

U.S. NUCLEAR REGULATORY COMMISSION
REGION I

Report No.: 50-352/93-01
50-353/93-01

Docket No.: 50-352
50-353

License No.: NPF-39
NPF-85

Licensee: Philadelphia Electric Company
2301 Market Street
Philadelphia, Pennsylvania 19105

Facility Name: Limerick Generating Station, Units 1 and 2

Inspection At: Limerick, Pennsylvania

Inspection Conducted: January 11-15, 1993

Inspectors: Nancy T. McNamara
N. McNamara, Laboratory Specialist
Effluents Radiation Protection Section (ERPS)

2/4/93
Date

J. J. Kottan
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Facilities Radiological Safety and Safeguards
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2-4-93
Date

Approved By: M. T. Miller
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Division of Radiation Safety and Safeguards

2-4-93
Date

Areas Inspected: Announced inspection of the radiological and non-radiological chemistry programs. Areas reviewed included: Confirmatory Measurements - Radiological, Standards Analyses - Chemistry, Laboratory QA/QC, and Audits.

Results: The licensee had in place effective programs for measuring radioactivity in process and effluent samples and for measuring chemical parameters in plant systems samples. No safety concerns or violations of regulatory requirements were observed.

DETAILS

1.0 Individuals Contacted

Principal Licensee Employees

- * J. Doeering, Plant Manager
- * J. Dougherty, QA/QC Chemist
- D. Fay, Technical Monitor
- E. Frick, Chemist
- K. Gordon, Supervisory Chemist
- * T. Jackson, Senior Chemist
- M. Kaminski, Engineer, QA
- * G. Madsen, Regulatory Supervisor
- * J. Phillabaum, Engineer
- * G. Roach, Services Superintendent

NRC Employees

T. Kenny, Senior Resident Inspector

- * Denotes those present at the exit meeting on January 15, 1993. The inspectors also interviewed other licensee personnel, including the chemistry technicians who performed the analyses for this inspection.

2.0 Purpose

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

1. The licensee's ability to measure radioactivity in plant systems samples and effluent samples, and the ability to measure chemical parameters in various plant systems samples.
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 - Radiochemistry

During this part of the inspection, liquid, airborne particulate (filter) and iodine (charcoal cartridge), and gas samples were analyzed by the licensee's chemistry department and the NRC for the purpose of intercomparison. The samples were actual split samples with the exception of the particulate filter, charcoal cartridge, and offgas samples. In those cases, the samples could not be split and the same samples were analyzed by the licensee and the NRC. Where possible, the

samples were actual effluent samples or in-plant samples which duplicated the counting geometries used by the licensee for effluent sample analyses. The samples were analyzed by the licensee using routine methods and equipment and by the NRC Region I Mobile Radiological Measurements Laboratory. Joint analyses of actual samples were 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 sample was sent to the NRC reference laboratory, Department of Energy, Radiological and Environmental Sciences Laboratory (RESL) for analysis requiring wet chemistry. The analyses to be performed on the sample are Sr-89, Sr-90, Fe-55, H-3 and gross alpha. 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 sample split between the licensee and the NRC during a previous inspection on February 5-9, 1990 (Combined Inspection Report No. 50-352/90-06 and 50-353/90-07) could not be compared at the time of this inspection because the licensee could not retrieve the sample analysis results. The licensee stated that they will forward to RI the results from the sample split from this inspection as soon as they are received.

The results comparisons for all of the above samples, for which results were available, which are presented in Table I, indicated that all of the measurements were in agreement under the criteria for comparing results. (See Attachment I to Table I). No safety concerns or violations were identified in this area.

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 Oak Ridge National Laboratory (ORNL) 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 analytical procedures with respect to accuracy and precision. The standards were submitted to the licensee in triplicate at three concentrations spread over the licensee's normal calibration and analysis range. The boron analyses were performed at only one concentration on the auto-titrator in order to duplicate the concentration normally encountered during standby liquid control tank boron analysis. The remainder of the boron standards were analyzed on the inductively coupled plasma emission spectrometer (ICP) in order to duplicate the boron concentrations which would be encountered when performing a post-accident sample.

Also, a feedwater sample was spiked with a standard anion solution and sent to ORNL for analysis. The analyses to be performed on the sample are chloride and sulfate. The licensee will perform the same analyses on an aliquot of this spiked sample. The results of these analyses will be compared when received at a later date and will be documented in a subsequent inspection report. The analysis of spiked samples permits comparisons from an actual sample matrix.

The results of the standards measurements comparisons indicated that all of the measurements were in agreement or qualified agreement under the criteria used for comparing results. (See Attachment I to Table II). The chloride results, which are approximately eight parts per billion (ppb) as reported in Table II were obtained after the recalibration of the ion chromatograph (IC). The licensee calibrated the IC at 40, 20 and 10 ppb and implemented a lower limit of detection (LLD) at two ppb. Thus, the licensee routinely reported results which were below the lowest calibration point (10 ppb) and above the LLD. The inspector discussed this matter with the licensee and noted that the licensee had not formalized the definition of LLD and the method for determination of the LLD. The licensee stated that this area would be examined and appropriate corrective action taken. The inspector stated that this area would be reviewed during a subsequent inspection. Additionally, the inspector noted that the licensee had put a new ICP and IC into service and was in the process of formalizing plans for an expanded chemistry laboratory. The new instrumentation and the expanded laboratory were indicative of licensee management support for the chemistry program. No safety concerns or violations were identified in this area.

4.0 Laboratory QA/QC

The licensee's laboratory QA/QC program was described in general terms in Procedure CH-1000, "Chemistry QA/QC Program." This procedure defined the administrative program used by the licensee to assure the quality of analytical measurements and referenced specific implementing procedures. The specific implementing procedures provided for both an intralaboratory and interlaboratory QC program. The intralaboratory program consisted of the use of instrument and procedure control charts for trending performance, and the analysis of spiked samples on a semi-annual basis. The interlaboratory program consisted of the analysis of unknown samples from outside laboratories for both chemical and radiochemical constituents. Included in the interlaboratory program was the vendor laboratory utilized by the licensee for performing selected radiochemical analyses of effluent samples. Also, the QC procedures contained detailed instructions for the preparation and use of control charts, spiked sample analyses and the evaluation of laboratory QC data.

The inspector reviewed selected data generated by the licensee's laboratory QC program for 1992 and 1993 to date and noted that the licensee was implementing the program as required. In particular, the inspector noted that the control limits for the gamma

spectrometry were now based on an experimentally determined estimate of the standard deviation. During the previous inspection in this area, the licensee used fixed values or tolerance limits for the control limits but stated that consideration would be given to changing to statistically determined limits. The licensee had implemented this change. No violations were identified in this area.

5.0 Audit Activities

The inspector reviewed the report for Audit No. A0391330, LGS Chemistry/Radiochemistry, which was conducted from May 21, 1992 through August 21, 1992. The audit was performed using detailed check lists, which had comprehensive comments in each reviewed area, and the audit team included a technical specialist. Additionally, the inspector reviewed an industry audit, NUPIC Audit-NYPA Audit No. 92-18, of the licensee's vendor laboratory used for selected radiochemical analyses of effluent samples, which was conducted on August 3-6, 1992. The above audits were of good technical depth, sufficient to identify programmatic problems in the areas being audited. The inspector also reviewed the licensee's master audit plan and audit schedule, in order to verify the frequency at which audits of the licensee's chemistry program were conducted.

The licensee also performed surveillance activities of specific chemistry tasks and documented these activities in technical monitoring reports. The inspector reviewed selected monitoring reports for 1992 and noted that the reports were generated following specific guidelines for each monitored activity.

Based on the review of the above audits and technical monitoring activities, the inspector determined there was independent oversight and assessment of chemistry activities. No safety concerns or violations were identified.

6.0 Exit Meeting

The inspector met with the licensee representatives denoted in Section 1.0 at the conclusion of the inspection on January 15, 1993. The inspector summarized the purpose, scope, and findings of the inspection.

TABLE I

Limerick Units 1&2 Verification Test Results

<u>SAMPLE</u>	<u>ISOTOPE</u>	<u>NRC VALUE</u>	<u>LICENSEE VALUE</u>	<u>COMPARISON</u>
<u>Results in MicroCuries per milliliter</u>				
ED Surge Tank	Cr-51	$(1.33 \pm 0.02)E-4$	$(1.33 \pm 0.06)E-4$	Agreement
0934 hrs	Mn-54	$(6.4 \pm 0.2)E-6$	$(6.2 \pm 0.7)E-6$	Agreement
01/14/93	Co-58	$(6.5 \pm 0.3)E-6$	$(6.3 \pm 0.2)E-6$	Agreement
(Detector No. 2)	Co-60	$(1.27 \pm 0.04)E-5$	$(1.33 \pm 0.03)E-5$	Agreement
	Zn-65	$(2.81 \pm 0.08)E-5$	$(2.70 \pm 0.09)E-5$	Agreement
	Ba-140	$(1.46 \pm 0.09)E-5$	$(1.42 \pm 0.05)E-5$	Agreement
	Cs-137	$(7.0 \pm 0.2)E-6$	$(6.7 \pm 0.2)E-6$	Agreement
	I-135	$(5.9 \pm 0.2)E-5$	$(6.8 \pm 0.4)E-5$	Agreement
	I-133	$(5.68 \pm 0.04)E-5$	$(6.2 \pm 0.2)E-5$	Agreement
	I-131	$(1.02 \pm 0.03)E-5$	$(1.07 \pm 0.04)E-5$	Agreement
	Na-24	$(1.09 \pm 0.04)E-5$	$(9.8 \pm 0.5)E-6$	Agreement

TABLE I - Continued

Limerick Units 1&2 Verification Test Results

<u>SAMPLE</u>	<u>ISOTOPE</u>	<u>NRC VALUE</u>	<u>LICENSEE VALUE</u>	<u>COMPARISON</u>
<u>Results in MicroCuries per milliliter</u>				
ED Surge Tank 0934 hrs 01/14/93 (Detector No. 4)	Cr-51	$(1.33 \pm 0.02)E-4$	$(1.51 \pm 0.07)E-4$	Agreement
	Mn-54	$(6.4 \pm 0.2)E-6$	$(7.5 \pm 0.3)E-6$	Agreement
	Co-58	$(6.5 \pm 0.3)E-6$	$(7.0 \pm 0.3)E-6$	Agreement
	Co-60	$(1.27 \pm 0.04)E-5$	$(1.46 \pm 0.03)E-5$	Agreement
	Zn-65	$(2.81 \pm 0.08)E-5$	$(3.00 \pm 0.09)E-5$	Agreement
	Ba-140	$(1.46 \pm 0.09)E-5$	$(1.73 \pm 0.06)E-5$	Agreement
	Cs-137	$(7.0 \pm 0.2)E-6$	$(7.7 \pm 0.3)E-6$	Agreement
	I-135	$(5.9 \pm 0.2)E-5$	$(6.48 \pm 0.15)E-5$	Agreement
	I-133	$(5.68 \pm 0.04)E-5$	$(6.6 \pm 0.2)E-5$	Agreement
	I-132	$(9.0 \pm 0.4)E-6$	$(1.1 \pm 0.3)E-5$	Agreement
	I-131	$(1.02 \pm 0.03)E-5$	$(1.25 \pm 0.05)E-5$	Agreement
	Na-24	$(1.09 \pm 0.04)E-5$	$(1.08 \pm 0.04)E-5$	Agreement
South Stack Charcoal Cartridge 2052 hrs 01/08/93 (Detector No. 4)	I-131	$(6.2 \pm 0.7)E-13$	$(7.2 \pm 0.9)E-13$	Agreement
	I-133	$(1.4 \pm 0.3)E-11$	$(1.21 \pm 0.15)E-11$	Agreement

TABLE I - Continued

Limerick Units 1&2 Verification Test Results

<u>SAMPLE</u>	<u>ISOTOPE</u>	<u>NRC VALUE</u>	<u>LICENSEE VALUE</u>	<u>COMPARISON</u>
<u>Results in MicroCuries per milliliter</u>				
Unit 2 Offgas	Kr-85m	$(3.6 \pm 0.3)E-7$	$(4.2 \pm 0.2)E-7$	Agreement
Post Treatment	Xe-133	$(1.18 \pm 0.03)E-7$	$(1.4 \pm 0.6)E-7$	Agreement
1356 hrs				
01/13/93				
(Detector No. 1)				
Unit 2	I-132	$(4.38 \pm 0.08)E-2$	$(5.40 \pm 0.12)E-2$	Agreement
Reactor Water	I-133	$(2.59 \pm 0.04)E-2$	$(2.92 \pm 0.09)E-2$	Agreement
0800 hrs	I-134	$(1.63 \pm 0.06)E-1$	$(2.13 \pm 0.04)E-1$	Agreement
01/14/93	I-135	$(7.0 \pm 0.2)E-2$	$(7.0 \pm 0.2)E-2$	Agreement
(Detector No. 1)				
Unit 1	Cr-51	$(3.48 \pm 0.09)E-5$	$(3.6 \pm 0.2)E-5$	Agreement
Reactor Water	Mn-54	$(5.21 \pm 0.13)E-6$	$(5.3 \pm 0.2)E-6$	Agreement
Particulate Filter	Co-58	$(4.80 \pm 0.13)E-6$	$(4.9 \pm 0.2)E-6$	Agreement
0730 hrs	Co-60	$(6.1 \pm 0.2)E-6$	$(6.4 \pm 0.2)E-6$	Agreement
01/11/93	Zn-65	$(8.0 \pm 0.3)E-6$	$(9.0 \pm 0.4)E-6$	Agreement
(Detector No. 5)				

TABLE I - Continued

Limerick Units 1&2 Verification Test Results

<u>SAMPLE</u>	<u>ISOTOPE</u>	<u>NRC VALUE</u>	<u>LICENSEE VALUE</u>	<u>COMPARISON</u>
<u>Results in MicroCuries per milliliter</u>				
Unit 1	I-132	$(5.0 \pm 0.4)E-4$	$(5.7 \pm 0.2)E-4$	Agreement
Reactor Water	I-133	$(1.49 \pm 0.12)E-4$	$(1.33 \pm 0.10)E-4$	Agreement
0730 hrs	I-134	$(1.41 \pm 0.16)E-3$	$(1.57 \pm 0.07)E-3$	Agreement
01/13/93				
(Detector No. 5)				
Unit 2 Offgas	Kr-85m	$(1.8 \pm 0.2)E-2$	$(1.81 \pm 0.06)E-2$	Agreement
1232 hrs	Kr-87	$(1.156 \pm 0.010)E-1$	$(1.22 \pm 0.04)E-1$	Agreement
01/12/93	Kr-88	$(7.16 \pm 0.07)E-2$	$(7.4 \pm 0.2)E-2$	Agreement
(Detector No. 6)	Xe-133	$(5.8 \pm 0.2)E-3$	$(6.5 \pm 0.4)E-3$	Agreement
	Xe-135m	$(4.0 \pm 0.2)E-1$	$(4.28 \pm 0.14)E-1$	Agreement
	Xe-135	$(7.69 \pm 0.04)E-2$	$(7.8 \pm 0.3)E-2$	Agreement
	Xe-138	(2.01 ± 0.08)	(2.09 ± 0.06)	Agreement

Note: Reported uncertainties are \pm one standard deviation (1S) counting uncertainties for both NRC and licensee results.

TABLE II

Limerick Units 1 & 2

Chemical Analysis	Method of Analysis	NRC Known Value	Licensee Value	Comparison
Results in parts per million (ppm)				
Copper	ICP	0.202 ± 0.002	0.2100 ± 0.0010	Agreement
		1.62 ± 0.02	1.653 ± 0.012	Agreement
		4.03 ± 0.04	4.12 ± 0.05	Agreement
Iron	ICP	0.199 ± 0.002	0.200 ± 0.003	Agreement
		1.590 ± 0.014	1.627 ± 0.012	Agreement
		3.98 ± 0.04	4.14 ± 0.02	Agreement
Nickel	ICP	0.199 ± 0.002	0.190 ± 0.004	Agreement
		1.600 ± 0.016	1.60 ± 0.02	Agreement
		4.00 ± 0.04	4.03 ± 0.05	Agreement
Chromium	ICP	0.200 ± 0.002	0.1917 ± 0.0006	Agreement
		1.608 ± 0.014	1.57 ± 0.02	Agreement
		4.02 ± 0.04	4.010 ± 0.010	Agreement
Zinc	ICP	0.103 ± 0.001	0.105 ± 0.006	Agreement
		1.09 ± 0.03	1.09 ± 0.10	Agreement
		5.22 ± 0.07	5.19 ± 0.15	Agreement

TABLE II - Continued

Limerick Units 1 & 2

<u>Chemical Analysis</u>	<u>Method of Analysis</u>	<u>NRC Known Value</u>	<u>Licensee Value</u>	<u>Comparison</u>
<u>Results in parts per million (ppm)</u>				
Boron	ICP	10.49 ± 0.11	10.6 ± 0.4	*
	ICP	30.4 ± 0.4	31.3 ± 0.8	*
	Tit.	506 ± 8	497 ± 3	Agreement
<u>Results in parts per billion (ppb)</u>				
Silica	SP	12.17 ± 0.13	12.6 ± 0.6	Agreement
		28.4 ± 0.4	25.9 ± 0.4	Agreement
		60.1 ± 1.0	58.0 ± 0.6	Agreement
Sodium	IC	10.6 ± 0.4	10.20 ± 0.04	Agreement
		20.4 ± 0.6	19.32 ± 0.09	Agreement
		31.0 ± 0.8	30.2 ± 0.2	Agreement
Sulfate	IC	7.9 ± 0.2	6.90 ± 0.08	Qual Agreement
		19.4 ± 0.3	17.70 ± 0.09	Agreement
		38.8 ± 0.6	37.113 ± 0.016	Agreement

* The criteria for comparing boron results were based on the titration method. No criteria exists, at the present time, for comparing boron by ICP. However, these results would be in Agreement under the criteria used for analyzing metals by ICP.

TABLE II - Continued

Limerick Units 1 & 2

<u>Chemical Analysis</u>	<u>Method of Analysis</u>	<u>NRC Known Value</u>	<u>Licensee Value</u>	<u>Comparison</u>
<u>Results in parts per billion (ppb)</u>				
Chloride	IC	7.7 \pm 0.3	7.16 \pm 0.13	Agreement
		19.4 \pm 0.5	20 \pm 3	Agreement
		36.5 \pm 1.1	37.9 \pm 1.0	Agreement

Notes:

ICP	=	Inductively Coupled Plasma Emission
Tit.	=	Potentiometric Titration
SP	=	UV-Vis Spectrophotometry
IC	=	Ion Chromatography

ATTACHMENT I TO TABLE I

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 judgement limits are variable in relation to the comparison of the NRC Reference Laboratory's value to its associated 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 must be considered acceptable as the resolution decreases.

<u>Resolution¹</u>	<u>Ratio for Comparison²</u>
< 4	No Comparison*
4 - 7	0.5 - 2.0
8 - 15	0.6 - 1.66
16 - 50	0.75 - 1.33
51 - 200	0.80 - 1.25
> 200	0.85 - 1.18

*No comparison due to the large uncertainty of the result

1. Resolution = (NRC Reference Value/Reference Value Uncertainty)

2. Ratio = (Licensee Value/NRC Reference Value)

ATTACHMENT I TO TABLE II

Criteria for Comparing Analytical Measurements from 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 ($\pm 2Sd$) of the ORNL 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 ($\pm 3Sd$) of the ORNL known values are considered to be in qualified agreement. 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 ORNL known value are in disagreement. The standard deviations were computed using the average percent deviation values of each analyte in Table 2.1 of the NUREG.

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

<u>Analyte</u>	<u>Agreement Range</u>	<u>Qualified Agreement Range</u>
Chloride	$\pm 8\%$	$\pm 12\%$
Sulfate	$\pm 10\%$	$\pm 15\%$
Silica	$\pm 10\%$	$\pm 15\%$
Sodium	$\pm 14\%$	$\pm 21\%$
Copper	$\pm 10\%$	$\pm 15\%$
Iron	$\pm 10\%$	$\pm 15\%$
Boron	$\pm 2\%$	$\pm 3\%$
Nickel	$\pm 6\%$	$\pm 9\%$
Chromium	$\pm 10\%$	$\pm 15\%$
Zinc	$\pm 10\%$	$\pm 15\%$