U. S. NUCLEAR REGULATORY COMMISSION
REGION 1

Report No. 50-423/87-32

Docket No. 50-423

License No. NPF-49 Priority -- Category C

Licensee: Northeast Nuclear Energy Company
P. O. Box 270
Hartford, Connecticut 06101

Facility Name: Millstone Nuclear Power Plant, Unit 3

Inspection At: Waterford, Connecticut

Inspection Conducted: December 14-18, 1987

Inspectors: Harvey Zibulsky 1-29-88
H. Zibulsky, Chemist date

Jason Jang 1-29-88
J. Jang, Sr. Radiation Specialist date

Approved by: W J Pasciak 2/2/88
W. J. Pasciak, Chief, Effluents date
Radiation Section, DRSS

Inspection Summary: Inspection on December 14-18, 1987 (Report No. 50-423/87-32).

Areas Inspected: Routine, announced inspection of the nonradiological chemistry program. Areas reviewed included measurement control and analytical procedure evaluations.

Results: No violations were identified.

Details

1. Individuals Contacted

*C. Clement, Unit 3 Superintendent
*J. Waters, Chemistry Supervisor
*T. Burns, Assistant Chemistry Supervisor, Unit 3
*F. Mueller, Unit 3 Chemist
*S. Macklin, Unit 3 Chemistry Specialist
H. Haynes, Station Services Superintendent
G. D'Auria, Chemist
D. Peiffer, Unit 3 Chemistry Specialist

*Present at the exit interview.

The inspectors also interviewed other licensee employees including members of the chemistry staff.

2. Measurement Control Evaluation

Verification of the licensee's measurement capabilities on actual plant water samples is done by splitting samples with the licensee and the Brookhaven National Laboratory (BNL). The reactor water standby tank sample was taken for boron analysis and feedwater samples were taken for hydrazine, ammonia, iron, copper, fluoride, chloride and sulfate. A feedwater sample was spiked with a standard solution of iron and copper and another feedwater sample was spiked with a standard solution of fluoride, chloride and sulfate. The standard spiked solutions were prepared by BNL for the NRC. On completion of the analyses by BNL and the licensee, an evaluation will be made (Inspector Follow-up Item 50-423/87-32-01).

Two independent standard stock solutions for calibration and measurement control were being used. The licensee was able to identify degenerated standard solutions and verify the quality of the standards.

Single point calibrations were currently being performed on the ion chromatograph and the atomic absorption measurement systems. The licensee understood the need for multi-point calibrations and was in the process of revising their procedures to include five calibration data points. The calibrations will be done twice monthly and a control check will continue to be performed each day the measurement systems are used. The calibration curves will be statistically fit using a newly developed least squares program the licensee has written for calibration curves.

The inspectors reviewed the licensee's inter- and intra-laboratory standards program as described in Procedure CP 3800, "Chemistry Quality Assurance Program." The programs are being maintained and the results are documented.

3. Analytical Procedure Evaluations

During the inspection, standard chemical solutions were submitted to the licensee for analysis. The standard solutions were prepared by BNL for the NRC, and the standards were analyzed by the licensee using normal methods and equipment. The concentrations of the standards were adjusted to cover the calibration ranges of the analytical systems used. The analysis of standards was used to verify the licensee's capability to monitor chemical parameters in various plant systems with respect to Technical Specification, vendor, and fuel warranty requirements. In addition, the analysis of standards was used to evaluate the licensee's analytical procedures with respect to accuracy and precision.

The results of the standard measurements comparison indictated that two out of thirty comparisons were in disagreement under the criteria used for comparing results (see Attachment 1). The results of the comparisons are listed in Table 1.

The fluoride and chloride disagreements were due to the single point calibrations made on the ion chromatograph. Because of the low concentrations, these disagreements are not considered significant.

When the licensee's calibration program is fully implemented, the licensee's measurement program should be significantly improved to analyze the anions and other analytes to low concentrations with good accuracy and precision.

4. Exit Interview

The inspectors met with the licensee representatives (denoted in paragraph 1) at the conclusion of the inspection on December 18, 1987, and summarized the scope and findings of the inspection. At no time during this inspection was written material provided to the licensee by the inspector.

Table 1. Capability Test Results

Millstone Nuclear Power Plant, Unit 3

Chemical Parameter	Analytical Procedure	NRC Value	Lic. Value	Ratio Value	Comparison
		Results in parts per million (ppm)			
Boron	Titration	100 ±10	006±11	1.00	Agreement
		302 ±46	012±34	1.00	Agreement
		494 ±6	5044±23	1.02±0.01	Agreement
		Results in parts per billion (ppb)			
Chloride	Ion Chromatography	2.4±0.3	2.0±0.1	0.83±0.11	Agreement
		3.7±0.1	4.4±0.2	1.19±0.06	Disagreement
		8.1±0.2	8.4±0.3	1.04±0.05	Agreement
Fluoride	Ion Chromatography	2.3±0.1	1.9±0.1	0.83±0.06	Disagreement
		4.4±0.2	4.2±0.1	0.95±0.05	Agreement
		8.4±0.3	8.7±1.0	1.04±0.13	Agreement
Sulfate	Ion Chromatograpny	2.0±0.1	2.1±0.1	1.05±0.07	Agreement
		4.1±0.2	4.5±0.3	1.10±0.09	Agreement
		8.1±0.3	8.2±0.3	1.01±0.05	Agreement
Ammonia	Spec. Ion Electrode	87.6±5.3	90.5±1.4	1.03±0.06	Agreement
		314.0±26.0	302.2±6.7	0.96±0.08	Agreement
		234.5±21.3	247.0±8.9	1.05±0.10	Agreement
Hydrazine	Spectrophotometry	22.3±1.4	21.0±1.7	0.94±0.10	Agreement
		56.9±0.7	57.3±2.9	1.01±0.05	Agreement
		104.0±1.0	101.3±2.1	0.97±0.02	Agreement
Silica	Spectrophotometry	27.2±2.8	28.3±1.5	1.04±0.12	Agreement
		54.5±3.5	52.3±1.5	0.96±0.07	Agreement
		80.0±2.5	80.3±1.5	1.00	Agreement
Sodium	Graphite furnace	4.6±0.5	4.8±0.2	1.04±0.12	Agreement
		9.2±0.8	9.4±0.8	1.02±0.12	Agreement
		14.4±0.8	14.2±0.4	0.99±0.06	Agreement

Copper	Graphite furnace	4.7±0.2	4.8±0.3	1.02±0.08	Agreement
		9.7±0.5	9.8±0.4	1.01±0.07	Agreement
		14.5±0.6	14.3±0.5	0.99±0.05	Agreement
Iron	Graphite furnace	4.9±0.4	4.4±0.3	0.90±0.10	Agreement
		9.6±0.3	8.9±0.5	0.93±0.06	Agreement
		14.7±0.3	13.9±0.2	0.95±0.03	Agreement

ATTACHMENT 1

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

$$\left(\text{ratio} = \frac{\text{Licensee Value}}{\text{NRC Value}}\right);$$

(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-ratio| ≤ 2 uncertainty)

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

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