#### U. S. NUCLEAR REGULATORY COMMISSION REGION 1

Report No. 50-293/92-13

Docket No. 50-293

License No. DPR-63

Licensee: Boston Edison Company 800 Boylston Street Boston, MA 02199

Facility Name: Pilgrim Nuclear Power Station

Inspection At: Plymouth, Massachusetts

Inspection Conducted:

June 22-26, 1992

Inspectors:

N. McNamára, Physical Science Technician Effluents Radiation Protection Section (ERPS)

Date

7.21.92

7-21-92 Date

J. Kottan, Laboratory Specialist, ERPS Facilities Radilogical Safety and Safeguards Branch (FRSSB)

Approved By:

R. Bores, Chief, ERPS, FRSSB Division of Radiation Safety and Safeguards

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

<u>Results</u>: The licensee had in place effective programs for measuring radioactivity in process and effluent samples and for measuring chemical parameters in plant systems. No violations or deviations were observed.

#### DETAILS

#### 1.0 Individuals Contacted

#### Principal Licensee Employees

- \*E. Boulette, VP Nuclear Operations/Station Director
- \*W. Clancy, Deputy Plant Manager
- \*D. Ellis, Senior Compliance Engineer
- D. Fountain, Chemistry Supervisor
- C. Goddard, Radwaste/Chemistry Manager
- \*T. McElhinney, Acting Compliance Division Manager
- \*D. Montt, Chemistry Division Manager
- \*A. Muse, Chemistry Supervisor
- \*H. Oheim, Regulation Affairs Department Manager
- L. Savard, Chemistry Supervisor
- \*L. Schmeling, Nuclear Services Department Manager
- \*A. Shatas, Senior QA Engineer
- \*K. Snyder, Chemistry Supervisor

#### NRC Employees

D. Kern, Resident Inspector

\*J. McDonald, Senior Resident Inspector

\* Denotes those present at the exit meeting on June 26, 1992. The inspectors also interviewed other licensee personnel, including members of the chemistry, radiation protection, and quality assurance department staffs.

#### 2.0 Purpose

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

- 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.
- 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's Chemistry Department and the NRC for the purpose of intercomparison. The samples were actual split samples with the exception of the charcoal cartridge, particulate filter, and offgas 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 and process samples or other 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 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 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, 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 June 25-29, 1990 (Inspection Report No. 50-293/90-17) were also compared during this inspection.

The licensee's Radiation Protection Department possessed a gamma spectrometry system which was used to quantify radioactivity on in-plant samples for radiation protection purposes. During this inspection, the charcoal cartridge and particulate filter were also analyzed by the licensee's Radiation Protection Department and compared with NRC results. These types of samples were those normally analyzed by the licensee's Radiation Protection Department.

The results of the comparisons for all of the above samples, which are presented in Table I, indicated that all of the measurements were in agreement under the criteria for comparing results (see Attachment 1 to Table I) with the exception of the Fe-55 and Sr-90 results from the liquid sample split during the previous inspection. The specific reasons for the Fe-55 and Sr-90 disagreements could not be determined during this inspection. However, as stated above, a liquid sample was split for Fe-55 and Sr-90 analyses during

this inspection, and these results will be compared as soon as received in order to resolve this discrepancy. Some possible reasons for the disagreements could be a poor sample split or a matrix effect present in the sample. Additional precautions were taken and techniques employed during this inspection in order to ensure and verify a good split sample. Finally, the licensee's results for both the Fe-55 and the Sr-90 were higher than the NRC results and, hence, biased in a conservative direction, and would not have resulted in the licensee exceeding any radioactive effluat release limits. 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 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 boron analyses at approximately 1000 parts per million (ppm) were performed in duplicate due to the lack of sufficient volume of the NRC standard.

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, fluoride, 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 measurement comparisons indicated that all of the measurements were in agreement or qualified agreement under the criteria used for comparing results (see Attachment 1 to Table II). During the previous inspection in this area, the licensee's boron and nickel results were in disagreement with the NRC values. Subsequent to that inspection, the licensee modified both the boron and nickel analysis procedures and during this inspection, the licensee's results of those analyses were in agreement with the NRC known values. The data are presented in Table II.

#### 4.0 Laboratery QA/QC

The licensee's laboratory QA/QC program was described in procedure SI-CH.0100, Quality Control of Chemistry Laboratory Data, and procedure 7.4.9, Quality Control of Counting Room Instrumentation. These procedures provide for both an intralaboratory QC program and an interlaboratory QC program. The intralaboratory program consisted of the use of instrument and procedure control charts, and the interlaboratory program consisted of the analysis of spiked samples received from outside laboratories for both radioactivity and chemical measurements. Also included in the interlaboratory QC program was the vendor laboratory used for the analyses of radioactive effluent samples which required separation procedures. The inspector reviewed selected data generated by the licensee's laboratory QC program for 1991 and 1992 to date. The inspector noted no discrepancies between program requirements and program implementation.

During the previous inspection in this area, the inspector noted that, while the laboratory QC program was being implemented, the data generated by the laboratory QC program were not being reviewed and assessed. However, during this inspection, the inspector noted that an individual had been hired to oversee the laboratory QA/QC program. In reviewing the above laboratory QC data, the inspector noted the detailed review of this data performed by this individual and the comprehensive documentation of these reviews.

The inspectors also reviewed Audit Report No. 91-34, Yankee Atomic Environmental Laboratory, which assessed the QA program of the vendor laboratory used for effluent radioactivity analyses which require wet chemistry. Additionally, the inspectors reviewed selected surveillances for 1991 and 1992 to date covering various chemistry activities including Technical Specifications, training, chemical control, laboratory QC, hydrogen water chemistry, and post accident sampling system. The licensee had chosen to assess the effectiveness of the site chemistry program through a series of surveillances (28 in 1991) rather than through an annual audit. The licensee had developed an annual schedule for these chemistry surveillance activities. The surveillances were detailed and included comprehensive checklists. The inspector concluded that this approach provided adequate independent oversight and assessment of chemistry activities. No safety concerns or violations were identified in tshis area.

#### 5.0 Exit Meeting

The inspector met with the licensee representatives denoted in Section 1 at the conclusion of the inspection on June 26, 1992. The inspector summarized the purpose, scope, and findings of the inspection.

# TABLE 1

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	CGMPARISON
		Results in Microcuries Per Milliliter		
Reactor Water				
Particulate Filter	Cr-51	(3.6 ± 0.4) E-4	(4.4 ± 0.2) E-4	Agreement
4-28-92	Mn-54	(4.69 ± 0.05) E-5	(4.9 ± 0.2) E-4	Agreement
0800 hrs.	Co-58	(2.44 ± 0.05) E-4	(2.61 ± 0.08) E-4	Agreement
(Detector #3)	Fe-59	(5.47 ± 0.15) E-4	(5.69 ± 0.11) E-4	Agreement
	Co-60	(5.29 ± 0.05) E-4	(5.66 ± 0.11) E-4	Agreement
Reactor Water	I-131	(3.47 ± 0.15) E-4	(3.7 ± 0.2) E-4	Agreement
6-23-92	I-132	(1.054 ± 0.010) E-2	(9.8 ± 0.2) E-3	Agreement
0750 hrs.	I-153	(4.77 ± 0.03) E-3	(5.1 ± 0.2) E-3	Agreement
(Detector #3)	I-134	(3.92 ± 0.14) E-2	(3.78 ± 0.05) E-2	Agreement
	I-135	(1.18 ± 0.02) E-2	(1.218 ± 0.015) E-2	Agreement

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcuries Per Milliliter		
Rad Demineralizer				
Inlet	Na-24	(6.93 ± 0.06) E-5	(7.2 ± 0.2) E-5	Agreement
6-24-92	Co-58	(8.0 ± 0.3) E-6	(6.5 ± 0.3) E J	Agreement
1030 hrs.	Co-60	(2.02 ± 0.03) E-5	(2.04 ± 0.04) E-5	Agreement
(Detector #3)	Sr-91	(1.09 ± 0.02) E-4	(1.1i ± 0.02) E-4	Agreement
	Sr-92	(7.7 ± 0.2) E-5	(8.2 ± 0.2) E-5	Agreement
	I-131	(1.36 ± 0.03) E-5	(1.44 ± 0.04) E-5	Agreemeni
	1-132	(5.44 ± 0.13) E-5	(5.68 ± 0.11) E-5	Agreement
	1 .33	(1.229 ± 0.005) E-4	(1.33 ± 0.03) E-4	Agreement
	I-135	$(1.79 \pm 0.02)$ E-4	(1.77 ± 0.02) E-4	Agreement
	Cs-137	(4.9 ± 0.2) F 6	(5.6 ± 0.3) E-6	Agreement
	Ba-140	(3.07 ± 0.10) E-5	(3.08 ± 0.09) E-5	Agreement
	As-76	(1.37 ± 0.05) E-5	(1.41 ± 0.11) E-5	Agreement

Pilgrim Verification Test Results

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SAMPLE	<b>ISOTOPE</b>	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcurie: Per Milliliter		
Main Stack Gas				
6-23-92	Xe-133	(4.9 ± 0.4) E-7	(5.2 ± 0.3) E-7	Agriement
1002 hrs.	Xe-135	(1.2 ± 0.2) E-7	(1.55 ± 0.09) E-7	Agnæment
(Detector #1)				
			(3.9 ± 0.2) E-3	Agreament
Offgas	Kr-85m	(3.89 ± 0.09) E-3		
6-23-92	Kr-87	$(2.62 \pm 0.04)$ E-2	(2.43 ± 0.09) E-2	Agreement
1345 hrs.	Kr-88	(1.50 ± 0.04) E-2	(1.57 ± 0.08) E-2	Ag. cment
(Detector #2)	Xe-135m	(1.04 ± 0.04) E-1	(1.16 ± 0.05; E-1	Agreement
	Xe-135	(1.94 ± 0.92) E-2	(1.77 ± 0.07) E-2	/.greement
	Xe-138	(5.18 ± 0.13) E-1	(4.812 ± 0.014) E-1	Agreement

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcuries Per Milliliter		
"B" Chemistry				
Waste Tank	Fe-55	(1.7 ± 0.2) E-7	(1.02 ± 0.16) E-6	Disagreement
6-27-90	Gross Alpha	(0.4 ± 1.3) E-9	< 3.2 E-8	No Comparison
1424 hrs.	H-3	(3.14 ± 0.04) E-3	(2.8 ± 0.2) E-3	Agreement
	Sr-89	(3.63 ± 0.14) E-5	(3.7 ± 0.3) E-5	Agreement
	Sr-90	(3.3 ± 0.2) E-7	(1.57 ± 0.11) E-6	Disagreement
		Results in Total Microcuries		
Main Stack	Ba-140	(2.64 ± 0.08) E-3	(2.95 ± 0.09) E-3	Agreement
Particulate Filter				
6-11-92				
1000 hrs.				
(Detector #2)				

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Total Microcuries		
Main Stack				
Charcoal Cartridge	I-131	(1.20 ± 0.02) E-2	(1.16 ± 0.05) E-2	Agreement
6-23-92	1-133	(4.98 ± 0.11) E-2	(4.5 ± 0.2) E-2	Agreement
0925 hrs.				
(Detector #2)				
Main Stack	I-131	(9.8 ± 0.2) E-3	(8.4 ± 0.2) E-3	Agreement
Charcoal Cartridge	I-133	(1.24 ± 0.03) E-2	(9.7 ± 0.4) E-3	Agreement
6-18-92				
1250 hrs.				
Radiation Protection Analysis				
(Detector #2)				

## Pilgrim Verification Test Results

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcuries Per Milliliter		
Reactor Water				
Particulate Filter	Cr-51	(3.6 ± 0.4) E-4	(4.5 ± 0.2) E-4	Agreement
4-28-92	Mn-54	(4.69 ± 0.05) E-4	(4.95 ± 0.03) E-4	Agreement
0800 hrs.	Co-58	(2.44 ± 0.05) E-4	(2.65 ± 0.03) E-4	Agreement
Radiation Protection Analysis	Fe-59	(5.47 ± 0.15) E-4	(5.43 ± 0.08) E-4	Agreement
(Detector #1)	Co-60	(5.29 ± 0.05) E-4	(5.64 ± 0.03) E-4	Agreement

Note: Reported uncertainties are one standard deviation counting uncertainties for both NRC and licensee results.

#### ATTACHMENT 1 TO TABLE 1

#### 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.

Resolution <sup>1</sup>	Ratio for Agreement <sup>2</sup>
< 4	No Comparisor
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

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

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

# TABLE II

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# Pilgrim

# Chemistry Test Results

Chemical <u>Analysis</u>	Method of <u>Analysis</u>	NRC <u>Known Value</u>	Licensee <u>Value</u>	Ratio ( <u>Lic/NRC</u> )	Comparison
		Results in parts pe	r billion (ppb)		
Chloride	IC	$1.90 \pm 0.03$	$1.90 \pm 0.04$	$1.00 \pm 0.02$	Agreenient
		3.60 ± 0.12	$3.92 \pm 0.10$	$1.09~\pm~0.05$	Qual.Agreement
		$7.5 \pm 0.3$	7.5 ± 0.3	$1.00 \pm 0.06$	Agreement
Fluoride	IC	$2.02 \pm 0.10$	$2.22 \pm 0.03$	$1.10 \pm 0.06$	Agreement
		$4.0 \pm 0.3$	$4.6 \pm 0.4$	$1.15~\pm~0.13$	Agreement
		$8.5 \pm 0.5$	9.1 ± 0.3	$1.07 \pm 0.07$	Agreement
Sulfate	IC	$1.94 \pm 0.03$	2.065 ± 0.013	$1.06 \pm 0.02$	Agreement
		$3.88 \pm 0.08$	$4.19 ~\pm~ 0.14$	$1.08 \pm 0.04$	Agreement
		$7.9 \pm 0.2$	8.27 ± 0.15	1.05 ± 0.03	Agreement

# **TABLE II** -Continued

# Pilgrim

# Chemistry Test Results

Comparison		Agreement	Agreement	Agreement	Agreement	Agreement	Agreement	Agreement	Agreement	Agreement
Ratio (Lic/NRC)		$1.02 \pm 0.1$	$1.056 \pm 0.015$	$1.08 \pm 0.05$	$0.86 \pm 0.04$	$0.88 \pm 0.03$	$0.89 \pm 0.03$	$0.954 \pm 0.012$	$0.953 \pm 0.012$	$0.961 \pm 0.009$
Licensee <u>Value</u>	r billion (ppb)	$15.7 \pm 0.6$	$30 \pm 0$	65 ± 3	$4.58 \pm 0.11$	$9.0 \pm 0.2$	13.8 ± 0.4	190.7 ± 1.5	383 ± 3	772.7 ± 1.2
NRC Knov 7 Value	Results in parts per billion (ppb)	15.4 ± 1.6	28.4 ± ~	$60.1 \pm 1.0$	$5.3 \pm 0.2$	$10.2 \pm 0.3$	$15.5 \pm 0.4$	200 ± 2	402 ± 4	804 ± 7
Method of Analysis		SP -			AAGF			ICP		
Chemical Analysis		Silica			Sodium			Chromium		

## TABLE II -Continued

# Pilgrim

# Chemistry Test Results

Chemical <u>Analysis</u>	Method of Analysis	NRC <u>Known Value</u>	Licensee <u>Value</u>	Ratio (Lic/NRC)	Comparison
		Results in parts po	er billion (ppb)		
Copper	ICP	$202 \pm 2$	194 ± 2	$0.960 \pm 0.014$	Agreement
		403 ± 4	396 ± 3	$0.983 \pm 0.012$	Agreement
		810 ± 10	796 ± 6	$0.983 \pm 0.014$	Agreement
Iron	ICP	199 ± 2	152 ± 2	0.965 ± 0.014	Agreement
		398 ± 4	390 ± 6	$0.98~\pm~0.02$	Agreement
		795 ± 7	778 ± 5	0.979 ± 0.011	Agreement
Nickel	ICP	192 ± 2	199 ± 2	$0.965 \pm 0.014$	Agreement
		400 ± 4	392 ± 5	$0.980 \pm 0.016$	Agreement
		800 ± 8	796 ± 3	0.995 ± 0.011	Agreement

## TABLE II -Continued

#### Pilgrim

## Chemistry Test Results

Chemical <u>Analysis</u>	Method of Analysis	NRC <u>Known Value</u>	Licensee <u>Value</u>	Ratio (Lic/NRC)	Comparison
		Results in parts p	er million (ppm)		
Boron	т	304 ± 4	311.3 ± 1.2	$1.024 \pm 0.014$	Agreement
		506 ± 8	5.5.1 ± 0.9	$1.018 \pm 0.016$	Agreament
		$1012 \pm 16$	*1028.6 ± 0.2	1.016 ± 0.016	Agreement

\* Duplicate analysis only

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V-Vis Spectrophotometry Si

AAGF = Graphite Furnace Atomic Absorption ICP = Inductively Coupled Plasma Spectrometry

= Potentiometric Titration T

#### ATTACHMENT 2 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 ( $\pm 2$ Sd) of the ORNL known values are considered to be in agreement. Licensee values outside the plus or minus two standard deviation range ( $\pm 2$ Sd) of the ORNL known values are considered to be within the plus or minus three standard deviation range ( $\pm 3$ Sd) 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 standard deviation values 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
Chloride Fluoride Sulfate Silica Sodium Chromium Copper Iron Nickel Boron	$\pm$ 8% $\pm$ 12% $\pm$ 10% $\pm$ 10% $\pm$ 14% $\pm$ 10% $\pm$ 10% $\pm$ 10% $\pm$ 2%	± 12% ± 18% ± 15% ± 15% ± 21% ± 15% ± 15% ± 15% ± 15% ± 3%