NRTSCNUCLEAR REACTOR TECHNOLOGY
AND SCIENTIFIC COMPUTATIONSDOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATIONReviewing
Official:*Joseph A. Lazzaro*
(Name and Title)
S. Engineer

Date:

*11/11/91*Keywords:
Gadolinium Nitrate
Localized Corrosion
Electrochemical Testing

Retention - Permanent

**SUPPLEMENTARY SAFETY SYSTEM
CORROSION STUDIES (U)**

by

M. H. Anderson

M. H. Anderson

Materials Applications and Corrosion Technology Group
Materials Technology Section

and

B. J. Wiersma

B. J. Wiersma

Materials Applications and Corrosion Technology Group
Materials Technology Section

ISSUED: May 21, 1991

D. Thomas Rindin

Authorized Derivative Classifier

6/3/91

Date

SRL

SAVANNAH RIVER LABORATORY, AIKEN, SC 29808

Westinghouse Savannah River Company

Prepared for the U. S. Department of Energy under Contract DE-AC09-89SR18035

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.

MASTER

DOCUMENT: WSRC-TR-91-389
                      SRL-MTS-913001

DATE: May 21, 1991

TITLE: SUPPLEMENTARY SAFETY SYSTEM
                      CORROSION STUDIES (U)

APPROVALS

_____ DATE: 6-3-91
P. E. Zapp, TECHNICAL REVIEWER
MATERIALS TECHNOLOGY

_____ DATE: 3-Jun-91
J. E. Marra, MANAGER
MATERIALS TECHNOLOGY

_____ DATE: 6/4/91
T. L. Capeletti, MANAGER
MATERIALS TECHNOLOGY

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, P.O. 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 Rd., Springfield, VA 22161.

INTRODUCTION AND SUMMARY

This memorandum presents experimental data from electrochemical and immersion tests to support the continued use of two sections of nonconforming steel in the Supplementary Safety System (SSS). The Reactor Corrosion Mitigation Committee (RCMC) met on May 16, 1991 to evaluate materials that had been installed in the SSS. The materials lacked complete Corrosion Evaluation (CE) and/or Certified Mill Test Reports (CMTR)¹ and had been installed during recent modifications (Project S-4332). Items that lacked proper documentation included AISI Type 304 stainless steel (304) instrument tubing (0.375" OD) associated with the pressure transmitters and a two-foot section of 304 pipe located on the far side of the system downstream of the pneumatic valves. The RCMC emphasized the need for experimental data to support the general belief that these components could remain in the system until the next scheduled long shut-down.

Cyclic potentiodynamic polarization scans were performed on sensitized and solution-annealed 304 samples in as-mixed and acidified $Gd(NO_3)_3$ or "ink", solutions at room temperature to determine the susceptibility of 304 to localized corrosion in this environment². No localized attack was observed on the solution annealed or sensitized 304 in the $Gd(NO_3)_3$ solution. These tests revealed no significant differences in the behavior of the sensitized and solution-annealed 304 in gadolinium nitrate solution. Therefore, localized corrosion of the nonconforming components is not anticipated, and the performance of the nonconforming components should not differ from that of corrosion evaluated and certified materials. Previous studies have shown that AISI Type 304L stainless steel (304L) did not pit during a three-month exposure in gadolinium nitrate solutions of pH 2 or 5. These solutions also contained Rhodamine B, a chloride containing dye which increased the pitting potential and the aggressiveness of the test solution.³ These combined results support the continued use of the nonconforming steels until replacement can be made at the next scheduled long shut-down.

EXPERIMENTAL PROCEDURE

Cyclic polarization scans were conducted according to ASTM standard G61-86. A Princeton Applied Research (PAR) Model 273A Potentiostat/Galvanostat was utilized to control the electrical potential during the test. PAR 342 corrosion measurement software was used to record the current response. The scan rate selected for these experiments was 0.166 mV/s. The test solution was deaerated with nitrogen during the test. The potential was measured with respect to a saturated calomel electrode (SCE). The potential of this electrode was checked against an unused SCE prior to each test. At the completion of each test, the specimen was examined under a light microscope at a magnification of 70X to see if pitting had occurred.

A gadolinium nitrate solution was prepared in the as-mixed and acidified conditions. The concentration of gadolinium in each solution was 0.22 g/ml. The pH of the as-mixed solution was 3.39. For the acidified solution, nitric acid was added to reduce the pH to 2.07. The solution was deaerated with a nitrogen gas purge, and remained at a temperature of 23 °C for the duration of each test.

304 stainless steel was tested in the solution annealed and furnace sensitized conditions. The carbon content of the 304 was certified by the manufacturer to be 0.06% (*Attachment 1*). In order to simulate the sensitized condition two specimens were held in a furnace at 650 °C, one for 6 hours and another for 24 hours. The degree to which the specimens had been sensitized was evaluated qualitatively with the oxalic acid etch test and then quantitatively with electrochemical potentiokinetic reactivation (EPR). The oxalic acid etch test consists of applying a current density of 1 A/cm² to the specimen for 90 seconds in a 10% oxalic acid solution and then observing the microstructure on a metallograph at a magnification of 250X. For EPR, the specimen is passivated in a 0.5 M H₂SO₄ + 0.01 M KSCN solution and then the potential is scanned in the cathodic direction towards the open circuit potential.⁴ As the potential is scanned, the current, which is an indicator of the localized dissolution occurring at the grain boundaries, is measured. At the completion of the scan, the total electrical charge density passed during the scan is calculated to determine the degree of sensitization. EPR values greater than 2 C/cm² indicate that the material is susceptible to intergranular stress corrosion cracking (IGSCC).⁵

RESULTS AND DISCUSSION

Microstructure Evaluation

Welding of austenitic stainless steels results in a sensitized microstructure in a narrow band adjacent to the weld. Sensitization occurs at the grain boundaries where chromium carbides have precipitated thereby leaving a chromium depleted region. Due to the depletion of the chromium the region is susceptible to intergranular attack.

The oxalic acid etch test provides a qualitative estimate of the degree of sensitization. During the test the carbides are preferentially etched indicating the presence of chromium depleted regions. There are three structures which may result:

1. Step   Steps at grain boundaries; non-sensitized
2. Dual   Grains partially encircled by carbides; sensitized
3. Ditch   Grains completely encircled by carbides; heavily sensitized

Figure 1 shows the solution annealed specimen after the oxalic acid test. A step microstructure is evident indicating that the material is not sensitized. Figures 2 and 3 show the specimens which had been heat treated for 6 and 24 hours respectively. The 6 hour specimen has a dual microstructure while the 24 hour specimen has a ditched microstructure. The results of the oxalic acid test indicate that the samples have been sensitized and can be used to compare the localized corrosion behavior of sensitized and non-sensitized material.

EPR has been used to quantitatively determine the degree of sensitization of welded and flame washed 304 pipe sections in the process water system at SRS. EPR values for flame washed regions on the outer diameter of the pipe range from about 5-20 C/cm²,⁶ while for pipe butt welds the values are approximately 15 C/cm².⁷ The EPR values determined for the solution-annealed, 6 hour and 24 hour specimens used in the electrochemical tests were 0.0027, 6.2 and 13.7 C/cm² respectively. Thus, the sensitization levels of the materials which were tested approximate those in the heat affected zones of welded 304 pipe. Figures 4, 5, and 6 show post-EPR microstructures for these specimens. The micrographs of the sensitized microstructures indicate that the grain boundaries were preferentially etched.

Cyclic Polarization Tests

The purpose of these tests was to investigate whether sensitization of 304 adversely affected its localized corrosion behavior in a gadolinium nitrate environment. Cyclic polarization is an electrochemical technique which provides a quick assessment of a material's susceptibility to pitting. Figure 7 illustrates how a cyclic polarization curve may be utilized to assess pitting susceptibility. Initially, the potential is scanned from the corrosion or open circuit potential (E_{corr}) towards more positive potentials. Since stainless steels possess a protective oxide film at the surface, the current density remains quite low over a wide potential range. At a high positive potential, a significant increase in the current density occurs. This potential (E_b) may indicate the initiation of pitting, or it may be another anodic reaction occurring at the oxide surface. At a current density of 5 mA/cm² the scan is reversed, and the potential is returned to E_{corr} . Pitting susceptibility is indicated if the return scan current density at potentials less than E_b exceeds that of the forward scan by more than an order of magnitude⁸ (negative hysteresis). Conversely, if the current density of the reverse scan is less than that of the forward scan (positive hysteresis) the specimen is not susceptible to pitting.

A matrix giving conditions for each scan is shown below:

Specimen	Heat Treatment Time (hr)	Solution pH
A	solution annealed	3.39
B	solution annealed	3.39
C	6	2.07
D	6	3.39
E	24	3.39

Figure 8 shows the polarization curve for the 24 hour specimen conducted in the as-mixed gadolinium nitrate solution. During the forward scan the current density remains quite low over a wide potential range of approximately 1.2 V. This result demonstrates that the oxide film protects the material very well in the gadolinium nitrate environment. The current density during the initial portion of the return scan is slightly greater than that of the forward scan. This result indicates a small amount of crevice corrosion which frequently occurs during these tests under a gasket at the edge of the specimen. However, from +1000 mV, E_b , back to E_{corr} the current density of the reverse scan is less than that of the forward scan. Thus, 304 is not susceptible to pitting in the gadolinium nitrate environment. As confirmation of this result, microscopical observation revealed no pits on the specimen face.

Similar results were obtained for polarization tests performed on the solution annealed and 6-hour specimens in the as-mixed gadolinium nitrate solution, as well as for the 6-hour specimen in an acidified solution. Therefore, localized corrosion of 304 is not anticipated in the gadolinium nitrate environment regardless of the degree of sensitization of the material.

Immersion Tests

Although electrochemical testing serves as a good predictor of the corrosion behavior of a material in a particular environment, coupon immersion tests are frequently performed to confirm these predictions. Immersion testing involves exposing specimens to environments that simulate anticipated field conditions for a period of several days or weeks. The specimens are then examined to determine the extent of corrosion.

Immersion testing of 304L rods in simulated SSS ink was performed previously in a study of the corrosion of liquid level conductivity probes used in the main ink storage tanks, probe pots, and reservoir tanks of the SSS. 304L rods in an as-received condition were exposed to solutions of gadolinium nitrate (0.18 g/ml Gd) for a period of three months. Variables for this program included acidification of the solution to pH 2, application of an alternating potential to the probe rod, and addition of Rhodamine B, a chloride-containing dye, to the

solution. These factors, particularly the application of an alternating potential, served to increase the aggressiveness of the test environment.

Pitting was not observed on 304L rods exposed to gadolinium nitrate solution containing Rhodamine B with pH values of 2 or 5 after a three-month period with no applied voltage to the rods. Nor was pitting observed under an applied voltage when the solution pH was raised to a value of 5 and the Rhodamine B was not added to the solution. These results suggest that the gadolinium nitrate solution alone, even in an acidified condition, is not sufficient to cause localized corrosion of 304L in the as-received condition. Because the cyclic potentiodynamic polarization scans indicated no significant differences in corrosion behavior of sensitized and non-sensitized 304 in various gadolinium nitrate environments, the immersion data can be extended to suggest that 304 would not have pitted under similar test conditions.

CONCLUSIONS

The data obtained during cyclic potentiodynamic polarization scans reveal that no significant differences in corrosion behavior exist between sensitized and non-sensitized 304 in as-mixed and acidified gadolinium nitrate solutions at room temperature. These results are supported by immersion data which indicates that 304L will not pit as a result of immersion in acidified gadolinium nitrate solutions for a period of three months. The combined data provide strong evidence that allowing the nonconforming SSS components to remain in place temporarily does not threaten the structural integrity of the system. The data corroborate the technical justification provided by the RCMC allowing for the components to remain in place until the next scheduled long reactor shut-down.

REFERENCES

1. J. E. Marra to J. D. Spencer (Reactor Corrosion Mitigation Committee), "Meeting Minutes - May 16, 1991 (U)," SRL-MTS-913000, Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina 29808 (May 17, 1991)
2. M. H. Anderson, Laboratory Notebook, WSRC-NB-91-110, Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina 29808 (1991)
3. M. H. Anderson, "Supplementary Safety System Liquid Level Probe Corrosion Study (U)," WSRC-NB-90-505, Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina 29808 (October, 1990)
4. W. L. Clarke, "The EPR Method for the Detection of Sensitization in Stainless Steels," Prepared for U. S. Nuclear Regulatory Commission and General Electric Company, GEAP 24888, NUREG/CR-1095, (April, 1981)
5. W. L. Clarke and D. C. Carlson, "Nondestructive Measurement of Sensitization of Stainless Steel: Relation to High Temperature Stress Corrosion Behavior," Materials Performance, Vol. 19, No. 3, March, 1980.
6. K. J. Stoner, WSRC-RP-89-229, "An Evaluation of Sensitization in Type 304 Stainless Steel Pipe Sections Removed from Service (U)," Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina 29808 (July 31, 1989)
7. G. R. Caskey, R. S. Ondrejcin, R. L. Sindelar and E. W. Baumann, WSRC-TR-91-12, "Effect of Neutron Irradiation on Stress Corrosion Cracking of Type 304 Stainless Steel in Simulated Savannah River Reactor Environments (U)," Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina 29808 (January, 1991)
8. P. E. Zapp, DPST-88-399, "Electrochemical Study of Corrosion Inhibition During Sludge Washing," Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina 29808 (March 14, 1988)

ATTACHMENT 1

CERTIFIED MILL TEST REPORT OF 304 MATERIAL USED FOR TESTS

<u>Element</u>	<u>wt %</u>
Carbon	0.06
Manganese	1.84
Phosphorus	0.037
Sulfur	0.002
Silicon	0.43
Chromium	18.28
Nickel	8.07
Molybdenum	0.42
Copper	0.48
Nitrogen	0.06
Cobalt	0.15
Iron	bal.

Figure 1. Oxalic Acid Etch Of Solution Annealed 304.

Figure 2. Oxalic acid etch of 304 that has been heat treated for 6 hours at 650° C.

Figure 3. Oxalic Acid Etch Of 304 That Has Been Heat Treated For 24 Hours At 650° C.

Figure 4. Post-EPR microstructure of the solution annealed 304.

Figure 5. Post-EPR microstructure of the 304 that was heat treated for 6 hours at 650° C.

Figure 6. Post-EPR microstructure of the 304 that was heat treated for 24 hours at 650° C.

Figure 7. Example of cyclic polarization curve which illustrates pitting susceptibility.

Figure 8. Cyclic polarization curve for 24 hour 304 specimen in a gadolinium nitrate solution with a pH of 3.39.

END

**DATE
FILMED
9/16/92**