U.S. NUCLEAR REGULATORY COMMISSION
REGION I

Report No.: 50-289/93-17

Docket No.: 50-289

License No.: DPR-50

Licensee: GPU Nuclear Corporation
P.O. Box 480
Middletown, Pennsylvania 17057

Facility Name: Three Mile Island Nuclear Station, Unit 1

Inspection At: Middletown, Pennsylvania

Inspection Conducted: August 2-6, 1993

Inspectors: N. T. McNamara — 8/17/93
N. McNamara, Laboratory Specialist — Date
Effluents Radiation Protection Section (ERPS)

for N. T. McNamara — 8/17/93
J. Kottan, Laboratory Specialist, ERPS — Date
Facilities Radiological Safety and Safeguards Branch (FRSSB)

Approved By: Robert J. Bores — 8/17/93
R. Bores, Chief, ERPS, FRSSB — Date
Division of Radiation Safety and Safeguards

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

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 NRC requirements were observed.

DETAILS

1.0 Individuals Contacted

Principal Licensee Employees

* G. Chevalier, Chemist
* E. Fuhrer, Manager, Plant Chemistry
* L. Lucas, Chemist
* A. Miller, Licensing Engineer
* B. Parfitt, Rad Engineer

U.S. Nuclear Regulatory Commission Employees

* R. Bores, Chief, Effluents Radiation Protection Section
  M. Evans, Senior Resident Inspector

* Denotes those present at the exit meeting on August 6, 1993.

The inspectors also interviewed other licensee personnel, including the chemistry and radiation protection 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 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 and charcoal cartridge. 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 were actual effluent samples or in-plant samples which duplicated the actual 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 analyses requiring wet chemistry. The analyses to be performed on the sample are Sr-89, Sr-90, H-3, Fe-55 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 September 24-28, 1990 (Inspection Report No. 50-289/90-17) were also compared during this inspection.

The licensee's radiation protection department performed gamma spectrometry analyses of in-plant samples for radiation protection purposes. During this inspection, the charcoal cartridge and reactor coolant particulate filter were also analyzed by the licensee's radiation protection department and compared with the NRC results. These types of samples were those normally analyzed by this department.

The comparisons for all of the above samples results that were available indicated that all of the measurements were in agreement under the criteria for comparing results (see Attachment 1 to Table I) with two exceptions. The exceptions were the Fe-55 and Sr-90 results from the sample which was split during the previous inspection. The specific reasons for the disagreement could not be determined during this inspection. However, the licensee has subsequently switched vendor laboratories for these analyses. 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. The data are presented in Table I.

During the previous inspection in this area the inspector discussed with the licensee the quantification and reporting of I-135 on effluent charcoal cartridge samples. At that time the licensee did not report I-135 results, even though I-135 was present on charcoal cartridge samples, because the samples had undergone more than ten half-lives of decay. (The charcoal cartridge sample results were decayed to the mid-point of a seven-day sampling period.) The licensee reviewed this item after the previous inspection and concluded that the practice of not reporting I-135 would be continued because it is insignificant with respect to I-131 in terms of offsite dose consequences. Also, the licensee's Technical Specifications do not specifically require that I-135 be quantified and reported.

The inspector stated that this item would be forwarded to the Office of Nuclear Reactor Regulation (NRR) for review and resolution.

Also, during this inspection, the initial results of the intercomparison from the Waste Gas Decay Tank samples were in disagreement. After resampling and reanalysis the results were in agreement. The inspector discussed this matter with the licensee and stated that the differences between the two sample results appeared to be due to sampling techniques. The licensee stated that this area would be reviewed and appropriate action taken to ensure that representative samples of the Waste Gas Decay Tanks could be taken and analyzed.

Subsequent to the exit interview (see Section 5.0), but prior to the inspectors leaving the site, a waste gas decay tank sample was again split between the licensee and the NRC. In this case, however, the licensee took four sequential samples in order to check the sampling technique. The analysis results of all four of the licensee's samples were in close agreement with each other, and they were also in agreement with the NRC results. The inspector stated that the licensee's complete actions in this area would be reviewed during a subsequent inspection in this area.

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

3.2 Standard Analyses - Chemical

During this part of the inspection, standard chemical solutions were submitted to the licensee for analyses. The standards were prepared by the 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.

Standards were also analyzed using the licensee's in-line ion chromatography (IC) systems. These samples were analyzed only in duplicate and the anion analyses were performed at two concentrations and the ammonia analyses performed at one concentration. Additionally, low level boron standards (one ppm or less) were submitted to the licensee for analysis. Low level boron analyses were used by the licensee to assess the performance of the Accident Generated Water (AGW) evaporator which is used to process water from TMI-Unit 2. The low level boron analyses were performed in triplicate at two concentrations.

Also, a sample was spiked with a standard anion solution and sent to ORNL for analyses. The analyses to be performed on the sample are fluoride, chloride, and sulfate. The licensee will perform the same analyses on an aliquot of the 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 standard measurements 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). The hydrazine data presented in Table II were determined from a hand plot of the calibration data rather than using the internal UV-Vis spectrophotometer calibration curve. The licensee determined that the UV-Vis spectrophotometer software fits the calibration data such that the calibration curve will pass through the origin of the graph regardless of the intercept obtained from the actual calibration data. Since the hydrazine calibration curve did not pass exactly through the intercept, the hydrazine results were initially in disagreement with the NRC results. The licensee stated that this area would be reviewed and appropriate corrective action taken to ensure that accurate spectrophotometer calibration curves were used for sample analyses. The inspector stated that this area would be reviewed during a subsequent inspection. It should be noted that at the present time the NRC has no criteria for comparing analytical results from in-line instrumentation. However, in this case, the in-line instrumentation met the criteria used for laboratory instrumentation. In addition, the NRC has no criteria for comparing results from low level boron analyses either. The licensee's low level boron results were biased lower than the NRC values and indicated a need to determine the reason for the low bias. The licensee stated that the low bias may be due to the environmental conditions (the high humidity) in the chemistry laboratory. The licensee further stated that this area would be reviewed and appropriate action taken. The inspector stated that this area would be reviewed during a subsequent inspection in this area. The data are presented in Table II.

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 two procedures. Procedure N1828, Quality Assurance Program for Radiological Effluent Monitoring, which addressed radiochemistry activities, and Procedure N1826, Control of Analytical Performance, which addressed analytical chemistry activities. Both of these procedures provided for both an intralaboratory QC program and an interlaboratory QC program. The intralaboratory program consisted of instrument and procedure control charts for assessing and trending performance and the analysis of duplicate samples. The

interlaboratory program consisted of the analysis of unknown samples received from outside laboratories.

The inspector reviewed selected data generated by the licensee's laboratory QA/QC program for 1991, 1992, and 1993 to date and, based on this review, noted that the licensee was implementing the laboratory QA/QC program as required. The licensee performed thorough reviews of the laboratory QC data, documented these reviews, and utilized the QC data in a proactive manner to improve analytical methods and procedures.

Additionally, the inspector reviewed Audit Report S-TMI-92-13, TMI Chemistry, dated February 2, 1993. The audit team included a technical specialist, and the technical depth of the audit was sufficient to identify any programmatic breakdowns. Based on the review of the above audit, the inspector determined there was independent oversight and assessment of chemistry activities.

No safety concerns or violations were identified in this area.

5.0 Exit Meeting

The inspectors met with the licensee representatives denoted in Section 1.0 at the conclusion of the inspection on August 6, 1993. The inspectors summarized the purpose, scope, and findings. The licensee representatives acknowledged the inspection findings.

TABLE I

Three Mile Island Radiochemistry Test Results

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcuries per Milliliter		
RMA-5 Charcoal	I-131	(2.288±0.005)E-8	(1.98±0.06)E-8	Agreement
Cartridge	I-133	(4.77±0.03)E-8	(4.02±0.14)E-8	Agreement
2053 hrs	I-135	(7.1±0.5)E-6	Not Reported	-----
07/31/93				
(Detector No. 1)				
		Results in Total Microcuries		
Reactor Coolant	Cr-51	(2.6±0.2)E-1	(2.52±0.15)E-1	Agreement
Particulate Filter	Co-58	2.095±0.009	2.11±0.06	Agreement
0735 hrs	I-131	(1.58±0.03)E-1	(1.59±0.05)E-1	Agreement
08/02/93	I-133	(2.14±0.08)E-1	(2.19±0.14)E-1	Agreement
(Detector No. 4)				
Reactor Coolant	Cr-51	(2.6±0.2)E-1	(2.67±0.13)E-1	Agreement
Particulate Filter	Co-58	2.095±0.009	2.16±0.06	Agreement
0735 hrs	I-131	(1.58±0.03)E-1	(1.68±0.07)E-1	Agreement
08/02/93	I-133	(2.14±0.08)E-1	(2.16±0.10)E-1	Agreement
(Detector No. 5)				

TABLE I - continued

Three Mile Island Radiochemistry Test Results

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcuries per Milliliter		
RMA-5	Kr-85m	(5.16±0.02)E-5	(5.0±0.2)E-5	Agreement
Condenser Offgas	Kr-87	(4.53±0.04)E-5	(4.42±0.15)E-5	Agreement
1028 hrs	Kr-88	(1.009±0.007)E-4	(1.00±0.04)E-4	Agreement
08/05/93	Xe-133m	(3.12±0.13)E-5	(2.9±0.2)E-5	Agreement
(Detector No. 4)	Xe-133	(1.4200±0.0013)E-3	(1.49±0.06)E-3	Agreement
	Xe-135m	(3.13±0.06)E-5	(2.56±0.11)E-5	Agreement
	Xe-135	(3.538±0.006)E-4	(3.39±0.16)E-4	Agreement
	Xe-138	(2.49±0.12)E-5	(2.2±0.2)E-5	Agreement
Reactor Coolant	I-131	(4.55±0.03)E-2	(4.7±0.2)E-2	Agreement
0730 hrs	I-132	(5.12±0.06)E-2	(5.9±0.3)E-2	Agreement
08/03/93	I-133	(6.21±0.03)E-2	(6.4±0.3)E-2	Agreement
(Detector No. 1)	I-134	(9.1±0.7)E-2	(8.9±0.4)E-2	Agreement
	I-135	(7.31±0.13)E-2	(7.0±0.4)E-2	Agreement
RCBT "C" Water	Co-60	(6.0±0.5)E-7	(6.8±1.2)E-7	Agreement
0830 hrs	Cs-134	(2.09±0.06)E-6	(2.2±0.2)E-6	Agreement
08/04/93	Cs-137	(5.71±0.09)E-6	(6.5±0.4)E-6	Agreement
(Detector No. 1)				

TABLE I - continued

Three Mile Island Radiochemistry Test Results

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Microcuries per Milliliter		
RCBT "C" Water	Fe-55	(1.21±0.01)E-4	(1.84±?)E-4	Disagreement
0745 hrs	H-3	(1.08±0.01)E-1	(9.31±?)E-2	Agreement
09/28/90	Sr-89	(1.1±1.1)E-7	(7.24±?)E-7	No Comparison
	Sr-90	(2.72±0.12)E-6	(1.26±?)E-6	Disagreement
	gross alpha	(1.1±1.8)E-8	<2.3E-7	No Comparison
Waste Gas Decay	Xe-133m	(4.00±0.12)E-3	(3.8±0.3)E-3	Agreement
Tank "B"	Xe-133	(3.591±0.004)E-1	(3.8±0.2)E-1	Agreement
1558 hrs	Xe-135	(2.16±0.03)E-3	(2.07±0.10)E-3	Agreement
08/05/93				
(Detector No. 4)				
RMA-5 Charcoal	I-131	(1.692±0.003)E-8	(1.57±0.05)E-8	Agreement
Cartridge	I-133	(2.91±0.02)E-9	(2.57±0.07)E-9	Agreement
0957 hrs	I-135	(1.07±0.05)E-9	(9.1±0.6)E-10	Agreement
08/04/93				
(Detector No. 2)				
(Health Physics				
Analysis)				

TABLE I - continued

Three Mile Island Radiochemistry Test Results

SAMPLE	ISOTOPE	NRC VALUE	LICENSEE VALUE	COMPARISON
		Results in Total Microcuries		
Reactor Coolant	Cr-51	(2.6±0.2)E-1	(2.41±0.11)E-1	Agreement
Particulate Filter	Co-58	2.095±0.009	2.10±0.06	Agreement
0735 hrs	I-131	(1.58±0.03)E-1	(1.60±0.05)E-1	Agreement
08/02/93	I-133	(2.14±0.08)E-1	(2.24±0.09)E-1	Agreement
(Detector No. 2) (Health Physics Analysis)				
		Results in Microcuries per Milliliter		
RCBT "C" Water	Co-60	(6.0±0.5)E-7	(4.8±1.1)E-7	Agreement
0830 hrs	Cs-134	(2.09±0.06)E-6	(2.2±0.2)E-6	Agreement
08/04/93	Cs-137	(5.71±0.09)E-6	(5.8±0.8)E-6	Agreement
(Detector No. 6)				

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

ATTACHMENT 1 TO TABLE I

CRITERIA FOR COMPARING RADIOCHEMICAL 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 the 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[1]	Ratio for Comparison[2]
<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

1.Resolution = NRC Value/one sigma counting uncertainty

2.Ratio = Licensee Value/NRC Value

TABLE II

Three Mile Island Analytical Chemistry Test Results

Chemical Analysis	Method of Analysis	NRC Known Value	Licensee Value	Comparison
		Results in parts per billion (ppb)		
Fluoride	ISE	40±2	45±3	Agreement
		84±4	85.7±0.6	Agreement
		202±8	205.3±1.2	Agreement
Chloride	IC	19.4±0.5	20.35±0.10	Agreement
		36.5±1.1	38.10±0.10	Agreement
		77±3	76.2±0.2	Agreement
Sulfate	IC	19.4±0.3	18±0	Agreement
		38.8±0.6	35±0	Agreement
		79±2	76±0	Agreement
Sodium	AAGF	1.02±0.03	0.93±0.06	Agreement
		3.10±0.08	2.6±0	Qual Agreement
		5.3±0.2	5.63±0.06	Agreement
Silica	SP	42.6±0.6	43.6±0.2	Agreement
		60.1±1.0	62.6±0.4	Agreement
		85.2±1.1	85.7±0.4	Agreement
Hydrazine	SP	56.5±1.0	57.15±0.15	Agreement
		68.2±0.6	69.85±0.10	Agreement
		102.4±1.0	104.6±0.3	Agreement

TABLE II - continued

Three Mile Island Analytical Chemistry Test Results

Chemical Analysis	Method of Analysis	NRC Known Value	Licensee Value	Comparison
		Results in parts per billion (ppb)		
Chloride	Inline IC	1.94±0.05	1.811±0.008*	-----
		3.65±0.11	3.34±0.08*	-----
Fluoride	Inline IC	2.02±0.08	1.824±0.013*	-----
		4.0±0.2	3.76±0.04*	-----
		Results in parts per million (ppm)		
Lithium	AA	0.493±0.007	0.506±0.006	Agreement
		1.24±0.02	1.218±0.007	Agreement
		2.43±0.03	2.389±0.009	Agreement
Boron	T	506±8	504.7±0.6	Agreement
		1049±11	1031.0±1.0	Agreement
		3040±4	3030±8	Agreement
Ammonia	Inline IC	1.10±0.03	1.16±0.03*	-----
Boron	SP	1.049±0.011	0.9152±0.0002	-----
		0.506±0.008	0.33205±0.00007	-----

TABLE II - continued

Three Mile Island Analytical Chemistry Test Results

*Duplicate analyses only

Notes:

IC = Ion Chromatography
SP = UV-Vis Spectrophotometry
T = Potentiometric Titration
AAGF = Graphite Furnace Atomic Absorption Spectrometry
AA = Atomic Absorption Spectrometry
ISE = Ion Specific Electrode

The NRC currently has no criteria for the comparison of results from inline instrumentation or from low level boron analysis.

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

ATTACHMENT 1 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 (±2Sd) of the ORNL known values are considered to be in agreement. Licensee values outside the plus or minus standard deviation range but within the plus or minus three standard deviation range (±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 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	± 8%	± 12%
Fluoride	± 12%	± 18%
Sulfate	± 10%	± 15%
Silica	± 10%	± 15%
Sodium	± 14%	± 21%
Boron	± 2%	± 3%
Ammonia	± 10%	± 15%
Hydrazine	± 8%	± 12%
Lithium	± 14%	± 21%