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**CORROSION ANALYSIS OF DECOMMISSIONED CARBON STEEL
WASTE WATER TANKS AT BROOKHAVEN NATIONAL LABORATORY**

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P. SOO and T.C. ROBERTS

JULY, 1995

**ENGINEERING RESEARCH AND APPLICATIONS DIVISION
DEPARTMENT OF ADVANCED TECHNOLOGY
BROOKHAVEN NATIONAL LABORATORY
UPTON, NY 11973-5000**

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ABSTRACT

A corrosion analysis was carried out on available sections of carbon steel taken from two decommissioned radioactive waste water tanks at Brookhaven National Laboratory. One of the 100,000 gallon tanks suffered from a pinhole failure in the wall which was subsequently patched. From the analysis it was shown that this leak, and two adjacent leaks were initiated by a discarded copper heating coil that had been dropped into the tank during service. The failure mechanism is postulated to have been galvanic attack at points of contact between the tank structure and the coil. Other leaks in the two tanks are also described in this report.

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EXECUTIVE SUMMARY

In late 1994, three "D Waste" tanks at Brookhaven National Laboratory were decontaminated and decommissioned. The 100,000 gallon carbon steel tanks were constructed in 1949 and provided storage for radioactive water and sludge until they could be pumped out for evaporation and solidification. The waste water was usually slightly alkaline (pH 8.0 - 8.5) and the sludge, which was diatomaceous earth, was reported to be acidic (pH 5 - 6). During service, two of the three tanks suffered from a total of three leaks in their containment structure. One was repaired but the other two leaks eventually led to the tanks being retired.

During tank dismantlement, sections from two tanks were obtained in order to determine the likely failure mechanisms. Unfortunately, not all of the leaking areas were available for analysis since funding for the study was not available until much of the tanks' structure had been sectioned and placed in containers in readiness for disposal. However, the section in Tank D3 which contained the first leak was procured and a detailed study was possible. A second leak occurred the base of Tank D3 but the point of penetration was never determined.

A third leak in Tank D1 was known to have occurred at a threaded nipple on a valve and was evaluated shortly after the leak was detected in 1982. After attempts to repair the leak were not successful, the tank was retired in 1984. The valve had been discarded before the current study was initiated and, therefore, could not be re-evaluated. Tank D2 saw the least amount of service and never leaked.

Below is given a summary of the corrosion analysis, with the main focus being on Tank D3 and the original pinhole leak that was detected in 1985 after 22 years of service:

- a) There is evidence to show that the chlorinated rubber paint that was initially applied to the tank interiors could be effective in retarding corrosion. However, the paint had to be applied according to the manufacturer's recommendations for maximum performance. Unfortunately, the coating was not properly applied and this led to accelerated attack in some areas of the tanks.
- b) Under the corrosion conditions for the D Wastes, the uniform corrosion rate for the tank walls was about 4 mils/y. It was considerably less, and close to zero, in locations where the paint was adherent.
- c) The tank welds that were studied, including some where a drain line penetrated the tank, were of good quality. Dye-penetrant tests did not reveal any evidence for cracking.
- d) The first (pinhole) leak in Tank D3 almost certainly began as a result of contact with a copper heating coil that was installed to prevent the waste water from freezing in winter. The leak, which was repaired with a patch, and two other adjacent holes that were discovered during the analysis are postulated to have been

caused by galvanic corrosion at the points of contact of the tank structure and the coil. This type of failure may be avoided by either selecting compatible materials for components that are to be used in the tanks during service, or by avoiding the disposal in the tanks of materials that could cause galvanic attack.

- e) Pitting corrosion was observed on the external and internal surfaces of the tanks, but some of the pits may have been present during tank construction before painting had taken place.

ACKNOWLEDGMENTS

The authors are indebted to the following BNL staff (past and present) who willingly provided anecdotal information on the service conditions and operational procedures for the decommissioned D Waste tanks: M. Clancy, P. Edwards, S. Kurczak, R. Howe, E. Klug, A. Lukas, L. Phillips, and W. Sells. Eric Klug was of particular help in locating documentation on the dates for tank heater leakage, repair, and replacement. Staff of ENSR Corporation, including D. Carbery, D. Hall, and W. Koenig, and A. Tope of BNL were responsible for supplying the tank sections for the corrosion study as well as providing information on the condition of the tanks immediately prior to dismantlement. B. Bowerman was responsible for taking the photographs of the tank sections after they were received from ENSR Corporation. R. Stoutenburgh was the photographer for Figure 1. J. Heiser prepared the computer graphics in Figures 3 and 8. D. Gupta and P. Wu of the Department of Energy, and W. Gunther, K. Bandyopadhyay, and M. Reich of BNL provided encouragement for the study. J. Weeks and C. Czajkowski reviewed the manuscript and offered helpful suggestions. Finally, we acknowledge Ms. G. Webster for finalizing the report and preparing it for publication.

1. INTRODUCTION

In late 1994, three "D Waste" tanks at Brookhaven National Laboratory (BNL) were decontaminated and decommissioned. The tanks were constructed in 1949 and provided storage for radioactive water and other wastes until accumulated water and sludge could be pumped out for evaporation and solidification. During service, two of the tanks suffered from a total of three leaks. One leak was repaired but another leak resulted in a tank being drained and removed from service in 1984. The other two tanks remained in service until 1987, after which they were also drained and retired.

During the tank dismantling process, sections from two of the tanks were obtained to carry out a corrosion analysis to determine the reason(s) for the failures. However, since parts of the tanks had already been sectioned and the pieces stored in containers in readiness for disposal, not all failure locations were available for study. Below is given a description of the tanks' service environments and a corrosion analysis of some of the available sections from the tanks.

2. TANK SERVICE ENVIRONMENTS

The following information was obtained from written and verbal descriptions of the history of the D Waste tanks at BNL. Most of the written material is from references 1 and 2, and the verbal information was obtained from numerous BNL staff who had worked at the tank complex or had knowledge of it.

There were, prior to dismantlement, three above-ground low-carbon (mild) steel tanks in the complex, identified as D1, D2, and D3 (see Fig. 1). The tanks were part of the BNL Waste Concentration Facility whose function was to receive D Wastes (viz. radioactive water with a gross beta activity greater than 90 pCi/ml) and volume reduce them prior to disposal off site. The D wastes were received from the Brookhaven Graphite Research Reactor (BGRR), the Brookhaven Linear-Accelerator Isotope Producer (BLIP), the Hot Laboratory complex (Building 801), the High Flux Beam Reactor (HFBR), and several much smaller facilities that periodically generated waste volumes of several gallons or so. Tank service began in the early 1950s. They were of 100,000 gallon capacity, measuring 30 ft. in diameter by 20 ft. in height. The bases, walls, and conical roofs were 3/8 in., 5/16 in., and 3/16 in. thick, respectively. During construction the tanks were assembled by lap welding sections of steel plate. Stress relieving of the welds was apparently not performed. The tanks were placed on concrete pads containing drainage channels which were aligned along weld joints to help locate leaks if they occurred. Each tank was equipped with a steam heating system to prevent freezing of the contents during cold weather. They were initially of a long U-tube design that were inserted radially via a bolted flange through the north-eastern quadrant of the tank wall into the interior at a height of about 6 inches above the base. Unfortunately, the tubes failed early and several major repairs were undertaken. Eventually, the U-tubes were taken out of service, but left in place, and substitute heaters with a coil design were installed through a manway in the tank roofs. This will be described in more detail below.

Figure 1. View of the Three D Waste Tanks Prior to Dismantlement

The tank exteriors were originally primed with an oil-based red lead paint, followed by two coats of an aluminum paint. Internally, they were painted with two layers of "Amercoat #33." However, in 1950, pre-service examination showed that the chlorinated rubber coatings were severely deteriorated. Some of the paint was scaling and pitting, and rust eruptions were much in evidence. The manufacturer of Amercoat concluded that the failure of the coating was due to three factors:

- a) Too much time had elapsed between initial tank wall sandblasting and coating application,
- b) The required number of coatings (4) were not applied, and
- c) There was a considerable amount of overspray of the finish coats.

Based on an analysis by the BNL Chemistry Department and Report #ORNL-382, it was concluded that Amercoat would not be resistant to all of the solvents that would likely be present in the tanks during service. A number of remedial actions were considered but, based on interviews with BNL staff, none were implemented. Apparently, the tanks were placed into service in the early 1950's with the coatings in the degraded condition.

During tank operation, radioactive wastes were initially received at Building 801. For the largest volumes of water, which originated from the BGRR, neutralization was not always practical and the water was pumped directly into the tanks. Some of this water was acidic and included nitric acid that was used to dissolve targets from BGRR during a period up to the late 1950's or early 1960's. For other smaller batches of liquid, neutralization was usually carried out with NaOH or HNO₃ to minimize the potential for tank corrosion. No pH adjustments were made on liquids once they were pumped into the tanks. The average pH of the liquids in the tanks ranged between 8.0 to 8.5. Most of the radioactivity in the tanks came from disassembly of BGRR fuel in the reactor canal. However, the total amounts of radioactivity were small (in the range of 10⁻¹¹ to 10⁻⁷ Ci/ml).

The tanks were periodically pumped to remove water to prevent overfilling. At any given time they were between about one-third to two-thirds full. The water was pumped to Building 811, and often was blended with more radioactive wastes prior to evaporation. Large volumes of liquid were evaporated to a few hundred gallons of slurry, which was then pumped into another tank (the so-called flying saucer tank because of its shape). The slurry was periodically solidified and shipped to a disposal site. The tanks saw most active service during the period from 1958 to 1968. This is because the BGRR was retired in 1967, and the new HFBR, which replaced it, generated far less D waste water.

In 1987, Chem-Nuclear Systems, Inc. (CNSI), removed about 3700 cu. ft. of sludge which was virtually all contained in Tanks D1 and D3. Its removal was accomplished by adding water to the tanks and mobilizing the material with a sparger. It was mainly diatomaceous earth (a naturally-occurring amorphous SiO₂) that was used as a filtering and sorptive medium in the

BGRR Canal Cleanup System. Table 1 gives a radiochemical analysis of the sludges which were stated to have a pH in the range 5 to 6. However, this was not documented. The slurry was pumped into a total of 35 liners and solidified by adding lime and cement. The solidified waste was tested by Enwright Laboratories of Greenville, SC, using the Environmental Protection Agency's Extraction Procedure Toxicity Test parameters. Typical test data are shown in Table 2. Since the concentrations of heavy metals in the leachate are many orders of magnitude less than those permitted by the Environmental Protection Agency, they show that the solidified waste was not classifiable as "hazardous" but only radioactive. The waste was shipped to Hanford, WA, for disposal. An analysis of the small amount of residual water in Tank D2 is given in Table 3. The pH of the liquid was not given but it probably was in the range of 8.0 to 8.5, as stated above for average tank liquids.

There is no documented information on the presence of Cl^- , SO_4^{2-} , or other anions, apart from NO_3^- and OH^- , that could influence the corrosion of the steel tanks. If Cl^- or SO_4^{2-} were present, they would be in small concentrations and would be removed as the tanks were regularly emptied during service.

If it is assumed that the 3700 cu. ft. of sludge was equally distributed between the Tanks D1 and D3, and that it was not mounded, calculation shows that each would have contained about 30 inches of material. Observations showed, in fact, that it was less deep on the north sides of tanks because the water/sludge mixture was pumped out via a pipe in that general location.

Table 4 gives an analysis of the radionuclide content of one of many soil sample removed in 1992 from regions adjacent to the D tank farm. It was found that the soils were more contaminated in locations north of the tanks. The soil was also contaminated with small quantities of methylene chloride, toluene, pentane, and bis(2-ethyhexyl)phthalate.

After the desludging operations, a significant amount of processing equipment was left in Tanks D1 and D3 by CNSI. Also remaining in these two tanks were failed U-tube heaters and copper steam coils, which will be discussed below.

Table 1. Analysis of Sludges from Tanks D1 and D3.

By Teledyne Isotopes, Inc.
May 1, 1986

Isotope	T-1/2 (years)	$\mu\text{Ci/gm (wet)}$
Gross alpha	-	$1.2 \text{ to } 2.0 \times 10^{-1}$
Gross beta	-	$4.6 \text{ to } 6.5 \times 10^0$
^{90}Sr	29	$2.1 \text{ to } 2.8 \times 10^0$
^{99}Tc	2.13×10^5	$1.0 \text{ to } 1.8 \times 10^{-3}$
^{137}Cs	30.17	$5.9 \text{ to } 9.6 \times 10^{-1}$
^{60}Co	5.27	$0.5 \text{ to } 1.8 \times 10^{-2}$
^{14}C	5730	$<1 \text{ to } 8.8 \times 10^{-5}$
^3H	12.3	$0.5 \text{ to } 1.2 \times 10^{-2}$
^{234}U	2.45×10^5	$0.8 \text{ to } 1.5 \times 10^{-3}$
^{235}U	7.04×10^8	$1.6 \text{ to } 4.4 \times 10^{-5}$
^{238}U	4.47×10^9	$0.8 \text{ to } 1.2 \times 10^{-3}$
^{238}Pu	87.74	$0.9 \text{ to } 1.7 \times 10^{-3}$
^{239}Pu	2.41×10^4	$0.7 \text{ to } 1.2 \times 10^{-1}$
^{240}Pu	6.56×10^3	$3.1 \text{ to } 5.2 \times 10^{-2}$
^{241}Am	432	$0.5 \text{ to } 4.8 \times 10^{-2}$
^{242}Am	152	$0.3 \text{ to } 9.0 \times 10^{-2}$

Table 2. Results of Leachability Tests on Solidified Sludge

ENWRIGHT
LABORATORIES
CERTIFICATE OF ANALYSIS

CLIENT: Chem-Nuclear

DATE RECEIVED: 12/21/87

PROJECT: Brookhaven National Lab

DATE COMPLETED: 01/16/88

SAMPLE ID: Tank D-1

DATE REPORTED: 01/22/88

LAB NO.: 87-46302

LAB CERTIFICATION NO: 23127

Parameters:

Results

Toxic Extraction Procedure:

Arsenic (ug/l)	<50
Barium	0.8
Cadmium	0.07
Chromium	<0.05
Lead	<0.2
Mercury (ug/l)	<0.5
Selenium (ug/l)	<5
Silver	<0.02

The above results are reported in milligrams per liter unless otherwise noted.

Analytical methods are those approved by the U.S. Environmental Protection Agency.

Please call Steve Hoeffner, your service representative, if you have questions concerning this report.

Respectfully submitted,

ENWRIGHT LABORATORIES, INC.

Charles H. Reece, Ph.D.
Laboratory Manager

Table 3. Analysis of Residual Water from Tank D2.

Waste Concentration Facility Tank D-2 Water Data (pCi/L)

Date	Zinc Sulf Alpha Act	Gross Alpha Act	Gross Beta Act	Gamma Spectroscopy Data					
				Cs-137 Act Top	Cs-137 Act Bottom	Cs-134 Act Top	Cs-134 Act Bottom	Co-60 Act Top	Co-60 Act Bottom
6/23/88	5.28E3 ±8%	NA	6.89E6 ±0.3%	5.574E6 ±0.5%	5.28E6 ±0.7%	9.29E3 ±15%	ND	ND	ND
6/30/88	1.06E4 ±6%	NA	7.35E6 ±0.3%	5.43E6 ±0.5%	5.14E6 ±0.4%	7.5E3 ±36%	ND	ND	ND
7/7/88	15.5 ±383% <139	NA	5.89E6 ±0.3%	5.76E6 ±0.3%	-	6.20E3 ±4%	-	2.43E3 ±27%	-

Mean Cs-137 Conc. = 5.436E6 ± 2.42E5 pCi/L (5%, 1σ) N=5
 Mean Cs-134 Conc. = 7.663E3 ± 1.55E3 pCi/L (20%, 1σ) N=3
 Mean Gross Beta Conc. = 6.71E6 ± 7.465E5 (11%, 1σ) N=3
 Estimated Sr-90 Conc. = (Gross beta conc. -1.110 Cs-137 - Cs-134)/2
 = 3.342 E5 pCi/L

Assumption

1. The quantity of material released from D-2 has been estimated to be 6000 gallons ±100 gallons.
2. To obtain the Sr-90 component from the gross beta data one can subtract gamma detected beta and then divide the answer by 2 to account for Y-90.

NA: Not Analyzed
 ND: Not Detected

Table 4. Analysis of a Soil Sample from the Waste Tank Site.

Isotope	Concentration (pCi/g)		
	Depth 0-2 ft	Depth 0-2 ft (Duplicate Sample)	Depth 5-7 ft
Actinium-228	1.36 +/-0.41	1.33 +/-0.31	0.93 +/-0.3
Americium-241	<0.1	<0.1	<0.1
Americium-243	<0.1	<0.1	<0.1
Californium-249	<0.1	<0.1	<0.1
Californium-250	<0.1	<0.1	<0.1
Californium-251	<0.1	<0.1	<0.1
Californium-252	<0.1	<0.1	<0.1
Cesium-137	0.33 +/-0.03	0.35 +/-0.02	0.05 +/-0.02
Cobalt-60	<0.03	0.3 +/-0.02	<0.02
Curium-242	<0.1	<0.1	<0.1
Curium-243	<0.1	<0.1	<0.1
Curium-244	<0.1	<0.1	<0.1
Curium-245	<0.1	<0.1	<0.1
Curium-247	<0.1	<0.1	<0.1
Curium-248	<0.1	<0.1	<0.1
Tritium	<0.5	<0.5	<0.5
Neptunium-237	<0.1	<0.1	<0.1
Plutonium-236	<0.1	<0.1	<0.1
Plutonium-238	<0.1	<0.1	<0.1
Plutonium-239	<0.1	<0.1	<0.1
Plutonium-240	<0.1	<0.1	<0.1
Plutonium-241	<0.1	<0.1	<0.1
Plutonium-242	<0.1	<0.1	<0.1
Polonium-210	<0.1	<0.1	<0.1
Potassium-40	5.9 +/-0.8	9.3 +/-0.5	7.4 +/-0.6
Radium-226	0.56 +/-0.09	0.70 +/-0.06	0.42 +/-0.07
Radium-228	1.4 +/-0.4	1.3 +/-0.3	0.9 +/-0.3
Strontium-90	1.68 +/-0.77	0.66 +/-0.40	<0.03
Technetium-99	<0.9	<0.9	<0.9
Thorium-228	<0.1	<0.1	<0.1
Thorium-230	<0.1	<0.1	<0.1
Thorium-232	0.99 +/-0.10	1.02 +/-0.07	0.56 +/-0.009
Uranium-232	<0.1	<0.1	<0.1
Uranium-233	<0.1	<0.1	<0.1
Uranium-234	<0.1	<0.1	<0.1
Uranium-235	<0.1	<0.1	<0.1
Uranium-238	<0.1	<0.1	<0.1

3. CHRONOLOGY OF TANK LEAKS

Tank D1 began service in January, 1952. In 1960 a leak developed in the U-tube heater. The level of sludge in the tank prevented it from being removed for repair and a new heater of a different design was installed in 1961. It was made from 3/4 in. diameter copper tubing that was bent into a coiled configuration about 2 ft. in diameter, with a pitch of about two inches. The coiled length was about 3 ft. long. The new heater was inserted through the manway in the tank roof which was close to the northwestern wall. After further leaks and repairs the heater was cut off in 1971 and allowed to fall to the bottom of the tank and a new similar coiled heater was installed, again through the manway. The tank developed a leak in late spring of 1982 around a threaded nipple on a valve on the base of the tank. The valve was located in a depression in the concrete pad about 12-18 in. away from the north-northwest tank wall. Due to the inaccessibility for repairs, the tank was taken permanently out of service in 1984, and as much free liquid as possible removed. Seepage continued to occur, however, because of residual water present in the sludge.

Initially, Tank D2, the spare, did not have a heater. It began to receive wastes in 1958 and a heater of the original straight U-tube design was installed in 1960. A leak developed a year later, and it was repaired and reinstalled in 1962. It was eventually replaced by a copper coil (year unknown) which, as for Tank D1, was inserted through the manway. This coil remained in place until tank dismantlement. The tank was retired in 1987.

Tank D3 entered service in April, 1953. The heater leaked in October, 1958, and it was replaced by a heater of the original design in December, 1960. New leaks occurred and were repaired until September, 1961, when a new coiled heater was installed through the manway. This also began leaking and it was replaced in October, 1963, and the old coil allowed to fall into the tank. A tank leak was detected in February, 1985, in the form of a pinhole on the northwest side of the tank about three inches from a weld and eight inches above the base of the tank. The leak rate was less than one gallon per day. An external patch was welded over the leaking area, and the tank was returned to service. A gap of about 1.5 inch existed between the patch and the tank wall, which would have allowed water to leak into the space. A second leak developed in January, 1987. It was concluded that the leak occurred as seepage in a welded seam between the base of the tank and the wall in the southeastern quadrant of the tank. However, this could not be verified. In fact, one BNL staff member believes that the leak could have been in the base of the tank, with water emerging at the wall/base interface. Liquid was removed from the tank in summer 1987; it was not returned to service. An attempt was made in the current study to locate the point of failure but the affected area had already been discarded.

In addition to the copper heater coils, other metal debris left on the bottoms of Tanks D1 and D3 during service included parts from the failed water-level gage system as well as debris that probably originated from the disassembly of BGRR fuel elements. This latter debris is thought to have been small pieces (1/4-3/8 in.) of crumbling uranium fuel. Additional debris left in the two tanks after desludging in 1987 consisted of miscellaneous contaminated processing equipment.

The tanks remained inactive until late 1994, when they were sectioned and removed for disposal by ENSR Corporation. Between 1987 and 1994 the tank interiors were still damp or wet. Therefore, a significant amount of corrosion probably continued in this period. Much of the loose rust on the tank interiors was removed by ENSR using a water jet procedure. The tanks were sectioned with a flame cutter, and the pieces were placed in containers in readiness for shipping to the disposal site. For the current study, selected pieces from Tanks D1 and D3 were obtained for corrosion-failure analyses.

Figure 2 summarizes the chronology of waste tank operations and decommissioning.

Key:

- a) Tank construction completed.
- b) Tank service begins.
- c) U-tube heater leaks.
- d) Copper heater coil installed through manway,
- e) New coil heater installed, old heater discarded in tank.
- f) Tank leak detected.
- g) Tank retired.
- h) Water and sludge removed to the extent possible.
- i) Tank dismantled.

Figure 2. Chronology of Tank Operations and Decommissioning.

4. TANK SAMPLE SELECTION

By the time funds were approved for the current study, much of the tank sectioning work had been completed, with tank pieces already stored in containers. No attempt was made to retrieve any of them because it would have been impossible to specify where individual pieces were originally located during service. The tank samples studied were from sections that were still in place.

Primary interest in this work was focussed on Tanks D1 and D3, since these were the ones that had leaked. The section from Tank D1 containing the leaking valve nipple was not traceable. However, a section of this tank's base was obtained for evaluation. The piece selected included areas that showed large as well as small amounts of corrosion so that a comparison could be made. Four pieces were selected from Tank D3. All were L-shaped pieces that included part of the tank wall and base. Figure 3 is a schematic of the locations of the pieces. Piece #3 is the most important since it contains the leakage area in the tank wall that was patched in 1985. It was interesting to note that, in addition to this leak, two more large holes were observed in the adjacent tank base. The three holes were large, measuring between 0.5 to 1.0 inches in diameter. It seems probable, that the base holes had increased to this size after the tank had been taken out of service and the water removed. If this were not the case, the leak rates would have been far higher than those observed, unless the scale and sludge were able to act as effective plugging materials.

Piece #1 from Tank D3 was selected since it contained a flange and section of 6 in. pipe that was part of the tank drain line that led to the evaporator. The intent was to examine the welds in this region to determine if they were potential sources of leakage because of the relatively complex geometry and extra welds which could cause high residual stresses. The other two pieces from Tank D3 (#s 2,4) were chosen as controls. Since, as noted above, the tank samples had their internal surfaces cleaned with high-pressure water to remove loose scale, some information on the nature of the corrosion processes within the tanks was unavoidably lost.

Figure 4 shows an as-polished section of the base of Tank D1. The cracked surface scale is on the external tank surface that contacted the concrete pad. Figure 5 is an etched section through the tank base interior surface, also showing corrosion scale. The metallurgical structure is a mixture of white ferrite grains interspersed between darker pearlitic material, which is typical of carbon steel. Table 5 gives a chemical analysis performed on the steel by the Long Island Testing Laboratories, Inc., as part of the current study. Except for the sulfur content, which is slightly in excess of the normal maximum of 0.05%, the steel conforms to low-carbon (mild) steel.

Figure 3. Schematic Showing Sample Locations Cut From Tank D3.

Figure 4. As Polished Section Through the Tank D1 Base Showing Surface that Contacted the Concrete Pad. Magnification 80X.

Figure 5. Etched Section Through the Tank D1 Base Showing Corrosion Scale and Steel Microstructure. Magnification 80X.

Table 5. Chemical Analysis of Steel From the D Waste Tanks

Element	Concentration (wt. percent)
C	0.209
Mn	0.40
P	0.011
S	0.051
Si	0.009
Cu	0.30
Fe	Balance

5. CORROSION ANALYSES

After CNSI had removed the sludges in 1987, the bases and walls of the tanks were cleaned with low-volume, high-pressure water. The water was removed and later incorporated into cement. Soon after this had been accomplished, BNL personnel entered the tanks and obtained the first direct information on interior tank corrosion. They found that the Tank D1 floor was in "fair" condition and still showed signs of the original Amercoat paint. On the other hand, the tank walls were in a "poor" and corroded state. Inside the tank were the remains of the original U-tube steam heater, replacement copper steam coil, piping, and other debris.

Tank D2, the newest and least used vessel, was in "good condition". This tank had no debris on its base and it accumulated very little sludge during its service life. The copper heater coil and its associated plumbing was still suspended from the manway, but it was in a degraded state. There remained about one inch of water plus a cement-like residue that was later removed during tank dismantlement in 1994. Except for the corroded heater coil, it was concluded that this tank could have been returned to service.

Tank D3 was in "poor" condition. The floor was pitted and the walls were heavily corroded with large sheets of loosely attached rust. Much debris was also present on the base of the tank, including a copper steam coil. The metal debris had not been removed by CNSI after desludging operations in 1987. It was retrieved by ENSR as part of the tank dismantlement effort in 1994.

5.1 Analysis of Tank D3

Figure 6 shows a photograph of Piece #3 (see Fig. 3). The base section was heavily rusted. The wall still shows the presence of the white Amercoat paint. A large slightly elongated hole about one inch in diameter is indicated by an arrow. This is the site of the original pinhole leak. Two additional holes were detected in the adjacent base section about two inches apart adjacent to a weld seam. One was about one inch in diameter and the other about half this size. The larger hole is also marked by an arrow in Figure 6, but the smaller base hole is not easily seen. Figure 7 shows the welded patch over the original leak. The 1.5 inch air gap between the patch and tank wall is clearly visible. Figure 8 is a schematic of Piece #3. As discussed, above, the holes in the tank floor probably increased in size after the tank had been drained.

Figure 9 is a horizontal section through the hole in the Tank D3 wall. Material on either side of the hole was mounted in separate epoxy samples. The circular structures in the figure are spring clips used to orient the metal specimens during mounting. The large loss in wall thickness is very evident, and the extended area of tapered metal in the vicinity of the hole is clearly seen. The flat side of the tapered material corresponds to the external surface of the tank. Figures 10 and 11 show, respectively, sections through the large and small holes in the base of Tank D3. Tapering of the steel in the vicinity of the hole is, again, very noticeable.

Figure 6. Photograph of Piece #3 from Tank D3 Showing Large Holes (Arrows). Ruler in Front of the Section is Six Inches Long.

Figure 7. Photograph of Piece #3 from Tank D3 Showing Patch Welded Over Site of First Pinhole Leak.

Figure 8. Schematic of Piece #3 from Tank D3 Showing Locations of the Three Holes.

Figure 9. Horizontal Section Through the Hole in the Tank D3 Wall. Note the Tapering of Material as it Nears the Edge of the Hole. Magnification 2.1X.

Figures 12 and 13 show micrographs of the surfaces on the tapered material around the hole shown in Figure 9. On the exterior wall of the tank a deep pit is seen covered by a lighter corrosion layer. Figure 13 shows the internal corroded area near the hole. A loose detached corrosion scale is seen, which itself is covered by a dark gray layer (between arrows) which is a remnant of the Amercoat paint. An interesting point to note is that the steel was corroded away, but the paint layer stayed in close proximity to the corroding surface. This suggests that as the Fe^{2+} ions entered solution during corrosion, they were able to pass through the Amercoat layer, either directly or through flaws in the paint. Possibly, the crevice region between the steel and paint was acidic, which prevented the precipitation of corrosion products.

Figure 10. Section Through the Larger Hole in the Tank D3 Base. Magnification 3X.

Figure 11. Section Through the Smaller Hole in the Tank D3 Base. Magnification 3.3X.

Figure 12. Section Through Material Close to the Hole in the Tank D3 Wall (Exterior Surface) Showing a Dark Pitted Area Covered by a Lighter Corrosion Layer. Magnification 80X.

Figure 13. Section Through Material Close to the Hole in the Tank D3 Wall (Interior Surface) Showing a Light Irregular Scale Covered by a Dark Paint Layer Between Arrows. Magnification 80X.

The sizes of all three holes in Piece #3 and the severe thinning of the adjacent steel are not typical of that expected for a simple pitting type failure. Therefore, an alternate failure mechanism must be postulated. Their close proximity to each other suggests that they are of related origin. None of the other three samples from Tank D3, or the other failure in Tank D1 at a threaded nipple on a valve, suffered from this type of shallow penetration.

It is postulated that the failures in Tank D3 were a result of galvanic corrosion arising from the presence of a discarded copper heater coil. The following facts are consistent with, but do not verify, this conclusion:

- a) The coils were suspended from the tank manway during service and were disconnected and allowed to drop into the tank when they had failed. The manway is directly above the location where the holes appear. Based on periodic sampling of the sludges it is known that they were highly fluid since small lead sampling "pigs" used during service readily contacted the bottoms of the tanks. Heavy copper coils would also have sunk into the sludge.
- b) Galvanic attack is likely for copper-steel couples and it can occur with great rapidity^(2,3). Since the steel is anodic to the copper, the tank will suffer corrosion and metal loss. The presence of NaOH and HNO₃ in the D waste water will increase electrical conductivity of the water, which will enhance the corrosion rate. The presence of paint apparently did not prevent attack and eventual failure.
- c) The distance between the two holes in the base of the tank is about two inches, which is approximately equal to the average pitch of the coils. Thus, these holes were probably formed by contact with adjacent loops in the coil. The coil also contacted the tank wall and gave rise to the first pinhole failure. Since the coil was dropped into the tank in 1963, and the pinhole leak was detected in 1985, it took 22 years to cause tank failure by galvanic attack. In the following years of service, the hole continued to increase in size, but the patch prevented further leakage from this area.
- d) The tapered metal loss around the holes is readily explainable in terms of the small angles of contact that a coil would have with the base and walls of the tank. This would encourage a large area of corrosion to occur around the points of coil-to-tank contact. Such a geometry is not consistent with a pitting type of attack. Indeed, if pitting alone was the cause of this failure, it is improbable that the three holes would have appeared in the same general location.

- e) No failures occurred in Tank D2 which contained no discarded coils. Tank D1 contained a copper coil but it was not discarded until 1971. Therefore, the time available for galvanic attack was about eight years less than for Tank D3 and penetration did not occur.

The above information, then, strongly supports the contention that the practice of discarding copper coils into Tank D3 resulted in galvanic corrosion failure. Since the steel tank is anodic to the copper, the steel enters solution as ferrous ion, releasing electrons that travel to the copper cathode. These electrons must be consumed if the corrosion process is to proceed. Two cathodic reactions may be postulated ⁽⁵⁾. If there is available oxygen in solution the following reaction is possible:

Since the sludge was very fluid, it would have been aerated as water was pumped into and out of the tanks.

The second possibility involves the reduction of hydrogen ions:

However, it has been stated that this reaction does not appear to be applicable for copper⁽⁶⁾.

Figure 14 shows a section through the Tank D3 wall about 4 in. below the site of the large hole. The presence of corrosion scale, and perhaps the Amercoat paint, is just visible as a gray broken layer. Little corrosion is seen and the wall thickness remains at the original 5/16 in. However, Figure 15, which is a section through the base also close to the hole, shows severe metal loss. The wavy nature of the inner tank surface indicates that there were local differences in the rate of corrosion, but attack was basically "uniform" at a rate of about 4 mils/y. This may be compared with the corrosion rate of 10 mils/y for low-carbon steel in water saturated with 6 ppm of oxygen⁽⁷⁾. If the sludge effectively reduces the oxygen level to a lower value, the observed 4 mils/y rate seems reasonable.

From the history of heater failures in the tanks described above, it seems quite possible that the short service lives of the original U-tube heaters could also have been caused by galvanic attack. The tubes were made of copper and were connected to steel flanges that contacted the tank walls. At least one recorded leak was in a rolled joint between the tube material and, presumably, the flange. Galvanic attack would be possible in this joint because of dissimilar metal contact. However, this mode of failure is speculative since actual failed U-tube heaters were not available for study.

Figure 14. Section Through the Tank D3 Wall About Four Inches Below the Site of the First Pinhole Leak. Magnification 2.3X.

Figure 15. Section Through the Tank D3 Base About Twelve Inches from the Two Holes. Magnification 1.8X.

Piece #1 from Tank D3 was also examined for evidence of corrosion, although this tank location, which contained a 6 in. drain line, had not been a source of leakage during service. Figure 16 shows the blanked off pipe on the tank's exterior. The arrow points to the remains of insulation that had been originally applied over the pipe-to-wall weld joint. Figure 17 shows the pipe from the inside of the tank. The inner surfaces still show the presence of the white Amercoat paint. A sharp instrument was used to remove the paint and corrosion scale from welded regions around the pipe and at wall-base locations. Following this, a small grinding tool attached to an electric drill was used to remove oxide scale until bare weld metal was reached. Dye penetrant tests were then conducted to determine if any of the welds had cracks present. None were observed. From the studies carried out on Piece #1, all weld material studied appears to be of good quality.

Piece #4, a control from the northeastern section of Tank D3, was examined also. Figures 18, 19, and 20 show the outer surface including a vertical lap weld, the inner surface, and the tank base, respectively. Visual observation indicated that all welded material was in good condition with no signs of attack. The base of the tank, which was in contact with the concrete pad, showed severe scaling but there did not appear to be any region where penetration was imminent. The other control sample, Piece #2, is shown in Figures 21 and 22. It was cut from the north wall and base of the tank. The Amercoat paint is still present on the internal wall but it had been lost from part of the tank base, possibly as a result of desludging operations or water jet cleaning prior to dismantlement. No evidence for excessive weld corrosion or cracking was found by visual examination.

The cause of the second failure in the southwestern quadrant of the Tank D3 cannot be determined at this time because of the inability to locate the exact point of penetration. It may not have been caused by galvanic attack because the copper coils were deposited on the other side of the tank.

Figure 16. Blanked Off Drainage Line from Tank D3. Remnants of Insulation Around Pipe Indicated by Arrow.

Figure 17. Drainage Line in Tank D3 Seen From Within the Tank. Scale From Wall-to-Base Weld Was Removed to Check Weld Integrity.

Figure 18. Outer Surface of Piece #4 from Tank D3 Showing Vertical Lap Weld.

Figure 19. Inner Surface of Piece #4 from Tank D3 Showing Lap Weld.

Figure 20. View of Piece #4 From Tank D3 Showing Corroded Surface that Contacted the Concrete Pad.

Figure 21. View of Piece #2 From Tank D3 Showing Remains of Amercoat Paint on Internal Tank Surfaces. Paint Was Lost From Part of the Tank Base.

Figure 22. View of Piece #2 From Tank D3 Showing Part of External Tank Wall.

5.2 Analysis of Tank D1

A sample was taken from the base of Tank D1 during dismantlement. The only leak in the tank was at a threaded nipple on a valve which, unfortunately, was unavailable for study. Figure 23 shows a section through one of most corroded locations. The Amercoat layer is still visible as a gray layer on the upper surface, but it did not prevent relatively severe corrosion from occurring. As was mentioned above, examination of the coating shortly after application showed that it had blistered and some regions had flaked away from the steel substrate. For the surface in contact with the concrete pad, non-uniform corrosion was also observed, including a large indented area.

Figure 24 is a section through the base in a region that was not severely corroded. After 32y of service and 10y in retirement, this section of the tank base had experienced little metal loss. Apparently, the Amercoat paint (shown on upper surface) was quite effective in this location. Also, little attack is seen for the surface that contacted the concrete pad.

Figure 23. Section Through the Base of Tank D1 in an Area Showing Severe Attack. Amercoat Paint Layer is Seen on Upper Surface. Magnification 3.1X

Figure 24. Section Through the Base of Tank D1 in an Area Showing Minimal Attack. Magnification 3X.

6. CONCLUSIONS

A corrosion analysis was conducted on available pieces of material obtained from the carbon steel D waste tanks at BNL, which were in service for up to about 35 years. This was followed by a retirement period of seven years during which residual moisture in the tanks would have allowed additional corrosion to occur. Below are given conclusions from the study, which are based on limited available tank material and service data:

- a) There is evidence to show that Amercoat #33 rubberized paint can effectively minimize local and uniform attack of carbon steel tanks under the water and sludge conditions for BNL D type wastes. The major criterion for success is that the paint be applied using the manufacturer's recommendations. If the paint is not properly applied, areas of poor adhesion will allow both localized and uniform corrosion to occur.
- b) Under Tank D3 service conditions, limited measurements from a sample taken from the wall gave an average uniform corrosion rate of about 4 mils/y. It was considerably less, even approaching zero, in areas where paint was effectively applied.
- c) The welds that were examined in the current study, including those at the 6 in. drain line from the tank wall, appear to be of good quality. Dye-penetrant tests did not detect any evidence for cracking in the small number of samples studied.
- d) The original U-tube heaters suffered early leakage. Since the tubes were fabricated from copper and were connected to steel flanges, it is possible that the leaks were a result of galvanic attack. This is speculative, however, since the actual heaters could not be examined.
- e) The first pinhole leak in the wall of Tank D3 almost certainly began as a result of contact with a discarded copper heating coil. Attack was in the form of galvanic corrosion with the anodic tank material corroding at the expense of the more noble copper. It took 22 years for the pinhole leak to appear. The presence of any Amercoat paint between the copper and steel was not effective in blocking corrosion currents. In fact, once corrosion commences beneath the coating a crevice could have formed and accelerated the attack because of the localized lowering of the pH. In essence, the mechanism of penetration would be a combination of galvanic and crevice corrosion. The leaks would have been avoided if the copper coil had not been discarded in the tank. During the period between 1987 and 1994, when the tanks were in retirement, additional corrosion probably occurred and led to an increase in the size of the holes in the Tank D3 base where wet conditions prevailed.
- f) In water storage tanks, failures such as those experienced in the D3 waste tank

may be avoided by either the selection of compatible materials for components that are to be used in tank operations, or by avoiding the disposal of foreign components into the tank where they could cause galvanic attack.

- g) Pitting was often observed in the tank samples, but some of this could have been initiated prior to the application of the internal and external paint layers. The pH of water in the tank was usually in the range of 8.0 to 8.5. Based on corrosion data for the high-level waste tanks at Hanford, WA, this is too low to prevent pitting in carbon steel⁽⁸⁾. A pH of about 11 is apparently needed to prevent this type of attack⁽⁸⁾.
- h) Corrosion of the external tank surfaces was not a problem during service. If rusting occurred the affected areas were usually cleaned and repainted.

7. REFERENCES

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