U. S. NUCLEAR REGULATORY COMMISSION REGION I

Report Nos. 50-317/91-04, 50-318/91-04

Docket Nos. 50-317, 50-318

License Nos. DPR-53, DPR-69

Licensee: Baltimore Gas and Electric Company P.O. Box 1475 Baltimore, Maryland 21203

Facility Name: Calvert Cliffs Nuclear Power Plant, Units 1&2

Inspection At: Lusby, Maryland

Inspection Conducted: January 14-18, 1991

N. T. McNamara, Physical Science Technician, 2-5-91 Inspectors: date Effluents Radiation Protection Section (ERPS), Facilities Radiological Safety and Safeguards Branch (FRSSB), Division of Radiation Safety and Safeguards (DRSS) L. A. Peluso, Radiation Specialist, ERPS, FRSBB, DRSS Jang 2-5-9/ date D. J. Kottan, Laboratory Specialist, ERPS, FRSSB, DRSS 2-5-7 date Approved by: R. J. Bores, Chief, ERPS, FRSSB, DRSS

Inspection Summary:

Inspection on January 14-18, 1991 (Combined Inspection Report Nos. 50-317/91-04, 50-318/91-04

Areas Inspected: Routine, unannounced inspection of the radiological and non-radiological chemistry programs. Areas reviewed included: confirmatory measurements-radiological, standards analyses-chemistry, and laboratory QA/OC.

Results: Of the areas reviewed, no violations were identified.

DETAILS

1.0 Individuals Contacted

Principal Licensee Employees

*P. Crinigan, General Supervisor, Chemistry

*C. Earls, Supervisor of Plant Chemistry

E. Eshelman, Chemist

J. Grigg, Chemistry Technician

*P. Katz, Superintendent, Technical Support R. Kreger, Sr. Chemistry Technician P. Majethia, Chemistry Technician

*C. Sly, Compliance Engineer

R. Sprecher, Chemical Analyst

*J. Volkoff, Compliance Enginer *L. Wenger, Principal Engineer, Compliance *J. Wood, Sr., Engineer, Quality Audits J. York, Chemist

NRC Employees

*L. Nicholson, Senior Resident Inspector A. How2, Resident Inspector

*Denotes those present at the exit meeting on January 18, 1991.

The inspectors also interviewed other licensee personnel, including members of the chemistry and radiation protection staffs.

2.0 Purpose

The purpose of this routine inspection was to review the following areas.

- The licensee's ability to measure radioactivity in plant systems and 1. effluent samples, and the ability to measure chemistry parameters in various plant systems.
- 2. The licensee's ability to demonstrate the acceptability of analytical results through implementation of a laboratory QA/QC program.

3.0 Radiological and Chemical Measurements

3.1 Confirmatory Measurements-Radiological

During this part of the inspection, liquid, airborne particulate (filter) and iodine (charcoal cartridge), and gas samples were analyzed by the licensee and the NRC for the purpose of intercomparison. The samples were actual split samples with the exception of the crud particulate filter and the charcoal cartridge samples. In these cases the samples could not be split, and the same samples were analyzed by the licensee and the NRC. Where possible, the samples are actual effluent samples or inplant samples which duplicated the counting geometries used by the licensee for effluent sample analyses. These samples were analyzed by the Chemistry Department using routine methods and equipment and by the NRC I Mobile Radiological Measurements Laboratory. Joint analyses of actual effluent samples are used to verify the licensee's capability to measure radioactivity in effluent and other samples with respect to Technical Specifications and other regulatory requirements.

In addition, a liquid effluent sample was sent to the NRC reference laboratory, Department of Energy, Radiological and Environmental Sciences Laboratory (RESL), for analyses requiring wet chemistry. The analyses to be performed on the sample are Sr-89, Sr-90, gross alpha and tritium. The results of these analyses will be compared with the licensee's results when received at a later date and will be documented in a subsequent inspection report.

The results of a liquid effluent sample split between the licensee and the NRC during a previous inspection on October 31, 1988 -November 4, 1988 (Combined Inspection Report Nos. 50-317/88-29 and 50-318/88-29) were also compared during this inspection.

The results of the above sample measurements comparisons, which are presented in Table I, indicated that all of the measurements were in agreement under the criteria used for comparing results. (See Attachment 1 to Table I). In reviewing the comparison results the inspector noted that the licensee's results for the liquid radioactive waste samples analyzed on Detector 1 appeared to be biased high by approximately 25%. The inspector discussed this bias with the licensee and noted that the data generated by the licensee's interlaboratory QA/QC program also revealed this same apparent bias. The licensee responded that a reason for the bias had not been determined, but that until the reason could be determined this counting geometry on Detector 1 would be taken out-of-service. The inspector stated that this item would be reviewed during a subsequent inspection.

In addition, the inspector determined that the licensee's Chemistry Department routinely analyzes inplant air particulate filters and charcoal cartridges combined rather than separately. The analyses were performed for the Health Physics Department. The inspector discussed this matter with the licensee and stated that although the air particulate filter and charcoal cartridge samples are taken together, they should be counted individually because the radioactivity distribution between the filter and the carridge can vary from sample to sample. Under these circumstances it is very difficult to prepare a calibration standard which accurately represents the radioactivity distribution in the particulate filter and charcoal cartridge. The licensee responded that inplant air particulate and charcoal cartridge samples would continue to be counted together for screening purposes, but that if radioactivity was detected during the screening, the particulate filter and charcoal cartridge would be analyzed independently. It should be noted that the effluent particulate filter and charcoal cartridge samples were counted separately.

The inspector had no further questions in this area. No violations were identified.

3.2 Standards Analyses (Chemical)

During this part of the inspection, standard chemical solutions were submitted to the licensee for analysis. The standards were prepared by Brookhaven National Laboratory (BNL) for the NRC, and were analyzed by the licensee using routine methods and equipment. The analysis of standards is used to verify the licensee's capability to monitor chemical parameters in various plant systems with respect to Technical Specifications and other regulatory requirements. In addition, the analysis of standards is used to evaluate the licensee's procedures with respect to accuracy and precision.

The standards were submitted to the licensee for analysis in triplicate at three concentrations spread over the licensee's normal calibration and analysis range. The sodium analyses, however, were performed at only two concentrations because the NRC supplied sodium solutions also contained lithium which appeared to interfere with the sodium analysis at the low parts per billion (ppb) levels. Additionally, the boron analysis at approximately 1000 parts per million (ppm) was performed only in duplicate because of the lack of sufficient volume of the NRC standards to perform these analyses in triplicate. The results of the standards measurements comparisons, presented in Table II, indicated that all of the measurements were in agreement or qualified agreement under the criteria used for comparing results. (See Attachment 2.) In addition, the inspector noted that during a previous inspection in this area, performed on January 9-13, 1989, (Combined Inspection Report Nos. 50-317/89-01 and 50-318/89-01) the licensee committed to review and implement corrective action as appropriate in order to resolve disagreements which occurred during that inspection. The inspector verified during this inspection that the licensee had implemented the required corrective actions.

No violations were identified in this area.

4.0 Laboratory QA/QC

The licensee's laboratory QA/QC program is detailed in Procedure CP-103, "Chemistry Quality Assurance Program". This procedure addresses responsibility, training and qualification, procedures, records, control of equipment and materials, and control of measurements and inspections. The control of equipment section requires a minimum of five calibration points for laboratory instrumentation with the resultant calibration curve to be generated using a computer-assisted best fit to the data. The control of measurements section addresses the construction and use of control charts. Each analyst is assigned an identifying number or symbol for identifying specific points plotted on a control chart. The additional activities section of this procedure describes the requirements for an interlaboratory and intralaboratory comparison program. The licensee participated in a bimonthly interlaboratory program sponsored by another utility for most routinely analyzed chemical parameters. The licensee also participated in an interlaboratory program with the National Institute of Standards and Technology (NIST) for radioactivity measurements. This included the licensee's vendor laboratory used for performing certain radioactivity analyses of effluent samples. The intralaboratory program consisted of analysis of spiked samples on a frequency which resulted in a analyst analyzing unknown sample, at least once every six months.

The inspector reviewed the licensee's data for the above programs, and noted that the licensee appeared to be implementing the programs as required. The utility which administered the interlaboratory chemistry program provided criteria for comparing results and the licensee had established criteria for the intralaboratory comparisons. However, no criteria had been established for the NIST interlaboratory program. The licensee stated that data from the NIST program was being reviewed in order to establish some comparison criteria. The inspector stated that this item would be reviewed during a subsequent inspection. Additionally, the inspector noted that an experienced individual had been assigned the responsibility for the laboratory QA/QC program on an ongoing basis. This individual was organizing the current and previous QA/QC data using spread sheets and had prepared trend plots of the data. This was being done in order to establish comparison criteria for some programs, such as the NIST program mentioned above, refine other comparison criteria currently in use, provide improved values for tolerance limits and detection limits, and provide for overall improved review of laboratory QA/QC data. The inspector stated that the actively ongoing organization and review of the laboratory QA/QC data were noted positive attributes of the licensee's chemistry program.

No violations were identified in this area.

5.0 Audits

The inspector reviewed Quality 'ssurance Audit #90-06, "Chemistry and Water Treatment", dated May 23, 1990 which war conducted during the period of March 12, 1990 through April 24, 199 't was performed to verify compliance and evaluate chemist' treatment activities. Also, the audit included chemistry (a coratory controls and procedures, performance of chemical and radiochemical analysis and equipment calibration and control charts. The inspector determined that the findings were resolved in a timely manner. The inspector also reviewed the audit schedule and determined that audits in the chemistry and radiochemistry areas were scheduled every two years by the Quality Assurance and Staff Services Department.

No deficiencies : ere identified and there were no further questions in this area.

6.0 Exit Interview

The inspector met with the licensee representatives denoted in Section 1 of this report at the conclusion of the inspection on January 18, 1991. The inspector summarized the purpose, scope, and findings of the inspection.

CALVERT CLIFFS VERIFICATION TEST RESULTS

Samole	ISOTOPE	NRC VALUE	Licensee Value	Comparison
		RESULTS IN MIC	CROCURIES PER MILLILITER	
Waste Gas Decay Tank 1-16-91 1330 hrs. (Detector 1)	Xe-135 Xe-133 Xe-133m	(1.83±0.04)E-3 (2.473±0.007)E-1 (1.6±0.2)E-3	(1.70±0.02)E-3 (2.409±0.004)E-1 (1.52±0.07)E-3	Agreement Agreement Agreement
Main Vent 1-18-91 1100 hrs. [Detector 2]	Xe-133 Xe-135	(5.0±0.2)E-7 (8.4±1.0)E-8	(5.8±0.3)E-7 (8.4±0.8)E-8	Agreement Agreement
Reactor Coolant 1-16-91 0850 hrs. (Detector 1)	1-131 1-132 1-133 1-135	(2.27±0.03)E-2 (6.58±0.07)E-2 (9.26±0.06)E-2 (7.5±0.3)E-2 (1.11±0.02)E-1	(2, 13±0.05)E-2 (7, 31±0.09)E-2 (8, 64±0.08)E-2 (7, 6±0.2)E-2 (1, 03±0.02)E-1	Agreement Agreement Agreement Agreement
#12 RCWM1* 11-10-88 1020 hrs.	H-3 Sr-89 Sr-90 gross alpha	(1.31±0.01)E-1 (4±2)E-8 (3±4)E-9 (2±7)E-9	(1.16+0.12)E-1 <1.7E-8 <7.0E-9 <1.6E-8	Agreement No Comparison No Comparison No Comparison
RCS Crud Filter 1-16-91 0850 hrs. (Detector 1)	1-131 1-132 1-132 1-135 Co-58	(3.60±0.15)E-5 (1.62±0.11)E-4 (1.32±0.03)E-4 (1.54±0.12)E-4 (2.74±0.05)E-4	$(3.8\pm0.2)E-5$ (1.20\pm0.04)E-4 (1.37\pm0.03)E-4 (1.94\pm0.10)E-4 (2.9\pm0.05)E-4	Agreement Agreement Agreement Agreement

*Sample split during a previous inspection

CALVERT CLIFFS VERIFICATION TEST RESULTS

CALVERT CLIFFS NUCLEAR POWER PLANT

CHEMISTRY TEST RESULTS

Comperison	Agreement Agreement Agreement	Agreement Agreement Agreement		Agreement Agreement Agreement	Qualified Agreement Agreement Qualified Agreement
Ratio	1.01±0.02	0.99±0.02	(m	1,03±0.02	0.97±0.02
[Lic/NRC]	1.011±0.011	1.05±0.03		1,03±0.03	1.001±0.014
pb]	0.973±0.008	1.04±0.05		0.981±0.015	0.98±0.02
Licensee	20.07±0.12	19.6±0.4	in Parts per Million (pp	1.023±0.006	*1002.8±0.5
Measured Value	30.13±0.15	30.5±0.6		1.507±0.006	2994±6
a in Parts per Eillion (p	39.4±0.2	40.9±1.5		1.943±0.006	4976±6
NRC	19.9±0.4	19.8±0.3	Result	0.990±0.015	1030±20
Known Value	29.8±0.3	29.0±0.5		1.46±0.04	2990±40
Results	40.5±0.3	39.2±1.0		1.98±0.03	5100±100
Method of Analysis	AA-GF	AA-GF		AA	Tit.
Chemica! Parameter	Copper	1 ron		Lithium	Boron

*Duplicate analysis

Notes: FE = Flame Emission AA = Flame Atomic Absorption Spectrometry AA-CF = Graphite Furnace AA SP = UN-Vis Spectrophotometry IC = fon Chromatography Tit. = Titration

CALVERT CLIFFS NUCLEAR POWER PLANT

CHEMISTRY TEST RESULTS

Chemica! Parameter	Method of Analysis	NRC Known Value	Licensee Measured Value	Ratio (Lic/NRC)	Comparison
		Result	s in Parts per Billion	[bbb]	
Fluoride	2	2.40±0.10 4.8±0.2 7.4±0.3	2.13±0.06 4.59±0.14 7.13±0.09	0.96±0.05 0.96±0.05 0.96±0.05	Agreement Agreement Agreement
Chioride	10	6.2±0.4 9.5±0.5 19.0±1.0	6.2±0.4 9.5±0.4 19.4±0.2	1,00+0.09 1,00±0.07 1,02±0.05	Agreement Agreement Agreement
Sulfate	2	6.0±0.4 12.0±0.8 19±3	6.6±0.4 32.6±0.3 21.1±0.2	1, 10±0, 10 1, 05±0, 07 1, 1±0, 2	Agreement Agreement Agreement
Aydrazine	45	10.2±0.3 42.3±0.9 84.4±0.6	10.2+0.7 41.3+0.2 83.2+1.3	1.00±0.07 0.98±0.02 0.98±0.02	Agreement Agreement Agreement
Ammors i a	SP	102±5 310±10 500±20	103±2 294+9 499±5	1,01±0.05 0,95±0.05 1,00±0.04	Agreement Agreement Agreement
Silica	SP	49±4 110±2 161±3	55.0±0.3 107.7±0.3 161.9±1.2	1,12+0.09 0,98+0.02 1,00±0.02	Qualified Agree Agreement Agreement
Sod i um	FE	5.1±0.2 9.9±0.2	5.3±0.4 9.4±0.3	1.04±0.09	Agreement Agreement

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ATTACHMENT 1

Criteria for Comparing Analytical Measurements of Table 1

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 judgement limits are variable in relation to the comparison of the NRC Reference Laboratory's value to its associated uncertainty. As the ratio, referred to in this program as "Resolution", increases the acceptability of a licensee's measurement should be more selective. Conversely, poorer agreement must be considered acceptable as the resolution decrease:

Resolution1	Ratio for Agreement ²
<3	No Comparison
8 - 15	0.6 - 1.66
16 - 50	0.75 - 1.33
>200	0.80 = 1.25 0.85 = 1.18

³Resoluti: (NRC Reference Value/Reference Value Uncertainty) ²Ratio = (License Value/NRC Reference Value)

ATTACHMENT 2

Criteria for Comparing Analytical Measurements of Table II

This attachment provides criteria for comparing results of capability tests. In these criteria the judgement limits are based on data from Table 2.1 of NUREG/CR-5244, "Evaluation of Non-Radiological Water Chemistry at Power Reactors". Licensee values within the plus or minus two standard deviation range (±2Sd) of the BNL known values are considered to be in agreement. Licensee values outside the plus or minus two standard deviation range but within the plus or minus three standard deviation range (±3Sd) of the BNL known values are considered. Repeated results which are in qualified agreement will receive additional attention. Licensee values greater than the plus or minus three standard deviations range of the BNL known value are in disagreement. The standard deviations were computed using the above average percent standard deviation value of each analyte in Table 2.1 of the NUREG.

The ranges for the data in Table II are as follows.

Analyte	Agreement Range	Qualified Agreement Range
Fluoride	2.1 - 2.7 4.2 - 5.4 6.5 - 8.3	2.0 - 2.8 4.0 - 5.6 6.1 - 8.7
Chloride	5.7 - 6.7 8.8 - 10.2 17.6 - 20.4	5.5 - 6.9 8.5 - 10.5 17.0 - 21.0
Sulfate	5.4 - 6.6 10.8 - 13.2 17 - 21	5.2 - 6.8 10.4 - 13.6 16 - 22
Hydrazine	9.4 - 11.0 39.0 - 45.6 77.9 - 90.9	9.0 - 11.4 37.4 - 47.2 74.6 - 94.2
Ammonia	92 - 112 280 - 340 452 - 548	87 - 117 265 - 355 428 - 572
Silica	44 - 54 100 - 120 146 - 176	42 - 56 95 - 125 138 - 184
Sodium	4.4 - 5.8 8.5 - 11.3	4.0 - 6.2 7.8 - 12.0

Analyte	Agreement Range	Qualified Agreement Range
Copper	18.0 - 21.8 26.9 - 32.6 36.6 - 44.4	17.1 - 22.7 25.5 - 34.0 34.7 - 46.3
Iron	17.9 - 21.7 26.2 - 31.8 35.4 - 43.0	16.9 - 22.7 24.8 - 33.2 33.6 - 44.8
Lithium	0.850 - 1.130 1.26 - 1.67 1.70 - 2.25	0.785 - 1.195 1.15 - 1.78 1.56 - 2.39
Boron	1008 - 1052 2926 - 3054 4991 - 5209	997 - 1063 2894 - 3086 4937 - 5263

ATTACHMENT 2

Criteria for Comparing Analytical Measurements of Table II