 3rd-stage wash solution.

- Specimens suspended in the vapor space above the solutions had higher uniform corrosion rates, and exhibited pitting (as much as 0.33 mm deep in the case of the 9-month original 3rd-stage wash test).

- For all the tests, the calculated uniform corrosion rates did not vary significantly with temperature between the test temperatures of 66°C and 88°C.

- Crevice corrosion was not apparent on the pairs of crevice specimens in any of the tests.

- No SCC was observed on U-bend specimens in any of the tests.

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