



Carolina Power & Light Company

SERIAL: NLS-84-127

MAR 20 1984

Director of Nuclear Reactor Regulation
Attention: Mr. D. B. Vassallo, Chief
Operating Reactors Branch No. 2
Division of Licensing
United States Nuclear Regulatory Commission
Washington, DC 20555

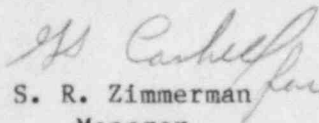
BRUNSWICK STEAM ELECTRIC PLANT, UNIT NOS. 1 AND 2
DOCKET NOS. 50-325 & 50-324/LICENSE NOS. DPR-71 & DPR-62
REQUEST FOR ADDITIONAL INFORMATION -
POST ACCIDENT SAMPLING SYSTEM

Dear Mr. Vassallo:

As a result of a telephone conversation with your staff on January 20, 1984, Carolina Power & Light Company (CP&L) was asked to clarify certain statements made concerning radiation effects on instrument accuracy in CP&L letter dated December 31, 1983 (LAP-83-579).

Please find enclosed the information requested. Should you have any questions concerning this letter, do not hesitate to contact a member of our Licensing Staff.

Yours very truly,


S. R. Zimmerman
Manager

Nuclear Licensing Section

PPC/ccc (9616PPC)
Enclosures

cc: Mr. D. O. Myers (NRC-BSEP)
Mr. J. P. O'Reilly (NRC-RII)
Mr. M. Grotenhuis (NRC)

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REQUEST FOR ADDITIONAL INFORMATION
POST ACCIDENT SAMPLING

NRC Comment

Provide additional information demonstrating applicability of laboratory instrumentation in the post-accident water chemistry radiation environment.

CP&L Response

Hydrogen or Total Gas Analysis: Hydrogen or total gas analysis will be performed by gas chromatography (GC). The GOW-MAC, series 550 GC (or equivalent) will be used. Adverse radiation effects on the GC components are not expected. The recording device used for the GC analysis will be located at a distance that will reduce the radiation levels well below these anticipated for post-accident samples. Gas chromatography is the method recommended in NEDC-30088. See attached reference - NEDC-30088, Page 3-3.

pH Measurement: The pH measurement (if required) will be made using a pH electrode, Cole Palmer catalog no. C-5990-45 or equivalent. This electrode has been successfully demonstrated for the determination of pH in the presence of gamma radiation through test and analysis. See attached reference - NEDC-30088, Pages 6-16, 6-17, D-1, and D-6.

Isotopic Analysis: Analysis by gamma spectroscopy will be conducted using extended shelves, sample dilutions and shielding as appropriate to reduce the radiation levels present. See attached reference - NEDC-30088, Pages 6-11.

Boron and Chloride Analysis: Analysis for boron and chloride will be performed by ion chromatography. The ion chromatograph uses a fixed sample volume of approximately 100 μ l. Adverse radiation effects on the components in the IC are not anticipated. Literature studies show that the cation resins begin to degrade at approximately 10^8 rads, that the electronic components are resistant to radiation exposure well above 10^5 rads, and that elastomers of the type used to make O-rings and silicon rubber sealing compounds are stable to about 10^6 rads. These values are well above those anticipated to be encountered by the IC during sample analysis. See the following attached references:

1. NEDC-30088, Pages 6-4, 6-13, and 6-14.
2. Evaluation of the GE and SEC Chemical Procedures for Post-Accident Analysis of Reactor Coolant Samples - Prepared by Exxon Nuclear Idaho Company, Inc., for the Nuclear Regulatory Commission, Pages 24, 25, and 26.
3. Analysis for pH, Chlorides, Dissolved Oxygen, Conductivity and Boron Under "Post-Accident" Conditions - Prepared by NUS Corporation, Pages 5, 9, 10, and 11.

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APRIL 1983

**RESPONSES TO NRC
POST-IMPLEMENTATION REVIEW
CRITERIA FOR POST-ACCIDENT
SAMPLING SYSTEM**

(This section is to be added to the PASS Manual)

4.5 Oxygen Analysis - Residual Hydrogen Method

In order to accommodate ALARA considerations, dissolved oxygen will be measured indirectly, whenever possible, using the residual hydrogen method. Using this method, dissolved oxygen is verified to be <0.1 ppm by measurement of a positive hydrogen residual of >10 cc/kg. Dissolved hydrogen concentration is determined by gas chromatography as described in Section 7. Gas chromatography has been successfully demonstrated for the determination of hydrogen in the presence of gamma radiation through testing and analysis by Babcock and Wilcox on TMI-2 post-accident gas samples.

6.2 DISCUSSION

6.2.1 Review of PASS System

The General Electric Post Accident Sample Station (1) was developed by the General Electric Company and a group of BWR owners in response to the requirements of NUREG-0578 (2) and subsequently NUREG-0737 (3). The system was designed to provide liquid and gaseous samples from one primary system, from the suppression pool, and from the primary containment atmosphere following a major reactor accident accompanied by a release of fission products as defined in Regulatory Guide 1.3 (4).

The development of the design specifications for this system involved a definite decision to avoid the use of inline analytical instrumentation, except for a conductivity monitor. The inline instrumentation was considered to have uncertain reliability under accident conditions. Instead, the emphasis was placed on the ability to obtain grab samples for laboratory analysis. Section 7 to Reference 1, includes suggested analytical procedures to meet the requirements of NUREG-0737 (3). It was the specific intent that only the analysis of immediate need would be performed at the reactor site, and the balance would be performed at an offsite, commercial analytical facility having the capability of processing multicurie samples. In several cases, it was intended that the onsite analysis would be of a scoping nature with more accurate analyses subsequently being performed at the offsite facility. This intent has been somewhat modified, depending on the particular reactor site and the various NRC clarification letters, with several of the sites having purchased ion chromatographs for boron and chloride analyses.

The PASS system was designed to obtain a variety of samples:

1. A 0.1 milliliter primary coolant or suppression pool sample diluted to 10.0 milliliters by the processing of flushing the sample valve contents into the sample system bottle. This sample is intended for radiochemical analysis and for initial site chemical analysis.

even under the best of conditions. Uncertainties on the order of 5% to 10% are more in keeping with the precision for repetitive analysis of a single sample. If the volumetric errors in the small volume sampling*, dilution, and equipment calibration are included, the overall analytical accuracies are more reasonably 10% to 20%. In addition, a requirement to analyze to zero concentration is a poorly defined limit and immediately raises the issue as to how sensitive an analysis procedure must be used. The need for an error limit other than zero becomes more acute when sample volumes are very restrictive or samples are diluted to reduce exposure. The error bands given in the clarification letter appear to be reasonable analysis limits; i.e., the boron analysis should be capable of detecting 50 ppm and the hydrogen method 5 cc/kg, etc.

Gross Activity, Gamma Spectra;

There should be no problem in meeting the accuracy requirement of a factor of 2 for the major nuclides nor in analyzing the range of activities given in Table 1. This capability is discussed in Section 6.2.2.4. Providing the precautions described in Section 7.6 of Reference 1 are followed, the background at the multichannel analyzer should not be a limiting factor for measuring the principal gamma emitters. There will be an increased uncertainty introduced as a result of successive dilutions, but all things considered, the accuracy for analyzing the initial aliquot should be within ± 30 to 40%. The major uncertainty lies in the representativeness of the initial sample. This subject is addressed in other tasks and is beyond the scope of the report. However, it should not be too significant for truly soluble nuclides. A major uncertainty may arise in analysis of the suppression pool water due to sample system contamination if the activity of the primary coolant is much higher than that of the suppression pool. The effect of cross contamination, however, can be minimized by adequately flushing the PASS between samples.

*Tests of the small volume samples (0.10 ml diluted to 10 ml) on the General Electric prototype PASS gave a sample and dilution precision of $\pm 5\%$ with a positive 6% bias in the 0.10 ml aliquot (i.e., 0.106 \pm 0.005 milliliters).

interfere when present in concentrations greater than 25 ppm while fluoride causes negative interference due to the formation of fluoroborate ion. These conditions are not expected to occur, however, in the BWR primary system.

Irradiation tests conducted by General Electric had reported in Appendix A, Chap. 7 Reference 1 showed that an energy absorption rate of 4.4×10^5 Rad/hr* during the color development phase of the analysis resulted in an error equivalent to 27 μ gm of boron or 270 ppm for a 0.1 ml coolant sample. Assuming the indication effect is proportional to dose, reducing the exposure to correspond to Reg. Guide 1.3 source terms and a one hour decay would result in only a 1 ppm error for the analysis of 2 ml of a 100:1 diluted, 0.1 ml primary coolant sample.

Chloride Analysis:

Chloride analysis of highly radioactive solutions with chloride concentrations in the range of 0.05 to 20 ppm cannot be performed in a normal laboratory using conventional techniques. Although a few of the BWRs using the General Electric PASS are planning to perform the analysis on site using an ion-chromatograph, most of the sites plan to send undiluted, 10 ml samples of the primary coolant to an offsite analysis facility. In the event of an accident involving extensive core damage, most BWRs would limit the chloride analysis at the site to a scoping analysis of samples of 0.1 ml primary coolant diluted at 10 milliliter volume. The PASS manual, Section 7.4.3, proposed the turbidimetric method as the most reasonable method for this purpose when handling highly radioactive samples. This method was taken from Reference 10 and was chosen as it did not involve boiling the sample

*This dose rate is approximately a factor of 50 larger than the 8×10^3 Rads/h calculated for a 0.1 ml primary coolant sample in a 25 ml analysis volume when using the Reg. Guide 1.3 source terms and a 1 hour decay. The 8×10^3 Rads/h absorption rate is not significantly different from the 1×10^4 Rads/h in the criteria (10) matrix.

with attendant risk of evolving radioactive iodine gas. The maximum sensitivity for this method is on the order of 0.1 ppm in the solution to be analyzed. Since the analysis will be performed on a sample diluted by a factor of 10, the initial concentration must be greater than 10 ppm, and more realistically, considering uncertainties in blank correction for chloride contamination in the diluent and the glassware, greater than 20 ppm. Consequently, the scoping procedure is barely capable of analyzing at the maximum specified concentration.

Depending on the particular procedure, a chloride analysis is subject to several interferences in terms of the element matrix listed in the NRC clarification letter. On an atom for atom basis, 40 ppm iodide is equivalent to 11 ppm chloride and will interfere in turbidimetric method by the formation of silver iodide. In addition, iodide is also expected to significantly interfere with the measurement of chloride using a solid state, specific ion electrode.* In ion-chromatography, the boron peak is immediately adjacent to that of chloride. Considering the high ratio of boron to chloride specified by the matrix and the chloride analysis requirements, there may also be serious boron interference in this method for chloride analysis.** Each utility planning to perform the chloride analysis on site should show that iodide or boron at the matrix specified concentrations will not effect the chloride analysis.

*Orion instrument Co. stated they have developed a specific ion electrode method for measuring chloride which involves elimination of iodide interference by oxidation of iodide to iodine with sodium bromate. This method is worthy of further consideration but will require special apparatus to avoid release of highly radioactive iodine vapor.

**Discussions with Dionex applications group revealed they are working on a method involving elution with 0.002 M sodium carbonate to separate chloride and borate. An application paper should be available in several weeks.

would still be 2% hydrogen which is readily measurable by gas chromatography using argon carrier. There is, however, the potential problem that attempting to optimize the analysis for low levels of oxygen may seriously effect the hydrogen sensitivity.

pH Analysis:

Section 7.4.4 of the PASS manual (1) suggested the possibility of using pH indicator paper for estimation of pH. This method, however, will not meet the Table accuracy requirements, and, as also described in Section 7.4.4, cannot be used at the required source term radiation levels due to total destruction of the indicator dye. Section 7.4.4 also described the possible use of a micro pH probe. Subsequent testing of this probe were unsatisfactory even without radiation and it was dropped from further consideration. Reference 12 describes the results of irradiation tests of a typical combination pH electrode (Fisher Model 13-639-104). The electrode performed satisfactorily at gamma flux levels up to 1.3×10^6 R/h in both buffered and unbuffered solutions at pH 4.0, 7.0, and 10.0. Readings in the buffered and unbuffered acidic solutions were stable over irradiation periods up to an hour. The unbuffered basic solution showed a decrease of approximately 0.1 pH units per minutes during a 5 minute test period. This type of electrode would meet the accuracy and stability requirements; however, the volume of sample required makes it impractical on the basis of personnel radiation exposure at the design basis source terms. A smaller combination electrode which would use 0.1 to 0.3 milliliters of solution was suggested.

- Two types of combination electrodes (semi-micro and flat-surface), which would use as little as 0.1-0.2 ml of sample for measurement, were tested under high radiation conditions at the Vallecitos test facility. The test results are given in Tables 6-2 and 6-3. The flat-surface electrode performed satisfactorily in the highest radiation field ($\sim 1.3 \times 10^6$ R/h) exhibiting <0.3 pH unit drift in all cases. For the

semi-micro electrode, the drift was less than 0.3 pH unit for a radiation field of 1×10^5 R/h. (Note that the standard test matrix recommended by the NRC suggests use of 10^4 R/hr). It was also found that the pH readings were not very stable for ~1 min. following the sample moving to or from the high flux zone. In some cases, the pH readings continued to deviate slowly for ~30 minutes from the pre-exposure reading. However, little or no change in pH readings before or after irradiation for ~20 minutes was observed in any of the cases.

Appendix D provides a revised Subsection 4.4 to Section 7 of the PASS procedures manual and describes the procedure for use of these pH electrodes. This write-up should replace the existing Section 4.4 discussion.

6.2.2.3 NUREG-0737 Criteria (5 and 2c)

6.2.2.3.a NUREG-0737 Criteria 5

"The time for a chloride analysis to be performed is dependent upon two factors: (a) if the plant's coolant water is seawater or brackish water and (b) if there is only a single barrier between primary containment systems and the cooling water. Under both of the above conditions the licensee shall provide for a chloride analysis within 24 hours of the sample being taken. For all other cases, the licensee shall provide for the analysis to be completed within 4 days. The chloride analysis does not have to be done on site."

6.2.2.3.b NRC Clarification Letter, Spring 1982

"BWRs on sea or brackish water sites, and plants which use sea or brackish water in essential heat exchangers (e.g., shutdown cooling) that have only single barrier protection between the reactor coolant are required to analyze chloride within 24 hours. All other plants have 96 hours to perform a chloride analysis. Samples diluted by up to a factor

4.4 MEASUREMENT OF pH WITH pH ELECTRODE

Because of the reliability, ease, and rapidity of measurement, as well as to be consistent with ALARA, two types of combination electrodes (semi-micro and flat-surface) have been found to be adequate to measure the pH of primary coolant samples. As little as 0.1-0.2 ml of undiluted sample is needed for the measurement. The flat surface electrode is preferred.

- a) For the flat surface combination electrode, the sample is taken directly into a regular 15 ml sample vial. Only 0.1 ml of the undiluted sample solution collected at the bottom of the vial is needed. For the measurement the electrode is inserted fully into the vial* with the flat surface in contact with the liquid at the bottom of the vial.
- b) For the semi-micro (0.6 cm dia.) electrode, the sample can be taken at the small volume sampler by using an air filled syringe to blow approximately 0.1 ml aliquots two or three times from the sample valve into a centrifuge tube (approx. 1.0 cm dia., 4.7 cm long) contained in a regular 15 ml sample vial**. Without completely removing the sample vial from the shielding cask, the vial cap is removed, and the electrode can be inserted into the centrifuge tube in the vial. The pH is measured directly in the undiluted solution by using a standard pH meter.

*The opening of the vial may be slightly too small for the electrode. Minor work may be needed to reduce the diameter of the plastic body of the electrode.

**It is noted that the centrifuge tube insert reduces the effective diameter of the sample vials which makes positioning of the sample vials very critical for insertion of the needles of the PASS. It is possible to overcome this restriction by bending the two hypodermic needles inward toward the center, and/or by using a sample vial with a larger diameter opening.

Three types of combination electrodes have been tested under high radiation fields. The test results are described in Appendix A. All three electrodes performed satisfactorily at 10^5 R/h radiation field, exhibiting a drift of less than 0.3 pH units in all buffer solutions. At 10^6 R/h radiation field, one electrode showed a greater deviation and poor stability during the test. It is difficult to identify the source of deviation and unstability. The true pH in the solution may be affected under high radiation fields. However, it is believed that with a small volume of sample, the radiation fields from the post accident coolant sample (assumed at 10^4 R/gm) should be much lower than the radiation fields to which the electrode was exposed under the test conditions (10^5 - 10^6 R/h).

APPENDIX A
EFFECT OF GAMMA IRRADIATION ON PH MEASUREMENTS BY PH ELECTRODES

Three combination electrodes⁽¹⁾ were tested with standard buffer solutions of pH 4.01, 7.0, and 10.0 in the Vallecitos Nuclear Center (VNC) gamma irradiation facility at gamma flux levels up to 1.3×10^6 R/h. The standard electrode was also tested with unbuffered diluted H_2SO_4 (pH=4) and NaOH (pH=10) solution. The electrodes were tested first in the laboratory using the integral leads supplied, and then with a 25-ft long coaxial cable, to connect the electrode with a pH meter (Orion's Ionalyzer, Model 801). The long cable was necessary for obtaining readings while the electrode was lowered into the gamma flux in a water pool. Although the long lead and poor connections did make the emf sensitive to movement of the cable or electrode and produced unstable readings at times, fairly reproducible pH readings were obtained.

The test electrode was placed in a 5/8-in. I.D. test tube containing ~3 ml of test solutions. The pH readings were taken at before irradiation, during irradiation at variable time intervals, and after irradiation. The results of pH measurements for the buffer and unbuffered solutions are given in Table 1 and 2, respectively.

(1) Three electrodes are:

1. Standard polymer body, gelfilled combination electrode with Ag/AgCl reference (Fisher Cat. No. 13-639-104)
2. Flat surface membrane combination electrode with Ag/AgCl reference (Fisher Cat. No. 13-039-83)
3. Epoxy-body, gelfilled combination electrode with Ag/AgCl reference, semi-micro size (6 mm dia.) (Cole Parmer Cat. No. C-5990-45)

In the buffer solutions, the standard and flat-surface electrodes performed satisfactorily under the highest radiation field ($\sim 1.3 \times 10^6$ R/h), exhibiting < 0.3 pH unit drift in all cases. For the semi-micro electrode, the maximum drift was near 1 pH unit under the same radiation field. However, the deviation was reduced to ≤ 0.3 pH unit when the electrode and solution were irradiated at a lower level of radiation field ($\sim 1 \times 10^5$ R/h). It was also found that the pH readings were not very stable for ~ 1 min following the sample moving to or from the high flux zone. In some cases, the pH readings continued to deviate slowly for ~ 30 min from the pre-exposure reading. However, little or no change in pH readings before or after irradiation for ~ 20 min were observed in any of the cases.

In the unbuffered solutions, the basic solution in particular, the measured pH seemed to decrease with increasing total exposure in a 5-min test period. However, such change was not observed in the acidic solution even after 1 hr of exposure.

TABLE 1

EFFECT ON GAMMA RADIATION ON pH MEASUREMENTS IN BUFFER SOLUTIONS

ELECTRODE	RADIATION FIELD (R/h)	IRRAD. TIME (MIN)	pH BUFFER SOLUTIONS		
			4.01	7.0	10.0
Standard	0 (pre-exposure)		3.958	7.000	9.901
	1.3×10^3	1-2	3.955	6.950	9.896
	1.3×10^4	1-2	3.963	6.922	9.895
	1.3×10^5	1-2	3.96	6.945	9.889
	1.3×10^6	1-2	3.8	6.822	9.734
	0 (post-exposure)		3.93	6.927	9.857
Flat Surface	0 (pre-exposure)		4.000	7.000	9.994
	1.2×10^6	5	4.271	7.301	10.149
		10	---	---	10.167
		15	---	7.202	---
		20	4.221	7.188	10.135
	0 (post-exposure)		3.945	6.951	9.935
Semi-micro	0 (pre-exposure)		(1)*4.017 (2) 3.996	7.000 7.000	10.000 9.997
	1.2×10^6	5	(1) 5.132 (2) 4.998	6.930 ---	10.932 10.744
		10	(1) --- (2) ---	6.966 7.813	10.917 ---
		15	(1) 5.074 (2) ---	6.985 ---	10.904 ---
		20	(1) 5.013 (2) ---	6.990 ---	10.885 10.724
	0 (post-exposure)		(1) 4.069 (2) 3.970	7.015 7.019	10.041 10.041
	0 (pre-exposure)		3.996	7.000	9.997
	1.0×10^5	5	4.217	7.075	10.050
		10	4.165	7.145	10.073
	0 (post-exposure)		3.970	7.019	10.014

* (1) and (2) indicate Tests 1 and 2, respectively

Table 2

Effect of Gamma Radiation on pH in Unbuffered Solutions
Using the Standard Combination pH Electrode

RADIATION FIELD (R/hr)	pH IN SOLUTION	
	H ₂ SO ₄	NaOH
0 (pre-exposure)	4.058	9.925
10 ³	4.066	9.922
10 ⁴	4.070	9.923
10 ⁵	4.070	9.915
10 ⁶ (1 min)	3.900	---
10 ⁶ (3 min)	3.859	9.55
10 ⁶ (5 min)	---	9.42
10 ⁶ (10 min)	3.846	*
10 ⁶ (40 min)	3.948	
0 (post-exposure)	4.107	9.475

*The reading was decreasing at ~0.1 pH unit per minutes after 3 minutes, and the measurement was terminated at ~5 min after exposed to the flux.

(c)
EVALUATION OF GE AND SEC CHEMICAL PROCEDURES FOR POSTACCIDENT
ANALYSIS OF REACTOR COOLANT SAMPLES

November 1981

Prepared by

Exxon Nuclear Idaho Company, Inc.
Idaho National Engineering Laboratory
Idaho Falls, Idaho 83401

for

The Nuclear Regulatory Commission

The advantage of the automatic mannitol titration procedure is its relative simplicity, remote operational characteristics, utility under routine and accident conditions, and wide measurement range.

The only apparent disadvantage of the procedure is the potential maintenance difficulty which might occur during replacement of sensing elements under accident conditions or rapid repair of the microprocessor. However, as backup capabilities to analyze boron samples are required for inline sample methods, the DigiChem analyzer should meet all measurement requirements.

The effects of high radiation fields have not been tested. ENICO feels that the effects probably will not be significant; however, this should be confirmed.

4.2.1.6 Ion Chromatography (IC). An ion chromatograph operates on the principle of selective retention and elution of ionic species on and from ion exchange media. It basically consists of a separator column and eluent, a suppressor column, a conductimetric detector, and a readout device. To perform an analysis for anions, such as borates or chlorides, the sample is first passed through the separator column - an anion exchange medium which retains the anions and replaces them with another anion from the exchange medium. The retained anions are then selectively removed from the separator column with the eluent, normally a dilute salt solution, and passed through the suppressor column. In the suppressor column - a cation exchange medium - the anions are converted to their acid forms which pass unretarded to the conductimetric detector. The conductivity of these dilute acid solutions is a function of the anion concentrations in the sample.

The time between sample injection and the appearance of conductivity peak for a particular anion depends on the sample size, the physical size of the columns, the types of exchange media, and the types, concentrations, and flow rate of the eluent. As a result different anions in a single sample can be separated and analyzed by proper selection of parameters.

(33)

In the development of an ion chromatographic procedure for the analysis of boron and/or chloride; SEC/NUS studied various combinations of eluents, separator columns, suppressor columns, and sample injection loop sizes. Initial testing resulted in a method which used a sodium tetraborate eluent and was applicable for chloride analysis of postaccident reactor coolant samples (cf Section 4.2.2.1). However, the analysis of boric acid solutions with the procedure showed inconsistent results.

Additional development and testing by Dionex, the manufacturer of the ion chromatograph used, resulted in a procedure for the simultaneous analysis of boron and chloride using a single sample.

In the test program a modified Dionex Model 10 Ion Chromatograph was used. The modifications included two 4 x 250 mm separator columns, a 3 x 250 mm suppressor column, a twenty cm (0.043 ml) sample injection loop, and a sodium carbonate/sodium hydroxide/mannitol eluent. An additional requirement identified was the need of a cation pre-column to remove excess base and convert borates to boric acid prior to loading highly basic samples into the injection loop. With a twenty-five percent pump stroke, the necessary times for the boron and chloride peaks to appear following injection to the sampling loop are respectively 5-6 and 9-10 minutes.

To consistently obtain satisfactory results, periodic washing and/or regeneration of the suppressor and pre-columns is necessary. The pre-column requires regeneration after the analysis of every two to three samples containing 0.4 M sodium hydroxide. The required frequency for washing and regeneration of the suppressor columns was not stated. However, based on the frequency noted in the initial chloride analysis development work, estimated frequency for regeneration is every four hours of continuous operation. The need for this is indicated by an erratic baseline on the readout device. The required frequency for washing the suppressor is once daily or prior to each regeneration.

If column washing and regeneration are not required, the analysis time is forty minutes. If column washing and regeneration are required prior to analysis, the sample analysis time is approximately two hours. Neither case includes system calibration time, which is fifteen minutes.

The IC procedure for simultaneous chloride and boron analysis has been laboratory tested using simulated postaccident reactor coolant samples, stable fission products, caustic, cooling water impurities, and normal reactor coolant chemical additives. No sample matrix effects were observed within the specified measurement range.

The advantages of the procedure are its adaptability to remote operation, the large chloride measurement range, the simplicity of operation, small sample sizes, potentially short sample analysis time, and the lack of chemical interferences.

The disadvantages of the procedure are the lack of a sufficient measurement range for boron, the need of a pre-column for basic samples, and the need for column washes and regeneration which might lead to long analysis times.

The effects of large irradiations associated with highly radioactive samples have not been evaluated. However, based on a literature study of radiation effects on the components of the IC and on limited laboratory tests used to determine the effects of 0-200 ppm hydrogen peroxide in samples, no radiological effects are anticipated. The literature showed that cation resins begin to degrade at approximately 10^8 rads and that the electronic components are resistant to exposure well above 10^5 rads. Both levels are well above those anticipated to be encountered by the IC during analysis of samples.

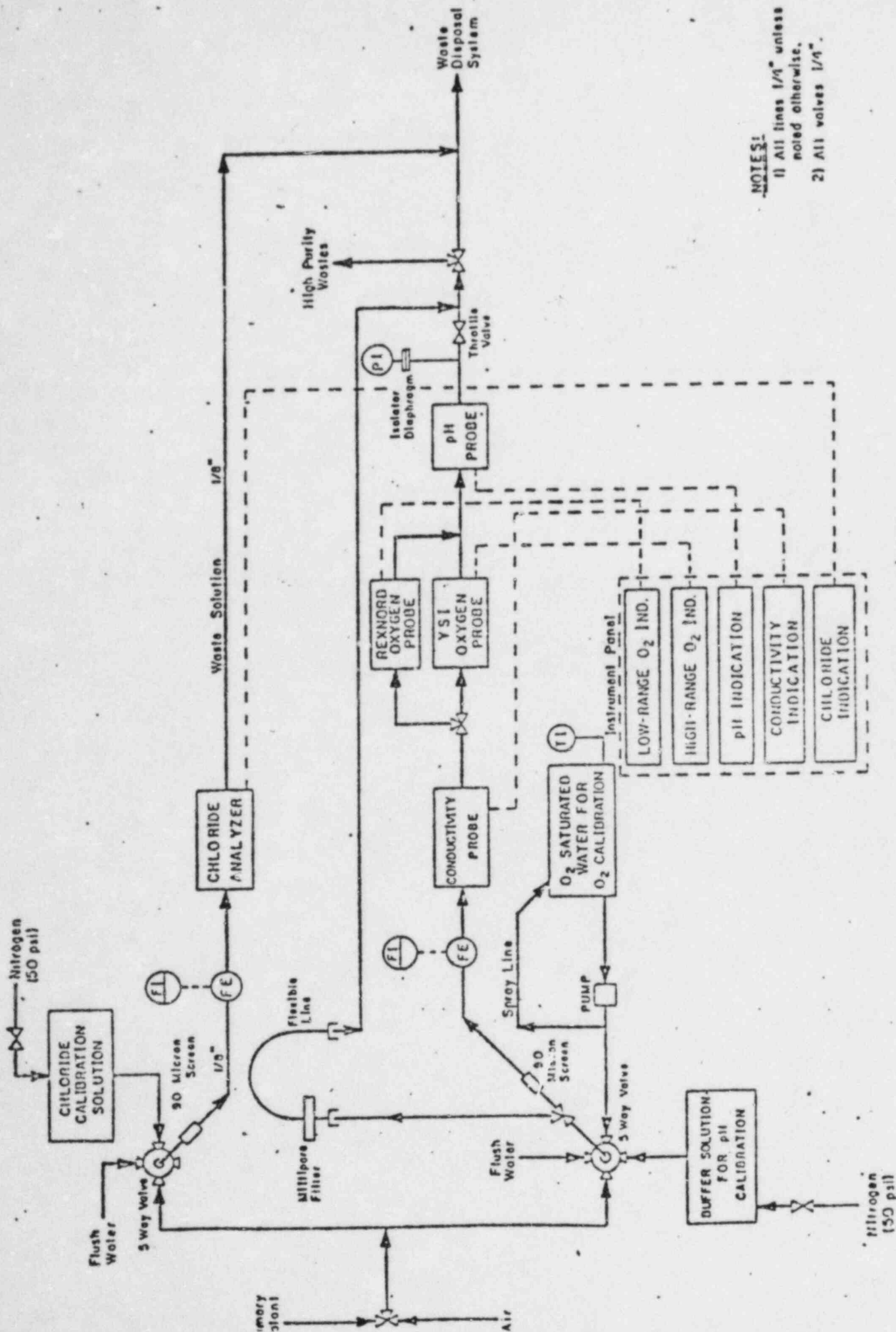
4.2.1.7 Carminic Acid Spectrophotometry. Two procedures were presented for boron analysis with carminic acid, one by SEC and one by GE. The one presented by GE was detailed; it was developed by HACH Chemical Company²⁰ and closely follows an ASTM procedure.²¹ The

ANALYSES FOR pH, CHLORIDES, DISSOLVED OXYGEN, CONDUCTIVITY
AND BORON UNDER "POST-ACCIDENT" CONDITIONS

BY

W. NESTEL, COMMONWEALTH EDISON
W. LECHNICK, NUS CORPORATION
R. C. RICE, NUS CORPORATION

FEBRUARY 1980



NOTES:

- 1) All times 1/4" unless noted otherwise.
- 2) All valves 1/4".

CECO COOLANT ANALYSIS SYSTEM

FIGURE 1

(21)

shielding requirements. The system as shown contains a Rexnorde oxygen probe which would not be used during post-accident sampling conditions. It is included as optional equipment at the request of CECO. Design capabilities of the system are shown in Table 3. All exposure times involved with operation of this system will be on the order of seconds.

Design of the automated system provides for precalibration of the instrumentation and final flush of the systems involved to reduce radiation levels after the analyses are complete. The system can be operated on a continuous or intermittent basis. For continuous operation, calibration is required on a once-per-day basis. Calibration would be performed prior to use when operated intermittently. Provision has been made to direct sample line purge and flush flow back to a high purity waste system or to the radwaste system. Buffer solutions used for pH-conductivity calibration and all chloride analyzer solutions will be directed to the radwaste system. Individual components within the system are described below:

A. CHLORIDE ANALYSES

The analyses will be performed by the use of ion chromatography. This is the only approach that can be used to analyze for chlorides that will not add significantly to radiation exposure. Analyzing a sample by IC is fairly straight forward requiring about 1 ml of sample transferred via hard piping into the sampling module to the IC. A fixed amount (400 μ l) of the sample is automatically transferred to the separator column for analysis. Typical results achieved under these conditions are shown in Figure 2. Excess sample is discharged to drain. Most of the other available methods for chloride analysis involve more exposure of the analyst to the radioactive solutions and for this reason were discarded as potential candidates for this application.

The Model 10 unit manufactured by the Dionex Corporation will be used in this application. This system can be used to analyze for chlorides.

down to a sensitivity of about 100 ppb without any pretreatment of the sample. However, this system cannot be used as is under accident conditions because of radiation exposure considerations. This system must be modified to provide for hard line piping to the sampling port. Also, shielding must be provided for that portion of the unit which will process the radioactive solution and secondary containment must be provided in the event of leakage.

B. CONDUCTIVITY MEASUREMENT

This will be provided by an in-line probe contained in a redesigned probe holder. The probe has a cell constant of 0.1. Calibration of the conductivity probe will be performed with the buffer solution used for pH calibration.

C. OXYGEN ANALYSES

These analyses will be performed by use of an in-line dissolved oxygen meter manufactured by the Yellow Springs Instrument Company. The probe holder has been redesigned to minimize fluid volume and reduce radiation exposure. Also, the probe holder is designed so that it can be flushed after it is used in this application. Design requirements includes provision for in-line calibration as is necessary to achieve accurate oxygen determinations. Calibration will be provided by use of a separate water source which will be saturated with respect to oxygen concentration. Normal calibration operations involving exposure to air cannot be used in this application because of radioactive contamination considerations.

D. pH DETERMINATION

An in-line probe will be used as is the case with the oxygen analysis system. The probe holder has been redesigned to minimize fluid volume. The pH probe like the oxygen probe is calibrated in place since

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it cannot be removed from the system. The loop design provides for the addition of buffer solution to the pH probe and for flushing of this solution from the system after calibration is complete.

E. OTHER DESIGN CONSIDERATIONS

1. Radiation Control

About six inches of lead will be used to provide for shielding of the tubing, probe assembly and valves which contain radioactive coolant. All components will be accessible from the back for ease of maintenance.

Secondary containment such as a hood will be used to provide for control of radioactive gases and iodine leaking from valves and fittings.

2. Pressure and Temperature Limitations

The analytical system operating pressure limitation is 75 psi. This is based on an operating pressure limitation of 100 psi for the pH probe. A margin of safety was arbitrarily added for conservative reasons.

Optimum temperature range for operation of the analytical system is in the range of 75-90°F. A small loss in accuracy for pH and conductivity determinations will result in operating at a higher temperature range. Maximum operating temperature is 125°F.

IV. RADIATION DEGRADATION

No problem is anticipated with radiation damage to instruments and/or O-rings that may be used in the system based on results of radiation damage effects reported in the literature. Results of a study performed by Doman

(20)

indicate that items such as semiconductors, resistors, capacitors, wire, insulators, etc., start suffering radiation damage in the range from 10^6 R to perhaps 10^{10} R. These exposure levels are several orders of magnitude higher than is expected for the use of the equipment shown in the system used under "post-accident" conditions.

Even if it were assumed that O-rings and silicon rubber sealing are stable to about 10^6 R or over as indicated by data presented, it is possible that O-rings or silicon rubber may be used in the system, however, exposure levels will be far below the 10^6 R range required to incur radiation damage.

There is some possibility that the silver chloride in the pH probe will eventually be reduced to metallic silver by gamma radiation. Should this occur, it would be indicated by sluggish response during use of the pH instrumentation. Operating procedures require daily calibration when the pH instrumentation is in use. Corrective action would require replacement of the probe assembly which is easily achieved.

V. BORON ANALYSES

A colorimetric method utilizing curcumin is currently recommended by NUS for boron determinations under "post-accident" conditions. The concentration range for this method is 0.2 to 2 mg/l boron, thus the samples will typically be diluted by about a factor of 1000. One ml of the diluted sample is required for analyses. All analytical operations must be carried out in an operating fume hood to provide containment of activity. The relative standard deviation for multiple analyses is about $\pm 13\%$. Total analyses time is two hours. The time frame does not meet NUREG-0578 requirements; however, it is considered justifiable from a safety analysis and personnel exposure viewpoint. The objective of the boron analyses is to determine that there is sufficient boron present to maintain the reactor in a subcritical condition during cooldown. Time requirements for cooldown will be on the order of many hours for all reactor systems.