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WVNS Tank Farm Process Support

**Experimental Evaluation of an
Inert Gas (Nitrogen) to Mitigate
External Corrosion of High-Level
Waste Storage Tanks**

M. R. Elmore

February 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
by Battelle Memorial Institute



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WVNS Tank Farm Process Support

Experimental Evaluation of an Inert Gas (Nitrogen) to Mitigate External Corrosion of High-Level Waste Storage Tanks

M. R. Elmore

February 1996

Prepared for
West Valley Nuclear Services
West Valley, New York
under Contract DE-AC06-76RLO 1830
with the U. S. Department of Energy

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Corrosion of the carbon steel waste storage tanks at West Valley Nuclear Services continues to be of concern, especially as the planned duration of waste storage time increases and sludge washing operations are conducted. The external surfaces of Tanks 8D-1 and 8D-2 have been exposed for more than 10 years to water that has intruded into the tank vaults. Visual inspection of the external tank surfaces using a remote video camera has shown indications of heavy corrosion in localized areas on the tank walls.

Tests on mild steel specimens under simulated tank vault conditions showed that corrosion is related to the availability of oxygen for the corrosion reactions; consequently, removing oxygen as one of the reactants should effectively eliminate corrosion. In terms of the waste tanks, excluding oxygen from the annular vault space, such as by continuous flushing with an inert gas, should substantially decrease corrosion of the external surfaces of the mild steel tanks (100% exclusion of oxygen is probably not practicable). Laboratory corrosion testing was conducted at Pacific Northwest National Laboratory to give a preliminary assessment of the ability of nitrogen-inerting to reduce steel corrosion. This report summarizes test results obtained after 18-month corrosion tests comparing "nitrogen-inerted" corrosion with "air-equilibrated" corrosion under simulated tank vault conditions.

Test results show that use of a nitrogen purge to inert the atmosphere and remove dissolved oxygen from "vault water" in contact with mild steel specimens at 30°C significantly decreased overall corrosion of wetted portions of the test specimens. General corrosion rates for the submerged portions of the air-purged specimens were much higher (~0.06 mm/yr) than for the nitrogen-inerted specimens (~0.002 mm/yr) in the same time period. Vapor space corrosion was not significant for either nitrogen- or air-purged specimens by the end of the 18-month test. Localized attack (primarily pitting) was extensive on the air-purged specimens and observed, but very limited, on the nitrogen-inerted specimens. Although the overall amount of pitting was much less, the deepest pits observed on the nitrogen-inerted specimens (0.6 mm after 18 months) were approximately the same as for the air-purged specimens (~0.5 to 0.6 mm after 18 months). Therefore, even lower dissolved oxygen concentrations are necessary to significantly affect the rate of pit growth once pits initiate on the surface of the steel.

As a result of this preliminary evaluation of nitrogen-inerting for corrosion control, additional similar testing is recommended but with more effort to exclude oxygen from the system to reach even lower concentrations and determine the effect, if any, on the pit deepening rate. This would help to better establish minimum operational requirements for the installed system. Test results showed the importance of eliminating water from the vault as part of a strategy for corrosion control. Consequently, it is recommended that the vaults and tanks be dried to the greatest extent practicable. Additional testing should be conducted with "low" water level (specimens embedded in perlite but with vault water level below the lower end of the specimens) to see if moisture that can be wicked through the perlite to the specimen surface will have as much effect on corrosion as when the specimens are half submerged in water, as for these tests.

Based on these limited laboratory tests, the most effective approach to controlling external corrosion of the tanks appears to be to 1) find and mitigate the source(s) of water intruding into the tank vaults, and 2) displace oxygen (and simultaneously remove additional water vapor from the vaults) with heated nitrogen purges of the vaults.

Contents

Summary	iii
1.0 Introduction	1.1
2.0 Experimental Approach	2.1
2.1 Test Materials	2.1
2.1.1 Steel Corrosion Specimens	2.1
2.1.2 Vault Water	2.2
2.1.3 Perlite	2.3
2.1.4 Purge Gases	2.3
2.2 Test Apparatus	2.4
2.3 Test Procedure	2.5
3.0 Results and Discussion	3.1
4.0 Conclusions and Recommendations	4.1
4.1 Conclusions	4.1
4.2 Recommendations	4.1
5.0 Reference	5.1

Figures

2.1	Apparatus with Test Specimens in Vessels Standing in Perlite/Water Mixture	2.5
3.1	Specimens Following 2-Month Exposure at 30°C, Half Submerged in Perlite/Vault Water to Nitrogen Purge and Air Purge	3.3
3.2	Specimens Following 18-Month Exposure at 30°C, Half Submerged in Perlite/Vault Water to Nitrogen Purge and Air Purge	3.4
3.3	Calculated Uniform Corrosion Rates for Nitrogen-Inerted Versus Air-Purged Specimens	3.5
3.4	Cleaned Specimens from 18-Month, 30°C, Air-Purged Test	3.7
3.5	Cleaned Specimens from 18-Month, 30°C, Nitrogen-Inerted Test	3.8

Tables

2.1	Composition of WVNS Vault Water Used in Nitrogen-Inerting Corrosion Tests	2.2
2.2	Typical Composition of Granular Perlite Used in the Nitrogen-Inerting Corrosion Tests	2.3
2.3	Analysis of Nitrogen Gas Used for the Nitrogen-Inerting Corrosion Tests, as Determined by Gas Chromatograph/Mass Spectrometer	2.4
3.1	“Measured” and “Adjusted” Uniform Corrosion Rates and Deepest Pit Depths for Specimens After 1-, 2-, 6-, and 18-Month Exposures in the Nitrogen-Inerting and Air-Purging Corrosion Tests	3.2

1.0 Introduction

Radioactive waste slurries resulting from spent fuel reprocessing operations at West Valley Nuclear Services (WVNS), West Valley, New York, have been stored in carbon steel underground storage tanks. During planned disposal operations at WVNS, the wastes in these tanks will be retrieved, pre-treated, and vitrified into a form suitable for geologic disposal. In the meantime, corrosion of the tanks, designated Tanks 8D-1 and 8D-2, is being addressed for the duration of waste storage time until retrieval begins and as sludge washing operations are conducted. The external surfaces of Tanks 8D-1 and 8D-2 have been exposed for more than 10 years to water that has intruded into the tank vaults. The water may include some ground water seeping through cracks in the vaults, but most of the water appears to enter through cracks and inadequate seals around penetrations in the roofs of the vaults. The water is periodically pumped out; however, not all of the water can be pumped out of either vault before loss of pump suction occurs, and the inflow of water is nearly continuous. Consequently, the vaults, and therefore the external tank surfaces, never dry out completely.

There is concern that long-term exposure of the tanks to the water may have caused significant corrosion to the tank walls. Visual inspection of the external tank surfaces using a remote video camera has shown indications of heavy corrosion in localized areas. Ultrasonic thickness inspection of the tank walls with sensors on remote crawlers is planned by WVNS but has not yet been performed. As part of the investigation into possible corrosion, WVNS asked Pacific Northwest National Laboratory^(a) (PNNL) to conduct laboratory corrosion testing.

PNNL recently completed long-term (30 months) laboratory corrosion testing with steel specimens exposed to simulated tank vault conditions (Mackey and Westerman 1995). After 30 months, the corrosion specimens showed a rate of general, or "uniform," attack of less than 0.1 mm/yr, consistent with what would be expected of a structural grade of carbon steel exposed to air-equilibrated, nonaggressive ground water. More importantly, however, the specimens exhibited severe nonuniform (pitting) attack. This attack is attributed to oxygen concentration cells present around particles of perlite (silicate mineral used for insulating brick under the tanks, also included in corrosion tests), and in the vicinity of the air-water interface on some of the specimens. The average rate of pit deepening of the deepest pits observed was ~ 0.25 mm/yr, and did not appear to diminish during the course of the test. Observations indicate that a pit deepening rate of greater than 0.5 mm/yr is possible under the conditions tested.

These pitting rates could not have been maintained on the actual tank walls since the tanks were constructed, or the tanks would already have been perforated. Therefore, either the test conditions were not representative of the vault conditions, or the 30-month test was not long enough to reach long-term steady-state conditions (where sufficiently thick layers of corrosion products may accumulate on

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the surface of the steel and thereby inhibit, to some extent, the corrosion reactions). The pitting rates observed in these tests are of concern, however, because the effect of even longer test times on pit deepening rate is unknown and corrosion on the inside of the tanks is not accurately known. Consequently, the thickness of the remaining tank wall steel cannot be accurately estimated. This concern led to the work discussed here.

Since corrosion of the mild steel specimens under these simulated tank vault conditions is related to the availability of oxygen for the corrosion reactions, removing oxygen as one of the reactants should effectively eliminate corrosion. In terms of the waste tanks, excluding oxygen from the annular vault space, such as by continuous flushing with an inert gas, should substantially decrease corrosion of the external surfaces of the mild steel tanks (100% exclusion of oxygen is probably not practicable). Based on this assumption, recommendations were given to displace the oxygen in the tank vault with an inert gas, such as nitrogen, as a means of mitigating external corrosion of the tank walls. At issue was 1) what degree of oxygen exclusion is necessary for effective corrosion control, and 2) is some other mode of corrosion favored under anoxic conditions. Laboratory corrosion testing was conducted at PNNL to give a preliminary assessment of the ability of nitrogen-inerting to reduce steel corrosion. This report summarizes test results obtained after 18-month corrosion tests comparing "nitrogen-inerted" corrosion with "air-equilibrated" corrosion under simulated tank vault conditions.

The main objectives of the work described here were to

- determine the magnitude of steel corrosion inhibition achieved by displacing oxygen from air in the tank/vault annulus using a commercially pure (>99.9%) nitrogen gas purge
- assess the possibility for exacerbating steel corrosion under the resultant anoxic conditions.

2.0 Experimental Approach

The overall approach to this testing was to expose steel corrosion specimens to environments simulating, as closely as practicable, the conditions presently existing in the tank vaults (with the exception of radiation) and conditions anticipated with nitrogen purge of the vault air space. Following exposures ranging from 1 to eventually 30 months, the specimens were removed from the vessels, cleaned, and examined for corrosion. General corrosion rates, calculated from weight loss measurements, and pitting density and depths were determined and reported (see Section 3.0, Results and Discussion).

2.1 Test Materials

The test materials included steel corrosion specimens (provided by WVNS from archived materials), vault water (water supplied by WVNS that had been pumped from the vault where it contacts the exterior surface of the waste tank), granular perlite (same material used for previous external corrosion tests), and purge gases (nitrogen and air). Details of these materials are given below.

2.1.1 Steel Corrosion Specimens

Test specimens used for the earlier external corrosion tests (Mackey and Westerman 1995) were procured to the ASTM A-516, Grade 55 specification. For the testing described here, WVNS requested that archived specimens of actual tank steel be used (specimens were originally fabricated from a section of plate removed from the top of Tank 8D-2 for new tank riser installations). Specimens were received from WVNS that had been used in other corrosion tests, then stored. As received, the specimens were coated with rust and bent into U-shapes, having been used as U-bend stress corrosion cracking specimens. At PNNL, these bent specimens were straightened and cleaned (per WVNS) so that the archived material could be used for the inerting tests.

Available records indicate that the ASTM designation for the type of steel used in fabricating Tanks 8D-1 and 8D-2 was ASTM A-201A. This designation has since been replaced with the designation ASTM A-516 (Grade 55 for carbon $< 0.18\%$), which has the same chemical composition and microstructure as material conforming to the earlier specification. [Microstructural and chemical analyses had previously been conducted, verifying conformance of the archived WVNS tank steel with the A-516 Grade 55 designation.]

Once the specimens were straightened, the surface was cleaned with 200-grit abrasive paper. [It should be noted that the specimens could not be restraightened to a uniformly flat surface during this preparation. Consequently, subsequent pit depth measurements were affected, as discussed in Section 3.0. Similarly, the surface preparation may not have removed all the surface defects that may have resulted from the previous corrosion testing, which may also have affected certain results for this test.] The dimensions of each specimen were measured with digital calipers to the nearest 0.025 mm. Typical specimen dimensions were 95 mm x 10 mm x 2.54 mm. A final thorough cleaning of the

specimens was performed in a 28-g/L tri-sodium phosphate/water solution, followed by deionized water rinsing and air drying. The specimens were then weighed on a 4-place analytical balance to the nearest 0.0001 g. Initial weights ranged from ~17.9 to ~18.5 g.

2.1.2 Vault Water

The water used in these tests was a portion of the supply sent by WVNS to PNNL for the earlier external corrosion tests. The analyzed composition of the water is shown in Table 2.1. The vault water was used for initial test setup. Deionized water was used for subsequent makeup water to compensate for evaporative losses over the course of the test.

Table 2.1. Composition of WVNS Vault Water Used in Nitrogen-Inerting Corrosion Tests

Chemical Species	Concentration, mg/L
Al	0.04
Ca	8.4
Fe	--
K	115
Mg	2.8
Na	99
Si	31.5
B	0.1
F ⁻	--
Cl ⁻	10.7
NO ₃ ⁻	3.26
SO ₄ ⁻	206
Total Carbon	34.4
Inorganic Carbon	32.3
Total Organic Carbon	2.1
pH	9.8
Conductivity, μ mho	925

2.1.3 Perlite

Perlite, a natural mineral, is the main component used to make the insulating bricks that lie underneath the tanks. Additionally, loose perlite was used to fill the joints between the bricks. This material is in direct contact with the tank bottom and may be a factor in corrosion of the steel. Therefore, perlite was used in contact with the corrosion specimens. The perlite material used for this test was taken from the same supply as used for the earlier external corrosion tests. This material was "unexpanded" perlite with a nominal particle diameter range of 2 to 4 mm (consistency of coarse sand). Table 2.2 shows the typical composition range for this product (originally obtained from Celite Corporation in Lompoc, California); however, this particular batch of perlite was not chemically analyzed prior to these tests.

2.1.4 Purge Gases

The purge gases used for this testing were bottled high-purity (99.997%) nitrogen and typical, laboratory-supply compressed air. Samples of the nitrogen gas were taken as each new supply bottle was placed into service. Table 2.3 shows the typical analysis for the nitrogen gas used for this test. The compressed air was filtered to remove any oils or other mists and particulates. Both gas streams were bubbled at ~100 mL/min through distilled water in "gas washing bottles" before the gas entered the test vessels to humidify the air and thus minimize water evaporation. This procedure was apparently effective since the amount of water evaporating from the vessels (that was periodically replenished by addition of deionized water) over an 18-month period was very small (typically from none to a few milliliters per month). Samples of the gas exiting the vapor space of the nitrogen-inerted vessel were taken at various times and analyzed to check for oxygen leaking into the vessel during the test. Typical analyses of the exiting gas indicated oxygen concentrations on the order of 0.1 to 0.6 mole %.

Table 2.2. Typical Composition of Granular Perlite Used in the Nitrogen-Inerting Corrosion Tests

Constituent	Range (wt%)
SiO ₂	72 - 75
Al ₂ O ₃	12 - 14
Na ₂ O	3 - 4
K ₂ O	4 - 5
CaO	0.5 - 1
Fe (total)	0.5 - 1
H ₂ O	3 - 5

Table 2.3. Analysis of Nitrogen Gas Used for the Nitrogen-Inerting Corrosion Tests, as Determined by Gas Chromatograph/Mass Spectrometer (GC/MS)

Species	Mole Percent
Nitrogen	99.92
Oxygen	0.055
Argon	0.01
Carbon Dioxide	0.0028
Carbon Monoxide	<0.01
Helium	<0.001
Hydrogen	<0.001
Methane	<0.01
Nitrous Oxide	<0.005
Other Nitrogen Oxides	<0.001
Ethane	<0.001
Other Hydrocarbons	<0.001
Ammonia	<0.001

which indicates that some oxygen was getting into the vapor space of the vessels. In a similar manner, it is expected that a nitrogen purge on the tank vaults would not be able to exclude 100% of the oxygen in the system.

2.2 Test Apparatus

The test apparatus consisted of two 4-L Teflon-lined vessels (similar to resin kettles) with removable lids. These vessels were partially immersed in and heated by a controlled temperature water bath, and were fitted with reflux condensers to minimize evaporation. A gas delivery system was set up to deliver constant low flowrates of humidified gases (one vessel with air, a second vessel with nitrogen gas) to the test vessels. Air and nitrogen flowrates were monitored by the rates of bubbles rising through each of the gas wash bottles. The vessel temperatures were monitored with thermocouples inserted through ports in the lids of the vessels. A sketch of the test setup is shown in Figure 2.1.

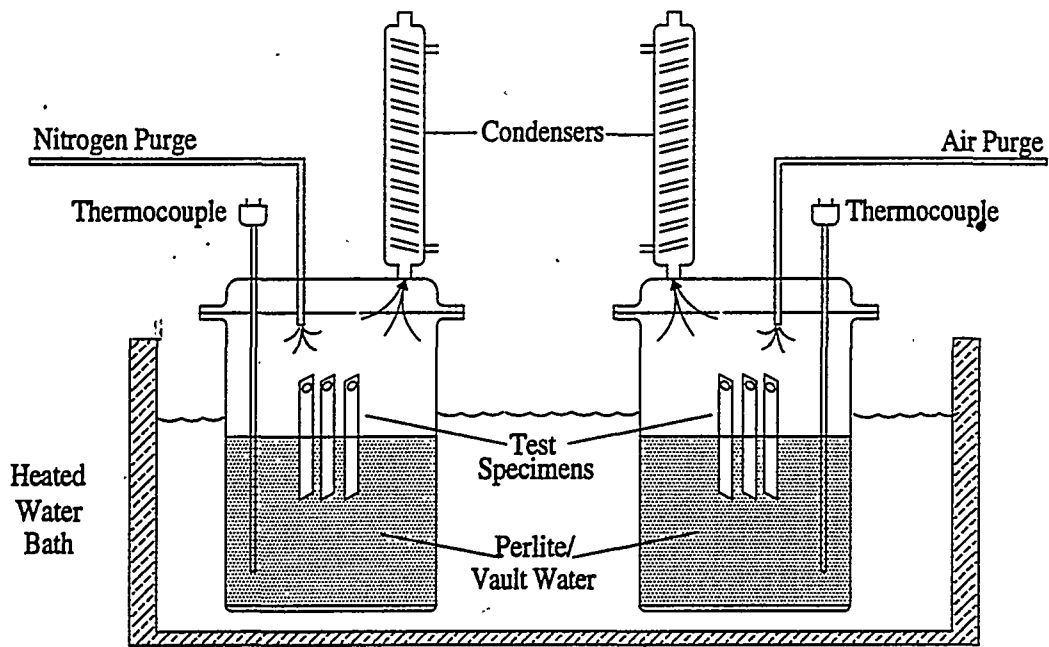


Figure 2.1. Apparatus with Test Specimens in Vessels Standing in Perlite/Water Mixture

2.3 Test Procedure

The tests exposed multiple steel specimens in vessels containing a mixture of water (water was pumped from the Tank 8D-1 vault and shipped by WVNS to PNNL) and granular perlite (simulating the perlite brick underlying the storage tanks). The gas supply tubing was run through the vessel lids down to near the bottoms of the vessels. The 4-L test vessels were then filled about one-half full with the granular perlite. Vault water was added to just cover the surface of the perlite. The nitrogen and air were bubbled up through the water-saturated perlite in the respective vessels for ~24 hr to equilibrate the water with the purge gas.

The vessels were reopened for a short period of time to insert the specimens. The specimens (nine per vessel) were arranged by pushing them down into the perlite so that the upper halves of their lengths were exposed to the vapor space of the vessels, and the lower halves were submerged in the perlite/water mixture. Once the vessels were sealed, the gas supply tubing was raised out of the perlite so that the purge gas flows were directed only into the head space (vapor space) of the vessels. The nitrogen-inerted vessel was purged in this manner for several minutes at a flowrate of several liters per minute of nitrogen to flush air from the vapor space. Meanwhile, the test vessels were placed in heated

water baths and maintained at $30^{\circ}\text{C} \pm 3^{\circ}\text{C}$ for the duration of the test. After the vapor space was flushed initially, the gas flowrates were decreased to ~ 100 mL/min and maintained at this rate for the duration of the test.

Originally, the test was to be conducted for 3 months. The test began with nine specimens in each vessel, with three specimens to be withdrawn from each vessel at the end of 1-, 2-, and 3-month exposures. Three specimens were taken out of each vessel at the end of the first and second months. However, at the end of the 3-month exposure, WVNS requested that the test duration be extended to 6 months. At 6 months, it was decided to remove one of the three remaining specimens from each vessel, and extend the duration of the test to at least 12 months. At the 12-month duration, an additional extension was made to add 6 more months. With the 18-month test it would then be roughly equivalent to, and could be more readily compared with, the 18-month examination of specimens from the earlier external corrosion tests.

Throughout the test, the vessels were monitored to ensure that the gas purge flowrates were constant, that water losses from humidifying the air and nitrogen in the gas wash bottles were replaced, that the temperature of the vessels (30°C) was constant, and that water did not evaporate from the vessels. What little water did evaporate from the vessels was periodically replaced to maintain the water level in the vessels just to the top of the perlite. Water needed for the nitrogen-inerted vessel was taken from the nitrogen wash bottle, since it had very low dissolved oxygen concentration.

Teflon tape was tied to the specimens to be removed without opening the top of the nitrogen-inerted vessel during the test (and therefore exposing the vapor space to air), and the tape was fed out through one of the ports in the vessel lid. The ports were then plugged with rubber stoppers. At the 1-, 2-, and 6-month intervals, those particular specimens were removed for examination by pulling them through the vessel port using the Teflon tape.

The coupons were examined by 1) observing the general appearance of the coupons as they were removed from the vessels, 2) cleaning the specimens in an inhibited acid cleaning solution to remove corrosion products, 3) weighing the cleaned specimens to then calculate corrosion rate from the weight loss, 4) microscopic examination to visually characterize the type(s) and extent of attack, and 5) measuring pitting depth with an optical micrometer.

3.0 Results and Discussion

Specimens were removed and examined at 1 month, 2 months, 6 months, and 18 months. Table 3.1 shows the results of corrosion rates calculated from the weight loss measurements. Two columns are presented for uniform corrosion rate: 1) "Measured," which is the calculated corrosion rate assuming uniform corrosion over the entire measured surface area of each specimen and 2) "Adjusted," since the corrosion was occurring almost entirely on only the bottom halves of the coupons. The adjusted values more accurately represent the actual uniform corrosion rates for the submerged halves of the specimens, assuming no significant metal loss due to nonuniform localized corrosion, such as pitting. The last column summarizes observations of localized corrosion and measured depths of deepest observed pits.

Following the 1-month exposure, those specimens removed for examination showed very little corrosion. The air-purged specimens had a little more "rust" colored oxide on the lower halves that had been embedded in the perlite/water. The specimens were then cleaned in inhibited hydrochloric acid to remove the corrosion products. The specimens were cleaned and dried and then reweighed to determine metal loss to corrosion. Calculated uniform corrosion for the lower halves of the nitrogen-inerted specimens averaged ~ 0.01 mm/yr, and for the air-purged specimens ~ 0.8 mm/yr. No pitting or other localized attack was noted on the 1-month specimens. The 1-month exposure specimens were then examined with the aid of a microscope and optical micrometer to identify and characterize areas of nonuniform attack.

Figures 3.1 and 3.2 show the typical appearance of the coupons after exposure in the test, and before removing the corrosion products with the inhibited acid cleaning. Figure 3.1 shows a specimen from each of the nitrogen-purged and air-purged vessels following 2 months exposure. The only visible attack was on the lower halves of the specimens that had been embedded in the perlite/water. Note that the vapor space exposure on the upper halves resulted in no corrosion on either of the specimens at this point. Following cleaning, uniform corrosion rates averaged about 0.013 mm/yr for the submerged portions of the nitrogen-inerted specimens, assuming no corrosion in the vapor space. A few shallow (< 0.025 mm deep) areas of localized attack were observed on the submerged areas as well, appearing as clusters of very small initiating pits.

Corrosion on the air-purged 2-month specimens was significantly greater on the submerged halves than on the nitrogen-inerted specimens. Calculated submerged uniform corrosion averaged ~ 0.08 mm/yr. These specimens also showed a greater number of areas of localized attack on the submerged halves with clusters of shallow pits ~ 0.025 mm deep or slightly greater.

The 6-month exposure specimens appeared very similar to the 2-month specimens (i.e., heaviest attack was on the submerged portions, insignificant corrosion in the vapor space). Calculated uniform corrosion rates for the submerged halves ranged from 0.0005 mm/yr for the nitrogen-inerted specimen to 0.07 mm/yr for the air-purged specimen. Pitting was observed on the lower halves of both specimens. The nitrogen-inerted specimen had far fewer pits with the deepest running to ~ 0.25 mm. The

Table 3.1. "Measured" and "Adjusted" Uniform Corrosion Rates and Deepest Pit Depths for Specimens After 1-, 2-, 6-, and 18-Month Exposures in the Nitrogen-Inerting and Air-Purging Corrosion Tests

Purge Gas	Exposure	Specimen ID	Corrosion Rate (mm/yr)		Observations & Pit Depths (mm)
			Measured ^(a)	Adjusted ^(a)	
Nitrogen	1 Month	X003	0.008	0.015	No pitting on vapor or submerged halves
Nitrogen	1 Month	X023	0.007	0.014	
Nitrogen	1 Month	X018	0.008	0.017	
Air	1 Month	X032	0.048	0.096	No pitting on vapor or submerged halves
Air	1 Month	X033	0.042	0.083	
Air	1 Month	X048	0.042	0.084	
Nitrogen	2 Months	X046	0.007	0.014	Few shallow pits (<0.025 mm) on submerged halves
Nitrogen	2 Months	X016	0.008	0.015	
Nitrogen	2 Months	X052	0.006	0.012	
Air	2 Months	X006	0.040	0.080	Slight vapor and interface pitting, heavier submerged corrosion (>0.025 mm)
Air	2 Months	X025	0.039	0.077	
Air	2 Months	X026	0.039	0.077	
Nitrogen	6 Months	X011	0.0002	0.0005	Few pits (0.25 mm) submerged only
Air	6 Months	X053	0.034	0.068	More pits (0.25 mm) submerged and vapor
Nitrogen	18 Months	X051	0.001	0.002	Few pits (0.6 mm) submerged only
Nitrogen	18 Months	X055	0.001	0.002	
Air	18 Months	X062	0.030	0.059	Much heavier (~0.5 to 0.6 mm) submerged
Air	18 Months	X063	0.030	0.061	

(a) "Measured" is calculated value for uniform corrosion, assuming weight loss is uniform over the entire surface of the specimen. "Adjusted" indicates that all the weight loss was assumed to occur only on the lower submerged half of the specimen.

air-purged specimen had a greater number of areas of localized attack on the submerged portion than on the nitrogen-inerted specimen. However, the deepest pits on this specimen also averaged ~0.25 mm.

Figure 3.2 shows similar specimens following 18 months exposure. As with the 2- and 6-month examinations, these specimens showed the heaviest corrosion on the lower, submerged portions. Additionally, there was slight but visible corrosion of the vapor space portions of the specimens, although for the "adjusted" uniform corrosion rate, corrosion on the vapor space portions was still considered

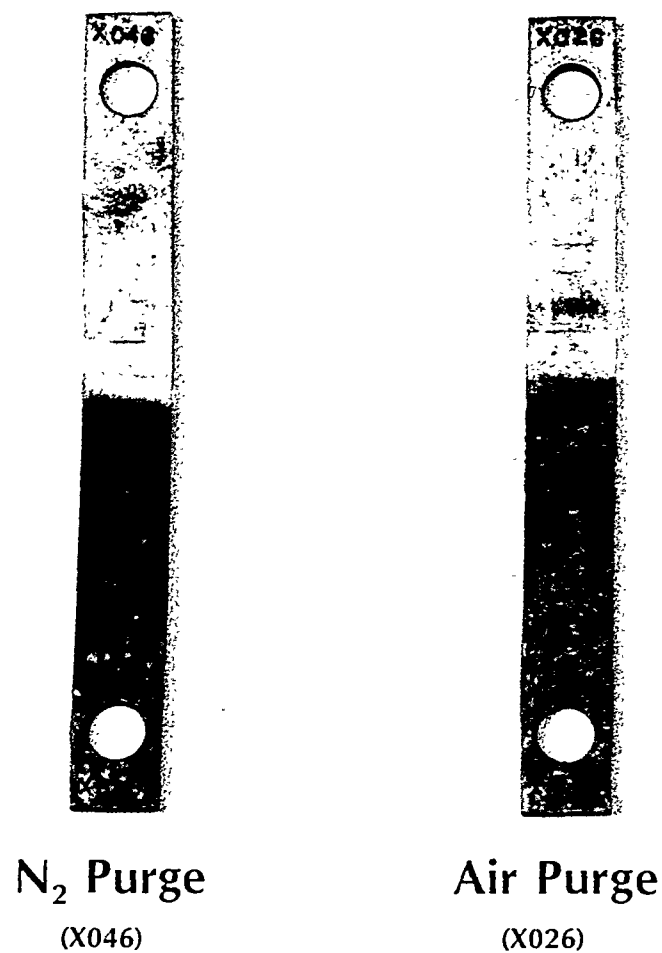


Figure 3.1. Specimens Following 2-Month Exposure at 30°C, Half Submerged in Perlite/Vault Water to Nitrogen Purge (Left) and Air Purge (Right). Both specimens show discoloration on the lower submerged halves, but actual corrosion of the air-purged specimen was noticeably heavier. Vapor space corrosion on both specimens was insignificant.

negligible. After these specimens were cleaned, the calculated uniform corrosion rates for the submerged halves ranged from 0.002 mm/yr for the nitrogen-inerted specimens to ~0.06 mm/yr for the air-purged specimens.

Overall, corrosion on both the nitrogen-inerted and air-purged specimens was significant only on the lower (submerged) halves of the specimens. Calculated uniform corrosion rates steadily decreased



N₂ Purge

Air Purge

Figure 3.2. Specimens Following 18-Month Exposure at 30°C, Half Submerged in Perlite/Vault Water to Nitrogen Purge (Left) and Air Purge (Right). Corrosion of the air-purged specimens was much heavier, resulting in perlite particles being trapped in the oxide layer on its surface. Vapor space corrosion on both specimens was negligible.

with time (as shown in Figure 3.3), and appeared to have reached an approximately steady-state condition by the end of the test at 18 months. The effect of the nitrogen-inerting is significant, decreasing the rate of metal corrosion by a factor of ~20 to 25. This corrosion inhibition was seen throughout the test from the 1-month examination to the final 18-month examination, having about the same magnitude of inhibition.

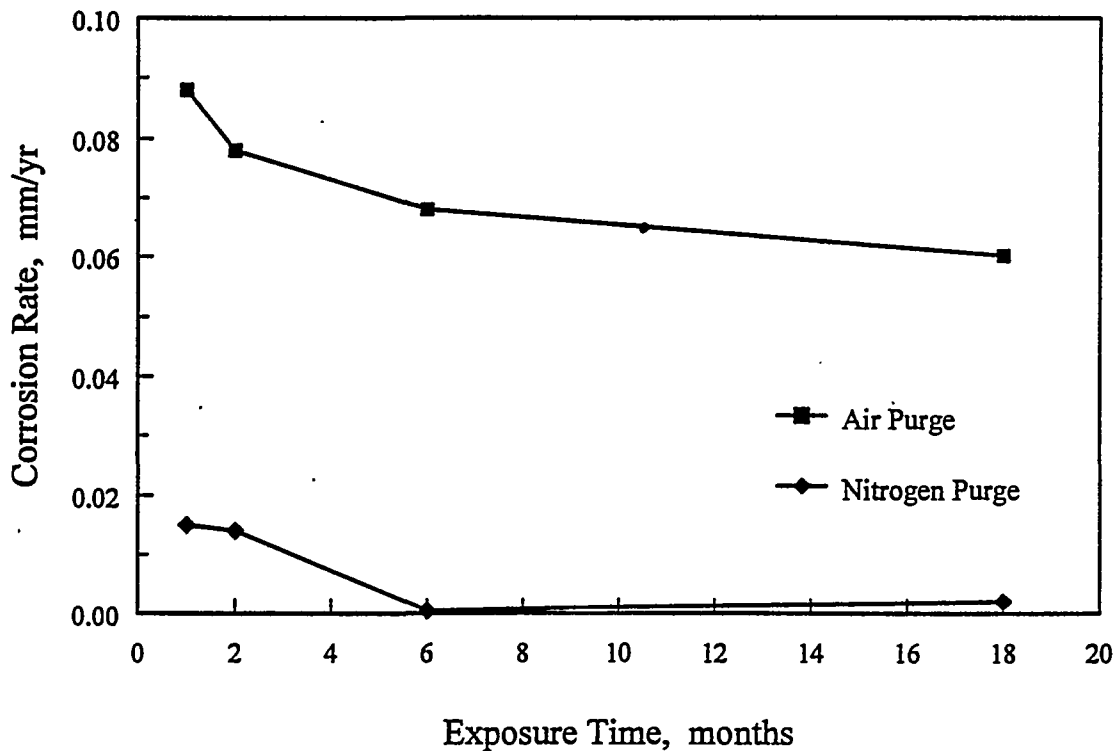


Figure 3.3. Calculated Uniform Corrosion Rates for Nitrogen-Inerted Versus Air-Purged Specimens. Rates adjusted for lower, submerged phase corrosion. Corrosion in the vapor space was negligible in all cases.

Corrosion in the vapor space was not a factor over the 18 months of the test. Some areas of localized vapor space attack were starting to appear on the 18-month specimens. However, it was negligible compared with the submerged attack. In the external corrosion testing (Mackey and Westermen 1995), by 18 months exposure, the corrosion in the vapor space was much more significant than at earlier intervals. One explanation may be that the corrosion products built up on the wetted, submerged portions of the specimens first, then began to accumulate at and finally above the air/water interface. These corrosion products then may have allowed the vault water to wick up higher on the specimens so that corrosion in the vapor space began to occur more rapidly after approximately 18 months. It is anticipated that the amount of vapor space corrosion occurring on the specimens from the nitrogen-inerting test would have continued to increase similarly.

An unexpected result from the nitrogen-inerting test was the apparent rate of pit deepening observed on the specimens. Like the calculated uniform corrosion rates, the number of pits that initiated and developed on the submerged portions of the nitrogen-inerted specimens were far fewer than those on the air-purged specimens. However, the depths of the deepest observed pits were similar for

nitrogen-inerted and air-purged specimens. This was consistent over the last several examination intervals of the test (2, 6, and 18 months) when pitting was observed. This result is more clearly illustrated in Figures 3.4 and 3.5. It should be noted that the depth of pitting on the air-purged 18-month specimens could only be estimated. Corrosion was heavy enough that there was no longer a clear point of reference to the original coupon surface from which pit depths could be accurately measured with the optical micrometer. In contrast, with the nitrogen-inerted specimens, nearly all the original surface was intact and the few pits had very sharply defined edges, providing excellent reference for the depth measurements.

This pitting observation suggests that, although the nitrogen purge takes nearly all the oxygen out of the vessel (and corrosion is significantly reduced as a result), there appears to be enough residual oxygen dissolved in the water to initiate a few pits. Once these pits initiate, there is apparently sufficient dissolved oxygen available to allow them (but only a very few of them) to continue to grow at a rate that is roughly the same as when oxygen is abundant.

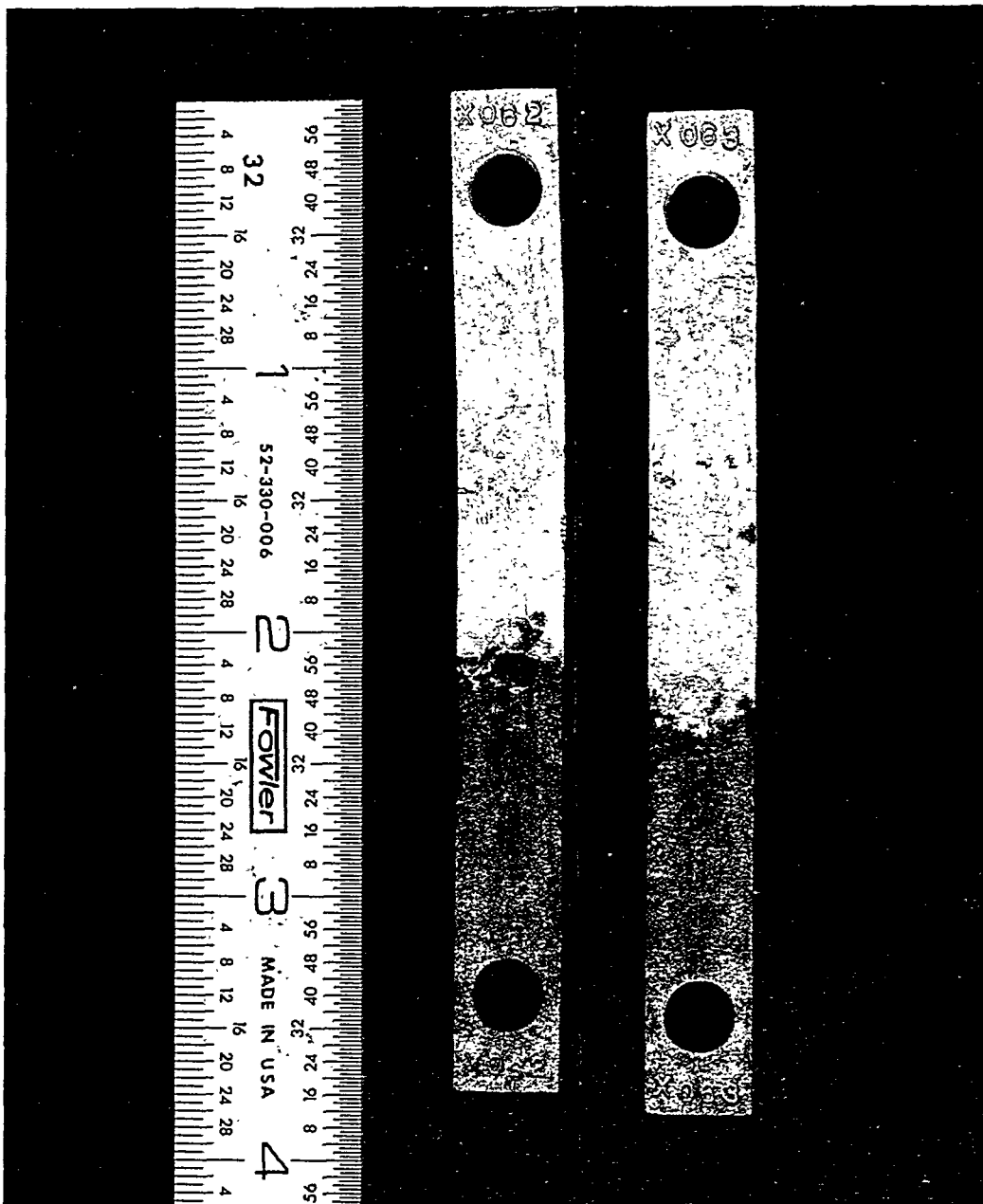


Figure 3.4. Cleaned Specimens from 18-Month, 30°C, Air-Purged Test. Corrosion on lower (submerged) half was extensive (estimated to be 0.5 to 0.6 mm penetration, and covered the entire wetted surface). Corrosion in vapor space was minimal.

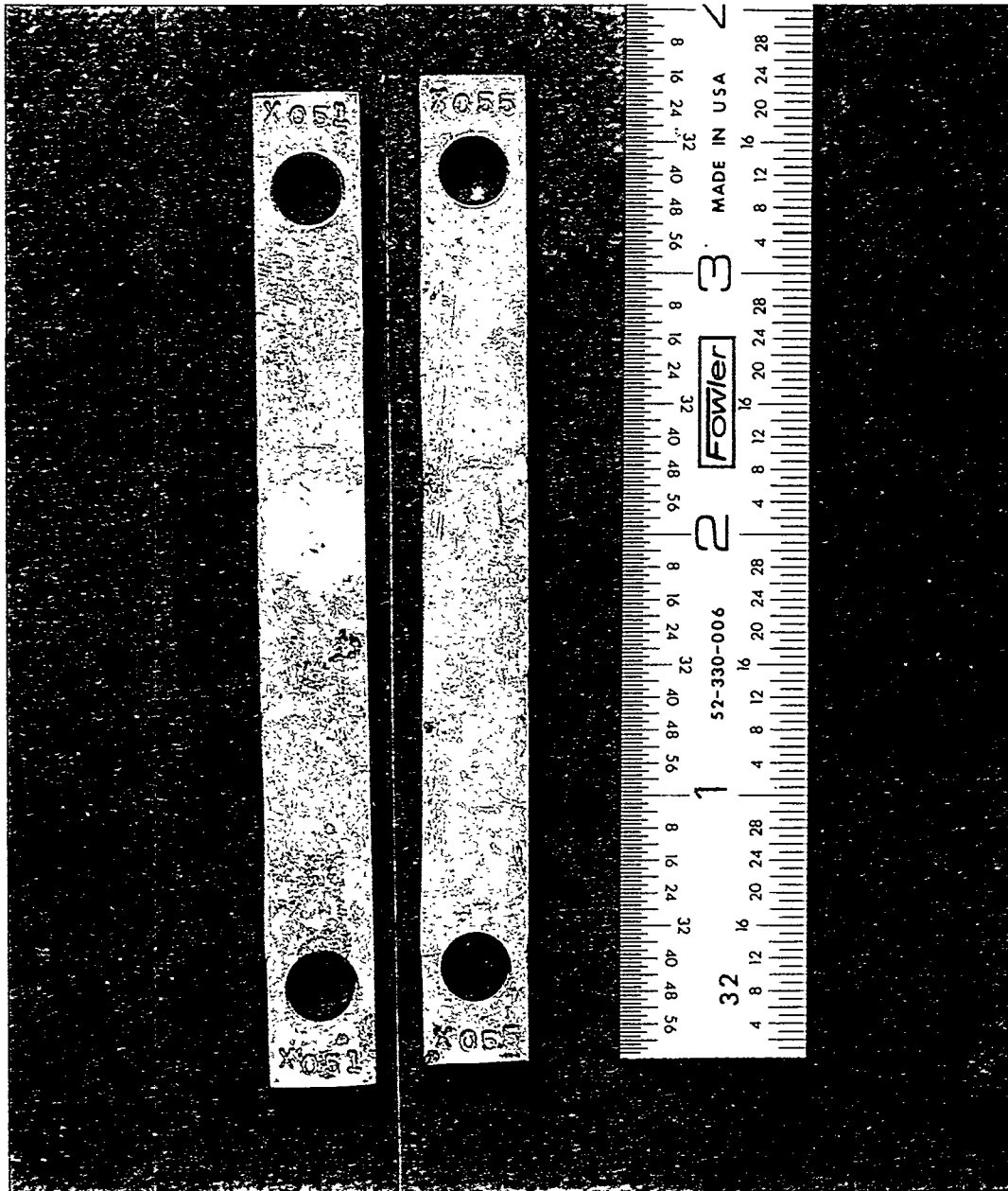


Figure 3.5. Cleaned Specimens from 18-Month, 30°C. Nitrogen-Inerted Test. Overall corrosion was minimal; most significant attack occurred on two areas on lower submerged half of each specimen where pitting was as deep as 0.6 mm. Vapor space corrosion was negligible.

4.0 Conclusions and Recommendations

The following conclusions and recommendations are based on the results of this study.

4.1 Conclusions

- Use of a nitrogen purge to inert the atmosphere and remove dissolved oxygen from water in corrosion tests of mild steel exposed to perlite/pan water at 30°C significantly decreased general corrosion (uniform corrosion and localized attack) of wetted portions of the test specimens.
- Exclusion of oxygen from the vapor space of the tank/vault annuli using an inert gas should greatly reduce corrosion of the mild steel tanks.
- General corrosion rates for the submerged portions of the air-purged specimens were much higher (~0.06 mm/yr) than for the nitrogen-inerted specimens (~0.002 mm/yr) by the end of the 18-month test.
- Vapor space corrosion was not significant for either nitrogen- or air-purged specimens by the end of the 18-month test.
- Amount of localized attack (primarily pitting) on the nitrogen-inerted specimens was much less than on the air-purged specimens. Although the overall amount of pitting was much less, the depths of the deepest observed pits on the nitrogen-inerted specimens (~0.6 mm after 18 months) were approximately the same as for the air-purged specimens (~0.5 to 0.6 mm after 18 months).
- The rate of pit deepening did not decrease significantly with time during the 18-month test (~0.5 mm/yr at 6 months and ~0.4 mm/yr at 18 months).
- The overall amount of pitting was significantly decreased by the lower oxygen potentials achieved by nitrogen inerting, but the rate of pit growth of the deepest pits was apparently not altered by the lower oxygen potential. Therefore, even lower dissolved oxygen concentrations may be necessary to significantly affect the rate of pit growth once pitting is initiated on the surface of the steel.

4.2 Recommendations

- Perform additional similar testing but with more effort to reduce oxygen to even lower levels to determine the effect, if any, on the pit deepening rate. This would help to better establish minimum operational requirements for the installed system.
- Dry the vaults and tanks to the greatest extent practicable. Test results show the importance of eliminating water from the vault.

- Perform additional similar testing but with “low” water level (specimens embedded in perlite but with vault water level below the lower end of the specimens) to see if moisture that can be wicked through the perlite to the specimen surface will have as much effect on corrosion as when the specimens are half submerged in water.
- Based on these laboratory tests, the most effective approach to controlling external corrosion of the tanks would be to 1) find and mitigate source(s) of intruding water and 2) displace oxygen and simultaneously remove additional water vapor from the vaults with heated nitrogen purges of the vaults.

5.0 Reference

Mackey, D. B., and R. E. Westerman. 1995. *West Valley Support Program - Final Report: External Corrosion of Tanks 8D-1 and 8D-2*. PNL-10570, Pacific Northwest National Laboratory, Richland, Washington.

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