

DOCKET No. 50-280 VEPCO.. SURRY I

Evaluation of OnLine Boron Analyzers

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ATTACHMENT 1

Criterion (2) - Provide a core damage estimate procedure.

Response:

Veeco has not implemented a specific procedure to provide an estimate of the degree of core damage as determined from radionuclide concentrations and core/plant status indicators. It is our intention to utilize a core damage assessment methodology which will be prepared by the Westinghouse Owners Group (pending approval of this task by the full Owners Group membership). This procedure/methodology would be implemented in a reasonable time period following availability of the information from the Westinghouse Owners Group. Upon approval of this program, the Westinghouse Owners Group will provide the NRC with information about the program scope and schedule.

Veeco's Emergency Response Plan provides for the assessment of core damage and its possible affects on operations. This is accomplished without formal procedures by individuals with expertise in the areas of core/fuel design, transient behavior, thermal hydraulics, and radiochemistry. These individuals are currently part of the Reactor Systems and Chemistry groups which comprise a portion of the corporate level Technical Support Staff. (It is this area of the corporate emergency response organization where formal procedure/methodology would be utilized for core damage assessment.) Our current Emergency Response Plan, its organization, and personnel represent an acceptable interim basis to provide estimates of core damage until a formalized methodology is available.

ATTACHMENT 2

Criterion (3) - Verify that PASS valves which are not accessible after an accident are environmentally qualified for conditions in which they must operate.

Response:

Veeco has reviewed procurement files and has determined that valves purchased for the PASS were procured with specifications which will qualify them for the post accident environment in which they must operate. Containment Isolation valves associated with the PASS were also purchased with the requirement that they be capable of operating in the environment in which they were to be installed. Veeco has documentation on file which supports their use in the post accident environment.

ATTACHMENT 3

Criterion (5) - Provide for an undiluted sample for analysis within 30 days.

Response:

North Anna Power Station - Veeco has available at Surry Power Station an in line Ion Chromatograph. Veeco considers this equipment to be portable. In the event that a chloride analysis would be required, the equipment would be transported to North Anna and put into operation. This will allow North Anna to perform an analysis for chlorides on an undiluted sample within the required 4 days.

ATTACHMENT 4

Criterion (10) - Provide information demonstrating applicability of procedures and instrumentation in the post accident water chemistry and radiation environment.

Response:

The Sentry High Radiation Sampling System was developed to provide in-line analyses and in-line dilutions for grab sample analyses which would meet the requirements of NUREG 0578, Section 2.1.8a, NUREG 0737, Item II B.3, and Regulatory Guide 1.97, Revision 2. Undiluted coolants and containment air samples can be captured in shielded containers for on-site or off-site analyses. The Sentry equipment can also be used for routine sampling and analyses.

The Cyrus Wm. Rice Division of NUS Corporation developed and tested the methods selected for post-accident boron, chloride, dissolved hydrogen and oxygen, and pH. The analytical requirements, selected method capabilities, and accuracies achievable based on testing are summarized in Table 5 except Boron. Vepco has installed on-line boron analyzer (DigiChem Analyzer) manufactured by the Ionics Corporation, and modified by Sentry Equipment Corporation. The analytical requirements, selected method, capabilities, and accuracy achievable based on testing are summarized in the attached report (NSAC/46), An Evaluation on On-Line Boron Analyzers. The NUS development and test program considered the following criteria in reviewing the analytical methods available to meet the post-accident requirement.

1. Chemical effect of the post-accident coolant matrix
2. Analysis time and radiological dose limitations
3. Radiation effect on method and/or equipment
4. Application to both normal and post-accident conditions
5. Compliance with sensitivity and range requirements
6. Applicability to in-line and grab sample analysis
7. Sample size requirements

The methods evaluated, testing performed, and reasons for selection of the appropriate method are summarized for each analysis in the following discussion. Complete details of the NUS development and testing program are presented in References 3 and 4.

Boron

The Ionics DigiChem Analyzer as modified by Sentry Equipment Corporation has been tested under normal conditions and at radiation levels as high as 10^5 to 10^6 R/hr. The accuracy of the analyzer, its reliability under normal conditions, its susceptibility to radiation damage, and its accuracy when exposed to high radiation levels are summarized in the Electric Power Research Institute's report titled "An Evaluation Of On-Line Boron Analyzers," NSAC/46, dated April 1, 1982 (Section 1 and 2).

Chloride

NUS evaluated several chloride analysis methods and selected ion chromatography as the method best suited for post-accident use. This method was selected primarily because of the need to analyze undiluted samples to meet the sensitivity required, and the subsequent radiological impact and chemical interferences associated with other methods.

The results of the evaluation and testing performed to qualify the ion chromatographic method are summarized below. The following methods were included in the evaluation:

Ion Chromatography

Selective Ion Electrode

Mercuric Nitrate Titration

Spectrophotometric Methods

Ion Chromatography is a powerful tool for the quantitative analysis of low ionic concentration solutions. The method, applicable to both anions and cations, is based on the elution selectivity of ion exchange media for different ionic species. Sample size, physical size of the ion exchange column, ionic capacity of the resin eluent concentration, and sample flowrate can all be held constant. The time after sample injection that a conductivity peak appears can be assigned to a specific ionic species. Ion chromatographs can be automated and can be operated remotely thus optimizing their use of in-line chloride analyses under post-accident conditions.

NUS testing was performed on a Dionex Model 10 ion chromatograph - the same model installed in the Sentry HRSS Chemical Analysis Panel. Testing was performed using post-accident matrix solutions containing various concentrations of chloride from 0.1 ppm to 20 ppm. The range of analyses can be extended with additional calibration curves and varying attenuation settings. The test results indicate the absolute mean bias for the ion chromatographic analysis of post-accident matrix samples is 7.6 percent for

chlorides in the range of 0.1 to 1 ppm and 5.8 percent for chlorides in the range of 1 to 10 ppm. The test results indicate the ion chromatographic method meets the range and accuracy requirements of the NRC post-implementation evaluation criteria guidelines.

Additional testing of the ion chromatographic method was conducted by NUS to determine if other contaminants, which could exist in the coolant through mixing with sump waters, would affect the chloride analysis. Contaminants tested included morpholine, hydrazine, ammonia, and natural and synthetic oils. No effects of morpholine, hydrazine, and ammonia were observed. Oil contamination increased the chloride results by about 10-30 percent. This result could be due to soluble chlorides present in the oils; however, this was not verified. Fouling of the resin columns was observed by progressive reduction on the time required for the appearance of the chloride peak. Approximately 10 to 15 oil contaminated samples could be analyzed under post-accident conditions without significant resin fouling. Details of the NUS development program and final verification testing are presented in Reference 1 and 2.

Dissolved Hydrogen

NUS reviewed various methods of measuring dissolved hydrogen concentration in reactor coolant and concluded in-line gas chromatographic techniques were best suited for post-accident applications. Hydrogen concentration in reactor coolant can be determined rapidly (20 to 30 minutes) and accurately by in-line gas chromatographic analyses using the Baseline 1030A which is installed in the HRSS chemistry analysis panel. The analytical sections of the gas chromatograph, installed in the rear of the Chemical Analysis Panel, employs a

dual column, thermal conductivity detector system to separate and measure hydrogen (as well as other gases). The controller for the gas chromatograph is installed in the Chemical Monitor Panel.

Hydrogen gas is initially stripped from a 30 ml coolant sample captured in an in-line sampling flask in the Liquid Sampling Panel. After collection of the liquid sample, hydrogen and other gases are stripped into a 300 cc evacuated flask. The stripped gas is routed to the Chemical Analysis Panel and to four 1 cc sampling loops of the gas chromatograph. Gas in the sampling loops is injected into the gas chromatograph by continuous flow of argon carrier gas. Residual water vapor is retained on the first column until the sample gases have eluted and then is back-flushed from the system.

Initial testing to establish optimum conditions was performed by NUS using a Fisher Model 1200 gas chromatograph. Both the Fisher and Baseline gas chromatograph have similar operating characteristics. Final calibration and identification testing was performed using a Baseline Model 1030A gas chromatograph as installed in the Sentry HRSS. The absolute mean deviation of results are 7.1 percent in a hydrogen range of 3.1 to 2.8 cc/kg at STP. The absolute mean deviation of results in the 21.7 to 186 cc/kg at STP was 8.8 percent. For the hydrogen range of 186 to 930 cc/kg at STP the absolute mean deviation was 7.6 percent. The absolute mean deviation was 2.8 percent in the hydrogen range of 930 to 1860 cc/kg at STP.

Based on the data, the Baseline gas chromatograph installed in the HRSS may be used to determine dissolved hydrogen concentration in the range of 3 to 2000 cc/kg at STP with an accuracy within the requirements of the NRC

post-implementation evaluation criteria guidelines. The accuracy statements apply to determinations made using separate calibration curves for each sample loop and for each of the four attenuation settings available. The operator must relate his determined peak height units to the calibration curve corresponding to the loop and attenuation scale used during the analysis.

Dissolved Oxygen

Since accurate dissolved oxygen results require analysis of undiluted samples with minimal exposure to air, in-line analyses methods must be performed.

NUS reviewed the capabilities of various in-line oxygen analyzers and concluded that two analyzers, a Yellow Springs Instrument analyzer and a Rexnord analyzer, were required to meet the objectives of providing monitoring capabilities under both normal plant operating conditions and post-accident conditions.

The Yellow Spring Instrument (YSI) Analyzer, while not as sensitive as the Rexnord analyzer, meets post-accident criteria. The YSI was selected for post-accident use because the response time of the probe was relatively short (i.e., 5 minutes) and the smaller probe holder volume would lower associated radiation levels. The Rexnord analyzer provides the sensitivity required during normal operating conditions. Preliminary testing to determine the effect of variable flow and high dissolved gases were performed. The conclusions drawn from this testing were:

1. The YSI Model 54 oxygen analyzer is relatively insensitive to flow rates from 58 ml/min to 547 ml/min.

2. Hydrogen in solution and microscopic bubbles of hydrogen in the water have no effect on oxygen readouts.

3. The YSI oxygen analyzer has adequate accuracy at 0.10 ppm oxygen.

Final verification testing was performed on both the YSI and Rexnord dissolved oxygen analysis systems as installed in the HRSS. Testing results in the YSI probe lead to the specified flow time of five minutes at 200 ml/min for obtaining probe equilibrium. Testing with the Rexnord probe indicated that 15 minutes was required to reach equilibrium.

Testing was performed using both a PWR and BWR post-accident matrix and comparing the dissolved oxygen concentration indicated by the probes with results obtained using the modified Winkler method. The absolute mean bias for YSI probe results on samples varying from 0.38 to 8.0 ppm dissolved oxygen was 8.2 percent. The mean absolute bias for the Rexnord probe was 5.7 percent on samples varying from 0.1 to 10 ppm oxygen.

Based on the final verification testing, the YSI probe can be used during post-accident conditions to determine dissolved oxygen concentrations with an accuracy of at least ± 10 percent in the test range of 0.1 to 10 ppm. The Rexnord probe data supports the value of ± 10 percent accuracy for dissolved oxygen in the test range of 0.1 to 20 ppm. Testing at oxygen concentrations up to 20 ppm were not performed, however, the linear response obtained indicates measurements at the higher concentration is achievable. This data indicate the requirements established by the NRC in the post implementation evaluation criteria guidelines can be met.

pH

pH analyses are performed in-line using a Cole-Parmer combination pH probe mounted within a probe holder. Calibration of the probe is conducted in-place using pH 7 and pH 4 or 10 buffer solutions. Readout indication is provided by a Beckman pH monitor mounted within the Chemical Monitor Panel.

During final verification testing, two calibration tests were performed. Initially a pH 7 buffer was flowed through the probe holder and the pH monitor adjusted to read 7.0. Then the probe was removed from the probe holder and immersed in a pH 10 buffer; the reading obtained was 9.8. The probe was rinsed and immersed in a pH 4 buffer and a reading of 3.8 obtained. The second calibration involved flowing calibration buffers of pH 7 and 10 from the calibration tanks. Readings of 9.7 were obtained for the pH 10 buffer.

Testing of the pH probe included flowing of PWR and BWR matrices through the Chemical Analyzer Panel, recording readings and comparing these readings with open grab sample measurements of the stream effluent. The data obtained indicates an absolute mean bias of ± 0.3 pH units over a pH range of 5 to 8.

Radiation Effects

A study made to determine the effect of radiation on equipment in the NUS analysis system indicates that the radiation levels anticipated will have no effect on accuracy of measurement and very little, if any, effect on operating lifetime of the individual components within the system. The study included a survey of personnel who have performed similar analysis under high radiation levels in hot cell conditions and a review of the literature concerning irradiation effects on materials of construction. In addition, laboratory experiments were performed to determine the effect of concentrations of

hydrogen peroxide on the conductivity of the reference solution. No effect was noted. The laboratory work was performed because there could be trace concentrations of peroxide in the coolant under zero or near zero hydrogen concentrations in the primary coolant.

In performing the survey, personnel were contacted at Battelle-Northwest and Oak Ridge Laboratories. In addition, a former employee of the naval test facility in Idaho was contacted concerning his hot cell experience with radiation chemistry at this location. Operational experience exists within the three laboratories concerning all phases of the analyses performed by the subject system. Results from these laboratories are consistent as all indicate the analytical measurements in question can be made at much higher radiation levels than will be experienced under post-accident conditions in the automated analysis system. One general conclusion that can be made from this survey, is that analytical instruments can be operated in a hot cell without loss of accuracy of results. There will be some reduction in operating lifetime of the system where continuing exposure at very high radiation levels is involved. Results of this survey as it applies to the individual analytical components within the system are discussed below:

a. Boron Determination

The Ionics DigiChem Analyzer, as modified by Sentry, performed properly at radiation levels of 8.64×10^4 R/hr. Its susceptibility to radiation damage and its accuracy when exposed to high radiation levels are summarized in the EPRI's report titled "An Evaluation of On-Line Boron Analyzers", NSAC/46, dated April 1, 1982 (Section 1 and 2).

b. Chloride Determination

Radiation levels for the chloride analysis equipment (ion chromatograph) will be lower than is the case for the other equipment in the analytical system. The reasons for this are as follows: (1) the maximum primary coolant volume contained within the ion chromatograph will be on the order of 1 ml, and (2) the system will be located further away from the radiation source than are other components in the system. Components in the ion chromatograph receiving relatively high radiation exposure include the following:

- Cation resin
- Anion resin
- Conductivity cell
- Transistors
- Capacitors
- Wire-wound pots
- Circuit board

No radiation damage is anticipated with resins based on experience developed at Battelle. Resins are conventionally used to separate various isotopes at Battelle without problems. Damage occurs after extended exposure; however, the degradation process is slow. Anion resin will start to degrade at about 10^8 rads and cation resins at 5×10^8 rads. This is several orders of magnitude higher than will be encountered for the resins in the ion chromatograph. It is anticipated that electronic components of the type included in the ion chromatograph will be resistant to cumulative exposure well above 10^5 rads.

In the absence of dissolved hydrogen, it is possible the primary coolant will contain low ppm concentrations of hydrogen peroxide from radiolysis of water. The effect of this peroxide on readout of the conductivity cell in the ion chromatograph was investigated by adding peroxide to a solution containing 2 ppm HCl and measuring conductivity before and after the addition of peroxide. The justification for using a 2 ppm HCl solution is noted below. Essentially no effect was observed on conductivity within the limits of the accuracy of the instrumentation.

Chloride determinations on an ion chromatograph are obtained by processing the water through resin columns and monitoring the conductivity of the effluent. The chloride (or other anions) will pass through the resin column in wave form at known time intervals after injection of the solution to be analyzed. Cations are removed by the suppressor column resulting in the formation of the corresponding acids from the anions in solution. Consequently, there will be a series of acids such as HCl, H₂SO₄ etc., passing through the conductivity cell in wave form, each at a different though known time interval, after the injection of the solution to be analyzed. Conductivity of the solution at a specific time interval is then related to acid concentration for the anionic species which passes through at that time.

Information developed in testing performed by NUS indicates that 5-10 ppm chloride in the sample size used will result in a maximum HCl concentration of about 2 ppm after it is separated in peaks as it passes through ion exchange columns in the ion chromatograph. The 2

ppm HCl concentration used in the peroxide test is based on the reasonable assumption that chloride level in the primary coolant will generally be below 10 ppm.

c. Dissolved Hydrogen

A review and evaluation of the components of the gas chromatograph i.e., molecular sieves, thermal conductivity cell, etc., indicates they are relatively insensitive to radiation damage. There are no radiation effects anticipated.

d. Dissolved Oxygen Determination

Readout equipment for this system is located remotely. The equipment exposed to radiationn contained in the oxygen and temperature detection probe includes the following:

- Gold cathode and silver anode
- Membrane made of 2 mil Teflon
- Electrolyte - saturated KCl
- Two metal oxide thermistors
- Connecting wires to anodes
- Synthetic rubber O-ring seals
- Stainless steel probe holder
- PVC block and Hysol Epoxy cement

The most sensitive component to radiation damage in the above list is the two-mil thick Teflon membrane. Unpublished data from Oak Ridge indicates that Teflon is resistant to radiation damage to about 10^6 rads. This data is supported by irradiation tests performed in

connection with the nuclear plane development effort. Results of this work indicate that high pressure (1400 psi) Teflon hoses would show incipient leakage at 10^6 rads exposure levels. Cumulative exposure levels for the Teflon membrane during post-accident conditions would be less than 10,000 rads. Thus, there is a safety factor of at least 100X associated with this component. It should be noted that the probe or the membrane itself can be easily replaced with very minimal exposure after the system is flushed, drained and blown dry.

The two anodes and stainless probe holder are not sensitive to radiation other than perhaps high-intensity neutron irradiation. There will be no neutrons present in the analytical system. The two metal-oxide thermistors are not expected to be affected by radiation; however, no problem would result if damage occurred. The temperature indication provided by the thermistors is not a critical measurement.

No radiation damage is anticipated to the PVC block below 10^6 rads based on data concerning the general resistance of organics to radiation. The Hysol epoxy cement is stable to radiation at exposure levels to 10^7 rads. Concerning other components (O-ring seals, insulation), the cumulative exposure levels anticipated are far below the area where damage will occur.

e. pH Determinations

Readout equipment for this system is located remotely. The equipment exposed to radiation includes the following:

Glass pH probe - Gel type with internal reference cell
Connecting wires to probe
Synthetic rubber O-ring seals
Stainless steel probe holder

Experimental work reported in literature indicates that pH electrodes of the type used in this system are stable at cumulative dosages up to $10^7 - 10^8$ rads. These results are in agreement with data presented in other references and experience reported by Battelle and the naval test facility in Idaho. Concerning selective ion electrodes, it was observed that the potential response of a fluoride electrode shifted with time at very high cumulative exposures; however, the affected electrode did not lose its effectiveness as long as calibrations were made periodically with standard solutions. A nitrate electrode began to give erratic readings as the cumulative dose approached 10^7 rad.

Cumulative exposure levels to the pH probe in the automated analysis panel during post-accident conditions will be less than 10,000 rads. Thus, there is a factor of at least 1000X below the point where incipient radiation damage can be anticipated. It is worthy to note that the data reported in the literature indicate that valid pH readings can be obtained even where a radiation effect was noted provided that the system is calibrated periodically. Operating instructions to be included with the automated analysis equipment will specify daily calibration when the system is in regular use.

Calibration prior to use will be specified for intermittent operation. Other components within the pH probe assembly will not be affected by the radiation exposure levels involved.

f. Pressure Indicator

A pressure transducer incorporating a strain gauge is used to sense pressure and transmit this pressure to the readout equipment which is located remotely. Only the transducer is exposed to radiation. This contains the following material:

Diaphragm made of 17-4 pH stainless steel

A strain gauge made of silicon doped with phosphorous

Synthetic rubber O-ring seal

Circuit board with resistors, capacitors and transistors

Die-cast aluminum housing for electronic components

Insulation on lead-in wire

The most sensitive component to radiation damage in the pressure transducer is probably the transistors. These should be resistant to cumulative exposure above 10^5 rads based on data presented in the literature. Maximum cumulative exposure for the transistors will be below 10,000 rads. There are no data available concerning radiation resistance of the strain gauge. Principle of operation for a strain gauge involves a change in resistivity that is proportional to the deflection in the gauge. It is very unlikely that resistivity of an

element will be affected by radiation exposures that will be experienced in the pressure-transducer driving a post-accident condition.

All other components in the pressure transducer can withstand cumulative exposure on the order of 10^6 rads or more.

Operation of the pressure indicator is not required for any of the post-accident analyses performed with the NUS system. The pressure indicator is included so that operating personnel can maintain a back-pressure of 40-50 psi or more in the system by suitable adjustment of the throttling valve. Back-pressure is required to keep dissolved gases in solution. Adjustment of the throttling valve to control back-pressure will be made during calibration of the system performed during normal power operations. Flow adjustment will be required only infrequently since inlet pressure will be relatively constant at about 60 psi. In the event that there was a significant change in pressure and the transducer failed, the change in pressure would be manifest by a change in flow rate. There can be no buildup of excess pressure since the system is pressure relief valve protected with valves in the Sentry system.

g. Valves

All valves use Teflon packing. The use of Teflon packing is specified because of its good sealing characteristics. Oak Ridge prefers Teflon-packed valves for handling radioactive solutions

containing high levels of radioactive iodine. Some radiation damage to the Teflon may be anticipated at 10^6 rads cumulative exposure; however, it is unlikely these valves will ever have 10,000 rads exposure. It is recognized that there are packing materials available that are more resistant to radiation than is Teflon. These were not specified because the primary concern is to maintain leak-tightness.

TABLE 5

ANALYSIS	REQUIREMENT		Method Selected	RESPONSE		
	Range	Accuracy		Range	Accuracy	Testing Method
Boron	0-2000 (PWR) 0-6000 (BWR)	+5% > 1000 ppm +50 ppm < 1000 ppm	Diluted Grab Sample Using Fluoroborate S.I.E.	500-6000 (1)	3.0% B >2000 ppm (2)(3) 10% B < 500 ppm	matrix
Chloride	0-20 ppm	+10% 0.5-20 ppm +0.05 ppm < 0.5 ppm	Ion Chromatography	0.1-20 5.8% 1-20 ppm	7.6% 0.1-1 ppm(3)	matrix
Hydrogen	0-2000 cm ³ /kg	+10% 50-2000 cc/kg +5 cc/kg < 50 cc/kg	Gas Chromatography	0.5-2000 cc/kg	7.1% 3.1-28 cc/kg 8.8% 267-186 cc/kg 7.6% 186-930 cc/kg 2.8% 930-1860 cc/kg	non-matrix
Oxygen	0-20 ppm	+10% > 0.5 ppm +0.05 ppm < 0.5 ppm	YSI in-line probe Rexnord in-line probe (4)	0.1-20 ppm	8.2% 0.38-8.0 ppm 5.7% 0.1-10 ppm	matrix
pH	1-13	+0.3 pH > 5 < 9 +0.5 pH < 5 > 9	in-line probe	1-13	0.3 -5.0 < pH < 8.0	matrix

- (1) The range is based on a 1 to 1000 dilution if the applicable range can be lowered by utilizing a small dilution, i.e., 1 to 100 dilution lowers the range to 50 ppm.
- (2) The accuracy stated is achievable if a boron standard is run immediately before the analysis and if the pH meter readout is adjusted to the correct response based on the calibration curve.
- (3) % error is the mean absolute bias
- (4) The Rexnord probe for routine (non-accident use) is installed parallel to the YSI probe.

REFERENCES

1. High Radiation Sampling System Operating and Maintenance Manual, Document 150-11-010, May 1981, Prepared for Sentry Equipment Corporation.
2. NUS Report R-27-3-1-1A "An Evaluation of the Baseline System for Determination of Total Gas Concentration During Normal or Post-Accident Conditions," Prepared for Commonwealth Edison Company, Chicago, Illinois, May 1981.
3. NUS Report R-27-4-1-1 "Development of Procedures and Analysis Methods for Post-Accident Reactor Coolant Samples," Prepared for Sentry Equipment Corporation, Oconomowoc, Wisconsin, April 1981.
4. NUS Report R-27-11-3 "Final Verification Testing of HRSS Chemical Analysis Panel," Prepared for Sentry Equipment Corporation, Oconomowoc, Wisconsin, November 1981.