REVIEW OF CORROSION ASPECTS OF HIGH-LEVEL WASTE STORAGE TANKS AT WEST VALLEY

Prepared for

Nuclear Regulatory Commission
Contract NRC-02-88-005

Prepared by

Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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ABSTRACT

This report provides an assessment of corrosion issues of importance to the integrity of high-level waste storage tanks at West Valley. The analysis is confined to the carbon steel tanks that contain wastes resulting from the Plutonium Uranium Recovery EXtraction (PUREX) process. Several degradation processes which can be related to the chemical composition of the wastes or sludge washing solutions, such as stress corrosion cracking, pitting corrosion, and crevice corrosion, are briefly examined, as well as the potential for external corrosion of the tanks. Results of the work currently conducted at West Valley to address these issues are examined. Planned activities, including inspection of the tanks, are discussed and evaluated, and a set of recommendations is provided.

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1 INTRODUCTION

1.1   DESCRIPTION OF THE WEST VALLEY DEMONSTRATION PROJECT

The West Valley Demonstration Project (WVDP) is being undertaken by the U.S. Department of Energy (DOE) pursuant to the West Valley Demonstration Project Act of October 1, 1980 (Public Law 96-368). This Act directs DOE to conduct at West Valley a radioactive high-level waste (HLW) management demonstration project comprising five major activities, as follows:

- Solidification of the HLW by vitrification or by such other technology determined to be the most effective for solidification;

- Development of containers suitable for permanent disposal of the HLW;

- Transportation of the waste to an appropriate federal repository for permanent disposal;

- Disposal of low-level radioactive waste (LLW) and transuranic (TRU) waste produced during the project; and

- Decontamination and decommissioning of the tanks and other facilities used in connection with the project.

The main task of the WVDP is to convert the HLW into borosilicate glass for ultimate disposal in a federal repository. The WVDP operations are controlled by DOE directives, with oversight provided by the U.S. Nuclear Regulatory Commission (NRC) to ensure no significant risk to the public radiological health and safety.

The West Valley site was a commercial nuclear fuel reprocessing center that operated from 1966 to 1972. It is located on the western plateau of the state of New York, near the community of West Valley and about 55 km south of Buffalo. The DOE, together with its prime contractor, Westinghouse Electric Corporation, officially took over the operation of the site in February of 1982. The prime contractor and site operator is West Valley Nuclear Services Co., Inc. (WVNS), a wholly-owned subsidiary of Westinghouse Electric Corporation. The HLW management demonstration project involves the cleanup of approximately 2.2 million liters (nearly 580,000 gallons) of nuclear spent fuel reprocessing wastes. Since the interruption of the reprocessing activities these wastes were stored in two underground tanks containing two different waste forms. Alkaline wastes from the Plutonium-Uranium Recovery EXtraction (PUREX) process were stored in Tank 8D-2 (approximately 2.1 million liters), and acidic THOrium Recovery EXtraction (THOREX) wastes were stored in Tank 8D-4 (approximately 31,000 liters). The THOREX wastes exist in essentially a single, liquid phase, but the PUREX wastes exist in two distinct phases, referred to as the supernatant (a liquid phase) and the sludge (a semi-solid phase). Approximately half of the radioactivity was contained in the supernatant and the other half in the sludge at the bottom of the tank.

The initial activities include decontamination of the HLW liquid, processing of the decontaminated HLW liquid into cement, and solidification of the ion exchange material used to decontaminate the waste together with the HLW sludge into borosilicate glass. To perform these activities, several supporting systems are needed. Two of the most important of these systems are the

Supernatant Treatment System (STS) and the Sludge Mobilization and Wash System (SMWS). The primary objective of the STS is to reduce the volume of liquid HLW, while the primary purpose of the SMWS is to remove sodium sulfate crystals present in the sludge which would be detrimental to the vitrification process. On the basis of our understanding of the operations conducted at West Valley in recent years and the modifications in the composition of the HLW stored in the tanks, this report presents an evaluation of the performance of the HLW storage tanks, as affected by plausible corrosion processes.

1.2 PURPOSE AND SCOPE OF THE REVIEW

This review addresses several issues related to corrosion processes which may affect the integrity of the HLW storage tanks used in various operations that are part of the vitrification process. With the delay in the initiation of the planned vitrification activities at West Valley, these storage tanks have been exposed, and will be exposed, for a greater duration than anticipated at design, to a variety of environmental conditions defined by the chemical composition of the HLW in different stages of the processing activities. Also, these tanks are used in the transfer of supernatant liquids and the mixing and washing processes. Although stress-relief heat treated during construction, the tanks have experienced chemical environments that could affect their integrity, particularly if differential settlement has modified the original stress conditions. During the washing and mixing process, the tanks could be subject to cyclic loading. This may contribute to the occurrence of environmentally assisted failures of the tanks, as caused by corrosion fatigue under cyclic stresses of moderately high frequency or stress corrosion cracking (SCC), either under cyclic stresses of very low frequency or sustained tensile loading. An understanding of the conditions and the propensity to failure, characterized by the occurrence of leaks, would provide a basis for the various tank monitoring requirements.

This document addresses the integrity of Tanks 8D-1 and 8D-2, which are made of carbon steel. Concerns about the integrity of these tanks arose from the experience accumulated with tanks made of carbon steels containing HLW from reprocessing operations at Savannah River and Hanford. Tanks made of type 304L stainless steel, in which THOREX wastes are stored such as Tank 8D-4, or Tank 8D-3 which currently contains decontaminated sludge wash liquid, are not the focus of this report since there is not such a concern at present regarding their integrity. These are smaller tanks, made of a corrosion resistant alloy which is not anticipated to be affected by localized corrosion in the presence of the liquid environments contained in both tanks. However, it will be reasonable to examine the operating conditions and the potential for failure of these tanks sometime in the near future.

2 BACKGROUND

2.1 HISTORY OF TANK CONTENTS

HLW resulting from the reprocessing of spent nuclear fuel using the alkaline PUREX process was stored since 1972 in an underground tank (8D-2), which is located within the WVDP waste tank farm (WTF). This tank originally contained a sludge layer, approximately 50 cm high, deposited in the bottom of the tank and mostly composed of insoluble hydroxides and oxides [$Al(OH)_3$, $Fe(OH)_3$, MnO_2, SiO_2, $UO_2(OH)_2$, and $Zr(OH)_4$] and precipitated salts [$Ca(CO)_3$, $FePO_4$ and $MgCO_3$]. A supernatant layer of about 2.1 million liters (nearly 560,000 gallons) containing about 39.5 weight percent total dissolved solids (TDS) was located on top of the sludge. The supernatant consisted of a relatively concentrated, alkaline (pH 10.0) salt solution, in which the predominant anions were reported to be nitrate, nitrite, sulfate, and bicarbonate/carbonate. Table 2-1 shows the chemical composition of the supernatant, as determined in 1987 prior to the initiation of the WVDP.

Table 2-1. Chemical composition of Tank 8D-2 supernatant (pH = 10.0) (Rykken, 1987)

Compound	Concentration	
	g/kg H_2O	moles/kg H_2O
$NaNO_3$	348.9	4.10
$NaNO_2$	180.3	2.61
Na_2SO_4	44.2	0.31
$NaHCO_3$	24.6	0.29
KNO_3	21.0	0.21
Na_2CO_3	14.6	0.14
$NaOH$	10.2	0.26
K_2CrO_4	3.0	0.02
$NaCl$	2.7	0.05
Na_3PO_4	2.2	0.01
Na_2MoO_4	0.4	0.002
Na_3BO_3	0.3	0.002
$CsNO_3$	0.3	0.002
NaF	0.3	0.007

Compounds with concentrations equal to or lower than 0.1 g/kg H_2O are not listed.

Through the STS, in conjunction with the Integrated Radwaste Treatment System (IRTS), approximately 75 percent of the alkaline supernatant was decontaminated in the initial phase of the operation (1988 through November 1990), mostly by the removal of ^{137}Cs. This was achieved through the use of zeolites as ion exchangers (Ionsiv IE-96® [1]) and the resulting LLW solution was concentrated and converted into a cement waste form. At that time, the operation was placed on standby because dilution of the supernatant and a decrease in the pH due to the absorption of atmospheric CO_2 caused the dissolution of fissile material out of the sludge. Associated with a decrease in the TDS concentration from 39.5 to 23 weight percent in the liquid in Tank 8D-2, the plutonium activity increased from 7.5×10^{-2} to 11.4×10^{-2} $\mu Ci/mL$ (Smith et al., 1992). A 20 percent NaOH solution was added in November 1991 to decrease the concentration of fissile material in the supernatant. Following this addition that increased the pH from 10.0 to 12.6, it was found that the concentration of plutonium in the supernatant was reduced 15 times and the uranium concentration 17 times (Smith et al., 1992). The supernatant processing phase of the project is considered complete and the sludge washing phase has begun.

Precipitated salts, in particular sodium sulfate crystals, are being removed from the sludge through the SMWS. Following the addition of 20 percent NaOH solution, the sludge is being mobilized using the sludge mobilization pumps. The caustic solution is added to avoid solubilization of actinides, such as uranium and plutonium, while the salts are being dissolved. After the washed sludge is allowed to decant, the washing solution is decontaminated by the IRTS using the Ionsiv IE-96® zeolite. A total of four washing cycles is planned. The resulting LLW solution will be concentrated and converted also in a cementitious waste form. At the present time, only one of the four planned washing cycles has been completed. As a consequence of radioactive decay, a radiogenic temperature of approximately 60°C is maintained in Tank 8D-2, but it is expected that by the action of the sludge mobilization pumps, the temperature may rise up to 95°C.

The radioactive species retained from the ion-exchange treatment of both the supernatant and the sludge wash solutions are stored as loaded zeolite at the bottom of another tank (8D-1) under a water cover about 2.4 m high as a radiation shield. The temperature of the loaded zeolite is expected to be about 60°C. This spare tank is also being used in the operation of the IRTS. Four ion-exchange columns connected in series and additional ancillary equipment of the IRTS are located inside Tank 8D-1. When the zeolites in these columns are exhausted, they are sluiced with process water into the tank. A zeolite mobilization pump serves to redistribute the zeolite over the bottom of the tank.

Tank 8D-1 currently contains 36,600 kg of Ionsiv IE-96® zeolite in water with a total volume of approximately 975,000 liters (257,600 gallons), whereas in Tank 8D-2 there are 1,458,000 liters (385,200 gallons) of sludge wash liquid covering the washed sludge (Meess, 1993). Although the precise chemical composition of both tank contents is not known, Tank 8D-1 contains Al_2O_3, SiO_2, and Fe_2O_3 as main solid constituents besides alkaline water. The source of Fe_2O_3 is obviously the corrosion of the reprocessing plant piping and vessels. The main components of the sludge contained in Tank 8D-2 are: $Al(OH)_3$, $CaCO_3$, $Fe(OH)_3$, MnO_2, $Ni(OH)_2$, $UO_2(OH)_2$, and SiO_2. The chemical composition in terms of the main constituents of the sludge wash solution currently in Tank 8D-2 is shown in Table 2-2 (Mahoney, 1992).

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[1] Ionsiv IE-96® is a registered trademark of UOP (formerly United Oil Production)

Table 2-2. Chemical composition of preliminary sludge wash solution from Tank 8D-2 (adapted from Mahoney, 1992)

Species	Concentration	
	g/l	moles/l
Na^+	69.0	3.00
NO_3^-	63.0	1.02
NO_2^-	56.0	1.22
SO_4^{2-}	23.0	0.23
Al^{3+}	0.30	0.012
Cl^-	0.49	0.014
OH (est.)	3.6	0.21
pH	12.5	

NOTE: Preliminary analyses from sample extracted January 18, 1992. One 48-hour mixing campaign was performed on the sludge in Tank 8D-2 after this sample was taken. Analytical results on a few species indicate no significant change in composition.

2.2 DESCRIPTION AND FABRICATION DETAILS OF TANKS

The principal HLW storage tanks are identified as 8D-1 and 8D-2. Both tanks are approximately 8 m high by 21 m in diameter and fully contained within a 61 cm thick reinforced concrete vault. An overall schematic view of Tank 8D-2 is shown in Figure 2-1 and a section view in Figure 2-2. The internal configuration of the tanks is illustrated in Figure 2-3, where it is seen that six steel columns, filled with concrete, exist inside each tank as an integral part of it. Additionally, there is a complex steel gridwork attached to the bottom supporting 40 steel columns with a diameter of 20.3 cm which are connected to the roof. A steel pan on which the tank is seated (Figure 2-1) has a liquid level detection system to identify any leakage from the HLW tanks. This pan does not provide containment and its use is confined to leakage detection. It appears, however, that the pan corresponding to the 8D-2 tank itself has a leak that allows water to pass to the vault. Leaked fluids can be returned to the tanks via pumps. Radioactive contamination of the surrounding area can be detected through monitoring wells located in the vicinity of the tanks. Both tanks have been modified in order to introduce the equipment required for the STS and the SMWS. In the case of Tank 8D-1 this equipment includes four zeolite (ion exchange) columns, the ion exchange feed tank, sluice feed tank, and the zeolite mobilization pump. Figure 2-4 shows some of these components and their locations within the STS process. The SMWS components include the Tank 8D-2 and five (5) sludge mobilization pumps, as well as a supernatant transfer pump. The arrangement is schematically shown in Figure 2-2.
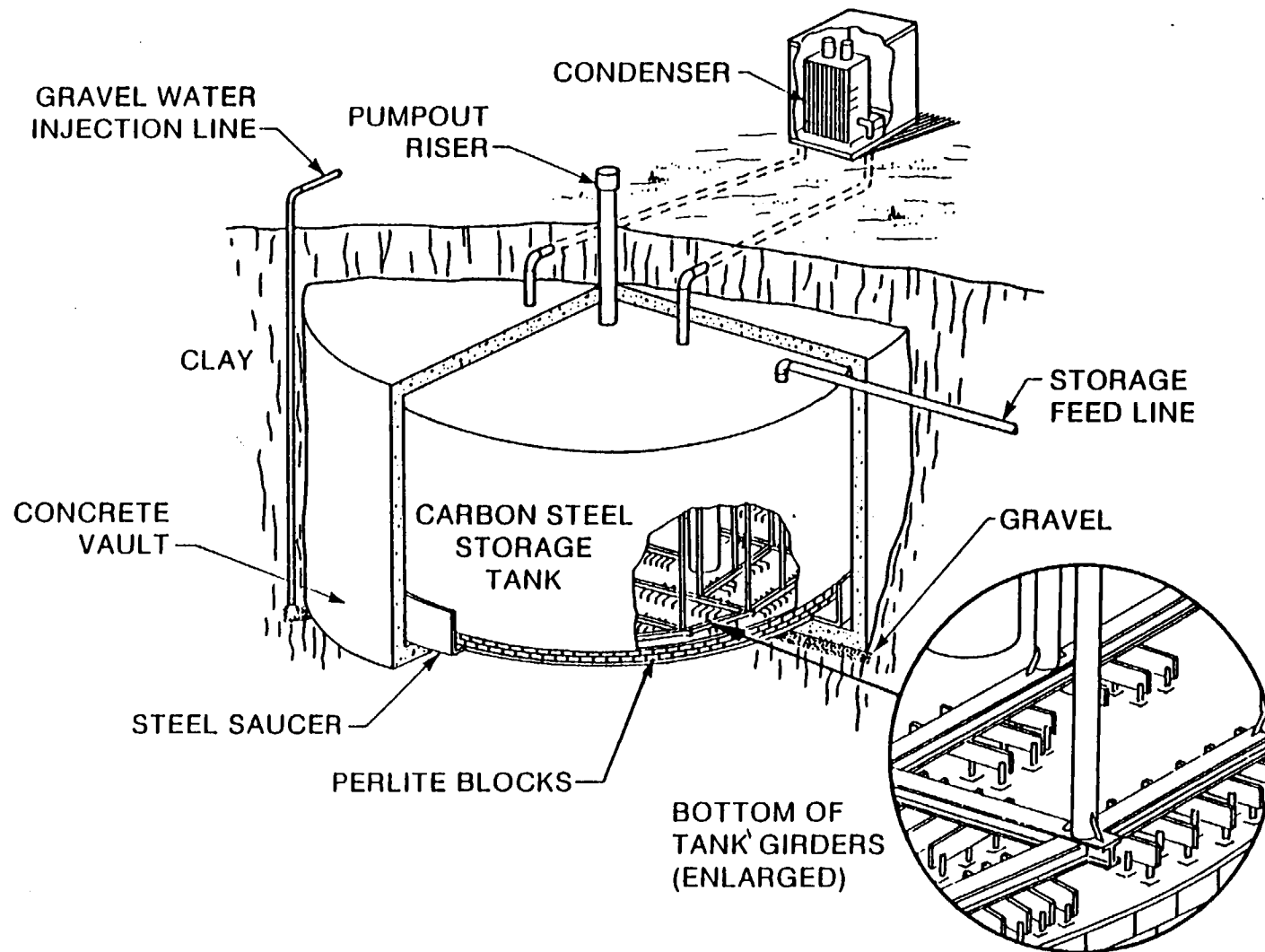
Figure 2-1. Schematic view of Tank 8D-2 (Prowse and Schiffhauer, 1991)
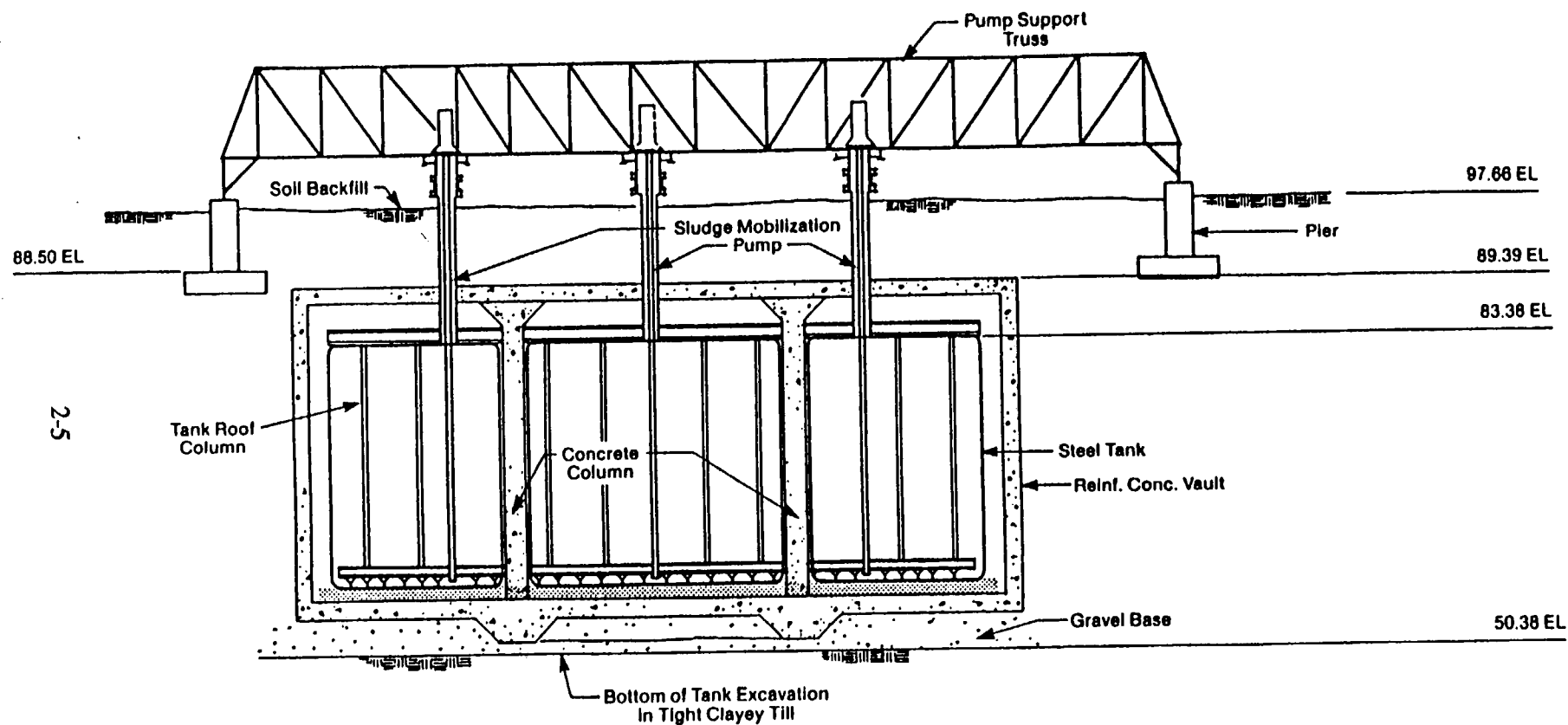
24

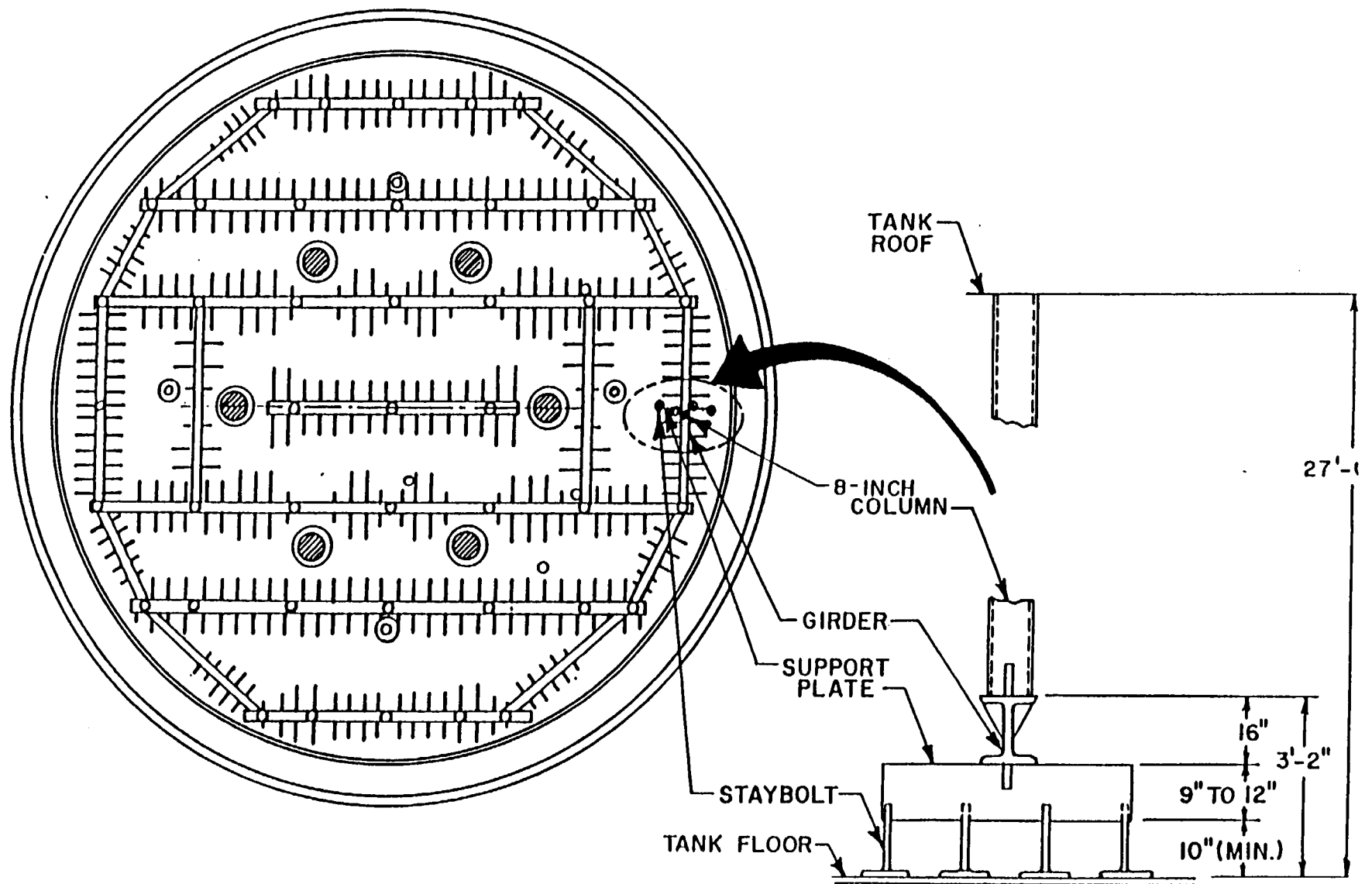**Figure 2-2. Section of Tank 8D-2 (Prowse and Schiffhauer, 1991)**

Figure 2-3. Plan and elevation above internal gridwork for Tanks 8D-1 and 8D-2 (Prowse and Schiffhauer, 1991)
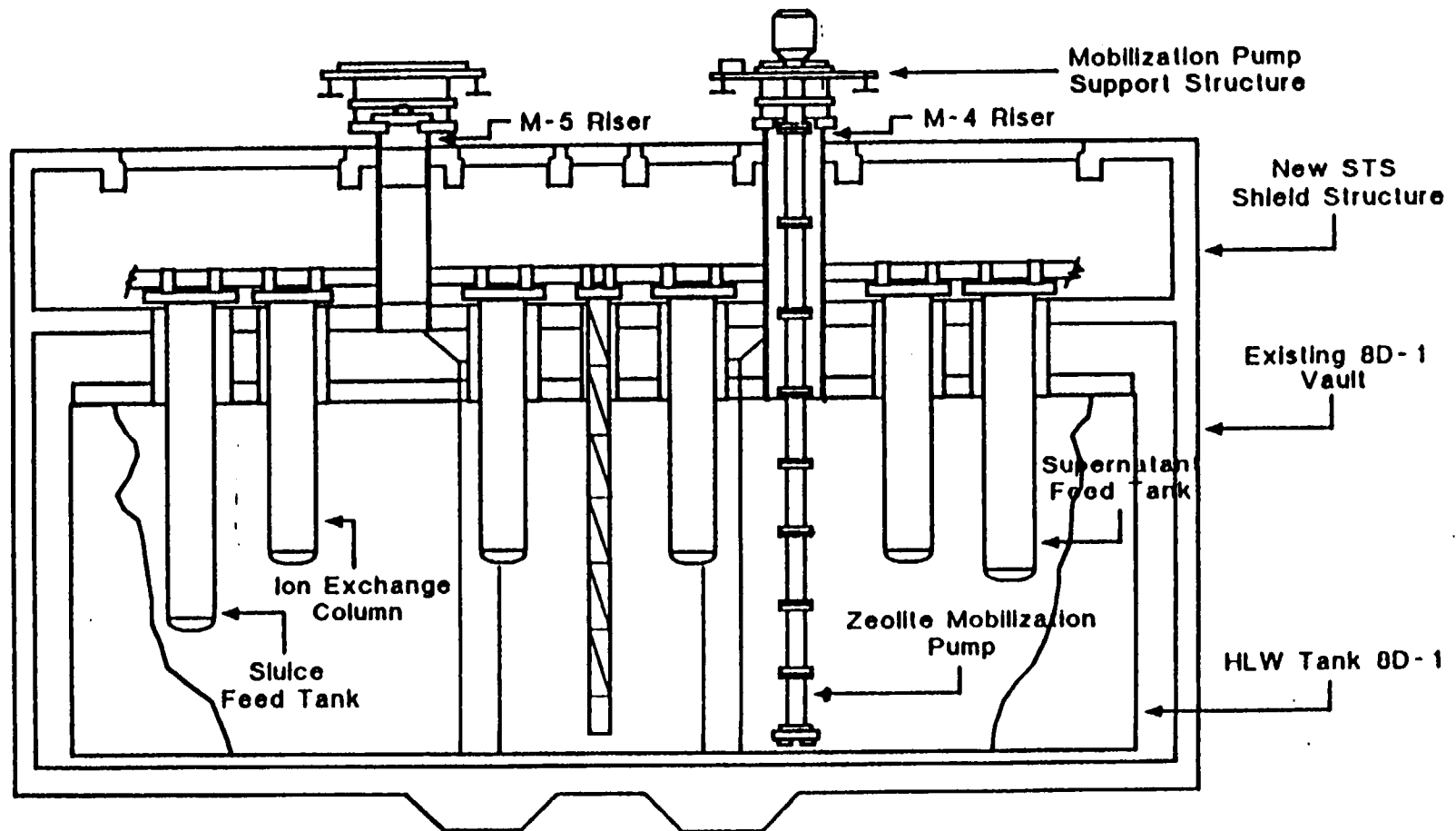
Figure 2-4. Section of Tank 8D-1 (Prowse and Schiffhauer, 1991)

The tanks were manufactured from carbon steel plates, according to ASTM A 201, Grade A, which was the standard specification for steels used in the fabrication of fusion-welded boilers and other pressure vessels. Table 2-3 shows the required chemical composition and Table 2-4 the mechanical properties. It should be noted that this standard specification was discontinued by ASTM in 1967 and replaced by A 515/A 515 M, originally published in 1964 and revised in 1990. There are no significant differences in terms of chemical and tensile requirements between both standards, although in the new version four different grades are included instead of two. It should be noted, however, that the manganese and silicon contents have been increased slightly, and the impurities content (sulfur and phosphorus) has been reduced to 0.035 max. After fabrication and welding, the tanks have been post-weld heat treated. However, the conditions and effectiveness of the stress relief heat treatment are not well known.

Table 2-3. Chemical composition range specified for ASTM A 201, Grade A (American Society for Testing and Materials, Annual Book of Standards, 1966)

Element	Content (percent)
Carbon, max	0.20 to 0.35
Manganese, max	0.80
Phosphorus, max Flange Firebox	 0.04 0.035
Sulfur, max Flange Firebox	 0.05 0.04
Silicon Ladle analysis Check analysis	 0.15 to 0.30 0.13 to 0.33

Table 2-3. Mechanical properties range specified for ASTM A 201, Grade A (American Society for Testing and Materials, Annual Book of Standards, 1966)

Tensile strength	55,000 to 65,000 psi
Yield point, min	30,000 psi
Elongation in 8 in., min Flange Firebox	 24 percent 25 percent
Elongation in 2 in., min Flange Firebox	 28 percent 29 percent

3 CORROSION PROGRAM ASSESSMENT

3.1 CURRENT PROGRAM ACTIVITIES

WVNS has established a limited program for monitoring and control of internal corrosion in carbon steel Tanks 8D-1 and 8D-2 (Meess, 1993). This was initially based on nondestructive examination (NDE) using ultrasonic testing. No evidence of thinning of the tank walls as a result of general corrosion was detected in an inspection conducted in 1982 (Prowse and Schiffhauer, 1991). Visual inspection of internal and external tank surfaces indicated the presence of surface scale and pitting, but no indication of the amount of pitting attack was reported. Corrosion control of the internal surfaces of the tanks was attained by a combination of high pH through the presence of a caustic solution and a relatively high concentration of nitrate, which acts as an efficient inhibitor for general corrosion of carbon steels. The corrosion allowance provided for these tanks is 6.4 mm (0.250 in.). In the report it was also noted that SCC has not been observed in corrosion coupons removed from Tank 8D-1 and Tank 8D-2.

WVNS responded to specific concerns or recommendations contained in the Safety Evaluation Report for the WVDP Supernatant Treatment System (Tschoepe et al., 1991), providing more details about the corrosion monitoring program. In the response (Rowland, 1992), it is pointed out that internal corrosion of Tank 8D-1 is being assessed by the use of two corrosion coupon racks, each holding various types of specimens. One of the racks rests on the tank floor, in the area covered by zeolite whereas the second one floats at the liquid/vapor interface, with coupons located in the liquid and vapor phases, as well as in the liquid/vapor interface. Table 3-1 lists the types and number of specimens and their location.

Table 3-1. Location of specimens in Tank 8D-1 (Rowland, 1992)

Specimen Type	Location			
	V	L	V/L	Z
Plain	2	4	1	4
Creviced	2	4	1	4
U-bend	2	3	0	3
Double U-bend	0	2	0	2
Compact tension	2	2	0	4

V: Vapor   L: Liquid   V/L: Vapor liquid interface   Z: Zeolite

Table 3-2 provides data obtained after nine months of exposure from December 1988 to September 1989 for different locations inside Tank 8D-1 (Rowland, 1992). It is seen that the rate of uniform corrosion was found to be higher in the vapor phase than in the liquid phase. Overall, the corrosion rates are all quite low. The relatively high value reported for the specimen located in the

Table 3-2. Corrosion rate data from 9-month exposure of specimens in Tank 8D-1 (Rowland, 1992)

Location	Corrosion Rates, mm/yr (mils/yr)	
	Maximum	Average
Vapor	0.031 (1.2)	0.020 (0.78)
Liquid	0.004 (0.14)	0.002 (0.07)
Zeolite	0.010* (4.1*)	0.016 (0.62)

* Pitting corrosion

zeolite-covered area was related to the occurrence of pitting corrosion. However, pit depth was not reported because it was stated that it could not be accurately measured. In order to control pitting corrosion, sodium nitrite ($NaNO_2$) was added into Tanks 8D-1 and 8D-2 as a pitting inhibitor in 1990, following the results of several studies conducted at Savannah River (Oblath and Congdon, 1987; Bickford et al., 1988; Congdon, 1988; Zapp and Hobbs, 1992). The inhibiting role of nitrite was planned to be assessed in 1992 following specimen removal for examination from Tank 8D-1, but the activity has been postponed. Similar data to that reported above is not available in the case of Tank 8D-2 because specimens were removed from this tank in 1982. At that time a general corrosion rate of 0.014 mm/yr (0.53 mils/yr) was measured in specimens located in the liquid phase (the supernatant) (Rowland, 1992).

It was also reported (Rowland, 1992) that crevice corrosion and SCC were not detected by inspection of the specimens located in Tank 8D-1. The examination of U-bends located in the various phases, as indicated in Table 3-1, is specifically mentioned. However, no information was reported regarding the double U-bend and the compact tension (CT) specimens.

Corrosion probes were installed in Tank 8D-2 in October 1991 for monitoring corrosion rates in the vapor and liquid phase, as well as in the sludge (Rowland, 1992). According to the available information (Meess, 1993), monitoring is conducted by using the CORROSOMETER® [2] probe. This probe measures metal loss through the increase in the electrical resistance of a metal conductor as a result of the decreases in cross section. Table 3-3 shows the average corrosion rate obtained initially (in a 60-day period) and after a six-month exposure (Meess, 1993). The data obtained in the vapor phase seem contradictory because one of the probes indicates a decrease in corrosion rate with time whereas the other one exhibited the opposite effect. It also appears that the corrosion rate in the vapor phase is slightly higher than that in the liquid and even in the sludge. In the last two cases, corrosion rates decrease with time. It should be emphasized that the corrosion rates in all cases are quite low. Each probe has a plain specimen attached to its end. However, no examination of these specimens has been reported yet.

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[2] CORROSOMETER® is a registered trademark of Rohrback Cosasco Systems

Table 3-3. Corrosion rate data from in situ probes located in Tank 8D-2 (Meess, 1993)

Tank Region	Corrosion Mode	Corrosion Rate, mm/yr (mils/yr)	
		Initial 60 Days	Six-Month Period
Sludge S1	Uniform	0.081 (3.2)	0.018 (0.7)
Liquid L2 L3 L4 L5	 Uniform Uniform Crevice Pitting	 0.058 (2.3) N/A 0.000 (0.0) 0.000 (0.0)	 0.000 (0.0) N/A 0.000 (0.0) 0.000 (0.0)
Vapor V6 V7	 Uniform Uniform	 0.046 (1.8) 0.094 (3.7)	 0.114 (4.5) 0.056 (2.2)

3.2   PLANNED PROGRAM ACTIVITIES

Most of the planned activities to be conducted at West Valley were presented by Meess (1993). The installation of a probe in Tank 8D-1 to conduct measurements of temperature, pH, and general corrosion in the liquid phase and in contact with zeolite is planned for in the near future. The probe that is being considered for general corrosion measurement is the CORRATER® [3] probe, based in a two-electrode polarization resistance method. New temperature indicators will be installed in Tank 8D-1; this is an ongoing activity in the case of Tank 8D-2.

There is some concern about external corrosion, and in particular that arising from microbially influenced corrosion. WVNS plans to determine the level of microbial activity for both tanks and to find means of reducing the extent of external corrosion (Meess, 1993). At the present time, WVNS is technically assisted by Savannah River Technology Center (SRTC), through the Equipment and Materials Technology Department, in order to conduct nondestructive examinations from the outer surface of the tanks using the space available in the annular gap between the tank walls and the concrete vault. Ultrasonic testing (UT) will be combined with a TV camera to conduct thickness measurements and detection of flaws as well as visual examination of the external surface of the tanks. SRTC, in addition to the design and fabrication of the appropriate equipment, will provide training and technical support for both operation of the equipment and analysis of the data.

It is also anticipated that changes in the operation of the zeolite mobilization pump may be needed if the probe to be located under the zeolite pile reveals the existence of potential corrosion problems.

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[3] CORRATER® is a registered trademark of Rohrback Cosasco Systems

At the laboratory level, simulations of the sludge wash are being conducted for the third cycle and planned for the fourth cycle. From the point of view of corrosion control and prevention, this activity is important in terms of defining the range of expected variations in the composition of the environment during the washing cycles. It is also being planned to conduct laboratory tests at Battelle Pacific Northwest Laboratories (PNL) to evaluate the magnitude of external corrosion due to the infiltration of surface water and groundwater. It was noted (Rowland, 1992) that SCC tests were being conducted at PNL to assess the possibility of this type of failure mode in the media contained in the tanks. However, the development of this activity has not been reported.

3.3   ASSESSMENT OF POTENTIAL CORROSION ISSUES

Although the exact chemical compositions of the liquids present in both tanks are not known, it is important to emphasize that nitrate is the predominant anion, resulting from the neutralization of the nitric acid solutions used in the PUREX process with sodium hydroxide. This anion is usually recognized as a good inhibitor of the general corrosion of carbon steels particularly at alkaline pHs, in which the relatively high concentration of hydroxide anions confers passivity to the steels. On the other side, anions such as chloride and sulfate which are also present in the waste liquids are well known as pitting promoters for carbon steels in alkaline solutions (Szklarska-Smialowska, 1986). However, it was reported that nitrate, sulfate, chloride, and fluoride can independently induce pitting of carbon steels in certain solutions simulating waste washing liquids from reprocessing operations, whereas nitrite was found to be a good inhibitor (Congdon, 1988; Zapp and Hobbs, 1992). Nitrite is naturally formed in reprocessing wastes by reductive radiolysis of nitrate in the strong radiation fields resulting mainly from the presence of ^{137}Cs.

In the solutions contained in both tanks, the chloride concentration appears to be almost two orders of magnitude lower than that of nitrate, if the composition given in Table 2-2 can be considered at least approximately representative. However, chloride is a very aggressive anion in terms of localized corrosion and it may be responsible for the occurrence of pitting. Under the conditions present in Savannah River, it was postulated that pitting occurred because the inhibiting action of hydroxide anions decreased as a result of the depletion in the hydroxide concentration that took place by absorption of atmospheric CO_2 in a very thin liquid film just above the waterline (Oblath and Congdon, 1987). As noted above, sodium nitrite was found to be an efficient inhibitor, compatible with the requirements of the overall waste processing (Zapp and Hobbs, 1992).

The main concern regarding the integrity of the tanks, however, is related to the well known susceptibility of carbon steels to SCC in hot nitrate-containing solutions. Although acidity of the nitrate solutions promotes cracking rapidly, the phenomenon has also been observed over a wide range of pH values (2.0 to 10.0). Intergranular SCC of radioactive waste storage tanks occurred several years ago at Savannah River in the presence of alkaline nitrate solutions at locations adjacent to weld beads (Holzworth et al., 1968).

Since that time, an extensive and systematic work on the SCC of ferritic steels has been conducted as reviewed by several authors (Parkins, 1977; Kowaka, 1990; Ciaraldi, 1992). The main conclusions of interest for the present case are as follows.

(i)   Susceptibility to SCC, expressed as a decrease in the threshold stress or minimum stress for cracking under tensile conditions, increases with increasing nitrate concentration and

with the following cation sequence: $Na^+ < K^+ < Li^+ < Ca^{2+} < NH_4^+$, but is independent of the cation at a fixed pH for the last three cations of the sequence.

(ii) Cracking occurs very rapidly in the pH range from 3 to 6, but the failure time increases significantly above pH 7.

(iii) Although SCC has been observed at temperatures as low as 35°C, the susceptibility to SCC is greatly accelerated by temperature, with activation energy ranging from 10 to 30 kcal/mole depending upon different material and environmental conditions.

(iv) Some anions may act as inhibitors of SCC or retard the cracking processes either by increasing the general rate of anodic dissolution, such as chloride and sulfate, or by producing more insoluble iron salts, such as carbonate/bicarbonate, phosphate, etc.

(v) SCC in hot nitrate solutions occurs over a wide range of potentials above a critical value, which is about $-0.3\ V_{SHE}$ in 4N NH_4NO_3. The corrosion potential of the steel in this solution lies within the cracking range, and oxidizing anions, such as MnO_4^- and $Cr_2O_7^{2-}$, tend to accelerate cracking.

(vi) The tendency to cracking decreases with increasing carbon content. However, carbon steels with up to 0.25 percent carbon, although relatively resistant to SCC, are still susceptible.

(vii) Residual tensile stresses arising from welding operations are a major contributor to SCC in hot nitrate solutions. Cracking is usually observed in areas immediately adjacent to the welds but it is not related to microstructural changes.

In the context of this discussion, it is important to note that tanks 8D-1 and 8D-2 have been reported to be fully stress relieved after fabrication (Prowse and Schiffhauer, 1991). It is known that stress relief of welded structures is one of the most successful means of preventing cracking of carbon steels in hot nitrate solutions. However, many problems arise in the application of stress relief methods to relatively large structures and components. In these cases, heat is applied locally to parts of the structure to obtain reduction in the peak residual stress, but it must be done with precision to avoid moving the regions of high residual stress to other areas. Usually, temperatures are lower than 650°C, which is the temperature necessary to attain full stress relief for carbon steels, to avoid the distortions caused by treatments at such higher temperatures. The specific conditions and methodology for the stress relief treatment of the tanks at West Valley are not known, and, therefore, a careful monitoring during the service life of the tanks is required.

An additional advantage arising from the addition of sodium nitrite to the reprocessing waste to prevent pitting of the tanks is that NO_2^- also prevents SCC in hot nitrate solutions by displacing the potential range for cracking to higher values (Parkins, 1984). The addition of 533 g/l of $NaNO_2$ to boiling 1M KNO_3 displaces the critical potential for cracking from $-0.16\ V_{SHE}$ to almost 0.64 V_{SHE}. It is, therefore, important to know the corrosion potential of the steel in the tank environment to evaluate the possibility of cracking by comparing the results with laboratory tests. Ondrejcin et al (1979) noted that the corrosion potential measured in several tanks at Savannah River ranged from -0.2 to $0.18\ V_{SHE}$, which is within the potential range for cracking in hot, concentrated nitrate solutions.

Ondrejcin (1979) conducted a comprehensive testing program using slow strain rate tests (SSRT) under a constant applied current in order to evaluate, through statistically designed experiments, the effects of temperature and concentrations of nitrate, nitrite, and hydroxide ions on the susceptibility to SCC of an ASTM A-285-B steel in simulated reprocessing wastes. This alloy is a carbon steel containing 0.12 percent carbon. It was found that ductility measurements (either elongation to failure or reduction in area) are the appropriate parameters for evaluating SCC susceptibility in this case. Temperature and nitrate concentration were the predominant factors in increasing susceptibility to SCC, and the addition of nitrite and hydroxide above certain minimum limits prevents the occurrence of cracking (the elongation limit adopted was 13 percent). The results for 5M $NaNO_3$ solution at 97°C are shown in Figure 3-1, where previous data obtained by Donovan (1977) using wedge-opening loaded (WOL) specimens were plotted by Ondrejcin (1979) for comparison with his own data. A straight line indicating a low limit in the combined concentration of both nitrate and hydroxide, as recommended by Ondrejcin, is also shown in the figure. The difference in the results between both SCC test methods at low hydroxide concentrations is attributed by Ondrejcin to the fact that Donovan conducted his tests in the absence of the minor components contained in the simulate waste. This may enhance the susceptibility at low hydroxide concentrations, even in the presence of nitrite concentrations beyond the recommended limit. In a latter publication (Ondrejcin et al., 1979), most of the important aspects of the program conducted at Savannah River are summarized. The combination of stress relief and environmental control, including temperatures lower than 70°C when the concentration of nitrate ion is too high, is recommended as a preventive measure for controlling SCC of storage tanks in the presence of radioactive waste resulting from the PUREX process.
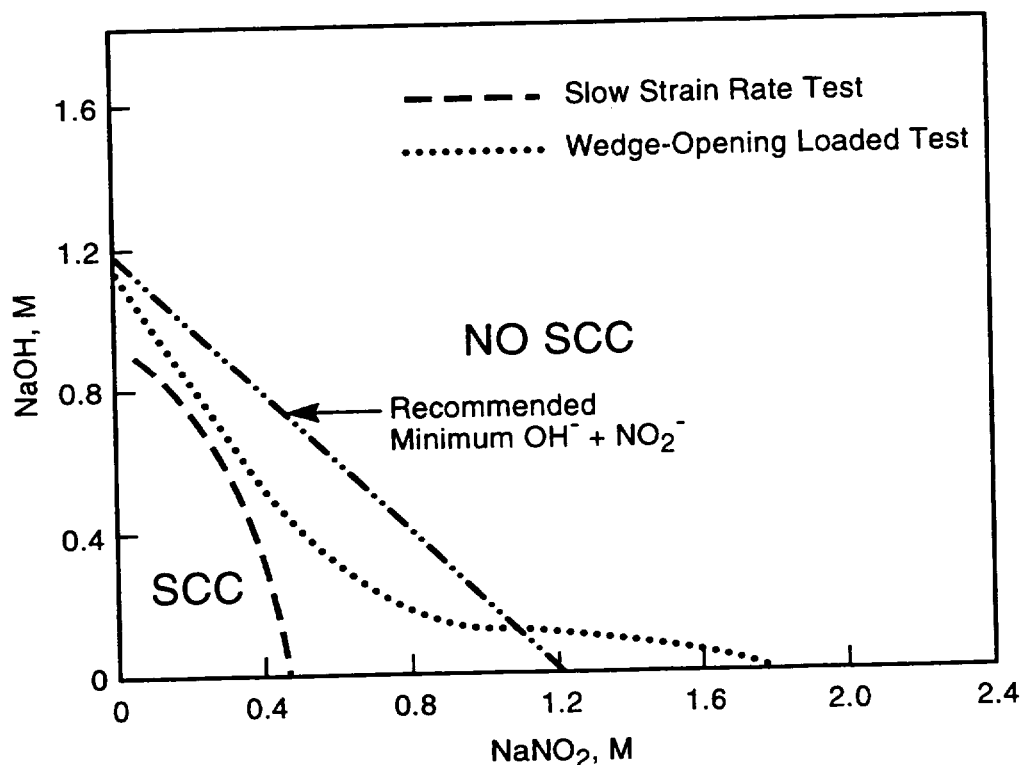

Figure 3-1. Effect of $NaNO_2$ and NaOH on SCC of A 285-B steel in 5 M $NaNO_3$ solution at 97°C. (Ondrejcin, 1979)

The previous discussion on SCC studies suggests that in the West Valley tanks the occurrence of SCC may be prevented by the presence of relatively high concentrations of nitrite and hydroxide with respect to that of nitrate, as shown by Table 2-2. The combined concentrations of OH^- and NO_2^- anions define a point located in the noncracking region of Figure 3-1. In addition, the concentration of NO_3^- in the 8D-2 tank is 1 M rather than 5 M as in the data shown in Figure 3-1 and the temperature is lower than 97°C. Therefore, it can be expected that the initiation and growth of stress corrosion cracks is inhibited. This consideration of environmental factors seems to be a valid approach for evaluating the potential risk of environmentally assisted cracking in the case of West Valley tanks. However, changes in the chemical composition of the waste or variations in temperature and corrosion potential may lead to the occurrence of cracking, which makes a monitoring and inspection program fully justifiable.

The potential corrosion problems discussed above arise from the action of the environment contained in the tanks. However, the possibility of external corrosion arising from the contact of the tanks with flooding water or groundwater should be considered also, particularly in the presence of microbial activity. In the last ten years, a large body of information has emerged regarding corrosion problems associated to microbial activity in many systems containing stagnant or intermittently flowing raw waters. In particular, containment vessels and auxiliary piping systems have been affected in the nuclear power industry in areas outside the containment structure (Licina, 1988), but microbiologically influenced corrosion (MIC) has also occurred in the presence of intense radiation fields (Wolfram et al., 1990).

An analysis of the present program at West Valley addressing issues related to internal and external corrosion, and some recommendations, are included in the following section.

3.4 REVIEW OF CURRENT AND PLANNED ACTIVITIES

The decision of WVNS to initiate a program of inspection of the carbon steel tanks with the technical support of SRTC is a step in the right direction. Periodic inspection of the tank walls using UT will allow detection of progressive thinning of the tanks by general corrosion, if changes in the chemical composition of the wastes lead to an acceleration of the attack. It may also permit detection of the initiation and growth of localized corrosion in the form of pitting or crevice corrosion, as UT indications of flaws or defects, before leaks develop. The same is valid for the detection of cracks. It should be noted, however, that the extension of the surface to be inspected and limitations regarding the accessibility of certain areas (i.e., the bottom of the tanks) make the task of detecting small pits or cracks difficult and, probably, the results of the inspection will not be completely reliable. This aspect has to be considered carefully in relation to stress corrosion cracks because the level of stress relief attained is not known with certainty, particularly at the bottom of the tanks, as a result of the complexity of the welded gridwork.

The visual inspection of the tank exterior will be useful for detecting any area in which localized attack may be initiated by the intrusion of groundwater or flooding water. In this context, the need for the evaluation of the potential for MIC should be emphasized. WVNS has included in their prevention plan the evaluation of microbial activity in relation to Tanks 8D-1 and 8D-2. We suggest to accelerate the development of the techniques and equipments for external remote inspection in order to have an integrated approach to inspection and monitoring of the tanks, in which all the possible causes of external corrosion, including MIC, are evaluated. In this regard, the development of appropriate remote tools for sample collection, in the eventual case of microbial activity, should be considered. The device to be

used as a cleaning crawler could be designed for collecting samples of corrosion products, including suspected bacterial colonies.

Although WVNS has indicated (Meess, 1993) that external corrosion is being quantified in a laboratory activity, the current extent of this activity is not known. Nevertheless, it appears extremely difficult to assess the potential or the degree of external corrosion of the tank without prior inspection. The result of this inspection should determine the scope of the program and the content of the activities to be conducted experimentally in the laboratory.

Regarding the activities reported to-date, it is important to note that a potential risk for pitting or crevice corrosion underneath the zeolite layer in Tank 8D-1 still exists despite the addition of nitrite. It appears that the occurrence of pitting corrosion in the laboratory tests conducted at Savannah River (Congdon, 1988; Zapp and Hobbs, 1992), as related to the depletion of hydroxide ions at the waterline, is not necessarily the same process that occurred on the specimens covered by zeolite in Tank 8D-1. Therefore, it would be desirable to initiate the monitoring in the zeolite region soon. In addition to the monitoring using electrical resistance or linear polarization methods, it will be valuable to have specimens attached to the probe in a similar manner to those currently located in Tank 8D-2 for periodic examination.

It will be extremely useful, in addition to the measurement of corrosion rates using linear polarization or electrical resistance methods, to monitor the corrosion potential of specimens immersed in the tanks, at least within the liquid phase. Corrosion potential monitoring combined with the planned laboratory activity related to SCC should allow the prediction of environmental conditions that may lead to the initiation and growth of cracks. Regarding the use of linear polarization methods for measurements of corrosion rates, a very important consideration is the periodic calibration of the equipment, because it is relatively common to obtain misleading results in field applications of electrochemical methods when measurements are conducted over extended periods.

An effort should be made to accelerate the removal and examination of the specimens located in Tank 8D-1. This activity was scheduled for 1992 and it will be highly desirable to complete the examination of these specimens as soon as possible to confirm the advantages of the nitrite addition as an inhibitor of pitting corrosion. It is also important to confirm the absence of stress corrosion cracks in the U-bend specimens and the lack of crack growth in the CT specimens. It is unfortunate, however, that, apparently, no welded SCC specimens are included in the set of specimens.

WVNS has initiated a program of evaluation and prevention of corrosion of the carbon steel tanks. This program should be continued, covering all the aspects related to external and internal corrosion of the tanks discussed in this report, to insure the integrity of the tanks, and, therefore, avoiding leaks that would lead to contamination of the groundwater.

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5 NOMENCLATURE — LIST OF ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CNWRA	Center for Nuclear Waste Regulatory Analyses
CT	compact tension
DOE	U.S. Department of Energy
HLW	high-level waste
IRTS	Integrated Radwaste Treatment System
LLW	low-level radioactive waste
LWTS	Liquid Waste Treatment System
MIC	microbiologically influenced corrosion
NACE	National Association of Corrosion Engineers
NDE	nondestructive examination
NRC	U.S. Nuclear Regulatory Commission
PNL	Pacific Northwest Laboratories
PUREX	Plutonium-Uranium Recovery EXtraction
SCC	stress corrosion cracking
SMWS	Sludge Mobilization and Wash System
SRTC	Savannah River Technology Center
SSRT	slow strain rate test
STS	Supernatant Treatment System
TDS	total dissolved solids
THOREX	THOrium Recovery EXtraction
TRU	transuranic
UT	ultrasonic testing
WOL	wedge-opening loaded
WTF	waste tank farm
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services Co., Inc.