

UNITED STATES NUCLEAR REGULATORY COMMISSION REGION II 101 MARIETTA STREET, N.W. ATLANTA, GEORGI/, 30323

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Report No.: 50-416/87-39

Licensee: System Energy Resources, Inc. Jackson, MS 39205

Docket No.: 50-416

Facility Name: Grand Gulf

Inspection Conducted: December 14-17, 1987

Inspector: Ross

Accompanying Personnel: C. A. Hughey

Approved by: J. B. Kahle, Section Chief Division of Radiation Safety and Safeguards

Date Signed

License No.: NPF-29

Date Signed

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SUMMARY

Scope: This special unannounced inspection was conducted in the areas of Standby Service Water and Circulating Water Systems chemical cleaning and plant chemistry control.

Results: One violation was identified - Failure to consider welds and crevice regions prior to performing chemical cleaning of the Standby Service Water System.

REPORT DETAILS

1. Persons Contacted

Licensee Employees

*R. Hutchinson, General Manager

*J. V. Parrish, Chem/Rad Superintendent

*T. Williamson, Chemistry Supervisor *G. D. Smith, Plant Chemist

J. Antoine, Cooling Tower Engineer, Chemistry R. Ducker, Standby Service Water System Engineer, Chemistry

*L. Daughtery, Compliance Supervisor

A. McCurdy, Manager of Operations

S. Davis, Instrument Specialist, Chemistry

S. Mahoney, Chemistry Training Specialist S. Thomas, Principal Mechanical Engineer

W. Fue, Chemist/Material Science

M. Tomincy, Senior Metallurgical Engineer

A. Holbrook, Chemistry Training Instructor

R. Meyers, Chemistry Shift Supervisor

NRC Resident Inspectors

*R. Butcher, Senior Resident Inspector J. Mathis, kesident Inspector

*Attended exit interview

2. Exit Interview

> The inspection scope and findings were summarized on December 17, 1987. with those persons indicated in paragraph 1 above. The inspector described the areas inspected and discussed in detail the inspection findings. No dissenting comments were received from the licensee. The licensee did not identify as proprietary any of the materials provided to or reviewed by the inspectors during this inspection. Licensee management was informed by telephone on January 6, 1987, that the adequacy of the safety evaluation of the chemical cleaning process had been resolved to be a violation of NRC requirements.

3. Licensee Action on Previous Enforcement Matters

This subject was not addressed in the inspection.

4. Unresolved Items

Unresolved items were not identified during this inspection.

5. Chemical Cleaning

At the time of this inspection, Grand Gulf Unit 1 was in the sixth week of its second refueling outage. Chemical cleaning of the A and C loops of the Standby Service Water System (SSW) was being completed, and chemical cleaning of portions of the circulating water system had begun in an attempt to remove oxidation and corrosion deposits and debris. Previous water treatment programs (Inspection Report No. 50-416/87-09) had not been effective in eliminating the microbiologically influenced corrosion (MIC) and fouling (blockage) of the SSW and preventing the formation of organic, inorganic and manganese oxide deposits on the ID of the stainless steel condenser trbes. Fouling and deposits, resulting in a reduction of flow through the SSW and reduction of heat transfer across the condenser tubes (with an associated power penalty of 13 MWe), prompted the licensee to pursue chemical cleaning of these systems.

The licensee decided to clean these systems using a vendor who supplied chemicals, engineering support, and water quality monitoring capabilities. The SSW cleaning was described in Grand Gulf Temporary Directive No. 04-1-01-P41-1-TEMP8, Rev. 0, approved December 2, 1987. The condenser tube cleaning was described in Grand Gulf Nuclear Station Modification Work Permit No. 87/1187, approved December 2, 1987. The cleaning program for the SSW consisted of the following basic steps:

- Iron deposits were initially conditioned by adding a tannin solution to the bulk water to penetrate and loosen the corrosion products by forming an iron-tannin complex.
- The bulk water pH was then lowersd to approximately 2.5 with sulfuric acid.
- 3) A mild organic acid (citric acid) was added to the bulk water. (This acid reacts with the insoluble iron-tannin complex to form a soluble complex, thus resulting in the removal of the iron oxide from the metal surface.)
- 4) The system was then drained, refilled, and treated with both a molybdate solution, to promote passivation of the "ciean" metal surface, and a biocide to reduce bacteria levels.

At the time of this inspection, the cleaning of the SSW had been completed. Although the effectiveness and results of the cleaning had not been formally summarized, the licensee informed the inspectors that about 6,000 lbs. of iron oxide had been removed. Flow testing of the SSW at minimum-basin level indicated full recovery of design flow, with no blockage of piping or heat exchanger tubes from loosened corrosion products.

Cleaning of the circulating water system (inlet and outlet water boxes and condenser tube IDs) had not been completed at the time of this inspection. The inspector was subsequently notified by the Grand Gulf Resident Inspector that cleaning had been completed and that preliminary assessments indicated that all iron oxide debris had been removed along with most of the manganese film.

To prevent future MIC and iron fouling problems in the SSW, a molybdate and biocide treatment program that had been started after the first refueling outage will be continued. To prevent iron/manganese deposition and MIC problems in the circulating water system a treatment program, also initiated after the first refueling outage and consisting of a non-oxidizing biocide, dispersant, and sulfuric acid additions, will be continued. A mechanical cleaning system (Amertap) that will use recyclable sponge balls to continuously clean the condenser tube IDs was installed during the second refueling outage.

The Standby Service Water System (SSW) is classified as a safety related system. Consequently, before the cleaning process could be initiated without prior NRC approval, the licensee was required by 10 CFR 50.59 to determine that this action was not an unreviewed safety question. Such a finding was made on the basis of a written safety evaluation of the process and the approval of Temporary Directive No. 04-1-01-P41-1-TEMP8, Rev. 0, on December 2, 1987.

The inspector reviewed the licensee's safety evaluation and found that it essentially consisted of the statement that "onsite tests confirm successful cleaning can be accomplished without degradation of the base metal or components." When the inspector requested documented justification for this statement, the licensee provided the following information:

a. NALCO Program Profile PR-2

This marketing document had been prepared by the NALCO Chemical Company of Oak Brook, Illinois and described the NALCO Delta T on-line cleanup program on which the licensee's procedures had been based. In a section of this document titled "Common Questions," the following statements were made: "Instantaneous corrosion rates on unprotected mild steel surfaces during the cleaning will normally range from 60 to 100 mpy (mil per year). But since the low pH usually lasts for only 24-30 hours, actual metal loss should be considerably less than one mil."

 Letter From Mr. Edward W. Ekis, Jr., of NALCO Chemical Company dated December 21, 1987

This letter provided corrosion rate data from other NALCO case studies and showed that corrosion of unprotected mild steel, at temperatures of 100 - 130°F had varied from 58 to 290 mpy - most of which was attributed to the citric acid step.

c. Data Extracted From Tests Performed by the SERI Corporate Engineering Department

These data had been produced in early 1987 during tests performed on mild steel and 90/10 copper-nickel alloys that represented the base metals present in the SSW pipe and heat exchanger tubes.

Metal	Reagent	Corrosion Rate - mpy
Mild Steel	Tannin Citric Acid	4.76 120.9 6.0
Copper-Nickel	Tannin Citric Acid	0.91 1.19

d. A paper "A Novel Approach to the On-Line Removal of Iron Deposits From Cooling Water Systems" authored by R. I. Kaplan and Edward W. Ekis, Jr., of NALCO Chemical Company

This paper describes the studies performed during the development of the NALCO Delta-T process but did not provide any corrosion data.

e. Test Pipe

Sections of two-inch diameter pipe that had been cut from the SSW to determine the degree of fouling and to be used in qualitative cleaning tests. These pipe sections revealed the following:

- Fouling from metal oxides had been reduced by a water treatment program which included the addition of a molybdate dispersant and which had been initiated after the first refueling outage.
- Some pipe were essentially plugged with metal oxides.
- Fouled pipe had been cleaned to the base metal by the NALCO Delta T process. All of the cleaned surfaces exhibited pitting. NALCO data indicated that this pitting was not caused by the chemical treatment; consequently, the pits were attributed to inorganic and organic fouling and corrosion mechanisms.

The inspectors expressed concern that, although this information provided some quantitative assurance that the base metals (carbon steel and copper-nickel alloys) would not be significantly degraded during the cleaning process, there was no similar data for butt and socket weld material or crevice regions where material degradation may also be significant. This concern was designated an unresolved issue at the conclusion of the inspection, and the licensee committed to provide any additional information that might be available to resolve the inspector's concern.

In a telephone call on December 23, the inspector was advised by the licensee that the NALCO letter dated December 21, 1987, was the only additional information that could be provided.

The unresolved issue was further evaluated by the inspector and Region II management and determined to constitute a violation of the requirements of 10 CFR 50.59. At the time that the licensee's Safety Evaluation was prepared, the potential for reducing the margin of safety of the SSW pipe had not been fully evaluated. During recent years, nuclear power plant operating experience has shown that although straight runs of pipe and tubes have been corroded/eroded through multiple mechanisms, most degradation has occurred in heat-sensitized weld regions, elbows, and crevices. The most obvious area of concerns during chemical cleaning of the SSW, therefore, should have been the unknown effect of a relatively acid solution (pH 2.0 to 2.5) in these regions. Also, since the licensee's tests had shown the small-diameter pipe to have been significantly pitted by the corrosion/fouling mechanisms, the licensee failed to consider the strength of the base metal after the corrosion products had been removed. The licensee's program did not include non-destructive testing of these pipes after they had been cleaned.

Although pre-cleaning test data related to corrosion had been collected by NALCO Chemical Company, the Corporate Engineering Department and the Plant Chemistry Department, the licensee did not maintain adequate written records to support the Safety Evaluation. Also, the Safety Evaluation did not consider the effect of the solvents on weld material or crevice regions. Consequently, the licensee is considered to be in violation of the requirements of 10 CFR 50.59 because of an inadequately prepared Safety Evaluation. Likewise, the licensee failed to perform an adequate safety review of Temporary Directive 04-1-01-P41-1 TEMP 8 by failing to recognize the potential detrimental effect of the process on the strength of the base and weld metals after the corrosion products had been removed.

Open. Violation 50-416/87-39-01 Failure to perform an acceptable safety review of the procedure used for chemical cleaning the Standby Service Water System.

6. Non-Radiological Confirmatory Measurement

The inspector submitted a series of non-radiological chemistry samples to the licensee for analysis to assess the capability of the chemistry staff to perform acceptable analyses. These "unknowns" were prepared for the NRC by Brookhaven National Laboratory (BNL). The licensee diluted the samples, as directed by the inspector, to bring the concentrations to within the ranges normally observed in the condensate, feedwater, or reactor coolant and were then analyzed by three different chemists. The results are presented in Attachment 1. The methodology for determining agreement or disagreement between NRC and the BNL values is discussed in Attachment 2.

7. Plant Chemistry (79701)

The inspectors re-assessed selected areas of the water chemistry control program to ensure chat the licensee was maintaining an effective level of chemistry control. This inspection was a continuation of Inspection Report No. 50-416/87-09, dated April 3, 1987. The following observations were made:

1) QA/QC

The licensee was in the process of revising the chemistry QA/QC program for monitoring the precision and accuracy of chemical measurements. The licensee planned to develop new accuracy and precision control charts constructed from data collected during 1987. New procedures describing the QA/QC program were in the approval process at inspection time.

As part of an intra-laboratory QA/QC program, at least one unknown spiked sample was being analyzed by each chemist once per month. The licensee was also carrying out an inter-laboratory comparison program with an outside vendor.

2) Training

The chemistry training program consisted of 17 weeks of initial training including classroom and laboratory training, a structured on-the-job (OJT) training program, and a continuing training program on various topics of interest. This total program had been accredited by INPO. To help implement this program, the laboratory chemists were scheduled to attend one week of training every second week of their six week rotation work cycle. This helped assure a consistency that made training easier to implement for chemistry management, the chemistry training staff, and the laboratory chemists.

The inspectors also toured the chemistry training laboratory. This laboratory contained instrumentation that was very similar to that being used in the plant laboratories. These facilities were considered to be adequate to support the licensee's training program.

3) Staffing

The inspectors noted no major changes in the chemistry department staff had occurred since the last inspection. There had been a stable work force with a low turnover rate. Some of the chemistry staff was on loan to the Health Physics group during the refueling outage to supplement the HP work force and to broaden their knowledge.

No violations or deviations were identified.

ATTACHMENT 1

NONRADIOLOGICAL INTERLABORATORY TEST RESULTS

GRAND GULF

DECEMBER 14-17, 1987

Analyte	Analysis Method	Dilution 1:X	NRC Y + s.d.(n)	Licensee X + s.d.(n)	Ratio $Z + s.d.$	$\frac{\text{Comparison}^{(5)}}{\pm 2 \text{ s.d.}}$
Chloride 86A (ppb)	IC	2000(1)	23.1 ± 0.5 (7)	19.9 ± 1.5 (3)	0.863 ± 0.066	D
Chloride 86A (Repeat) (ppb)	IC	2ú00 ⁽¹⁾	23 1 ± 0.5 (7)	21.1 ± 0.3 (3)	0.912 ± 0.013	D
Chloride 86B (ppb)	IC	2000(1)	43.5 ± 1.9 (7)	38.7 ± 0.6 (3)	0.899 ± 0.015	D
Chloride 86B (Repeat) (ppb)	IC	2000(1)	43.5 ± 1.9 (7)	36.9 ± 0.4 (3)	0.848 ± 0.009	D
Chloride 86C (ppb)	IC	1000	80.5 ± 2.2 (8)	88.5 ± 2.0 (2) ⁽²⁾	1.100 ± 0.024	D
Chloride 86C (Repeat) (ppb)	IC	1000	80.5 ± 2.2 (8)	80.9 + 1.9 (3)	1.005 ± 0.023	А
Sulfate 86A (ppb)	IC	1000	20.0 ± 0.9 (7)	20.7 ± 1.1 (3)	1.035 ± 0.057	A
Sulfate 86B (ppb)	IC	1000	41.0 + 2.4 (8)	40.6 <u>+</u> 0.4 (3)	0.989 + 0.010	A
Sulfate 86C (ppb)	IC	1000	80.8 + 3.0 (7)	84.3 <u>+</u> 0.8 (3)	1.043 ± 0.009	A

Attachment 1

Analyte	Analysis Method	Dilution 1:X	NRC Y + s.d.(n)	Licensee X + s.d.(n)	Ratio Z + s.d.	Comparison + 2 s.d.
Silica 86S (ppb)	VIS SPEC	1900	54.3 <u>+</u> 5.6 (7)	58.0 + 2.6 (3)	1.068 ± 6.049	А
Silica 86T (ppb)	VIS SPEC	1000	109 + 7 (7)	103 + 5 (3)	0.948 ± 0.046	A
Silica 86U (ppb)	VIS SPEC	1000	160 ± 5 (7)	148 ± 2 (3)	0.925 ± 0.013	D
Silica 86U (Repeat) (ppb)	VIS SPEC	1000	160 + 5 (7)	165 <u>+</u> 1 (3)	1.033 ± 0.013	A
Sodium 86J (ppb)	IC	1000(3)	4.6 ± 0.5 (6)	5.2 ± 0.3 (3)	1.138 ± 0.070	A
Sodium 86K (ppb)	IC	1000 ⁽³⁾	9.23 + 0.8 (6)	10.9 ± 1.7 (2)	1.178 ± 0.181	А
Sodium 86L (ppb)	IC	1000(3)	14.4 + 0.8 (6)	15.4 + 0.7 (3)	1.068 ± 0.048	A
Iron 86G (ppm)	AAS	25(4)	4.9 ± 0.4 (13)	5.6 ± 0.3 (3)	1.140 ± 0.005	A
Iron 86H (ppm)	AAS	25 ⁽⁴⁾	9.6 ± 0.3 (14)	9.9 <u>+</u> 1.3 (3)	1.037 ± 0.133	А
Iron 861 (ppm)	AAS	25 ⁽⁴⁾	14.7 ± 0.42 (13)	15.6 + 1.3 (3)	1.020 ± 0.090	A
Copper 86G (ppm)	AAS	25 ⁽⁴⁾	4.68 ± 0.24 (12)	5.45 <u>+</u> 1.6 (3)	1.165 ± 0.342	A

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Attachment 1

Analyte	Analysis Method	Dilution 1:X	NRC Y + s.d.(a)	Liceasee X + s.d.(n)	Ratio Z + s.d.	Comparison 2 s.d.
Copper 86H (ppm)	AAS	25 ⁽⁴⁾	9.7 ± 0.5 (14)	9.3 ± 0.6 (3)	0.962 ± 0.061	A
Copper 861 (ppm)	AAS	25 ⁽⁴⁾	14.5 ± 0.6 (13)	14.6 ± 0.5 (3)	1.004 ± 0.031	А
Nickel 86G (ppm)	AAS	25 ⁽⁴⁾	5.1 ± 0.3 (6)	5.4 ± 0.3 (2)	1.069 <u>+</u> 0.066	А
Nickel 86H (ppm)	AAS	25 ⁽⁴⁾	10.2 ± 0.3 (7)	9.4 ± 1.6 (3)	0.918 ± 0.158	A
Nickel 861 (ppm)	AAS	25 ⁽⁴⁾	15.3 <u>+</u> 0.4 (6)	16.7 <u>*</u> 0.8 (3)	1.089 ± 0.040	A
Chromium 86G (ppm)	AAS	25 ⁽⁴⁾	5.1 ± 0.3 (6)	5.4 ± 0.3 (3)	1.066 ± 0.060	Å
Chromium 86H (ppm)	AAS	25 ⁽⁴⁾	9.4 ± 0.3 (6)	9.3 ± 1.4 (3)	0.992 ± 0.154	A
Chromium 861 (ppm)	AAS	25 ⁽⁴⁾	14.3 ± 0.8 (6)	12.1 ± 1.4 (3)	0.846 ± 0.098	A

1) Licensee diluted 1:2000. For comparison purposes the licensee's values were multiplied by 2.

 Licensee analyzed unknown only two times. For comparison purposes, the licensee's value that was nearest the NRC's value was used as the third value in the standard deviation and mean calculations.

3) Licensee diluted 1:500. For comparison purposes the licensee's value were divided by 2.

4) In order to compare the NRC values, the licensee's raw values were multiplied by 25.

5) A = Agreement, D = Pisagreement.

ATTACHMENT 2

CRITERIA FOR COMPARING ANALYTICAL MEASUREMENTS

This attachment provides criteria for comparing results of the capability tests. The acceptance limits are based on the uncertainty (standard deviation) of the ratio of the licensee's mean value (X) to the NRC mean value (Y), where

- (1) Z = X/Y is the ratio, and
- (2) S, is the uncertainty of the ratio determined from the propagation of the uncertainties of licensee's mean value, S, and of the NRC's mean value, S, 1 Thus,

 $S_{2}^{2} = S_{2}^{2} + S_{2}^{2}$, so that $Z^{2} = \chi^{2} - \chi^{2}$

$$S_{z} = Z \cdot \begin{pmatrix} S_{z}^{2} & S_{z}^{2} \\ S_{z}^{2} & Y^{2} \end{pmatrix}^{2}$$

The results are considered to be in agreement when the bias in the ratio (absolute value of difference between unity and the ratio) is less than or equal to twice the uncertainty in the ratio, i.e.:

$$| 1 - Z | \le 2 \circ S_2$$

 National Council on Radiation Protection and Measurements, <u>A Handbook of</u> <u>Radioactivity Measurement Procedures</u>, NCRP Report No. 58, Second Edition, 1985, Pages 322-326 (see Page 324).