

U.S. NUCLEAR REGULATORY COMMISSION
REGION I

Report No. 50-293/85-23

Docket No. 50-293

License No. DPR-35 Priority -- Category C

Licensee: Boston Edison Company

800 Boylston Street

Boston, Massachusetts 02199

Facility Name: Pilgrim Station

Inspection At: Plymouth, Massachusetts

Inspection Conducted: August 12 - 16, 1985

Inspectors: J. J. Kottan
J. J. Kottan, Radiation Laboratory Specialist

9/17/85
date

M. E. Kramaric
M. E. Kramaric, Radiation Specialist

9/24/85
date

Approved by: W. J. Pasciak
W. J. Pasciak, Chief, BWR Radiological
Protection Section

9/17/85
date

Inspection Summary: Inspection on August 12-16, 1985 (Report No. 50-293/85-23)

Areas Inspected: Routine, unannounced inspection of the licensee's chemical and radiochemical measurements program using the NRC: I Mobile Radiological Measurements Laboratory and laboratory assistance provided by DOE: Brookhaven National Laboratory and Idaho National Engineering Laboratory, Radiological and Environmental Sciences Laboratory. Areas reviewed included: analytical procedures evaluation using standards, split samples for chemical analyses, performance on radiological analyses of split actual effluent and inplant samples, and program for the quality control of analytical measurements. The inspection involved 109 inspector hours on site by three NRC regionally based inspectors.

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

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DETAILS

1. Individuals Contacted

*J. Crowder,	Senior Compliance Engineer
R. Smith,	Chief Chemical Engineer
A. Shatus,	Senior Chemical Engineer
C. Grevenitz,	Chemical Engineer
*S. Stinson,	Chemical Engineer
*C. Mathis,	Plant Manager
D. Fountain,	CC and RP Technician
C. Goddard,	CC and RP Technician

The inspector also interviewed other licensee employees, including members of the chemistry and health physics staffs.

*Denotes those present at the exit interview.

2. Analytical Procedures Evaluation

During the inspections standard chemical solutions were submitted to the licensee for analysis. The standard solutions were prepared by the Brookhaven National Laboratory (BNL) for the NRC region I, and the standards were analyzed by the licensee using normal 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 Specification requirements 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 results of the standard measurements comparison indicated that, with the exception of two measurements, all of the results were in agreement under the criteria used for comparing results. (See Attachment I.) The two disagreements, both metal analyses, are not considered significant. Both values, although in disagreement, were within ten percent of the NRC values. The results of the comparisons are listed in Table I. The licensee performed all analyses in triplicate. The chloride and fluoride analyses were performed using ion chromatography, the metal analyses by plasma emission spectroscopy, and the boron analyses by the mannitol titration method.

No violations were identified in this area.

3. Chemistry Confirmatory Measurements

During the inspection actual inplant water samples were split between the licensee and the NRC in order to verify the licensee's measurement capabilities on actual plant water samples. The analyses will be performed by the licensee using normal methods and equipment and for the NRC Region I by BNL. The analyses to be performed are chloride and fluoride on a

reactor water sample; and iron, copper, nickel, and chromium on a feed-water filter sample. On completion of the analyses by both laboratories, the results will be compared, and the intercomparison will be documented in a subsequent inspection report.

4. Radiochemistry Confirmatory Measurements

During the inspection, liquid, particulate filter, charcoal cartridge, and gas samples were split between the licensee and NRC for the purpose of intercomparison. The split samples are actual effluent and inplant samples normally analyzed by the licensee. The samples were analyzed by the licensee using normal 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 samples with respect to Technical Specification requirements 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, Fe-55 and tritium. The results 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 an effluent sample split between the licensee and NRC:I during a previous inspection on May 9-13, 1983 (Inspection Report No. 50-293/83-13) were also compared during this inspection.

The results of the sample measurements comparison indicated that all of the measurements, with two exceptions, were in agreement under the criteria used for comparing results. (See Attachment II.) The results of the comparisons are listed in Table II. At the beginning of this inspection the licensee's chemistry gamma spectroscopy system was inoperative. The licensee counted samples on the health physics gamma spectroscopy system (the backup system) until the chemistry system was repaired. The sample counting system used for each sample is noted in Table II. The As-76 disagreement on a particulate filter sample resulted from an incorrect half life value being used by the licensee. The result was in agreement when calculated with the correct half life. The licensee corrected the isotope library prior to the conclusion of the inspection. The disagreement on a tritium measurement intercomparison will be resolved when the sample requiring wet chemistry which was split during this inspection is compared for the tritium results. This intercomparison will be performed as soon as both sample results are available.

No violations were identified in this area.

5. Laboratory QC Program

The inspector reviewed the licensee's program for the quality control of analytical measurements. The licensee maintains both an intralaboratory

and an interlaboratory QC program for chemical and radiochemical analyses. The intralaboratory program consists of daily or periodic source and background checks, and where applicable, gain and resolution checks in the radiochemistry area; and daily or periodic standard analysis in the chemistry area. All results are plotted on control charts. The interlaboratory program consists of periodic spike sample analyses in both the radiochemistry and chemistry areas. The data from this program is also plotted and includes graphs for the mean and range as well as technician performance. The inspector reviewed the QC data for the period January, 1985 to date.

No violations were identified in this area.

6. Exit Interview

The inspector met with the licensee representatives denoted on Paragraph 1 at the conclusion of the inspection on August 16, 1985. The inspector summarized the purpose and scope of the inspection and the inspection findings.

TABLE 1

CAPABILITY TEST RESULTS

PILGRIM STATION

CHEMICAL PARAMETER	NRC VALUE Results in parts per billion (ppb)	LICENSEE VALUE	RATIO	COMPARISON
Chloride	10.3 ± 0.7 70 ± 3 28 ± 3	9.7 ± 0.3 70 ± 1 30.7 ± 0.6	0.94 ± 0.07 1.00 ± 0.05 1.10 ± 0.11	Agreement Agreement Agreement
Fluoride	9.6 ± 0.4 75 ± 4 33 ± 2	9.9 ± 1.2 70.7 ± 1.2 30.7 ± 1.2	1.03 ± 0.13 0.94 ± 0.05 0.93 ± 0.07	Agreement Agreement Agreement
Boron	1014 ± 15 3050 ± 30 5040 ± 130	1060 ± 56 3030 ± 27 4915 ± 25	1.05 ± 0.05 .993 ± 0.013 .98 ± 0.03	Agreement Agreement Agreement
Copper	1.536 ± 0.016 1.040 ± 0.016 0.532 ± 0.004	1.548 ± 0.010 1.012 ± 0.004 0.498 ± 0.003	1.008 ± 0.012 0.973 ± 0.015 0.936 ± 0.009	Agreement Agreement Disagreement
Iron	1.37 ± 0.08 0.96 ± 0.04 0.51 ± 0.04	1.413 ± 0.014 0.982 ± 0.005 0.511 ± 0.005	1.03 ± 0.06 1.02 ± 0.04 1.00 ± 0.08	Agreement Agreement Agreement
Chromium	1.50 ± 0.11 1.08 ± 0.02 0.48 ± 0.04	1.442 ± 0.006 0.968 ± 0.002 0.489 ± 0.003	0.96 ± 0.07 0.90 ± 0.02 1.02 ± 0.09	Agreement Disagreement Agreement
Nickel	1.52 ± 0.03 1.03 ± 0.05 0.53 ± 0.06	1.519 ± 0.006 1.009 ± 0.006 0.494 ± 0.005	1.00 ± 0.02 0.98 ± 0.05 0.93 ± 0.11	Agreement Agreement Agreement

NOTE: All licensee analyses were run in triplicate. The F, Cl, and boron analyses were separate analyses and/or dilutions. The uncertainty associated with these analyses is an estimate of the total uncertainty of the measurement process. The metal analyses were repeat analyses of one dilution, and the uncertainty is an estimate of the instrument precision.

TABLE 2
VERIFICATION TEST RESULTS
PILGRIM STATION

SAMPLE	ISOTOPE	NRC VALUE Results in microcurie per milliliter	LICENSE VALUE	COMPARISON
*Drywell Particulate Filter C-19 August 10, 1985	Cr-51	(2.85 ± 0.03) E-10	(2.81 ± 0.02) E-10	Agreement
	Mn-54	(8 ± 2) E-13	(1.2 ± 0.2) E-12	Agreement
	Co-60	(8.5 ± 0.5) E-12	(1.04 ± 0.03) E-11	Agreement
	As-76	(8.5 ± 0.4) E-11	* (8.2 ± 0.3) E-12	*Disagreement
	Mo-99	(1.29 ± 0.07) E-10	(1.31 ± 0.04) E-10	Agreement
	Np-239	(4.7 ± 0.3) E-11	(5.51 ± 0.10) E-11	Agreement
	I-131	(6.1 ± 0.2) E-12	(5.9 ± 0.2) E-12	Agreement
	Te-132	(4.5 ± 0.4) E-12	(4.4 ± 0.2) E-12	Agreement
	I-133	(2.30 ± 0.05) E-10	(2.35 ± 0.04) E-10	Agreement
	Cs-137	(9 ± 2) E-13	(1.74 ± 0.14) E-12	Agreement
	Ba-140	(2.3 ± 0.2) E-11	(1.9 ± 0.8) E-11	Agreement
	Na-24	(2.50 ± 0.04) E-9	(2.67 ± 0.04) E-9	Agreement
	Co-58	(8.1 ± 0.3) E-12	(8.4 ± 0.2) E-12	Agreement
*Drywell Charcoal Cartridge C-19 August 10, 1985	I-131	(1.000 ± 0.014) E-10	(9.72 ± 0.06) E-11	Agreement
	I-133	(1.33 ± 0.02) E-9	(1.33 ± 0.01) E-9	Agreement
*corrected result is (8.8 ± 0.3) E-11. This result is in agreement. See Paragraph 4.				
Misc. Tank 1020 hours August 14, 1985	Cr-51	(2.5 ± 0.4) E-6	(3.4 ± 0.8) E-6	Agreement
	Mn-54	(2.7 ± 0.8) E-6	(4 ± 2) E-7	Agreement
	Co-60	(6.6 ± 0.2) E-6	(8.3 ± 0.4) E-6	Agreement
	Cs-137	(5.96 ± 0.11) E-6	(6.6 ± 0.3) E-6	Agreement
	As-76	(1.14 ± 0.14) E-6	(1.2 ± 0.3) E-6	Agreement
	Cs-134	(2.9 ± 0.8) E-7	(2.5 ± 1.2) E-7	Agreement
Main Stack Gas 1325 hours August 15, 1985 1st count	Kr-85m	(6.5 ± 0.3) E-7	(6.93 ± 7.91%) E-7	Agreement
	Kr-88	(3.7 ± 0.8) E-7	(4.71 ± 26%) E-7	Agreement
	Xe-133	(3.84 ± 0.08) E-6	(3.89 ± 4.65%) E-6	Agreement
	Xe-135	(8 ± 2) E-8	not identified	No Comparison
Main Stack Gas 1325 hours August 15, 1985 2nd count	Kr-85m	(6.5 ± 0.3) E-7	(6.67 ± 9.69%) E-7	Agreement
	Xe-133	(3.84 ± 0.08) E-6	(3.61 ± 4.19%) E-6	Agreement
	Xe-135	(8 ± 2) E-8	(1.24 ± 29.8%) E-7	Agreement

NOTE: Samples identified with an asterisk were counted on the Health Physics counting system.

TABLE 2 (con't)

VERIFICATION TEST RESULTS

PILGRIM STATION

<u>SAMPLE</u>	<u>ISOTOPE</u>	<u>NRC VALUE</u>	<u>LICENSEE VALUE</u>	<u>COMPARISON</u>
<u>Results in microcurie per milliliter</u>				
Reactor Water	I-132	(4.58 ± 0.06) E-3	(4.66 ± 1.54%) E-3	Agreement
1333 hours	I-134	(1.40 ± 0.03) E-2	(1.38 ± 4.64%) E-2	Agreement
August 14, 1985	I-135	(4.65 ± 0.15) E-3	(4.44 ± 2.22%) E-3	Agreement
1st count				
Reactor Water	I-131	(1.5 ± 0.2) E-4	(1.06 ± 4.56%) E-4	Agreement
1333 hours	I-133	(1.76 ± 0.03) E-3	(1.68 ± 1.03%) E-3	Agreement
August 14, 1985				
2nd count				
*Main Stack	I-131	(6.0 ± 0.3) E-3	(5.62 ± 0.12) E-3	Agreement
Charcoal Cartridge	I-133	(1.11 ± 0.05) E-1	(1.13 ± 0.02) E-1	Agreement
August 9, 1985				
*Main Stack	Ba-140	(1.1 ± 0.5) E-3	(8.5 ± 1.0) E-4	Agreement
Particulate Filter				
August 9, 1985				
Off Gas				
0918 hours	Kr-87	(5.55 ± 0.07) E-1	(5.46 ± 1.8%) E-1	Agreement
August 15, 1985	Kr-88	(4.85 ± 0.05) E-1	(4.30 ± 2.2%) E-1	Agreement
1st count	Kr-85m	(1.75 ± 0.02) E-1	(1.46 ± 2.0%) E-1	Agreement
	Xe-135	(8.08 ± 0.03) E-1	(7.01 ± 0.5%) E-1	Agreement
	Xe-133	(1.86 ± 0.02) E-1	(1.89 ± 2.9%) E-1	Agreement
	Xe-135m	(2.3 ± 0.3) E-0	(2.02 ± 7.6%) E-0	Agreement
Off Gas				
0918 hours	Kr-87	(5.55 ± 0.07) E-1	(5.12 ± 11.87%) E-1	Agreement
August 15, 1985	Kr-88	(4.85 ± 0.05) E-1	(4.52 ± 3.97%) E-1	Agreement
2nd count	Kr-85m	(1.75 ± 0.02) E-1	(1.61 ± 2.37%) E-1	Agreement
	Xe-135	(8.08 ± 0.03) E-1	(7.072 ± 0.53%) E-1	Agreement
	Xe-133	(1.86 ± 0.02) E-1	(1.946 ± 1.87%) E-1	Agreement
<u>Results in total microcuries</u>				
*Reactor Building Vent				
Charcoal Cartridge	I-131	(3.8 ± 0.3) E-3	(3.87 ± 0.09) E-3	Agreement
August 9, 1985	I-133	(1.01 ± 0.05) E-1	(1.04 ± 0.02) E-1	Agreement
Reactor Building Vent				
Particulate Filter	Ba-140	(8 ± 4) E-4	(7.9 ± 1.4) E-4	Agreement

TABLE 2 (con't)

VERIFICATION TEST RESULTS

PILGRIM STATION

SAMPLE	ISOTOPE	NRC VALUE Results in microcurie per milliliter	LICENSEE VALUE	COMPARISON
Misc. Tank 1400 hours May 10, 1983	gross alpha	(6.4 ± 0.8) E-8	not analyzed	No Comparison
	gross beta	(1.69 ± 0.06) E-4	(1.4 ± 0.1) E-4	Agreement
	H-3	(1.73 ± 0.06) E-5	(1.20 ± 0.24) E-5	Disagreement
	Sr-89	(2.5 ± 1.2) E-7	<2E-7	Agreement
	Fe-55	(4 ± 4) E-8	(8.7 ± 0.4) E-5	No Comparison

ATTACHMENT I

Criteria For Comparing Analytical Measurements

This attachment provides criteria for comparing results of capability tests. In these criteria the judgement limits are based on the uncertainty of the ratio of the licensee's value to the NRC value. The following steps are performed: (1) the ratio of the licensee's value to the NRC value is computed

$$\text{ratio} = \frac{\text{Licensee Value}}{\text{NRC value}} ;$$

(2) the uncertainty of the ratio is propagated.¹

If the absolute value of one minus the ratio is less than or equal to twice the ratio uncertainty, the results are in agreement. ($|1 - \text{ratio}| \leq 2 \text{ uncertainty}$)

$$Z = \frac{x}{y}, \text{ then } \frac{S_z^2}{Z^2} = \frac{S_x^2}{x^2} + \frac{S_y^2}{y^2}$$

(From: Bevington, P. R., Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1969)

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 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.

$$\text{RESOLUTION} = \frac{\text{NRC REFERENCE VALUE}}{\text{REFERENCE VALUE UNCERTAINTY}}$$

$$\text{RATIO} = \frac{\text{LICENSEE VALUE}}{\text{NRC REFERENCE VALUE}}$$

Resolution

<3
4 - 7
8 - 15
16 - 50
51 - 200
>200

Agreement

0.4 - 2.5
0.5 - 2.0
0.6 - 1.66
0.75 - 1.33
0.80 - 1.25
0.85 - 1.18