U.S. NUCLEAR REGULATORY COMMISSION

REGION III

Report No. 50-483/88017(DRSS)

Docket No. 50-483

License No. NPF-30

Licensee: Union Electric Company Post Office Box 149 - Mail Code 400 St. Louis, MO 63166

Facility Name: Callaway Plant, Unit 1

Inspection At: Callaway Site, Steedman, Missouri

Inspection Conducted: August 22-26, 1988 (Onsite) September 7 and 8, 1988 (Telephone discussions)

Inspector: R. B. Holtzman

m. schumach

M. C. Schumacher, Chief Approved By: Radiological Effluents and Chemistry Section

Inspection Summary

Inspection on August 22-26, 1988 (Report No. 50-483/88017(DRSS)) Areas Inspected: Routine, announced inspection of the chemistry program, including (1) procedures, organization, and training (IP 83722, 83723); (2) reactor systems water quality control programs (IP 79701); (3) quality assurance/quality control program in the laboratory (IP 79701); (4) nonradiolgical confirmatory measurements (IP 79701); and (5) the observation of collocated thermoluminescent dosimeters (TLD) (TI2500/22, IP80721).

Results: The licensee has an extensive water quality control program that conforms to the EPRI Steam Generator Owners and Primary Systems Guidelines. The nonradiological confirmatory measurements results were good, but demonstrated some weaknesses in the chemical measurements QA/QC program. The licensee identified weaknesses in the measurements program and corrected them. No violations or deviations were identified during this inspection.

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9/14/14 Date

5/16/11 Date

DETAILS

1. Persons Contacted

- ¹G. L. Randolph, General Manager, Nuclear Operations, UENO
 ¹J. D. Blosser, Manager, Callaway Plant, UENO
 ¹J. R. Peevy, Assistant Manager, Technical Services, UENO
 ¹J. R. Polchow, Superintendent, Chemistry and Radwaste, UENO
 ¹C. A. Riggs, Supervisor, Chemistry, UENO
 ¹C. C. Graham, Supervisor, Health Physics Technical Support, UENO-HP
 ¹L. H. Kanuckel, Supervisor, Engineering QA, UEQA
 ¹R. D. Miller, Engineer, UEQA
 ¹D. A. Widmer, Engineer, UEQA
 ²P. M. Bell, Chemist, UENO
 S. L. Leach, Chemistry Foreman, UENO
 G. D. Clark, Radiation/Chemical Technician (RCT)
 P. G. DeSautels, RCT
 D. A. Dutoi, RCT
- T. Rook, Instructor, Training, UENO
- ¹C. H. Brown, Resident Inspector, NRC

The inspector also interviewed other licensee personnel in various departments in the course of the inspection.

¹Denotes those present at the plant exit interview on August 26, 1988. ²Telephone discussions held on September 7 and 8, 1988.

2. Licensee Action on Previous Inspection Findings

- a. (Closed) Open Item (50-483/87017-02): Licensee to assess the causes of disagreements and repeat analyses of silica, hydrazine, iron, sodium and report the results to Region III. The results are presented in Table 1 with the criteria given in Attachment 1. The licensee achieved five agreements in eight analyses. The cause of the original disagreements in the silica analyses appeared to be due to a high silica blank in the deionized water, which was corrected prior to these analyses. The hydrazine analyses improved with better standards. The disagreements in the other measurements were not resolved, but quality of the results presented in Table 3 (this report) demonstrate improvement of the analyses, probably due to more experience and an improved measurements control program. Development of this program will be followed in future inspections under the QA/QC program.
- b. (Open) Open Item No. 50-483/88008-01: Licensee to analyze a liquid sample for gross beta, gross alpha, H-3, Fe-55, Sr-89 and Sr-90 and report the results to Region III. The licensee's results of the liquid sample are contained in Table 2; the comparison criteria are given in Attachment 2. Sr-90 and gross alpha (G-ALPHA) results were

not compared because they were below the lower limits of detection. The gruss beta (G-BETA) results were in disagreement because the licensee and NRC samples were counted at different times. One possible cause of the Fe-55 and Sr-89 disagreements appears to be the chronic problem of poor preservation of the split. The licensee is changing the procedure to mitigate this problem, and, if the containers from this split are still available at the licensee's contract laboratory, they will be tested for plate-out. The licensee agreed to determine the Fe-55, Sr-89, Sr-90 and gross beta concentrations in a sample supplied by the NRC reference laboratory and report the results to Region III for comparison.

3. Management Controls, Organization and Training (IP 83722, 83723)

The Chemistry Department has been reorganized since the previous inspection in this area (Inspection Report No. 50-483/87016). The Supervisor, Chemistry with the responsibilities formerly divided between the Primary System and Secondary System Supervisors, reports to the newly expanded position (to add radwaste) of Superintendent, Chemistry and Radwaste. The Superintendent reports to the Assistant Manager, Technical Services. A Chemist and Chemical Engineer, along with four laboratory foremen ard 17 Radiation Chemical Technicians (RCT), operate the laboratory. This personnel complement appears to be adequate for the required routine chemistry program.

The Superintendent recently came to this position from Supervisor, Health Physics Operations. He appears to be qualified as the "Radiochemist" under ANSI/ANS-3.1-1978 from education (Bachelor of Science, Physics), nuclear Navy, Rad/Chem Foreman at this plant, and Health Physics Operations experience. In addition, the direct-line laboratory Supervisor also qualifies from education and experience in power reactor radiochemistry.

The RCTs are all qualified as chemistry technicians under ANSI/ANS-3.1-1978. The licensee's Chemistry Technician training program was accredited by INPO April 24, 1986.

No violations or deviations were identified.

Water Chemistry Control Program (IP 79701)

The inspector reviewed the licensee's water chemistry control programs incorporated in administrative procedures APA-ZZ-01020, "Primary Chemistry Program," Revision 1, May 22, 1987 and APA-ZZ-01021, "Secondary Chemistry Program," Revision 1, March 4, 1988. These are based on and conform to the respective EPRI guidelines NP-4762-SR, "PWR Primary Water Chemistry Guidelines," Revision 0, September 1986, and NP-2704-SR, "PWR Secondary Water Chemistry Guidelines," Revision 1, June 1984. Waiver of the limits requires the approval of the Plant Manager or his alternate (Emergency Duty Officer). The licensee is working on various aspects of the secondary system to improve water chemistry. The concentration of efforts of the Chemical Engineer on the maintenance and operation of the makeup water system has resulted in greatly improved water quality. This system has inline process monitors for conductivity and silica as recommended by INPO. This improved the water quality in the secondary reactor system, which reduced maintenance of the full-flow polishers. Water quality parameters are monitored and recorded by inline process instrumentation, including cation and specific conductivity meters, sodium and dissolved oxygen analyzers in conformance with the EPRI guidelines.

The primary system sampling is done from two adjacent panels in the primary sampling room. These panels have sampling points for reactor coolant and for related systems, such as the RHR. The Post Accident Sampling System was designed to limit the number of samples drawn and processed from the RCS by the use of a continuous inline boron monitor, also used during normal operations and a remotely operated gamma spectrometer with a Ge detector for isotopic analysis of reactor coolant inline.

The Chemistry Department plots on a monthly basis, trend charts of chemistry parameters, including chloride, fluoride, conductivity, hydrogen, boron and dissolved oxygen. They also submit a monthly letter to the Assistant Plant Manager, Operations with information on significant trends and events.

No violations or deviations were identified.

5. Implementation of the Chemistry Program (IP 79701)

The inspector reviewed the chemistry programs including physical facilities and laboratory operations. Both the hot and cold laboratories had sufficient room, good instrumentation, and good maintenance.

The inspector observed several technicians analyze the confirmatory measurements samples, including boron by an autotitrator, hydrazine by spectrophotometry, and chloride and sulfate by ion chromatography (IC). They appeared to be generally knowledgeable about the work and followed the procedures.

Overall, the housekeeping was good and the laboratories appeared to be adequate for the proper operation of the plant.

No violations or deviations were identified.

6. Nonradiological Confirmatory Measurements (IP 79701)

The inspectors submitted chemistry samples to the licensee for analysis as part of a program to evaluate the laboratory's capabilities to monitor nonradiological chemistry parameters in various plant systems with respect to various Technical Specification and other regulatory and administrative requirements. These samples had been prepared, standardized, and periodically reanalyzed (to check for stalility) for the NRC by the Safety and Environmental Protection Division of Brookhaven National Laboratory (BNL). The samples were analyzed by the licensee using routine methods and equipment.

The samples were diluted by licensee personnel as necessary to bring the concentrations within the ranges normally analyzed by the laboratory, and run in triplicate similarly to routine samples. The results are presented in Table 3 and the nonradiological chemistry criteria for agreement in Attachment 1. These criteria for agreement are based on comparisons of the mean values and estimates of the standard deviations (SD) of the measurements. Consideration was given to the possibility that the uncertainties (SD) of the licensee's results were not necessarily representative of the laboratory's because they were obtained by one analyst over a short period of time. Consequently when the licensee SD was less than that of BNL, and a disagreement resulted, the BNL value was substituted for that of the licensee in calculating the SD of the ratio Z (S, in Attachment 1).

The licensee also prepared two samples, each containing a matrix to be split with BNL. To these were added analytes supplied by the inspector. Reactor water was spiked with the anions chloride, sulfate and fluoride, and a steam generator blowdown sample was spiked with the copper, iron, nickel and chromium (only copper and iron are to be analyzed). The licensee will determine the concentrations of the analytes in each of the samples and report the results to Region III for comparison with the values to be determined by BNL. This will be followed under Open Item (50-483/88017-01).

The licensee analyzed 10 analytes at three concentrations each. Of the initial 30 analyses, 19 of the results (63%) were in agreement with those of BNL. The disagreements included the two lower-level boron, the two higher-level fluoride, a copper, two sodium, a lithium and all three hydrazine results. Most of the differences were resolved when the licensee reanalyzed the samples with disagreements, except for the boron, and obtained agreements. The fluoride specific ion electrode, which is very temperature sensitive, was recalibrated. New standards were made for copper, sodium and lithium and the sodium samples were diluted carefully to prevent contamination. There appeared to be a substantial difference between the commercial aqueous lithium standard used originally and the new made from reagent grade LiCl. The hydrazine analytical procedure was revised to require that the acidities of the calibration and check standards and of the samples were the same.

The boron analyses showed low biases of about 4%, with otherwise good precision of the measurements for both the BNL and licensee results. This appears to be due to differences in the methods of analysis; the licensee diluted the sample only minimally to less than 10 ml, did not

adjust the starting point, and used an inflection endpoint, while diluted to 100 ml, adjusted to a starting point of pH 7.6, and ray a dead-stop endpoint of pH 8.6. The licensee's method used milli rather than pH units, so that a comparison of the endpoints is difficult to make. The dilution affects the equivalence points and may result in the observed bias. Checks by the licensee of a laboratory standard made from from reagent-grade boric acid and of a commercial aqueous standard (Fisher) were within one-half percent of the reported 1000-ppm concentrations. Similar negative biases were observed at other licensees in Region III that used methods similar to those of this plant. As noted in a previous report (Region III Inspection Reports (50-266/88017; 50-301/88015)), the source of this bias has not yet been ascertained. The inspector will try to resolve this problem prior to subsequent inspections.

Overall, the results of the analyses were good. Laboratory personnel demonstrated a willingness and good ability in determining the causes of the disagreements. This appears to be due to the improvements in the QA/QC program since last year. Improvements in the licensee performance will be examined in subsequent routine inspections.

No violations or deviations were identified.

7. Quality Assurance and Quality Control for Nonradiological Chemistry

The inspectors reviewed the nonradiological QA/QC program in for both the primary and secondary systems laboratories. This program is controlled by Chemistry Departmental Procedures

- CDP-ZZ-00300 Control of Chemistry Instrumentation and Equipment, Revision 13, January 6, 1988, and
- CDP-ZZ-00700 Laboratory Quality Control Program, Revision 9, August 22, 1988,

and Chemistry Technical Procedures

- CTP-ZZ-04701 Control Chart Construction and Use, Revision 1, October 29, 1987, and
- CTP-ZZ-04702 Quality Control Verification Program, Revision 1, July 29, 1986.

The second procedure above gives the key nonradiological parameters for analysis as boron, chloride, fluoride, sulfate, silica, iron, copper and sodium. Control charts were implemented for these analyses with warning limits of two standard deviations (SD) and control limits of three SD's. Other analytical methods required that the results from the performance standards give values of the results within certain limits before the RCT may proceed with the analyses.

This program has been modified extensively to address the concerns expressed in the previous inspection in this area (Region III Inspection Report No. 50-483/87016). The warning and control limits were calculated periodically at six-month intervals from the performance check standard data, themselves, and the limits were changed to two and three SD's. All of the more significant analytical procedures, such as that for boron, now have control charts, and separate logsheets were implemented for the control chart data. The calibration and control standards are now from different sources, i.e., different manufactures or different lots. The procedures also take into account the possible nonlinearity of calibration curves.

The inspector noted further suggestions on improvements to the QA program:

- a. The control chart mean and SD values should be determined more frequently than the present six month interval to present more current values of these parameters, possibly monthly or quarterly, and each chart should show several months of data (60-100 points). Alternatively, the monthly charts may be kept together. Charts for infrequently done analyses should accumulate 30 or more points, representing periods of many months, to give a better picture of analytical operations.
- b. Consideration should be given to using control limits at two standard deviations to give better control of the procedure. The basis is that some action should be considered, anyway, when a set of data points begins to approach one of the two-SD limits, which demonstrates a nonstatistical behavior of the analysis, within the two-SD limits, such as a set of data points approaching, but not at, the control limit.
- c. The baseline (100% recovery) should be based on the mean, rather than the "true" value of the performance standard, so that the control limits are symmetrically placed on either side to show the statistical behavior of the performance checks. If there is a bias between the mean and "true" values, the use of the latter as the baseline may result in this line being too close to the control limit. A stable, but innocurate standard, is still useful in the determination of instrumental stability; determination of its correct value is a separate problem.
- d. The comments on the charts should be readily available to the analyst by placing them on the logsheets, rather than in a separate file.

e. All quantitative analyses should have control charts as part of the quality assurance of the measurements program, regardless of the immediate concern to the NRC, such as cooling tower water treatment materials. These may be eventually of interest to the NRC, and at present they may be economically useful to the plant. Having fewer types of programs may also simplify the administration of the QA/QC program.

Licensee representatives agreed to consider these suggestions and will submit a letter with their proposed actions to the Region III office by November 1, 1988. Progress in this will be followed in subsequent inspections under Open Item No. 50-483/88017-02.

Licensee representatives were very aware of the value of a good QA/QC program and they have spent much effort on its development and implementation. They appear very receptive to initiatives for improvement.

No violations or deviations were identified.

8. Verification of Collocated TLDs (TI 2500/22, IP 80721)

The inspector examined six locations where licensee and NRC TLD dosimeters were believed to be collocated. At four of the locations they were on the same poles, and at a fifth, they were on adjacent poles. The sixth was not collocated.

No violations or deviations were identified.

9. Open Items

Open items are matters which have been discussed with the licensee, which will be reviewed further by the inspector, and which involve some action on the part of the NRC or licensee, or both. Open items disclosed during the inspection are discussed in Sections 6 and 7.

10. Exit Interview

The scope and findings of the inspection were reviewed with licensee representatives (Section 1) at the conclusion of the inspection on August 26, 1988. The inspector discussed concerns about the quality control program and the confirmatory measurements addressed in Sections 6 and 7. Licensee representatives agreed to consider these items relating to these concerns by November 1, 1988 and submit a letter to Region III. Telephone conversations were held with licensee representatives on September 7 and 8, 1988 relating to the confirmatory measurements results. During the exit interview, the inspector discussed the likely informational content of the inspection report with regard to documents or processes reviewed by the inspector during the inspection. Licensee representatives did not identify any such documents or processes as proprietary.

Attachments:

- Table 1, Nonradiological Interlaboratory 1.
- Test Results, May 1987 Attachment 1, Criteria for Comparing Analytical Measurements (Nonradiological) 2.
- 3. Table 2, Radiological Interlaboratory Test Results, Callaway Nuclear Plant, Second Quarter 1988
- Attachment 2, Criteria for Comparing 4. Analytical Measurements (Radiological)
- 5. Table 3, Nonradiological Interlaboratory Test Results, August 22-26, 1988

TABLE 1 Nonradiological Interlaboratory Test Results Subsequent to Inspection Open Item 50-483/87016-0xx Callaway Nuclear Plant May 1987

Anal- Analysis yte Method ^a		NRC		Licensee			Ratio		Comparison		b
		Y ± 4	5D	×	± SD		Z ±	SD ±2	S	D	
				Con	centrat	ion	, ppb				
Chloride	IC	80.5	±	2.2	71.6	±	2.2	0.889	±	0.037	D
Iron	AAS	14.7	±	0.42	19.3	*	0.6	1.313	±	0.054	D
Sodium	AAS	14.4	±	0.8	25.5	±	5.6	1.736	±	0.401	A
Hydra- zine	Spec	22.3 56.9 104		1.4 0.7 1	20.7 50.6 101	± ± ±	0.2 0.4 1		±	0.061 0.016 0.013	A, D A
Silica	Spec	109 160	± ±	7 5	98 146	± ±	77			0.086 0.052	A A

 Methods: IC Ion chromatography AAS Atomic absorption spectrophotometry Spec UV/Vis spectrophotometry

b. A = Agreement D = Disagreement

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* Substituted the BNL uncertainty for licensee's uncertainty.

TABLE 2

U S NUCLEAR REGULATORY COMMISSION

OFFICE OF INSPECTION AND ENFORCEMENT.

CONFIRMATORY MEASUREMENTS PROGRAM FACILITY: CALLAWAY FOR THE 2 QUARTER OF 1988

SAMPLE	1SOTOPE	REBULT	ERROR	RESULT	NSEE	RATIO	SEEINRC RES	
L WASTE	H-3 SR-89 SR-90 G-ALPHA	6.05-02 5.9E-07 3.0E-09 3.0E-09	1.5E-03 3.0E-08 4.0E-09 2.0E-09	5.0E-08 43.0E-08 41.0E-08	1.0E-04 0.0E-01 0.0E-01 0.0E-01	8.56-02	4.0E 01 2.0E 01 7.5E-01 1.5E 00	ADZZ

T TEST RESULTS: A×AGREEMENT D=DISAGREEMENT *=CRITERIA RELAXED N=NO COMPARISON

1.

	Non-R	adiolog		TAB al Inter Callawa ugust 22	y Plant		/ Test	Results		
Comparison	Analysįs		RC	b	Licenseeb		0	Ratio	Compagi-	
Parameter	Method		+	SD	X ±	SD		Z ± SD	son +2 S	D
			C	oncentra	tion, p	pb				
Fluoride	SIE	165.6	± ±	1.6 3.4			1.5	0.800 ± 0.831 ± 0.894 ±	0.022	D*
(rerun)		84.6	±	4.0 1.6 3.4	41.0 80.7 164		1.2 1.2 1.2	0.911 ± 0.954 ± 0.990 ±	0.026	Α,
Chloride	IC	18.65	±	0.05 0.30 0.60	9.53 19.30 38.80	±	0.30 0.10 0.40	1.035 ±	0.017	A
Sulfate	IC	19.15	±	0.70 1.35 1.15	9.20 18.3 39.7	±		0.956 ± (0.068	A A A
Iron	AA/FU	18.6 39.8 58.5	* * *	0.5	18.2 35.1 55.5			0.978 ± (0.882 ± (0.949 ± (0.074	A A A
Copper	AA/FU		* * *	1.5 1.5	21.8 41.8 64.0	±	4.7	1.090 ± 0 1.037 ± 0 1.067 ± 0).049).083	D* A A+
(rerun)		20.0	±	0.3	20.9	±	0.5	1.045 ± (0.030	A [*]
Sodium	AA/FL	212 316	**	14 12 18		大土土	45 56 28	1.595 ± 0. 1.774 ± 0. 1.608 ± 0.	283	A D D
(rerun)		212 316	* *	12 18		2 2	9 4	1.028 ± 0. 1.070 ± 0.	062	A* A
Lithium		985 1500 2065	* * * *	20 35 50	1432 1897	* * *	9 13 15	0.963 ± 0. 0.955 ± 0. 0.919 ± 0.	024 031	A A D*
(rerun)		2065	ż	50	2023	*	21	0.980 ± 0.	026	A

		1	ABLE 3	(continued	1)			
Hydra- Spec zine (rerun)	19.9 49.9 100 19.9 49.9 100	*1 *1 *1 * 1 * 1 * 1	0.5 1 0.3 0.5	$ \begin{array}{r} 21.0 \pm \\ 52.7 \pm \\ 106 \pm \\ 20.5 \pm \\ 50.2 \pm \\ 100.9 \pm \\ \end{array} $	0.0 0.6 0.6 0.3 0.1	1.056 ±	0.012	D* D*+ A+ A
Silica Spec	52.8 104 157	*	2.8 4 2	53.7 ± 107 ± 162 ±	1.2 1 2	1.017 ± 1.029 ± 1.032 ±	0.041	A A A
			Concen	tration,ppm	1			
Boron Titr	1040 3089 5000	* * *	10 41 90	996 ± 2950 ± 4874 ±	: 9		± 0.01 ± 0.01 ± 0.01	8 D*
a. Methods:								

TABLE

Methods: SIE Specific in electrode IE Ion Chromatography AA/FU Atomic absorption spectrophotometry/furnace AA/FL Atomic absorption spectrophotometry/flame Spec UV/VIS spectrophotometry Titr Titration potentiemetric/mannitol method

- b. Value * standard deviation (SD); the number of analyses is from 6 to 9 for BNL and three for the licensee.
- c. A = Agreement D = Disagreement

* Substituted the BNL uncertainty for licensee's uncertainty.

+ Rerun A/D.

ATTACHMENT 1

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

1. 4

(2) S, is the uncertainty of the ratio determined from the propagation of the uncertainties of licensee's mean value, S_x, and of the NRC's mean value, S_y.¹ Thus,

$$\frac{S_z^2}{Z^2} = \frac{S_x^2}{X^2} + \frac{S_y^2}{Y^2}, \text{ so that}$$
$$S_z = Z \cdot \left(\frac{S_x^2}{X^2} + \frac{S_y^2}{Y^2}\right)^{\frac{1}{2}}$$

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 | ≤ 2•S, .

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

4/6/87

ATTACHMENT 2

CRITERIA FOR COMPARING ANALYTICAL MEASUREMENTS

This attachment provides criteria for comparing results of capability tests and verification measurements. The criteria are based on an empirical relationship which combines prior experience and the accuracy needs of this program.

In these criteria, the judgment limits are variable in relation to the comparison of the NRC's value to its associated one sigma uncertainty. As that ratio, referred to in this program as "Resolution", increases, the acceptability of a licensee's measurement should be more selective. Conversely, poorer agreement should be considered acceptable as the resolution decreases. The values in the ratio criteria may be rounded to fewer significant figures reported by the NRC Reference Laboratory, unless such rounding will result in a narrowed category of acceptance.

RESOLUTION	RATIO = LICENSEE VALUE/NRC REFERENCE VALUE
	Agreement
<4	0.4 - 2.5
4 - 7	0.5 - 2.0
8 - 15	0.6 - 1.66
16 - 50	0.75 - 1.33
51 - 200	0.80 - 1.25

0.85 - 1.18

Some discrepancies may result from the use of different equipment, techniques, and for some specific nuclides. These may be factored into the acceptance criteria and identified on the data sheet.

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