**CORROSION EVALUATION OF LLW2 SKID-B
WELD FAILURE MECHANISMS**

Topical Report

By
Ji Young Chang

May 2001

Work Performed Under Contract No. DE-AC24-81NE44139

Prepared by
West Valley Nuclear Services Co.
10282 Rock Springs Road
West Valley, NY 14171-9799

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical information, PO Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

**CORROSION EVALUATION OF LLW2 SKID-B
WELD FAILURE MECHANISMS**

Topical Report

By
Ji Young Chang

May 2001

Work Performed Under Contract No. DE-AC24-81NE44139

Prepared for
U.S. Department of Energy
Assistant Secretary for Nuclear Energy

Prepared by
West Valley Nuclear Services Co.
10282 Rock Springs Road
West Valley, NY 14171-9799

THIS PAGE INTENTIONALLY LEFT BLANK

TABLE OF CONTENTS

Section	Page
LIST OF ILLUSTRATIONS	iii
LIST OF TABLES	iv
EXECUTIVE SUMMARY	vii
1.0 INTRODUCTION	1
2.0 BACKGROUND	2
3.0 THE LLW2 SKID-B SYSTEM AND RELATED FACILITIES	3
4.0 APPLIED MATERIALS	4
5.0 WELDING AND QA INSPECTION PROCEDURE	5
6.0 ENVIRONMENT	6
6.1 Empirical Scaling Index	7
6.2 Water Chemistry	7
7.0 EVALUATION OF THE POSSIBLE WELD DEFECTS AND CORROSION PRODUCT	8
7.1 Videoscope Inspection	8
7.2 Radiographic Inspection (ASME B31.3)	9
7.3 Stereoscope Examination of the Rust-Nodule (Corrosion Product and Weld-Spatter)	9
7.4 Microbiologically Influenced Corrosion (MIC) Examination	9
7.5 Failure Analysis	10
7.5.1 Acceptable Weld and Typical Weld Defects	10
7.5.2 Macro-Photograph	10
7.5.3 Metallographic Evaluation of Weld	11
A. Sensitization	11
B. Intergranular Stress Corrosion Cracking (IGSCC)	12
7.5.4 SEM and EDS Analysis	12

7.6	Ultrasonic Test (UT)	12
7.7	Pitting Initiation Mechanism at Heat Tints Site (HTS)	13
7.8	Mechanism of Chloride Pitting Corrosion	14
8.0	SUMMARY AND CONCLUSIONS	15
8.1	Stress Corrosion Cracking (SCC) and General Corrosion (GC)	15
8.2	Microbiologically Influenced Corrosion (MIC)	15
8.3	Chloride Pitting Corrosion	15
9.0	RECOMMENDATIONS AND PROPOSAL SELECTION	17
10.0	ACKNOWLEDGMENT	18
11.0	REFERENCES	19
12.0	BIBLIOGRAPHY	21
13.0	ACRONYMS	22
	APPENDIX A - FIGURES REFERENCED IN REPORT	A-1
	APPENDIX B - LLW2 SKID-B CORROSION EVALUATION	B-1

LIST OF ILLUSTRATIONS

Figure	Page
Figure A-1. North Plateau Groundwater Remediation System (NPGWR). Well water is pumped to Surge Tank 02-D-001 and sent to LLW2 Skid-B.	A-2
Figure A-2. Low-Level Waste Treatment System, LLW2 Skid-B. Influent comes from NPGWR.	A-3
2a. Surge Tank 02-D-001 and PVC process lines in NPWGR.	A-3
2b. Ion-exchange columns and stainless steel process lines. Materials are Type 304L, ER308L, and CF-3M (cast 316L).	A-3
Figure A-3. Chloride Pitting Corrosion of Type 304L pipe ER308L filler metal, and cast Type 316L T-connector material after 7 months exposure in groundwater. Weld No. 3-236B, 02-WW-1-1/2-3094, LLW2 Skid-B.	A-4
3a. Weld No. 3-230D, 02-WW-1-1/2-3136	A-4
3b. Weld No. 3-236B, 02-WW-1-1/2-3094	A-4
Figure A-4. Chloride Pitting Corrosion of Type 316L T-connector. ER308L filler metal, and Type 304L pipe and cast Type 316 valve flanges after 7 months exposure in groundwater.	A-5
4a. Weld No. 2-229B, 02-WW-1-1/2-3130	A-5
4b. Weld No. 3-236B, 02-WW-1-1/2-3094.	A-5
Figure A-5. Radiograph showing cavities (four top spots and others) in the weld zone (white ring) and in the HAZ center dark lines. Radiograph of Skid-B, Package 97-236B, DTS weld #7, DWG 3013, after J. Reynolds.	A-6
Figure A-6. Rust nodule attached to the inside of the pipe where pitting took place. It is $\text{Fe}(\text{OH})_3$, containing Cr: 12.1%, Ni:0.32%, and Cl:2.78%. The dome is facing toward the center of the pipe. Original magnification = 46X.	A-7
Figure A-7. The other side of the same nodule as in Figure A-6, showing Fe_3O_4 (dark line at the top) that apparently was electronically connected to the base metal and acted as a cathode to deposit the material coming from the inside of the pits. Original magnification = 46X.	A-8
Figure A-8. Thin corrosion layer on the top of the dome is a Fe_3O_4 section. The original metal had a pit and formed a corrosion product outside the pit. Original magnification = 116X.	A-9
Figure A-9. A typical electrochemically deposited positive ion from an <i>occluded pit cell</i> by <i>auto-catalytic action</i> in weld filler material ER304L. The orange-red colors are $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The material is a mixture of oxides: Cr: 12.1%, Ni: 0.32%, and Cl: 2.78%, which probably came from the ER308L pits. Original magnification = 465X.	A-10
Figure A-10. Typical defects, (a) through (d), that occur in the arc welding of heat-resistant alloys. Sketch (e) represents a weld with no defects and good reinforcement. (Ref. 12)	A-11
Figure A-11. As-received pipe. Top cutting marking is arbitrarily chosen as 0 degrees and clockwise, 90 degrees specimen (W4) is named "sec. B 50" (Right). The section with the 179 degrees to 359 degrees sample is named "Sec. B 64" (Left).	A-11
Figure A-12. As-received inside of pipe showing improper welds, e.g., <i>oxide tints-scale</i> , <i>drop-through</i> , and chloride pitting corrosion cavities.	A-12

Figure A-13. Weld defect area in Figures A-12 shown at a higher magnification.	A-12
Figure A-14. Type 304L SS pipeline seam weld not affected by the corrosion and close to the original color.	A-13
Figure A-15. The coloration and the oxide film thickness of stainless steel. The blue color away from the HAZ is 720 Å and is acting as a protective oxide. However, the thickness of the dark-brown color tints-scale is over 5,000 Å and, as a result, the chromium-depleted 304L surface becomes susceptible to chloride pitting corrosion.	A-13
Figure A-16. As-received pipe, Section B64, showing pitting in the thick tints-scale near the weld. This shows incomplete fusion of the weld material to the base metal and <i>drop-through</i>	A-14
Figure A-17. Pits in the Type 304L HAZ (Section 64). Notice the <i>weld tints-scale</i> that will initiate pitting.	A-14
Figure A-18. Drop-through weld defects and large pits at the cut surface. These are connected to the internal surface of the pipe and formed by chloride pitting corrosion during 7 months of exposure.	A-15
Figure A-19. The mating end of the same drop-through (Section 50).	A-15
Figure A-20. Close-up of the pit cell. Shows connection to the surface and cup-shaped internal pit cell surface. Metallography of this surface is shown in Figure A-23 and the SEM is shown in Figure A-32.	A-16
Figure A-21. Sketch showing locations of metallography cross-sections from LLW2 Skid-B. Pipe OD = 1.900 in., ID = 1.610 in., Wall thickness = 0.145 in.	A-16
Figure A-22. Weld porosity and corroded material in Section 64, also shown in Figures A-12 and A-13. The Type 304L pipe is on the left, weld filler material ER308L is in the middle, and Type 316L cast flange is on the right.	A-17
Figure A-23. The result of the chloride pitting corrosion started at the oxide layers between the root-weld and the final weld. Shows root-pass, drop-through, and pitting corrosion at the HAZ.	A-17
Figure A-24. Pitting found in the HAZ. The welded zone was well defused; however, post-weld surface cleaning of the tints-scale and chromium-depleted zone was not done, thereby initiating chloride-pitting corrosion at the HAZ.	A-18
Figure A-25. Shows a good diffusion penetration between the base metal and the filler metal. Shows good fusion between the root-pass and final-pass.	A-18
Figure A-26. Weld HAZ in Type 304L pipe at the weld interface (ER308L). No evidence of carbide precipitation at the grain boundaries associated with sensitization (500X).	A-19
Figure A-27. Weld HAZ in Type 304L pipe ID.	A-19
Figure A-28. EDS analysis of Type 304L pipe used in LLW2 Skid-B.	A-20
Figure A-29. EDS analysis of ER308L weld filler material.	A-20
Figure A-30. EDS analysis of cast stainless steel CF-3M (Type 316L).	A-21

Figure A-31. SEM picture of the remaining metal surrounding the pits (white).	A-21
Figure A-32. EDS analysis of pit cell No. 3. Shows Cl content of 1.67%. <i>Occluded pitting cell</i> formed by the <i>auto-catalytic action</i> . The deeper, smaller holes are initiated by oxide inclusion (slag) and depleted chromium in local areas. Low pH (<i>pH 1</i>) <i>pitting soup</i> dissolves the stainless steel making round cells by forming <i>galvanic cells</i>	A-22
Figure A-33. EDS analysis of pit cell No. 2. Shows Cl content of 0.68%.	A-23
Figure A-34. EDS analysis of pit cell No. 1a. Shows Cl content of 0.22%.	A-23
Figure A-35. EDS analysis of pit cell No. 2a. Shows Cl content of 0.77%.	A-24
Figure A-36. Polarization curves for Type 304L (UNS S30403) and ER 308 filler metal. Comparison is between as-welded without post-weld cleaning and cleaning by the pickling process (after P. Li, Ref. 16).	A-25
Figure A-37. Chloride Pitting Corrosion Mechanism: Auto-catalytic action in occluded pit cells will take place after pits are initiated at weld defects and under heat tints-scale in 304LSS with ER308L filler metal welded to Type 316L stainless steel in underground water with 200 ppm chloride at room temperature.	A-26

LIST OF TABLES

Tables	Page
Table 1. Composition of Materials and Scanning Electron Microscope - Energy Dispersive Spectroscopy (SEM-EDS) Analysis of LLW2 Skid-B Materials After Welding	4
Table 2. Applicable National Standards, Codes, Local Control Procedures, and Specifications	5
Table 3. Special Local Rules	5
Table 4. An Average Concentration of Chloride, Sulfate, and Iron in Monitoring Wells Between 1991 and 1996 (Ref. 6)	6
Table 5. Chlorine Analysis of Skid-A and Skid-B Analysis in January 1999 (Ref. 9 & 19)	6

THIS PAGE INTENTIONALLY LEFT BLANK

EXECUTIVE SUMMARY

An independent investigation of pipe welding leaks from the Low-Level Waste 2 (LLW2) Skid-B System for the possibilities of improper welding (IW), microbiologically influenced corrosion (MIC), sensitization, chloride pitting corrosion (CPC), and intergranular stress corrosion cracking (IGSCC) was conducted. The results show the prevailing mechanisms that caused the leaks are identified as IW, CPC, and the improper selection of weld filler material for the base metals in an environment of the North Plateau underground water. There is no evidence of MIC, sensitization, or IGSCC. The chloride pitting corrosion mechanism that took place at all the welds are also described. All the pipelines were replaced with polyvinyl chloride (PVC) for cost saving and the LLW2 Skid B System has been successfully operating since 1999. This report summarizes the findings and recommendations associated with preventive measures for future operations.

1.0 INTRODUCTION

This report documents the corrosion evaluation and failure mechanisms of the stainless steel pipe welds in the Low-Level Waste Treatment System (LLW2) Skid-B. Independent evaluation of the metallographic samples from Skid-B was conducted by the Westinghouse Science and Technology Center (WSTC). A videoscope tape of the pipe internals was evaluated by ChemMet, PC, and Welding & Joining Management Group-West. All results were incorporated in this report.

2.0 BACKGROUND

The LLW2 Facility is a replacement for an existing waste treatment system. The Facility processes two different waste streams through two different "skids." After seven months of operation, one of the two skids began to leak. Extensive evaluation of the corrosion mechanisms and the contributing factors are documented in this report. This report principally evaluates the physical and chemical configurations that led to the corrosion and leaks. Chloride pitting corrosion, exacerbated by weld defects, is the corrosion mechanism. The report also discusses fabrication and Quality Assurance (QA)/Quality Control (QC) actions that would have prevented their occurrence. It is believed that in the absence of either the defects or the chloride concentrations, corrosion would not have occurred.

In developing the specification for processing skids to be used in the Facility, high chloride was not identified as a parameter of concern. As such, piping fabrication and inspection standards for the system did not identify more rigorous welding standards that could have prevented the corrosion and subsequent leaks.

3.0 THE LLW2 SKID-B SYSTEM AND RELATED FACILITIES

The LLW2 Skid-B system started operation April 1, 1998. The general location of the Low-Level Waste Treatment System (LLWTS) and the names of associated facilities are shown in Figure A-1. Water containing chloride and Sr-90 in the North Plateau (NP) wells is collected in the North Plateau Groundwater Remediation System (NPGWR) in the North Plateau cargo container as shown in Figure A-1. Figure A-2a shows the polyvinyl chloride (PVC) process pipelines of the NPGWR. The water flows through the PVC pipelines and is stored in a polyethylene tank (02-D-001). Water is then pumped out to the Skid-B surge tanks, which are made of plastic-lined carbon steel (02-D-002) and are located in the 0-LLW2 Facility as shown in Figure A-1. The LLW2 pipelines are made of Type 304L stainless steel (SS) (pipe), ER308L (filler metal), and CF-3M (cast 316L flanges and elbows). The typical 1-1/2 inch Schedule 40 pipelines used in Skid-B are shown in Figure A-2b.

In the LLW2 system, water is treated with ion-exchange resins (IONAC® C-249) in three exchange columns to capture Sr-90. A Piping and Instrumentation Diagram (P&ID) of the Skid-B system, along with the leak spots, is shown in Appendix C. The treated water is then sent to Lagoon 4 or 5. Water in Lagoons 4 and 5 is either sent to Lagoon 3 for holding and chemical analysis or sent back to Lagoon 2 for further treatment. If the chemical analysis is acceptable, then the water is discharged to Erdman Brook. The locations of Lagoons 2 and 3 in relation to the West Valley Demonstration Project (WVDP) Main Building and Erdman Brook/Franks Creek are shown in Appendix E.

The first signs of leaks from the Skid-B pipelines were detected October 26, 1998 after 209 days (approximately seven months) of operation. At that time, 12 spots were detected as weeping-type leaks. Typical indications of leak spots are shown in Figures A-3 and A-4. The locations of the leaks are illustrated on the piping flow diagram (Appendix C). The pitting corrosion rate of the weld at the mixed base metal was 253 mils penetration per year (145 mils [1-1/2 inch pipe wall thickness] x 365 days/209 days = 253 mpy). The composition of Type 304L (pipe), ER308 (filler), Type 316L (flange) is shown in Table 1. The oxide heat tints-scale formed in the heat-affected zone (HAZ) had not been removed after the welding process. Tables 2 and 3 show specifications and special local rules that may apply for current activities. The average chloride concentration at the WVDP site is between 165 mg/L and 460 mg/L as shown in Tables 4 and 5.

In contrast to the Skid-B system, waste water coming from the Main Plant is collected at the interceptors as shown in Figure A-1 (bottom right corner). This water is then drained to Lagoon 2. The waste water is treated in Skid-A (with IE®-95 resin and IONAC® C-249 resin) and sent out to Lagoons 4 and 5. The water is then sent to Lagoon 3. When the water quality is acceptable to applicable regulations, it is discharged to Erdman Brook.

4.0 APPLIED MATERIALS

The materials used in the construction of Skid-B, and of primary concern in this report, are listed below and the compositions are given in Table 1:

Pipe: 1.5 inch, Type 304L, Schedule 40, longitudinal seam welded pipe
 Elbow: 1.5 inch, Type 316L, SS
 Tee: 1.5 inch, Type 316L, SS
 Valve-Flange: CF-3M (Cast Type 316L, SS)
 Weld Filler Rod: ER 308L (Max. carbon content of 0.03) was used for the filler metal (Ref. 1 and 2).

It was noted that a different material (ER-309) was tested during welding procedure qualification, and that ER308L was used for the LLW2 Skid-B pipe field welding (Ref. 3). However, this practice is accepted by the involved parties.

As noted above, the construction materials of the LLW2 Skid-B were mixed. The elbows, T-connectors, and valve-flanges welded to the pipes were 316L stainless steel using ER308L filler material. The 316L material did not show any sign of corrosion. However, the ER308L that was used as a filler material between the 316L flange and the 316L elbow (Figure A-4), and between the 304L pipe and the 316L T-connector (Figure A-3) showed significant pitting corrosion. Filler material 308L is not an appropriate material to use between Type 316L elbows and flanges because of a lack of molybdenum in the filler material that will set up galvanic conditions. Also, Fe-18Cr-8Ni alloy (304L) is more susceptible to pitting corrosion than Fe-18Cr-8Ni-3Mo (316L) (Ref. 4, p. 1:175). However, it is important to avoid sweeping generalizations regarding the propensity of an alloy to pit or of the infinite properties of anions. Each system must be considered individually (Ref. 5). Further discussion of this topic is in Section 8.1.

Table 1. Composition of Materials and Scanning Electron Microscope - Energy Dispersive Spectroscopy (SEM-EDS) Analysis of LLW2 Skid-B Materials After Welding

Element	Pipe (304L)*	Weld (ER 308L)*	Flange (cast 316L)*
Fe	70.62(65-71)	68.12(64.0-69.36)	67.47(61.9-68.6)
Cr	16.75(18-20)	17.93(19.5-22.0)	15.66(16-18)
Ni	9.71(8.0-12.0)	9.95(9.0-11.0)	10.62(10.0-14.0)
Mo	0.29(0.0)	0.81(0.75)	3.74(2.3-3.0)
Si	0.73(1.0)	0.80(0.3-0.65)	1.08(1.0)
Mn	1.74(2.0)	2.10(1.0-1.5)	1.27(2.0)
P	---(0.045)	0.09(0.03)	---(0.045)
S	0.00(0.03)	0.00(0.03)	0.00(0.03)
C	0.32(0.03)	0.19(0.03)	0.22(0.03)
Na	---(0.00)	---	
Cl	0.09(0.11)	0.10	
O	0.07(—)	0.09(—)	0.08(—)

* The italicized numbers are the handbook specification numbers for Type 304L (pipe), ER 308L (weld filler material), and Type 316L (flange) materials before welding. The numbers that are not italicized are the EDS analysis of the welded conditions after seven months exposure in water.

5.0 WELDING AND QA INSPECTION PROCEDURE

Gas tungsten-arc welding (GTAW) methods were used to weld the piping on Skid-B. All applicable weld procedures and QA inspection procedures are shown in Table 2. Special local rules are summarized in Table 3.

The pipes were preheated and argon gas was used for welding, as well as for back-purging, to prevent surface oxidation and increase the pitting corrosion resistance. The electrode used was 2% thoriated tungsten. The applied potential and current were 10 to 15 volts and 60 to 120 amps, respectively. Other parameters such as gas flow rate, travel speed, and metal specifications are shown in Ref. 3. The welding was performed manually.

Table 2. Applicable National Standards, Codes, Local Control Procedures, and Specifications

<i>Activities</i>	<i>National Standards and Codes</i>	<i>Local Control Procedures and Specifications</i>
Design and Fabrication	ANSI B31.1	Per System Specifications and QA-QIP-20
Materials	ASME Code Section II	Per System Specifications
Inspection	ASTM Inspection	QA-QIP-14, QA-QIP-24, QA-TEST-01
Testing	ANSI B31.1	QA-QIP-13
Welder Qualifications	ASME Code Section IX	QA-QIP-24
Weld Procedure	ASME Code Section IX	GT-8-8

Table 3. Special Local Rules

For Materials List, see Bill of Materials in the system drawing.

- # All socket welds are to be fit-up and welded in accordance with ANSI B31.1; minimum fillet size is 3/16 inch.
- # All weld fit-up and final weldment (root weld inspection is not identified) shall be visually inspected in accordance with QA-QIP-24 and QA-TEST-01 prior to hydrostatic testing. (The type of water to be used is not identified.)
- # Threaded joints are to be assembled per DTS-RWO-004.
- # Tubing should slope upward towards gauges or instruments, and loops should be minimized whenever possible.
- # Flush the assembly with potable water prior to installation. (The internal cleaning of all welds by pickling to remove internal pipe oxide film was not mentioned.)
- # Minimum tubing bending radius is 3 times the tube diameter.
- # Instrument line size is specified by the instrument line number on the System P&ID and defined by Engineering Standard DTS-ENG-S-2000.

Note: The items in parentheses will significantly affect chloride pitting corrosion. Thus, the recommendation is to specify and rigorously implement them in future projects.

From the experience of Dr. J. A. Grantham, welding engineer/metallurgist (Appendix B), the above manual welding procedures and workmanship standards were not enforced during fabrication in the industry.

6.0 ENVIRONMENT

Skid-B influent has been supplied from underground wells in the NPGWR as shown in Appendix E. The water is contaminated mainly with Sr-90. The temperature of the influent contacting the piping is between 45° and 55°F. The pH of the influent to Skid-B is <pH 7.6 (23°C) with a standard deviation of 0.05. The maximum chloride content of wells in the vicinity of the North Plateau cargo container (Figure A-1 and Appendix E) is less than 200 mg/L for the years 1991-1997 (see Table 4) and increased slightly to reach the 281 level in January 1999 (see Table 5). The dissolved oxygen concentration in the various locations of the LLW2 system averaged 8.5 ppm (influent to Skid-B from NPGWR-02-D-01).

For comparison, Skid-A influent is approximately 10% from the NPGWR and 90% from Lagoon 2 since 1996, and contains a lower chloride level. The pH of Lagoon 2 is routinely adjusted to achieve a target operating pH of between 9.5 and 10.5 Standard Units (S.U.). This milder condition of the chloride concentration in Skid-A could be considered a contributing factor in the lack of leaking welds after 7 months exposure. A chlorine analysis of Skid-A, Skid-B, and soft water was conducted in January 1999. The results are shown in Table 5. The results provided a caution that the higher percent of influent from underground water may shorten the life of Skid-A (It is expected that Skid-A was built the same way as Skid-B.). The differences with Skid A influents are the higher pH, the higher hardness of water in the influent, and the lower chloride content of Lagoon 2. However, once pitting corrosion is established on Type 304L stainless steel, it is very difficult to stop due to the auto-catalytic actions that raise the concentration of chloride in the pits.

Another factor influencing corrosion is the flow rate of the fluid. High-flow conditions, preferably over 0.7 m/sec are required, to minimize corrosion. The flow rate of the water in the 1-1/2 inch pipe averages 0.63 m/sec (6.5 gpm) in Skid-B (Appendix C). In addition, Skid-A process pipeline legs were shut off for a 3-month period which created a stagnant region in the system, as shown on the P&ID (Appendix C). This low flow rate and the stagnant condition set up an environment suitable for chloride pitting corrosion. Thus, an effort should be made to flush the piping often to prevent deposits inside the pipeline, especially where HAZ chloride pitting corrosion can easily take place.

Table 4. An Average Concentration of Chloride, Sulfate, and Iron in Monitoring Wells Between 1991 and 1996 (Ref. 6)

<i>Monitoring Well No.</i>	<i>Chloride Cl (mg/L)</i>	<i>Sulfate SO₄ (mg/L)</i>	<i>Iron Fe (ppm)</i>
401	460 (13 s)*	27.7 (12 s)	13,436 (12 s)
502	176 (11 s)	31.1 (11 s)	12,003 (23 s)
801	197 (10 s)	29.2 (10 s)	499 (9 s)
106	165 (10 s)	65.1 (10 s)	18,494 (10 s)

* The number 460 mg/L indicates the average of 13 samples(s) taken from Well No. 401. Well No. 401 is located close to the Main Parking Lot. Wells Nos. 502, 801, and 106 are located close to the WMA2 area and, thus, are considered more representative of influent water to the LLW2 system. (See Appendix E.)

Table 5. Chlorine Analysis of Skid-A and Skid-B Analysis in January 1999 (Ref. 9 & 19)

<i>Sampling Date</i>	<i>Soft Cold Water</i>	<i>Skid-A Cl ppm</i>		<i>Skid-B Cl ppm</i>	
	<i>(Cl ppm)</i>	<i>Influent (1058)</i>	<i>Effluent (1066)</i>	<i>Influent (1067)</i>	<i>Effluent (1063)</i>
01/04/99	-----	162	184	246	-----
01/26/99	9.37	160	167	281	-----
02/02/99	10.90	141	146	285	280

6.1 Empirical Scaling Index

North Plateau influent, Lagoon 2 influent, and combined effluent water analysis data were used to calculate the Langelier Index (LI), assuming the temperature is 23°C (Ref. 20, Dr. Divine). The LI is an empirical scaling index used to predict the formation of scales on metal walls. It is commonly used in carbon steel systems to predict corrosion; with the presence of scale tending to decrease corrosion. The LI for the North Plateau influent, based on the water analysis, is minus 1.2 (-1.2) suggesting a strong tendency to dissolve carbonate scale in LLW2 Skid-B piping. On the other hand, Lagoon 2 influent water, with a higher carbonate concentration and pH, resulted in a LI value of plus 0.4 (+0.4), resulting in moderate scaling taking place in Skid-A. Skid-A was fed with Lagoon 2 water and showed no leaking compared to Skid-B (12 weld leaks) which was fed by North Plateau water. It is possible that the reason the Skid-A welds remained in better condition than the Skid-B welds was due to the combination of the following conditions:

- # Fewer numbers of defective welds (1 vs. 12). These weld defects could not be identified by radiography before the start of Skid-B.
- # Lower chloride content ($\text{Cl} = 136 \mu\text{g/mL}$ vs. $321 \mu\text{g/mL}$)
- # Higher pH ($\text{pH} = 10.5$ vs. <7.6)
- # Moderate scaling ($\text{LI} = +0.4$ vs. dissolved carbonate $\text{LI} = -1.2$)

The effects of a coating/scale on stainless steel have been rather vague because of many contributing factors. The effect of a coating/scale property on corrosion will be a function of several factors:

- # If the scale were impermeable, then it would be definitely protective.
- # If the scale becomes separated from the surface of the stainless steel, the scale can lead to crevice corrosion.
- # If the scale is porous, then solution can get down to the metal surface in spots.
- # Pores can lead to pitting on carbon steel; there will be a stronger tendency to pit.

In addition, the flow rate of the water in the piping also has an effect. Additionally, there is typically an incubation period before anything occurs. These all result in uncertainty as to what will actually happen. However, it is clear that the higher the pH, the smaller the concentration of chloride and the higher the flow velocity (the flow velocity should be above 0.7 m/s) and the better the weld quality, the lower the probability of localized corrosion (Ref. 19).

6.2 Water Chemistry

The analytical results of North Plateau (NP) and Lagoon 2 water samples taken from LLW2 in March 1999 can be found in Reference 20.

The current chloride levels in Lagoon 2 water may be a direct result of the near-term operations of directing NP water to Lagoon 2 prior treatment at the LLW2. Lagoon 2 water has sufficient hardness to lead to scale formation in Skid-A components. If most of the operation with Skid-A occurred during periods of lower chloride content, the same plating effect will actually help protect the Skid-A components. Behind the deposits in Skid-A, any chloride ions will find conditions ($\text{pH} 10.5$) not as susceptible to pitting corrosion (Ref. 19).

7.0 EVALUATION OF THE POSSIBLE WELD DEFECTS AND CORROSION PRODUCT

Longitudinal, seam-welded pipe was used for the LLW2 System. The original pipe seam-weld did not show any signs of corrosion. Only a small number (12 welds) of the manually welded field-welds and the HAZ were perforated (1-1.2 inch pipe with a wall thickness of 145 mils) after 209 days of operation in an average of less than 300 ppm chloride in the water.

Videoscope inspection, radiographic inspection, stereoscope examination, microbiologically influenced corrosion (MIC) examination, metallograph, and scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) examinations were conducted to identify the major cause of the pipe leaks. The cause was identified as chloride pitting corrosion. Internal weld defects and improper welding techniques provided initiation sites for this corrosion mechanism. The following sections (7.1 through 7.8) describe these investigations and the results.

7.1 Videoscope Inspection

Videoscope tape was examined for four out of the 13 welds at location Nos. #2, #3, #4, and #7. Welds #2 and #7 were leaking before shutdown of the system. The videotape clearly shows discontinuity of the welds, drop-throughs, undercut, and oxide heat-tints scale deposits that can provide initiation sites for pitting corrosion. The videotape was sent to an independent welding expert for further evaluation. The following are independent observations from Dr. Divine, P.E., Chief Engineer of ChemMet, Ltd., PC; and Dr. Grantham, P.E., Welding Engineer/Metallurgist (Ref. 7 and Appendix B):

- # The observed manual weld defects are: lack of penetration, lack of fusion, excessive concave root (suck-back), undercut, excess internal reinforcement (wagon tracks), excess weld metal (dingle berries), porosity, slag, burn-through, excess spatter, and weld fissures (cracks).
- # There are remnants of slag remaining on several manual welds as though a consumable backing strip was used for an atmospheric barrier instead of inert gas inside the pipe. Areas of white "sugar" that appear on the welds are generally nitrides and oxides. They indicate a lack of cleanliness and improper shielding with inert gas during fabrication.
- # The weld defects noted were observed in the filler metal area of the manual welds. The HAZ in the base metal on each side of the manual welds appeared to be in satisfactory condition without deterioration. (Comment by J.Y. Chang: Cavities were identified in the base metal during destructive evaluation.) The manufacturing seam in the pipe appeared satisfactory, without any indications. Seamless pipe is generally used in corrosive applications. (Comment by W. L. Zuppinger: Skid-A and -B systems were not identified as a corrosive environmental application.)
- # The areas of filler metal deterioration could indicate that an incompatible filler metal was used with the base material or an incorrect base material was used for the filler metal. Further analysis is recommended. (Comment by J.Y. Chang: ER 309L is a better filler material for Type 316 valve flanges or elbows.)
- # In addition, the pipes should be cross-sectioned at the points of failure to determine the type of attack and, in the case of pits, the pit profile. Microbiologically influenced corrosion (MIC) pits generally have a different shape than plain chloride-induced pits. (Comment by J. Y. Chang: The pipe cross-section was examined. Results are reported in Section 7.5.3. MIC is reported in Section 7.4.)

7.2 Radiographic Inspection (ASME B31.3)

Radiographic inspection was conducted to examine weld defects on Skid-B, Skid-A, and the Off-Skid components (Ref. 8). Only the results of Skid-B are reported here. Radiographic inspection of Skid-B after seven months exposure shows that out of the six welds inspected, three welds were rejected due to large cavities. One example of the radiographic inspection, dated January 5, 1999, is shown in Figure A-5. These cavities appear in the welded area as well as in the HAZ, as depicted in Figure A-5.

7.3 Stereoscope Examination of the Rust-Nodule (Corrosion Product and Weld-Spatter)

A piece of rust-nodule that was attached to the inside of the pipe was removed and evaluated. It shows the typical brown-orange rust color of a $\text{Fe}(\text{OH})_3$ deposit as shown in Figures A-6 through A-9. The rust was a very powdery-brittle deposit accumulated on the internal weld-spatter. The thin-shell form of the weld-spatter is black-rust Fe_3O_4 . Fe, Mn, Mo, Si, and S were found in the corroded material with the SEM-EDS analysis as described in Section 7.5.4. In reference to Figure A-6, the upper portion of the surface, including the dome, may be facing the higher pH (7.6 pH, 23°C) and an oxygen level of 8.5 ppm. The top of the dome shows thin corrosion product layers as can be seen in Figure A-6. However, below this thin, black-scale surface where crevices were formed, a significant amount of electrochemically deposited oxides were observed. This can be more clearly seen in Figures A-7, A-8, and A-9. Notice that at the top of the layers of weld-spatter, there is pitting inside the dome and deposits of oxide surrounding the pit hole. This will be further discussed in Section 7.8. Figure A-9 displays the morphology of electrochemically deposited metallic ions. Even though only chemical elements were identified, it is expected that these elements may have been in the form of $\text{Fe}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, and MoO_2 at the cathode and successively oxidized to the state of $\text{Fe}(\text{OH})_3$ and Fe_2O_3 (orange-red). The original thin weld-spatter that was not removed oxidized to what appears as a greenish-black color in Figures A-6, A-7, and A-8 (magnetite = Fe_3O_4). The weld-spatter becomes the crevice corrosion initiation site.

The chemical composition of the deposit on the weld-spatter was analyzed indicating that the Cr content was 12%, the Ni content was 2%, and the chloride content was 2.7%. Other elements were not tested. The $\text{Fe}(\text{OH})_3$ content is expected to be the balance (68.92%) of the material. This material must have come from deep inside the pitting of the corroded weld-filler material (anode) as soluble Fe^{2+} , Cr^{3+} , Ni^{2+} , and Mn^{2+} . Hydrolysis took place when these elements reached the cathode at the surface (the thin magnetite layer shown in Figures A-6 and A-8). These ions reacted with hydroxyl ions and possibly formed an insoluble deposit of $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, and $\text{Mn}(\text{OH})_2$.

7.4 Microbiologically Influenced Corrosion (MIC) Examination

The metabolic activity of bacteria can change the local environment and lead to MIC in situations where the metal would otherwise maintain corrosion resistance (Ref. 9 and 10). The bacteria growth could also be attributed to aerobic, anaerobic bacteria (AAB), or acid-producing bacteria (APB) rather than sulfur-reducing bacteria (SRB). WVNS has been investigating North Plateau SRB counts in Tank 8D-1. The counts were very low during the last five years. A recently failed pipeline at the Interim Waste Storage Facility (IWSF) showed bacteria counts were less than 1,000 SRBs and 2,460,000 counts for other types of bacteria that are aerobic, anaerobic, or acid-producing types. Additionally, as of January 20, 1999, the existence of the *Gallionella* sp. bacteria was not confirmed at Skid-B, Weld No. 4.

The results of the bacteria counts after the 28-day incubation period are shown in Appendix D. The presence of SRB counts and APB will support other interwoven mechanisms of corrosion. However, North Plateau groundwater supplied to LLW2 Skid-B did not indicate the presence of SRB. The microbe counts should be in the order of over 10,000 to one million to be a major cause of MIC. Thus, MIC was not the principal cause of the pipe failure.

7.5 Failure Analysis

A section of the LLW2 Skid-B weld sample (236-B W4) was decontaminated at the WVDP and sent to the WSTC for independent failure analysis by R. Kunig and R. J. Jacko. The failure analysis report, completed by WSTC, is summarized in the report entitled, "Failure Analysis of WVNS LLW2 Skid-B Pipe Weld" (Ref. 11). Additionally, WVNS independently evaluated the metallographic, SEM-EDS, and chloride pitting corrosion evidence for the mechanisms leading to failure. These are summarized in Sections 7.5.1 through 7.8.

7.5.1 Acceptable Weld and Typical Weld Defects

Before proceeding to examine the cross section of the sample, it is worth reviewing the terminology that will be used in these following sections. Figure A-10 depicts the typical defects that occur during arc welding of heat-resisting alloys (Ref. 12) and also describes the defects using standard welding terminology. This terminology can also be applied to the gas tungsten-arc welding (GTAW) of stainless steel. Using Figure A-10 as the basis, the appropriateness of the weld was evaluated as follows:

7.5.2 Macro-Photograph

The weld sample that was sent for evaluation to WSTC is shown in Figure A-11. Figures A-12 and A-13 detail the inside of the pipe that was cut open longitudinally. The "drop-through" defect can be seen. The depth of the pipe appearing in this photo is approximately 80% of the pipe thickness, meaning the depth of the drop-through is (pipe wall thickness [0.145 in.] $\times$ 0.8 = 0.116 in.) approximately 0.116 inches. If the convex and concave depth of the root pass at the internal surface allowed for $\pm 3/32$ inches (0.094 in.), then this fault is not within an acceptable limit and provides the basis for rejection.

The unaffected pipe seam weld lines are shown in Figure A-14. Figure A-15 depicts a color close to the true color of the pipe's surface in contrast to the color of a white and blue paper napkin. The blue color area at the end of the pipe has a film thickness of 720 angstrom (72 nm) and is unaffected by the chloride (<300 ppm) corrosion after seven months of service. However, where the color is dark brown, the film thickness is over 5,000 angstrom (500 nm). This area shows significant pitting. If this oxide film and the chromium-depleted underlying area were removed, there is a high probability that chloride pitting could have been prevented.

The pits at the HAZ having thick oxide scales are shown in Figures A-16, A-17, and A-18. These pictures also present the "incomplete fusion" and "overlap" weld defects that provided initiation sites for crevice pitting corrosion in the weld filler material (ER 308L). The pitted region in Type 304L and the bottom section is cast Type 316L stainless steel, which was not corroded. Also, one can almost predict that some weld-spatter rested on this pitted area forming a crevice between the weld-spatter and the pipe thereby initiating crevice-chloride-pitting corrosion. This is why it is recommended to complete the post-weld cleaning and passivate the piping with 10% to 15% nitric acid before operation. Weld-spatters, oxide layers, and Cr-depleted layers should be removed.

Figure A-19 shows the short segment of good welds that did not show any pitting. Figure A-20 displays the segments of the defective weld drop-through that provided the initiation site for the pitting corrosion in the filler metal and also shows "insufficient fusion and oxide slag entrapment" between the root weld and the final weld. These will be discussed in detail in Section 7.5.3.

Before proceeding to the next figures, one can visualize how drop-through appears to the inspectors when looking inside a pipe from the flange side (Figure A-15) if the section of the leg could be disassembled. Internal visual inspections are rarely, if ever, required. However, welds at the end of a fabricated spool piece can easily be inspected.

An important action required in the future is to remove all post-weld oxide film and flush the pipes occasionally to remove contaminants. The system should be run in this mode to mitigate stagnant areas and promote drainage in order to prolong the life of the pipes against chloride pitting corrosion.

7.5.3 Metallographic Evaluation of Weld

WSTC used metallographic and SEM-EDS analyses of the samples to perform the failure analysis. At the same time, WVNS made an independent interpretation from the SEM-EDS data and photographs. As mentioned earlier, the chemical composition of the welded materials and the analysis of the corrosion product are shown in Table 1. The italicized numbers in parentheses in the table are the original specification numbers for Type 304L (pipe), ER 308L (filler), and Type 316L (flange) materials before welding.

The samples were sectioned into smaller pieces. Five pieces were mounted, polished, and etched by WSTC. The general locations of these pieces are illustrated in Figure A-21. Cross-sections of the etched samples are shown in Figure A-22 through A-27.

Figure A-22 indicates that chloride pitting corrosion was initiated at the defective weld. That is, the root-weld exhibited excessive drop-through (Figure A-10(d)) and should have been repaired. A root-weld inspection would probably have identified the defect. By cleaning the oxide slag deposits, the welder could have made the repair-pass and the final weld-pass successfully. The oxide layer may have been left between the root-pass, repair-pass, and final weld. The repair root-pass did not fuse satisfactorily to the base metal, as shown in Figure A-22. The result is the formation of a large, chloride-pitting corrosion cavity in the three weld layers after seven months exposure, as shown in Figures A-22 and A-23. A good supply of shielding-inert gas, backing-gas, and cleaning the surfaces would have prevented the pitting initiation site (see Appendix B).

Pitting corrosion in the HAZ is shown in Figure A-24. As already mentioned in Section 7.5.1, it is necessary to prevent oxidation of the surface by providing enough backing gas for each of the first three passes. Additionally, post-weld cleaning should be conducted. Post-weld cleaning of the surface is a good practice to prevent pitting initiation sites, as described in Section 7.8 and Figure 36.

Type 304L is not the preferred material to use, especially when operating in a high chloride environment. The pitting resistance equivalent (PRE) that is $\%Cr + 3.3 Mo + 30N$ is a measure of the susceptibility to pitting. The PRE of Type 304L is 18, which is one of the lowest values of PRE. This is discussed in more detail by Agarwal, D. C. (see Bibliography).

Figures A-24 and A-25 depict satisfactory weld sections without pitting. Skid-B has many good welds. A Skid-B repair project can be accomplished by implementing proper welding practices and selection of materials. Reducing the amount of salt used in snow removal may help to maintain the chloride concentration of underground water below a 200 ppm level.

A. Sensitization

The weld interface between the 304L and ER308L (Ref. 11) is shown in Figures A-26 and A-27. The weld HAZ in the 304L and the filler metal ER308L interface shows no obvious indications of carbide precipitation at the grain boundaries usually associated with sensitization. This is due to the standard WVNS practice of using only low carbon content (0.03%) materials. Other supporting evidence is shown in Ref. 11 (see Figures A-20 through A-30).

B. Intergranular Stress Corrosion Cracking (IGSCC)

In the cross-section photos (Figures A-22 through A-27) there is no evidence of intergranular stress corrosion cracking. Sharp advancing crack tips that would indicate IGSCC cannot be identified. Figures A-22 and A-23 are examples of the current failure mode that is significantly different from IGSCC. Additional evidence can be found in Ref. 11 (Appendix A, Figures A-3 through A-35). The pitting morphology is round-shaped cavities connected to each other. The pictures and IGSCC mode of failure can be found in Ref. 13 (page 108).

7.5.4 SEM and EDS Analysis

Figures A-28 through A-35 represent the SEM-EDS analysis of: Type 304L, weld material ER308L, and cast stainless steel Type 316L. These numbers are put side by side with the material composition specification in Table 1. Note that the carbon contents are out of specification. It is suspected that EDS cannot accurately measure light-element carbon, thus a separate test for carbon content would be required. Since IGSCC and sensitization were not observed, the carbon content is expected to be low (0.03%). A separate carbon content test was not conducted.

The cross-section of the internal structure of the nodules appears to be formed by occluded cells (cells in which the anolyte and catholyte are separated from one another). The nodules are a product of the oxidizing cations that came from the bottom of the advancing pitting cell and were deposited at the cathode as an insoluble hydroxide.

The occluded cell of pitting is revealed in Figures A-32 and A-33. Figure A-31 shows the same area as Figure A-23 (Metallograph). It clearly shows the metal surrounding the pitting holes was curved by the pitting soup as shown in Figures A-32 and A-37. These many different layers of round chambers contain progressively higher concentrations of chloride. The EDS analysis indicated the chloride content in these chambers is different. Figure A-32 shows a chloride content of 1.67% (16,700 ppm). In Figure A-33, the chloride content is slightly less; 0.68% (6,800 ppm). The influent water contains approximately 0.028% (280 ppm). The chloride concentration of the last chamber touching the outside of the pipe is 31.7% (3.17E+5 ug/g). This will create a pH gradient in the occluded cell from less than pH 1 at the leaking end of the cell pipe surface to pH 7.6 at the top of the cell touching influent water (23°C).

The results indicate that chloride pitting corrosion initiated at defective weld sites, and the galvanic chloride concentration mechanism (auto-catalytic action), took place at the advancing end of the pitting. The SEM-EDS analysis shows that the high pitting-soup composed of HCl, FeCl₂, MCl₂, and H₂S had been ionizing Fe, Cr, and Ni into the solution and was carried away to the pitting entrance (cathode) by a potential differential (0.5 to 1.2 volts) created by the occluded cell leaving the empty cavities. Figures A-34 and A-35 also show the formation of a chloride gradient (0.22% and 0.68%).

SEM-EDS analysis established that the failure was due to the chloride pitting corrosion initiated at the defective welds and was propagated by the electrochemical process (called auto-catalytic action) in the many interconnected occluded pit-cells.

7.6 Ultrasonic Test (UT)

Ultrasonic inspection of the remaining pipe has not been conducted. However, UT inspection is recommended for inclusion of future inspection of the welded stainless steel pipe lines.

7.7 Pitting Initiation Mechanism at Heat Tints Site (HTS)

The following text describes why it is necessary to perform post-weld internal cleaning and passivation of welds in order to prevent pitting initiation.

As mentioned in Section 7.5.1 and Figures A-14 through A-20, various discolorations of the surface of stainless steel has been observed. These discolorations are called "heat tints." When iron is heated above 200°C (390°F), an oxide film appears on its surface. The color will indicate the amount of oxide film thickness (Ref. 14). Oxide film less than the wave length of visible light is considered a protective layer and will not cause the pitting corrosion as observed in Figure A-15. The film thickness of different colors that are close to blue are not susceptible to corrosion. In the WVDP environment, no corrosion was observed in the film thickness identified by the following colors (also described in Section 6.0):

- # Yellow = 40 nm (400 Å)
- # Orange = 52 nm (520 Å)
- # Red = 58 nm (580 Å)
- # Purple 63 nm (630 Å)
- # Violet = 68 nm (680 Å)
- # Blue = 72 nm (720 Å).

However, where the dark-brown colored rust formed, the number of pitting corrosion sites were more prevalent, as shown in Figures A-16 through A-18.

Arthur H. Turhill and Richard E. Avery state in Ref. 15 that when the oxide developed sufficient thickness to absorb all light, then the metal appears dark and the film scale is visible to the naked eye (Figure A-14 through A-20). The dark heat tint formed alongside a weld during the welding of stainless steel in the HAZ is a thicker chromium oxide scale (500 nm [5,000 Å]), with a mixture of iron, nickel, and other oxides. When heat tint scale forms, as observed in Figures A-16 to A-18, chromium diffuses outward from the base metal in the heated zone. The zone extends as far as the elevated temperatures allow chromium diffusion to occur. The diffusion of chromium into the scale leaves a thin, chromium-reduced layer just beneath the heat tint scale. This thin layer contains less chromium, the primary constituent that gives stainless steel its higher corrosion resistance. Reference 15 continues stating that corrosion that would not occur elsewhere can be initiated in the HAZ if the heat tint scale and the layer just beneath it are not removed. The reference also suggests using removal methods such as a rotating fiber brush, pickling, or electropolishing to readily restore the weld area to a normal base-metal with high corrosion resistance. Reference 15 also reports the results of a study done by University of Tennessee Laboratory (UTL) investigators (Ref. 16). The UTL tested Type 304L (UNS S30403), welded with ER filler metal (the same material used at the WVDP), using a polarization technique. The cleaned weld surface, free of heat tint scale, is passive and resistant to corrosion. Figure A-36 shows the results of the UTL polarization curves. The vertical section of the dotted curve indicates the normal passive range of typical stainless steel. However, the solid line shows the stainless steel welds that were not cleaned. In addition, the heat tint scale or underlying chrome-depleted layers were not removed. This solid curve presents no significant vertical line between the current density 10 μA and 50 μA at a potential between 100 mV to 850 mV. In other words, at a potential of 600 mV to 800 mV, the corrosion rate of the stainless steel will go up from 10 to 30 times faster at the local area.

For all oxide layers over 5,000 Å (500 nm), the dark brown colored oxide and chromium-depleted layers must be removed. These layers will become a pitting initiation site. Nitric acid pickling can be used to accomplish the removal.

As mentioned earlier, most pitting may have started under the heat tints oxide, other oxide deposits from the fluid, remaining weld-spatter, or weld defects. In the beginning, micro-organisms may have assisted initiation of the corrosion, but such evidence could not be confirmed during this investigation.

7.8 Mechanism of Chloride Pitting Corrosion

After pitting initiation took place, the chloride pitting corrosion mechanism will immediately take over to increase the chlorine concentration from the 250 ppm level of water to the 16,700 to 27,000 ppm level at the advancing pitting front, and continue to concentrate to the level of 100,000 ppm to 317,000 ppm Cl at the time when the advancing pitting front had reached the outside of the pipe. The corrosion rate may have reached 700 mpy at this high HCl concentration. From the initiation to the time of pipe weld perforation, the corrosion rate may have been changing from 0.1 mpy to the final accelerated corrosion rate of 700 mpy, thus establishing an average perforation rate of 253 mpy (actual data), and taking only seven months to perforate a 1-1/2 inch stainless steel, Schedule 40 pipe.

Many of the factors that affect corrosion are equally applicable to pitting corrosion, e.g., the large cathode/small anode area relationship, difference in concentration of the cathodic reactant, and auto-catalytic formation of acid within the occluded cell (Ref. 17).

It must be stressed that providing reducing conditions at the protective oxide film of Type 304L will initiate pitting. Furthermore, oxide scale (produced by welding) or any crevices (formed by incomplete fusion) will greatly accelerate pitting corrosion by concentrating the pit acid solution; HCl, FeCl₂, H₂S, or FeMnCl (pitting agent); formed by an auto-catalytic process in the occluded pit cell. The local concentration of Cl⁻ and H⁺ ions are required for continued propagation of the pits.

The pitting was indeed initiated through the oxide layers between the base metal and the root-pass and also the oxide layer between the root-pass and final weld as shown in Figures A-17, A-18, A-22, A-24, and A-32. An operating pitting mechanism was constructed from all the information accumulated during this investigation and is summarized in Figure A-37.

The stagnant environment and high chlorine concentration in the water created ideal conditions for chloride pitting corrosion. Apparently, negatively charged chloride ions (Cl⁻) were attracted by the anode when positively charged proton (H⁺) concentrations are high at the bottom of the crevice formed by the connected porosity (anode) as shown in Figures A-32 and A-37. HCl concentration will be increased (H⁺ + Cl⁻ = hydrochloric acid) and will increase the corrosion rate significantly. At the 15 to 30 wt% of HCl, the corrosion rate of Type 304L stainless steel increases from a passive state to an alarming corrosion rate of 700 mpy/year (Ref. 18). The results of the analysis support the chloride pitting corrosion mechanism that caused the leaking of the LLW2 stainless steel pipe welds.

It is interesting to note that Skid-A was shut down for 3 months and provided more stagnant areas than Skid-B piping, however, Skid-A did not develop leaks. In the WVDP environment, it is likely that other effects, such as pH, calcium carbonate, and chloride concentration, resulted in much greater combined effects on corrosion resistance than stagnant conditions alone.

8.0 SUMMARY AND CONCLUSIONS

A major chemical company investigated the causes of failure and the failure type of austenitic stainless steel in the U.S.A. The results of their statistical data in 954 cases revealed that stress corrosion cracking (SCC) dominated the failure rate at 38.0%. Pitting corrosion cracking is next at a rate of 25.0%. General corrosion (GC) cracking follows at 17.8%. The intergranular corrosion (IGC) rate is 11.5%, with all other types, such as MIC, reported at a rate of 7.7% (Ref. 18.).

WVNS evaluated all the above corrosion cracking mechanisms. The results are summarized below:

8.1 Stress Corrosion Cracking (SCC) and General Corrosion (GC)

Metallographic evaluations of the cross-sections of the leaking pipe support there was not carbide precipitation associated with sensitization nor were there indications of SCC or intergranular stress corrosion cracking (IGSCC). General corrosion of the pipe seam weld was minimal. The inside of the sectioned pipe away from the weld displayed the original bluish thin film that was untouched by the influent water, while the welded area and thin brown-scaled area showed many pits. The conclusion is that general corrosion (GC) of Type 304L did not cause the perforation of the pipe welds.

8.2 Microbiologically Influenced Corrosion (MIC)

The sulfur-reducing bacteria (SRB) population in the influent of Skid-B was investigated using MIC KIT III® bacteria incubation in their favorite nutrient. After 28 days of incubation, a number of bacteria were evaluated, indicating no presence of SRB.

Gallionella sp. (iron/manganese-oxidizing bacteria) was investigated with a stereoscope and the chemical analysis data of the deposits. It was concluded that the deposit was formed by an electrochemical deposition mechanism set by the auto-catalytic process in the occluded pitting cell, and not by the Gallionella sp. bacteria.

For other bacteria, such as APB, aerobic bacteria (AB), and anaerobic bacteria (AAB), the counts were too small to be considered responsible as the prevailing mechanism of the pipe weld leaks.

8.3 Chloride Pitting Corrosion

The result of the WVNS investigation established the cause of the Skid-B pipe weld leaks was chloride pitting corrosion caused by the combined effects of pitting initiation at the defective welds and at the HAZ heat-tints scale, by the high chloride concentration in the groundwater, and by a slow-moving water condition near the closed valves that enabled the auto-catalytic process in the occluded pit cells. This created a high concentration of acid-pit solution (<pH 1), which rapidly pitted through the imperfect area of the welds and perforated the pipe within 209 days. The effective pitting corrosion rate was 253 mpy for Weld No. 4.

Evidence is sufficient to support the above conclusions. SEM-EDS analysis showed the spherical, bowl-shaped pitting indicating typical chloride pitting corrosion. This also implies a low pH pitting acid solution (HCl, FeCl₂, MCl₂, H₂S) in specific locations. EDS confirmed the presence of a high chloride concentration gradient. This clearly demonstrated that the auto-catalytic process took place in the occluded pit cells.

Also, chemical analysis of the leaked material deposited outside the pipe, the true front line of pitting, showed a 31.7E+5 µg/g (31.7%) chloride concentration. This fact also supports that the main cause of the LLW2 Skid-B leaks was due to chloride pitting corrosion initiated by defective weld sites and a lack of cleaning.

The rust nodule attached to the inside of LLW2 pipe Weld #2 was examined with a stereoscope at 46X, 166X, and 465X magnifications at the WVNS Environmental Lab. It was identified as the deposit of corrosion products on the weld spatter. A low-density powdery material, $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ (orange-brown color), exhibited the structured patterns of electrochemically deposited layers. The analysis concluded that weld spatter attached to the internal surface of the pipe was acting as a cathode of the occluded cell that was located and exposed in water containing a higher oxygen (8.0 ppm average) and pH (< pH 7.5) level compared with the inside of the weld-filler metal pit-cavities. The cathode collected metal ions from inside the occluded pit cells. The chemical analysis using acid digestion methods revealed the deposited rust contained: Cl = 27,800 ppm, Cr = 121,000 ppm, and Ni = 3,200 ppm, indicating a much higher chloride concentration than the influent water (300 ppm, max.). Again, this suggests that crevice/pitting chloride corrosion was involved. The internal near-surface, weld-defects, oxide scale, slags, and insufficient fusion provided the ability for the site to initiate pitting. The auto-catalytic process took over to establish occluded pit cells that were able to perforate the pipe weld filler material (ER308L) within 209 days.

9.0 RECOMMENDATIONS AND PROPOSAL SELECTION

The analysis has identified the leaks were caused by chloride pitting corrosion initiated as weld-defects and uncleaned thick heat tints-scale at the HAZ. However, it should be noted that the majority of Skid-B pipes, including the original seam weld in the piping, has not been affected by the <300 ppm chloride. The pipe skin and original seam weld, away from the welds, were as clean as the original pipe shown in Figures A-14 and A-15. This means that even if Type 304L is known as "not a very good pitting-resistant material," it is still an adequate material that can withstand the present WVDP environment. It is believed that in the absence of either the defects or the chloride concentrations, the corrosion as described in this report would not have occurred.

With these facts in mind, WVNS has three possible approaches to repair the Skid-B system. They are briefly outlined in the following proposals:

Proposal 1

Repair only the defective welds with LOKRING™ fittings and, if necessary, replace any Type 304L pipe-lines with Type 316 stainless steel (using Type 316 filler metal where welding is required). Flush the system with 10 to 15% nitric acid to remove the oxide scale that caused pitting initiation.

Proposal 2

Replace Skid-B Type 304L pipelines (1-1/2 inch) with polyvinyl chloride (PVC) or chlorinated polyvinyl chloride (CPVC) plastic material, at a minimum. Cost savings may be recognized. However, a redesign of this system is required for mechanical endurance.

Proposal 3

Replace all Type 304L stainless steel/Type 316 stainless steel with an AL-6XN alloy that is a higher pitting corrosion-resistant material, and flush the system to remove the oxide tints scale. This will make the system more reliable; however, it will cost three times more.

WVNS accepted Proposal 2. The LLW2 Skid-B System has been successfully operating since 1999 without incident.

10.0 ACKNOWLEDGMENT

The author wishes to acknowledge the encouragement and support provided by Fred W. Damerow, Manager, High-Level Waste Closure Engineering, who contributed the insightful Background Section; Daniel C. Meess, Manager, Tank Farm and Integrated Radwaste Treatment System Engineering, for corrosion management internal funding support; and Thomas E. Cottrell, Manager, Site Operations Projects and Support, for his general guidance. Thanks are also extended to William L. Zuppinger, Operations Technical Support, who reviewed the manuscript, contributed valuable comments. In addition, thanks to the external funding support provided by Joseph F. Jablonski, Manager, Main Plant Operations.

11.0 REFERENCES

1. AWS Specification A5.9-93 or SFA-5.9, Part C, Appendix "Guide to Specification for Bare Stainless Steel Welding Electrodes and Rod," p.218, 1998.
2. G. G. Page, Materials Performance, Vol. 28 (7), p. 58, 1989.
3. Larry E. Beets to J. Z. Kwiatkowski, fax transmittal on "QW-48 Welding Procedures Specification (WPS); (Diversified Technologies, Knoxville, TN, WPS No. GT 8-8, 6/27/95; Supporting PQR(s): GTAW 01802, Rev. A, 10/24/97; Welding Process: GTAW; Type: Manual)," November 23, 1998.
4. Taylor Lyman, et al., ed., "Arc Welding of Stainless Steel," Welding and Brazing, Metals Handbook, Vol. 6, 8th Ed., pp. 245-276, 1971.
5. L. L. Shreir, R. A. Jarman, and G. T. Burstein, eds., "Corrosion, Metal Environmental Reactions," Vol. 1, p1:175, Butterworth-Heinemann Ltd., Linacre House, Jordan Hill, Oxford OX2 8DP, 1994.
6. Tom Whelan, "Welding Problems, Skid-B at LLW2," WVNS Meeting Minutes, January 29, 1999.
7. J. R. Divine, "Videoscope Tape Evaluation," e-mail - divine@chem, 10:20pm, January 7, 1999 and Report, "LLW2 Skid-B Corrosion Evaluation" by ChemMet, Ltd., PC: Dr. James R. Divine, PE, February 3, 1999.
8. J. Reynolds, "Radiograph Surveillance and Interpretation Report," WVNS, December 10, 1998.
9. Helmut Thielsch and Susan Freeman, "Microbiological Corrosion in Municipal Water Treatment Piping," Water/Engineering and Management, pp. 18-19, May 1997.
10. Gregory Kobin, "Corrosion by Microbiological Organisms in Natural Water," NACE, Corrosion/76, Paper No. 147, 1976.
11. Rosemarie Kunig and Rich Jacko, "Failure Analysis of WVNS LLW2 SKID-B Pipe Weld," Westinghouse Science and Technology Center, January 20, 1999.
12. Taylor Lyman, et al., ed. "Arc Welding of Heat Resistant Alloy," Welding and Brazing, Metals Handbook, Vol. 6, 8th Ed., pp. 277-295, 1971.
13. R. F. Steigerwald, ed., "Intergranular Corrosion of Stainless Alloys," by ASTM, Stp. 656, p. 108, 1978.
14. S. L. Shawla, R. K. Gupta, "Selection of Stainless Steel," Materials Selection for Corrosion Control, ASM International, Chapter 11, p. 145, 1993.
15. Arthur H. Tuthill and Richard E. Avery, "Heat Tints on Stainless Steels Can Cause Corrosion Problems," pp. 72-73, Materials Performance, February 1999.
16. P. Li, et al., "Effects of Weldments in Microbial Fresh Waters," Corrosion/95, Paper No. 151, Houston, TX, NACE, 1995.
17. A. John Sedriks, "Corrosion of Stainless," John Wiley & Sons, Inc., NY, 1979.
18. Metal Handbook, Vol. 13, Corrosion, pp. 350, ASM International, Metals Park, Ohio, 1987.

19. J. R. Divine, "Calculation of Langelier Index for Combined Effluent and Influent of North Plateau Water and Lagoon 2 Influent Water," Letter to J. Y. Chang, March 19, 1999.
20. J. L. Mahoney, "Evaluation of LLW2 Water Samples - Corrosion," Memo #: II:99:0006, March 8, 1999.

12.0 BIBLIOGRAPHY

Agarwal, D. C., "Defy Corrosion with Recent Nickel Alloys," Chemical Engineering Progress, pp. 62-66, January 1999.

ASTM Designation: F493-97, "Standard Specification for Solvent Cement for Chlorinated Polyvinyl Chloride (CPVC) Plastic Pipe and Fittings, November 1997.

ASTM Designation: D3915-80, "Standard Specification for Polyvinyl Chloride (PVC) and Related Plastic Pipe and Fitting Compounds," pp. 777-781, 1980.

Chang, Ji Young, "MCI Test Results of 8D-1 Vault Water," Presentation, July 24, 1995.

Craig, Bruce D., ed., "Handbook of Corrosion," pp. 457-468, ASTM International, 1989.

Dillon, C. P., ed., "Forms of Corrosion - Recognition and Prevention," pp. 31-32, NACE Corrosion Handbook, 1982.

Kelly, James, Private Conversation on "Alloy AL-6XN and Relative Fabrication Cost Calculation," January 29, 1999.

McIntyre, Dale R., Cortest Laboratories, Inc., Material Tech Institute of the Chemical Process Industry, Inc., I Publication No. 27, "Experience Survey Stress Corrosion Cracking of Austenitic Stainless Steel in Water," February, 1987.

Maurer, Jack R., "Optimizing Surface Quality of Stainless Alloys and Using a Modified ASTM G 48B Procedure for Acceptance Testing," Materials Performance, pp. 77-78, January 1999.

Private Conversation with Dr. Chester Dacres, DACCO SCI, Inc., Nov. 12, 1998.

Private Conversation with Oscar Lopez and Don Kay on January 29, 1999.

Schalert, K. W., "Radiographic Inspection Report," Job No. 9802742, Quality Inspection Services, Inc., December 5, 1998.

Steigerwald, R. F., ed., ASTM Special Technical Publication 656, May 1997.

Streicher, Michael A., "Material Problems with Temporary and Permanent Storage of High-Level Nuclear Wastes," Materials Selection & Design, Materials Performance, Vol. 38, No. 1, January 1999.

Whelan, Tom, "Summary of LLW2 Welding Issues and Related Topics," Presentation at WVNS, January 8, 1999.

13.0 ACRONYMS

AAB	Anaerobic Bacteria
AB	Aerobic Bacteria
APB	Acid-Producing Bacteria
CPC	Chloride Pitting Corrosion
CPVC	Chlorinated Polyvinyl Chloride
GC	General Corrosion
GTAW	Gas Tungsten-Arc Welding
HAZ	Heat-Affected Zone
HTS	Heat Tint Sites
IGC	Intergranular Corrosion
IGSCC	Intergranular Stress Corrosion Cracking
IW	Improper Welding
ISWF	Interim Waste Storage Facility
LI	Langelier Index
LLW	Low-Level Waste
LLW2	Low-Level Waste Treatment System
LLWTS	Low-Level Waste Treatment System
MIC	Microbiologically Influenced Corrosion
NP	North Plateau
NPGWR	North Plateau Groundwater Remediation System
P&ID	Piping and Instrumentation Diagram
PQR	Procedure Qualification Record
PRE	Pitting Resistance Equivalent
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
RT	Radiographic (Examination) Test
SCC	Stress Corrosion Cracking
SEM-EDS	Scanning Electron Microscope - Energy Dispersive Spectroscopy
SRB	Sulfur-Reducing Bacteria
SS	Stainless Steel
UT	Ultrasonic Examination
UTL	University of Tennessee Laboratory
WMA2	Waste Management Area 2
WOQ	Welder Qualifications
WPS	Welding Procedure Specification
WSTC	Westinghouse Science and Technology Center
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services Company

THIS PAGE INTENTIONALLY LEFT BLANK

APPENDIX A
FIGURES REFERENCED IN REPORT

THIS PAGE INTENTIONALLY LEFT BLANK

Figure A-1. North Plateau Groundwater Remediation System (NPGWR). Well water is pumped to Surge Tank 02-D-001 and sent to LLW2 Skid-B.

2a. Surge Tank 02-D-001 and PVC process lines in NPWGR.

2b. Ion-exchange columns and stainless steel process lines. Materials are Type 304L, ER308L, and CF-3M (cast 316L).

Figure A-2. Low-Level Waste Treatment System, LLW2 Skid-B. Influent comes from NPGWR.

3a. Weld No. 3-230D, 02-WW-1-1/2-3136

3b. Weld No. 3-236B, 02-WW-1-1/2-3094

Figure A-3. Chloride Pitting Corrosion of Type 304L pipe ER308L filler metal, and cast Type 316L T-connector material after 7 months exposure in groundwater. Weld No. 3-236B, 02-WW-1-1/2-3094, LLW2 Skid-B.

4a. Weld No. 2-229B, 02-WW-1-1/2-3130

4b. Weld No. 3-236B, 02-WW-1-1/2-3094.

Figure A-4. Chloride Pitting Corrosion of Type 316L T-connector. ER308L filler metal, and Type 304L pipe and cast Type 316 valve flanges after 7 months exposure in groundwater.

Figure A-5. Radiograph showing cavities (four top spots and others) in the weld zone (white ring) and in the HAZ center dark lines. Radiograph of Skid-B, Package 97-236B, DTS weld #7, DWG 3013, after J. Reynolds.

6a.

6b.

Figure A-6. Rust nodule attached to the inside of the pipe where pitting took place. It is $\text{Fe}(\text{OH})_3$, containing Cr: 12.1%, Ni:0.32%, and Cl:2.78%. The dome is facing toward the center of the pipe. Original magnification = 46X.

Figure A-7. The other side of the same nodule as in Figure A-6, showing Fe_3O_4 (dark line at the top) that apparently was electronically connected to the base metal and acted as a cathode to deposit the material coming from the inside of the pits. Original magnification = 46X.

8a.

8b.

Figure A-8. Thin corrosion layer on the top of the dome is a Fe_3O_4 section. The original metal had a pit and formed a corrosion product outside the pit. Original magnification = 116X.

9b.

Figure A-9. A typical electrochemically deposited positive ion from an *occluded pit cell* by *auto-catalytic action* in weld filler material ER304L. The orange-red colors are $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The material is a mixture of oxides: Cr: 12.1%, Ni: 0.32%, and Cl: 2.78%, which probably came from the ER308L pits. Original magnification = 465X.

Figure A-10. Typical defects, (a) through (d), that occur in the arc welding of heat-resistant alloys. Sketch (e) represents a weld with no defects and good reinforcement. (Ref. 12)

Figure A-11. As-received pipe. Top cutting marking is arbitrarily chosen as 0 degrees and clockwise, 90 degrees specimen (W4) is named "sec. B 50" (Right). The section with the 179 degrees to 359 degrees sample is named "Sec. B 64" (Left).

Figure A-12. As-received inside of pipe showing improper welds, e.g., *oxide tints-scale*, *drop-through*, and chloride pitting corrosion cavities.

Figure A-13. Weld defect area in Figures A-12 shown at a higher magnification.

Figure A-14. Type 304L SS pipeline seam weld not affected by the corrosion and close to the original color.

Figure A-15. The coloration and the oxide film thickness of stainless steel. The blue color away from the HAZ is $720 \text{ \AA}$ and is acting as a protective oxide. However, the thickness of the dark-brown color tints-scale is over $5,000 \text{ \AA}$ and, as a result, the chromium-depleted 304L surface becomes susceptible to chloride pitting corrosion.

Figure A-16. As-received pipe, Section B64, showing pitting in the thick tints-scale near the weld. This shows incomplete fusion of the weld material to the base metal and *drop-through*.

Figure A-17. Pits in the Type 304L HAZ (Section 64). Notice the *weld tints-scale* that will initiate pitting.

Figure A-18. Drop-through weld defects and large pits at the cut surface. These are connected to the internal surface of the pipe and formed by chloride pitting corrosion during 7 months of exposure.

Figure A-19. The mating end of the same drop-through (Section 50).

Figure A-20. Close-up of the pit cell. Shows connection to the surface and cup-shaped internal pit cell surface. Metallography of this surface is shown in Figure A-23 and the SEM is shown in Figure A-32.

Figure A-21. Sketch showing locations of metallography cross-sections from LLW2 Skid-B. Pipe OD = 1.900 in., ID = 1.610 in., Wall thickness = 0.145 in.

Figure A-22. Weld porosity and corroded material in Section 64, also shown in Figures A-12 and A-13. The Type 304L pipe is on the left, weld filler material ER308L is in the middle, and Type 316L cast flange is on the right.

Figure A-23. The result of the chloride pitting corrosion started at the oxide layers between the root-weld and the final weld. Shows root-pass, drop-through, and pitting corrosion at the HAZ.

Figure A-24. Pitting found in the HAZ. The welded zone was well defused; however, post-weld surface cleaning of the tints-scale and chromium-depleted zone was not done, thereby initiating chloride-pitting corrosion at the HAZ.

Figure A-25. Shows a good diffusion penetration between the base metal and the filler metal. Shows good fusion between the root-pass and final-pass.

Figure A-26. Weld HAZ in Type 304L pipe at the weld interface (ER308L). No evidence of carbide precipitation at the grain boundaries associated with sensitization (500X).

Figure A-27. Weld HAZ in Type 304L pipe ID.

Element	Weight (%)
O	0.07
Na	
Si	0.73
P	
S	0.00
Cl	0.09
Cr	16.75
Mn	1.75
Fe	70.62
Ni	9.71
Mo	0.29

Figure A-28. EDS analysis of Type 304L pipe used in LLW2 Skid-B.

Element	Weight (%)
O	0.09
Na	0.00
Si	0.80
P	0.09
S	0.00
Cl	0.11
Cr	17.93
Mn	2.10
Fe	68.12
Ni	9.95
Mo	0.81

Figure A-29. EDS analysis of ER308L weld filler material.

Figure A-30. EDS analysis of cast stainless steel CF-3M (Type 316L).

Figure A-31. SEM picture of the remaining metal surrounding the pits (white).

Figure A-32. EDS analysis of pit cell No. 3. Shows Cl content of 1.67%. *Occluded pitting cell* formed by the *auto-catalytic action*. The deeper, smaller holes are initiated by oxide inclusion (slag) and depleted chromium in local areas. Low pH (*pH 1*) *pitting soup* dissolves the stainless steel making round cells by forming *galvanic cells*.

Element	Weight (%)	Element	Weight (%)	Element	Weight (%)
O	6.23	S	0.00	Fe	60.15
Na	2.01	Cl	1.67	Ni	6.01
Si	1.33	Cr	20.29	Mo	0.65
P	0.10	Mn	1.58

Element	Weight (%)
O	4.32
Na	1.24
Si	8.31
P	0.64
S	0.28
Cl	0.68
Cr	22.58
Mn	1.22
Fe	56.28
Ni	3.66
Mo	0.79

Figure A-33. EDS analysis of pit cell No. 2. Shows Cl content of 0.68%.

Element	Weight (%)
O	1.77
Na	
Si	1.57
P	
S	0.00
Cl	0.22
Cr	25.70
Mn	1.29
Fe	62.94
Ni	3.48
Mo	3.04

Figure A-34. EDS analysis of pit cell No. 1a. Shows Cl content of 0.22%.

Element	Weight (%)
O	4.67
Na	1.14
Si	1.61
P	0.25
S	0.32
Cl	0.77
Cr	23.89
Mn	1.22
Fe	60.41
Ni	3.42
Mo	2.29

Figure A-35. EDS analysis of pit cell No. 2a. Shows Cl content of 0.77%.

Figure A-36. Polarization curves for Type 304L (UNS S30403) and ER 308 filler metal. Comparison is between as-welded without post-weld cleaning and cleaning by the pickling process (after P. Li, Ref. 16).

A-26

THIS PAGE INTENTIONALLY LEFT BLANK

APPENDIX B
LLW2 SKID-B CORROSION EVALUATION

ChemMet, Ltd., PC
Dr. James R. Divine, P.E.

Welding & Joining Management Group, West
Dr. Jesse A. Grantham, P.E.

THIS PAGE INTENTIONALLY LEFT BLANK

CHEM MET, LTD., PC

PO Box 4068
West Richland WA 99353

(509) 967-2309 or (800) 570-2309 FAX (509) 967-2459

Your Single Source for Chemical, Materials, and Environmental Technology

February 3, 1999

Dr Ji Young Chang, PE
West Valley Nuclear Services
Rock Springs Road
MS N-AOCN 07
POB 191
West Valley NY 14171-0191

Dear Dr Chang:

Attached is my report discussing the Corrosion of LLW2 Skid-B. With it, I am enclosing a copy of a letter received from Dr J A Grantham, PE, of Welding & Joining Management Group, West that discusses the quality of the welds, based on information provided by your video tape.

The overall conclusions are that you started with poor welds that resulted in crevices. The crevices together with high chloride concentrations and occasional stagnant conditions in inappropriate alloys led to the formation of crevice corrosion and to pitting. During normal operating conditions, the 304L stainless steel probably would have been satisfactory. However, the presence of chloride, crevices (or other of the unsatisfactory weld conditions), or stagnant conditions or any of the three, individually, could have initiated pitting.

Please contact me if you have questions.

Sincerely,

James R. Divine, PhD, PE
Chief Engineer

Attachment: **Letter from Welding & Joining Management Group, West**

E-mail: divine@chemmet.com

<http://www.chemmet.com>

CHEM MET, LTD., PC

PO Box 4068
West Richland WA 99353

(509) 967-2309 or (800) 570-2309 FAX (509) 967-2459

Your Single Source for Chemical, Materials, and Environmental Technology

LLW2 Skid-B Corrosion Evaluation

Introduction

West Valley Nuclear Services Company, Inc. (WVNS) requested CHEM MET to provide technical/engineering assistance in support of the subject program. Specific tasks included:

- Provide an independent technical review of video tapes taken of the interior of the subject equipment piping.
- Recommend examination techniques and provide interpretation of the results of such examinations
- Contribute to and review the WVNS draft report on the failure mechanism.
- Participate in a presentation, on request, at WVNS on the failure mechanism and proposed corrective measures.

This report documents the independent technical review. All other items, with the exception of participating in a presentation, have been completed in previous correspondence with Dr Ji Young Chang, PE, of WVNS.

This report is based on a review of the video tape of the boroscope examination of interior of the Skid-B piping, of water data supplied by Dr Chang, and of fax copies of photographs and sketches from the metallographic study performed on the failed piping. Additional information is provided in the attached letter report from Dr J A Grantham, PE, who commented on the quality of the welding based on a review of the video tape.

Background

The sensitivity of the 300 series austenitic stainless steel alloys is well known. It is known to be susceptible to stress corrosion cracking by chlorides, to pitting, and to crevice corrosion. The latter two are similar but in the case of pitting, a pit has to be initiated whereas in crevice corrosion, the "pit" exists from some

construction artifact such as formation of oxide on the surface by the heat of welding (heat tint), by weld spatter, or by gaps left between two components joined by welding.

If the alloy does not contain sufficient chromium, as suggested by Table 4 of Dr Chang's report¹, then the alloy is more susceptible to corrosion. Examples of failures are common, but one is particularly meaningful². It shows pitting corrosion, nearly identical to the examples from the current failure and is attributed to chloride induced pitting. A related example occurred recently at Hanford. A 304 stainless steel tank was exposed to concentrated chloride solution at 20 to 40°F. The 0.25-inch thick wall penetrated in three to four months. Although the concentrations were higher, the temperature was lower; the solution was also stagnant.

Discussion

From the discussions by Drs Chang and Grantham, there is evidence of heat tint, weld drop-through, weld spatter, and crevices. In the presence of chloride concentrations of 450 ppm at room temperature, particularly in stagnant conditions, these features are sufficient to initiate pitting directly without the need to invoking crevice corrosion.

Once started, pits further concentrate chloride and become acidic, often to a pH of less than 1. As noted in the Hanford example above, corrosion rates of over 1,000 mpy (1 inch or 25.4 mm per year) are feasible without the need to invoke microbial induced corrosion (MIC).

It is acknowledged that disproving MIC by the absence of measurable microbe concentrations is difficult - they may have been missed in some way. Nevertheless, as noted, their presence or absence is moot because the corrosion rate can be sufficiently great without their presence.

Conclusions

Stainless steel with an insufficiency of chromium, an excess of carbon, which is improperly welded is, in the presence of chloride and especially under stagnant

¹ Chang, Ji Young, *Corrosion Evaluation of LLW2 Skid-B*, Draft Copy dated 29 January, 1999, WVNS, West Valley, NY.

² Metals Handbook, Volume 13, p 350, *Corrosion*, ASM International, Metals Park, OH, 1987.

conditions, is expected to pit. Depending on the interaction of the various operating parameters, pitting rates of the order of 1,000 mpy are not unexpected.

Though 304 stainless steel is not considered ideal for use with chloride containing solutions, it has been used even in seawater. For use in chloride systems, the chromium concentrations should be above the minimum specified, welding should be done in accordance with standard procedures by qualified welders, and the system should be flushed and drained when not in use.

Welding & Joining Management Group, West

FAKED

1/5/99

Dr. James Divine
ChemMet, Inc.
P.O. Box 4068
West Richland WA 99353-0017

Reference: Weld Leak Evaluation, MIL@LLW2, Dr. J.Y. Chang, WJMG Project 99001,
Borescope Video WVNS W/O 9802488, Skid B, DTS Dwg, WPS-M-3009 Rev A.

Dear Dr. Divine,

As we discussed by telephone, the following is a summary of my initial observations.

There are numerous manual welding defects that are immediately rejectable by visual examination in accordance with accepted standards for pipe welding. These indications could be readily determined and rejected using common nondestructive evaluations, either ultrasonic examination (UT) or radiographic examination (RT) during fabrication.

The observed manual weld defects were: lack of penetration, lack of fusion, excessive concave root (suck-back), undercut, excess internal reinforcement (wagon tracks), excess weld metal (dingle berries), porosity, slag, burn-through, excess spatter and weld fissures (cracks).

There are remnants of a slag remaining on several manual welds as though a consumable backing strip was used for an atmospheric barrier instead of inert gas inside the pipe. Areas of white "sugar" that appear on welds are generally nitrides and oxides. They indicate a lack of cleanliness and improper shielding with inert gas during fabrication.

The weld defects noted were observed in the filler metal area of the manual welds. The heat-affected zone (HAZ) in the base metal on each side of the manual welds appeared to be in satisfactory condition without deterioration. The manufacturing seam in the pipe also appeared satisfactory, without any indications. Seamless pipe is generally used in corrosive applications.

The areas of filler metal deterioration could indicate that an incompatible filler metal was used with the base material or an incorrect base material was used for the filler metal. Further analysis is recommended.

It would be beneficial to examine the official, signed welding documents and material certifications related to the manual and automatic pipe welds. These would include the welding procedure specification (WPS), procedure qualification record (PQR) and welder qualifications (WOQ). From my experience, these manual welding procedures and the workmanship standards were not enforced during fabrication.

Additional review is pending your authorization.

Sincerely,

Jesse A. Grantham, PhD., P.E.
Welding Engineer/Metallurgist

Technology • Training • Testing

1-303-451-6759
1-800-987-9269

2200 E. 104th Ave. Suite 203
Denver, Colorado 80233-4403
P.O. Box 21813, 80221-0813

Fax 1-303-280-4747
<http://www.wjmg.com>
Jesse_A_Grantham@prodigy.net

THIS PAGE INTENTIONALLY LEFT BLANK

Appendix C. Weld Leak Locations in LLW2 Skid-B (900D-7392, Sh. 7)

OPERATIONS TECHNICAL SUPPORT
MAKE SURE - WRITE IT

TO: JF Jablonski MS WV-205
 FROM: EF Dinsmore ex 2039
 DATE: December 16, 1998
 cc: TE Whelan MS WV-AA7
 JY Chang AOC-07

SUBJECT: 28 day MIC results

The final analyses of the samples that were collected Nov. 18 are summarized below as number of bacteria per ml of sample in the table below. In addition, I took pictures of all the samples that I hope to have developed shortly.

	Cap color	Green	Red	Blue	Yellow
Sample	Valve #	SRB	APB	Anaer	Aer
Skid A Inf	1058	0-10	1000-10000	100-1000	1-10
Skid A Eff	1066	0	10000-100000	100-1000	1-10
Skid B Inf	1067	0	1-10	0	0
Skid B Eff	1063	0	10-100	0	1-5
Soft Water	Cold water	0	1-10	0	0

The green capped bottles detect sulfate reducing bacteria. The red organic acid producers, the blue anaerobic or facultatively anaerobic, and the yellow for aerobic bacteria.

There was little change from last week other than the continued growth of the acid producers from Skid A.

Please call me at 2039 if you need more information.

Sincerely,

EF Dinsmore
Operations Technical Support

COPY TO:

Name	Mail Stop	Name	Mail Stop
<u>X</u> WL Zuppinger	AA7	<u> </u> JF Jablonski	205
<u>X</u> TE Cottrell	207	<u> </u> SA MacVean	201

Appendix D

THIS PAGE INTENTIONALLY LEFT BLANK

THIS PAGE INTENTIONALLY LEFT BLANK

DOE/NE/44139-92

WEST VALLEY DEMONSTRATION PROJECT

DOE

**Corrosion Evaluation of LLW2 Skid-B
Weld Failure Mechanisms**