

U.S. NUCLEAR REGULATORY COMMISSION  
REGION I

Report No.: 50-244/92-14

Docket No.: 50-244

License No.: DPR-18

Licensee: Rochester Gas and Electric Corporation  
49 East Avenue  
Rochester, New York 14649

Facility Name: R. E. Ginna Nuclear Generating Station

Inspection At: Ontario, New York

Inspection Conducted: September 14 - 18, 1992

Inspectors:

Larry T. McNamara  
N. T. McNamara, Laboratory Specialist  
Effluents Radiation Protection Section (ERPS)

10/6/92  
date

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Branch (FRSSB)

10-6-92  
date

Approved By:

Marie Miller  
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Division of Radiation Safety and Safeguards

10-7-92  
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

#### 1.1 Principal Licensee Employees

- \* B. Dahl, Senior Chemist
- \* D. Fillion, Radiochemist
- \* R. Gaspar, Lead Technician
- \* A. Harhay, HP and Chemistry Manager
- \* G. Jones, Control Chemist
- \* N. Leoni, Quality Improvement Specialist
- \* R. Marchionda, Maintenance Superintendent
- \* J. Widay, Plant Manager

#### NRC Employees

T. Moslak, Senior Resident Inspector

- \* Denotes those present at the exit meeting on September 18, 1992. The inspectors also interviewed other licensee personnel, including members of the chemistry and health physics staff.

### 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 Laboratory Organization and Operation

Since the previous inspection in this area, (Inspection Report No. 50-244/90-16, performed August 6-10, 1990), the licensee's chemistry organization had changed in that parts of the chemistry organization no longer reported to offsite organizations. The licensee's chemistry program was now wholly contained within the Health Physics and Chemistry Department onsite. Primary systems chemistry and radiochemistry were performed under the direction of the Radiochemist. Primary system sampling and analysis were performed by shift technicians. These technicians performed both chemistry and health physics tasks. Secondary side chemistry and related tasks were performed by chemistry technicians under the direction of the Senior Secondary Chemist. These technicians were chemistry technicians only and performed no health physics tasks.



Both the Radiochemist and the Senior Secondary Chemist reported now to the Health Physics and Chemistry Manager.

#### 4.0 Radiological and Chemistry Measurements

##### 4.1 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 filters and charcoal cartridge. 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 effluent 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, 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 August 6-10, 1990 (Inspection Report No. 50-244/90-16) were also compared during this inspection.

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). In reviewing the above results the inspector noted that the licensee analyzed certain gaseous effluent samples using a "nominal" 4 liter Marinelli Beaker. The licensee had been using 4000 ml for the volume of the Marinelli Beaker when calculating effluent noble gas concentrations. However, the actual volume is approximately 4600 ml. The licensee stated that the actual volume of the Marinelli Beaker would be utilized in future calculations. The inspector noted that the use of the smaller volume was a conservative error by the licensee and stated that this would not result in the licensee exceeding any effluent release limits. The vent stack and condenser air ejector data present in Table I were determined using the



actual volume of the Marinelli Beaker. No safety concerns or violations were identified in this area.

#### 4.2 Standard 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.

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 standard measurements comparisons indicated that all of the measurement results were in agreement or qualified agreement under the criteria used for comparing results (see Attachment 1 to Table II). The copper and chromium results were reanalyses which were performed after the licensee recalibrated the atomic absorption spectrometer (AA). Initially, the licensee utilized the auto-sampler of the AA to perform dilutions of the calibration standards and then performed a non-linear fit to the resulting calibration points. At the lower part per billion (ppb) concentrations this technique resulted in values which were biased high and in disagreement from the ORNL known value. The recalibrations were performed with the chemist, rather than the auto-sampler, preparing the calibration standards and the data were fit to a linear curve. The licensee stated that as a result of these results comparisons, the AA calibration procedure would be modified so that the calibration standards would be prepared by the analyst and the data would be fit to a linear curve. The inspector stated that this area would be reviewed during a subsequent inspection in this area. The data are presented in Table II.





## 5.0 Laboratory QA/QC

The inspector reviewed the licensee's chemistry and radiochemistry laboratory QA/QC program. The laboratory QA/QC program was defined in Appendix G of the Ginna Station Quality Assurance Manual. Appendix G defines the laboratory QA/QC program in a general manner and references laboratory procedures for specific implementation of various aspects of the program. In reviewing the laboratory procedures the inspector noted that procedures addressed the intralaboratory aspects of a laboratory QC program. This included the construction and use of instrument and procedure control charts, duplicate and spiked sample analyses, and the review of the intralaboratory QC data. The inspector noted that the licensee participated in an interlaboratory comparison program with the National Institute of Standards and Technology (NIST) for radioactivity measurements. The NIST program included the vendor laboratory used by the licensee for performing radioactivity analyses of effluent samples which require separation chemistry. Additionally, the licensee participated in a quarterly interlaboratory comparison program with a vendor laboratory that supplied standards for the measurement of various chemical parameters. The licensee also used this same vendor laboratory to supply chemical standards on a semi-annual basis for the technician requalification program. However, the licensee did not have in place any procedures which described the interlaboratory aspects of the laboratory QA/QC program. The inspector discussed this matter with the licensee and the licensee stated that this area would be reviewed and appropriate corrective action would be taken.

The inspector reviewed selected laboratory QA/QC data for 1991 and 1992 to date and noted that the licensee participated in the above interlaboratory programs on a routine basis. Although the interlaboratory aspects of the laboratory QA/QC program were not formally documented, the licensee did, in fact, have in place a comprehensive overall laboratory QA/QC program. The inspector stated that the detailed data reviews and statistical analyses of the QC data by the licensee were noteworthy. The licensee now had a specific individual, the Quality Improvement Specialist, who was responsible for overall coordination and review of the laboratory QA/QC program. In discussing the QC data with the Quality Improvement Specialist, the inspector suggested that the interlaboratory chemical analysis data be trended by analyte as well as by instrument, as the licensee was currently doing. The Quality Improvement Specialist stated that this would be incorporated into the review of the interlaboratory data. The inspector stated that the above areas would be reviewed during a subsequent inspection. No safety concerns or violations were identified in this area.

## 6.0 Audit Activities

The inspector reviewed Audit Report No. 92-13:CJK, performed June 22 to July 10, 1992, and Audit Report No. 91-17:GFS, performed June 3-19, 1991. These audits included the licensee's Health Physics, Chemistry and Radwaste Programs. The sections of the audit which addressed the chemistry area appeared to be of good technical



depth, sufficient to identify programmatic problems in the areas being audited, and were performed by individuals with technical expertise in the areas being audited. In particular, the inspector noted that both audit reports addressed the chemistry laboratory QA/QC program implementation.

The inspector noted that the above audits appeared to provide adequate independent oversight and assessment of chemistry activities. No safety concerns or violations were identified in the area.

#### **7.0 Exit Meeting**

The inspector met with the licensee representatives listed in Section 1.0 at the conclusion of the inspection on September 18, 1992. The inspector summarized the purpose, scope, and findings of the inspection.



TABLE I

GINNA 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>		
Waste Gas Decay Tank 1110 hrs 09/17/92 (Detector No. 2)	Xe-133	(3.040±0.013)E-3	(2.871±0.001)E-3	Agreement
	Xe-135	(5.8±0.7)E-6	(4.1±0.3)E-6	Agreement
Reactor Water Particulate Filter 0100 hrs 09/10/92 (Detector No. 2)	Cr-51	(4.05±0.09)E-5	(4.42±0.15)E-5	Agreement
	Co-58	(4.28±0.03)E-5	(4.52±0.05)E-5	Agreement
	Co-60	(1.16±0.07)E-6	(1.10±0.12)E-6	Agreement
	Sb-124	(4.2±0.2)E-6	(5.1±0.3)E-6	Agreement
	Sb-122	(1.58±0.06)E-5	(1.73±0.15)E-5	Agreement
	Zr-95	(5.3±0.2)E-6	(5.7±0.2)E-6	Agreement
Reactor Building Effluent Radiation Monitor R-10A Charcoal Cartridge (Detector No. 1)	I-131	(2.4±0.2)E-12	(2.4±0.5)E-12	Agreement
	I-133	(2.4±0.2)E-12	(2.9±0.8)E-12	Agreement



TABLE I - cont'd

Ginna 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>				
Liquid Waste	Co-58	$(1.451 \pm 0.007)E-4$	$(1.59 \pm 0.02)E-4$	Agreement
Holdup Tank	I-131	$(4.82 \pm 0.05)E-5$	$(5.5 \pm 0.2)E-5$	Agreement
0110 hrs	Cs-134	$(1.415 \pm 0.007)E-4$	$(1.55 \pm 0.02)E-4$	Agreement
09/16/92	Cs-137	$(2.369 \pm 0.007)E-4$	$(2.58 \pm 0.02)E-4$	Agreement
(Detector No. 1)	Mn-54	$(1.09 \pm 0.04)E-5$	$(1.42 \pm 0.14)E-5$	Agreement
	Co-60	$(9.85 \pm 0.06)E-5$	$(1.21 \pm 0.02)E-4$	Agreement
	Sb-125	$(2.58 \pm 0.11)E-5$	$(3.1 \pm 0.4)E-5$	Agreement
Reactor Coolant	I-134	$(1.20 \pm 0.02)E-1$	$(1.29 \pm 0.03)E-1$	Agreement
0834 hrs	Cs-138	$(1.15 \pm 0.02)E-1$	$(1.32 \pm 0.04)E-1$	Agreement
09/17/92				
(Detector No. 2)				
First Count				
Reactor Coolant	I-131	$(3.54 \pm 0.02)E-3$	$(3.4 \pm 0.3)E-3$	Agreement
0834 hrs	I-132	$(6.50 \pm 0.11)E-2$	$(6.43 \pm 0.14)E-2$	Agreement
09/17/92	I-133	$(3.93 \pm 0.04)E-2$	$(3.32 \pm 0.04)E-2$	Agreement
(Detector No. 2)	I-135	$(8.4 \pm 0.2)E-2$	$(6.7 \pm 0.2)E-2$	Agreement
Second Count				





TABLE I - cont'd

Ginna 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>		
Vent Gas 1338 hrs 09/15/92 (Detector No.1)	Xe-133	(2.32±0.05)E-6	(2.88±0.05)E-6	Agreement
	Xe-135	(7.4±0.7)E-8	(5.3±0.5)E-8	Agreement
Condenser Air Ejector Gas 1545 hrs 09/17/92 (Detector No. 1)	Kr-85m	(5.49±0.07)E-6	(6.57±0.09)E-6	Agreement
	Kr-87	(9.6±0.2)E-6	(9.6±0.2)E-6	Agreement
	Kr-88	(1.28±0.03)E-5	(1.28±0.02)E-5	Agreement
	Xe-133	(6.01±0.04)E-5	(7.20±0.05)E-5	Agreement
	Xe-135	(5.96±0.02)E-5	(5.84±0.02)E-5	Agreement
Liquid Waste Holdup Tank 1400 hrs 08/07/90	gross alpha	(1.1±0.2)E-7	(5.75±?)E-8	Agreement
	H-3	(1.48±0.02)E-1	(1.42±?)E-1	Agreement
	Sr-89	(1.47±0.13)E-6	(1.40±?)E-6	Agreement
	Sr-90	(2.37±0.11)E-6	(2.27±?)E-6	Agreement
	Fe-55	(9.35±0.10)E-6	(7.85±?)E-6	Agreement

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

<u>Resolution</u> <sup>1</sup>	<u>Ratio for Agreement</u> <sup>2</sup>
<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 Reference Value/Reference Value Uncertainty)

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



TABLE II

Ginna Chemistry Test Results

<u>Chemical Analysis</u>	<u>Method of Analysis</u>	<u>NRC Known Value</u>	<u>Licensee Value</u>	<u>Percent Difference</u>	<u>Comparison</u>
<u>Results in parts per billion (ppb)</u>					
Fluoride	<sup>1</sup> IC	20.2±1.0	20.4±0.5	+ 1%	Agreement
		40±3	37.5±1.1	- 6%	Agreement
		85±5	75.7±0.3	- 11%	Agreement
Chloride	<sup>1</sup> IC	19.0±0.3	20.0±0.6	+ 5%	Agreement
		36.0±1.2	35.5±0.2	- 1%	Agreement
		75±3	72.4±0.6	- 4%	Agreement
Chloride	<sup>2</sup> IC	7.5±0.3	6.9±0.4	- 8%	Agreement
		19.0±0.3	18.7±1.3	- 2%	Agreement
		28.5±0.5	29.6±1.4	+ 4%	Agreement
Sulfate	<sup>2</sup> IC	7.9±0.2	8.4±0.5	+ 6%	Agreement
		19.4±0.3	20.2±1.4	+ 4%	Agreement
		29.1±0.5	31.8±1.6	+ 9%	Agreement
Sodium	IC	5.3±0.2	5.5±0.4	+ 4%	Agreement
		10.2±0.3	10.3±0.2	+ 1%	Agreement
		15.5±0.4	15.4±0.2	- 1%	Agreement
Ammonia	SP	110±3	106.7±0.6	- 3%	Agreement
		482±7	488±6	+ 1%	Agreement
		915±15	917±9	0%	Agreement



TABLE II- cont'd

Ginna Chemistry Test Results

<u>Chemical Analysis</u>	<u>Method of Analysis</u>	<u>NRC Known Value</u>	<u>Licensee Value</u>	<u>Percent Difference</u>	<u>Comparison</u>
<u>Results in parts per billion (ppb)</u>					
Silica	SP	15±2	13±0	- 13%	Qual Agree
		28.4±0.4	28±0	- 2%	Agreement
		60.1±1.0	63±0	+ 5%	Agreement
Hydrazine	SP	13.26±0.06	12±0	- 9%	Agreement
		34.1±0.3	32.7±0.6	- 4%	Agreement
		56.5±1.0	53±0	- 6%	Agreement
Copper	AAGF	8.06±0.08	9.0±0.3	+ 12%	Qual Agree
		16.2±0.2	17.2±0.6	+ 6%	Agreement
		20.2±0.2	21.37±0.15	+ 6%	Agreement
Iron	AAGF	7.96±0.08	8.7±0.8	+ 9%	Agreement
		15.90±0.14	16.7±0.9	+ 5%	Agreement
		19.9±0.2	19.0±1.3	- 5%	Agreement
Chromium	AAGF	8.04±0.08	8.8±0.4	+ 9%	Agreement
		16.08±0.14	16.2±0.3	+ 1%	Agreement
		20.0±0.2	19.7±0.5	- 2%	Agreement





TABLE II - cont'd

Ginna Chemistry Test Results

<u>Chemical Analysis</u>	<u>Method of Analysis</u>	<u>NRC Known Value</u>	<u>Licensee Value</u>	<u>Percent Difference</u>	<u>Comparison</u>
<u>Results in parts per million (ppm)</u>					
Lithium	AA	0.493±0.007	0.513±0.006	+ 4%	Agreement
		1.24±0.02	1.167±0.015	- 6%	Agreement
		2.43±0.03	2.36±0.05	- 3%	Agreement
Boron	T	304±4	301.9±1.0	- 1%	Agreement
		506±8	505.2±1.5	0%	Agreement
		1049±11	1033.1±0.9	- 2%	Agreement

IC = Ion Chromatography

SP = UV-Vis Spectrophotometry

AAGF = Graphite Furnace Atomic Absorption Spectrometry

AA = Flame Atomic Absorption Spectrometry

T = Potentiometric Titration

1. Tetraborate Eluent

2. Hydroxide Eluent



## 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 ( $\pm 2Sd$ ) 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 computer 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.

<u>Analyte</u>	<u>Agreement Range</u>	<u>Qualified Agreement Range</u>
Chloride	$\pm 8\%$	$\pm 12\%$
Fluoride	$\pm 12\%$	$\pm 18\%$
Sulfate	$\pm 10\%$	$\pm 15\%$
Silica	$\pm 10\%$	$\pm 15\%$
Sodium	$\pm 14\%$	$\pm 21\%$
Chromium	$\pm 10\%$	$\pm 15\%$
Copper	$\pm 10\%$	$\pm 15\%$
Iron	$\pm 10\%$	$\pm 15\%$
Boron	$\pm 2\%$	$\pm 3\%$
Ammonia	$\pm 10\%$	$\pm 15\%$
Hydrazine	$\pm 10\%$	$\pm 15\%$

