

NUREG/CR-5365  
ORNL/TM-11168

---

# Iodine Speciation and Partitioning in PWR Steam Generator Accidents

Final Report

---

Prepared by E. C. Beahm, S. R. Daish, J. Hopenfeld,  
W. E. Shockley, P. Voillezue

Oak Ridge National Laboratory

Prepared for  
U.S. Nuclear Regulatory Commission

8911020276 e91031  
PDR NUREG  
CR-5365 R PDR

## AVAILABILITY NOTICE

### Availability of Reference Materials Cited in NRC Publications

Most documents cited in NRC publications will be available from one of the following sources:

1. The NRC Public Document Room, 2120 L Street, NW, Lower Level, Washington, DC 20555
2. The Superintendent of Documents, U.S. Government Printing Office, P.O. Box 37082, Washington, DC 20513-7082
3. The National Technical Information Service, Springfield, VA 22161

Although the listing that follows represents the majority of documents cited in NRC publications, it is not intended to be exhaustive.

Referenced documents available for inspection and copying for a fee from the NRC Public Document Room include NRC correspondence and internal NRC memoranda; NRC Office of Inspection and Enforcement bulletins, circulars, information notices, inspection and investigation notices; Licensee Event Reports; vendor reports and correspondence; Commission papers; and applicant and licensee documents and correspondence.

The following documents in the NUREG series are available for purchase from the GPO Sales Program: formal NRC staff and contractor reports, NRC-sponsored conference proceedings, and NRC booklets and brochures. Also available are Regulatory Guides, NRC regulations in the *Code of Federal Regulations*, and *Nuclear Regulatory Commission Issuances*.

Documents available from the National Technical Information Service include NUREG series reports and technical reports prepared by other federal agencies and reports prepared by the Atomic Energy Commission, forerunner agency to the Nuclear Regulatory Commission.

Documents available from public and special technical libraries include all open literature items, such as books, journal and periodical articles, and transactions. *Federal Register* notices, federal and state legislation, and congressional reports can usually be obtained from these libraries.

Documents such as theses, dissertations, foreign reports and translations, and non-NRC conference proceedings are available for purchase from the organization sponsoring the publication cited.

Single copies of NRC draft reports are available free, to the extent of supply, upon written request to the Office of Information Resources Management, Distribution Section, U.S. Nuclear Regulatory Commission, Washington, DC 20555.

Copies of industry codes and standards used in a substantive manner in the NRC regulatory process are maintained at the NRC Library, 7020 Norfolk Avenue, Bethesda, Maryland, and are available there for reference use by the public. Codes and standards are usually copyrighted and may be purchased from the originating organization or, if they are American National Standards, from the American National Standards Institute, 1430 Broadway, New York, NY 10018.

## DISCLAIMER NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability of responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

---

---

# Iodine Speciation and Partitioning in PWR Steam Generator Accidents

Final Report

---

---

Manuscript Completed: May 1989  
Date Published: October 1989

Prepared by  
E. C. Beahm, S. R. Daish,<sup>1</sup> J. Hopenfeld,<sup>2</sup>  
W. E. Shockley, P. Voilleque<sup>3</sup>

Oak Ridge National Laboratory  
Operated by Martin Marietta Energy Systems, Inc.

Oak Ridge National Laboratory  
Oak Ridge, TN 37831

<sup>1</sup>Visiting Scientist From AERE Harwell, England

<sup>2</sup>U.S. Nuclear Regulatory Commission

<sup>3</sup>Science Applications International Corporation

Prepared for  
Division of Safety Issue Resolution  
Office of Nuclear Regulatory Research  
U.S. Nuclear Regulatory Commission  
Washington, DC 20555  
NR-ENR B0453  
Under Contract No. DE-AC05-84OR21400



### ABSTRACT

Measurements of iodine speciation in aqueous solution at 285°C and 1000 psig show a higher percentage as I<sub>2</sub> in solutions at tracer concentrations than at higher concentrations. A 1 × 10<sup>-9</sup> M I<sup>-</sup> solution resulted in 2% I<sub>2</sub> whereas a 1 × 10<sup>-4</sup> M I<sup>-</sup> solution had only 0.1% I<sub>2</sub>. Tests of primary coolant from operating reactors had a peak in percent I<sub>2</sub> at shutdown, with an increase in volatile species up to 20% of the total iodine. During normal power operation, primary coolant percent I<sub>2</sub> was generally lower than the detection limit.



## CONTENTS

ABSTRACT . . . . .	iii
FOREWORD . . . . .	vii
LIST OF FIGURES . . . . .	ix
LIST OF TABLES . . . . .	xi
EXECUTIVE SUMMARY . . . . .	xiii
PART 1: MEASUREMENTS OF RADIOIODINE SPECIES IN SAMPLES OF PRESSURIZED WATER REACTOR COOLANT . . . . .	1
1. INTRODUCTION . . . . .	1
2. ANALYTICAL METHODS . . . . .	2
3. RESULTS . . . . .	3
3.1 PLANT OPERATING CONDITIONS . . . . .	3
3.2 DATA FOR RADIOIODINES . . . . .	4
4. DISCUSSION . . . . .	22
5. CONCLUSIONS . . . . .	31
6. ACKNOWLEDGMENTS . . . . .	31
7. REFERENCES . . . . .	31
APPENDIX A. TABULATION OF PLANT MEASUREMENT DATA . . . . .	33
PART 2: IODINE PARTITIONING IN PRESSURIZED WATER REACTOR STEAM GENERATOR ACCIDENTS . . . . .	47
1. INTRODUCTION . . . . .	47
1.1 BACKGROUND . . . . .	47
1.2 BEHAVIOR AT LOW AQUEOUS CONCENTRATIONS . . . . .	48
2. EXPERIMENTAL PROCEDURE . . . . .	49
2.1 SIMULATED STEAM GENERATOR TESTS . . . . .	49
3. EXPERIMENTAL RESULTS . . . . .	52
3.1 LABORATORY TESTS . . . . .	52
3.1.1 Partition Coefficient . . . . .	52
3.1.2 Adsorption of Iodine from Solution . . . . .	54
4. DISCUSSION . . . . .	55
4.1 FORMATION OF I <sub>2</sub> AT TRACE CONCENTRATIONS . . . . .	55
4.2 HI AS A SOURCE OF IODINE VOLATILITY . . . . .	57
4.3 INTERRELATION OF PRIMARY COOLANT TESTS AND SIMULATED TESTS . . . . .	58
5. CONCLUSION . . . . .	59
6. REFERENCES . . . . .	60

## FOREWORD

The evaluation of iodine behavior in steam generator tube rupture accidents in pressurized water reactors requires information on both iodine speciation and on iodine partitioning between aqueous solution and the gas phase. This work was carried out in two experimental programs: (1) Measurements of Iodine Speciation in the Primary Coolant of Two Nuclear Power Plants and (2) Studies in a Pressure Vessel System to Measure Iodine Partitioning and Iodine Speciation as a Function of pH and Oxygen Environment.

Results of these experimental programs are described in the two parts of this report. Both parts are presented in form and content as virtually stand-alone documents. The final sections of Part 2 provide a correlation of the two methodologies.

# LIST OF FIGURES

## Part I

<u>Number</u>		<u>Page</u>
1	Power level changes with time near shutdown (time = 0) at the two PWRs studied . . . . .	5
2	Changes in hydrogen ( $H_2$ ) concentration in reactor coolant as a function of time near shutdown (time = 0) at the two PWRs . . . . .	6
3	Changes in reactor coolant temperature and pressure with time near shutdown (time = 0) at Plant 1 . . . . .	7
4	Changes in reactor coolant temperature and pressure with time near shutdown (time = 0) at Plant 2 . . . . .	8
5	Changes in boron concentration and pH of the reactor coolant at Plant 1 . . . . .	9
6	Changes in boron concentration and pH of the reactor coolant at Plant 2 . . . . .	10
7	Measured concentration of $^{131}I$ in reactor coolant near the time of shutdown (time = 0) at the two PWRs . . . . .	11
8	Measured concentrations of $^{132}I$ , $^{133}I$ , and $^{135}I$ in reactor coolant near the time of shutdown (time = 0) at Plant 2 . . . . .	13
9	Measured elemental iodine fractions (F3) for $^{131}I$ in reactor coolant near the time of shutdown (time = 0) at the two PWRs (open points indicate values below detection limit) . . . . .	20
10	Measured iodate/periodate fractions (F2) for $^{131}I$ in reactor coolant near the time of shutdown (time = 0) at the two PWRs (open points indicate values below detection limit) . . . . .	21
11	Simple model of radioiodine transport from fuel pellets to reactor coolant . . . . .	23



Number

Page

12	Calculated average inputs of radioiodine isotopes to reactor coolant at Plant 2. Upper plot contains data for $^{131}\text{I}$ (solid points) and $^{132}\text{I}$ (open points); lower plot contains data for $^{133}\text{I}$ (solid points) and $^{135}\text{I}$ (open points) . . . . .	26
13	Product of thyroid risk-weighted radioiodine concentration (CV*) and coolant pressure ratio (PR) computed using data from Plant 2 . . . . .	30

Part 2

1	Experimental system for investigating iodine transport from a simulated steam generator . . . . .	50
---	---	----

# LIST OF TABLES

## Part 1

<u>Number</u>		<u>Page</u>
1	Total coolant concentrations and radioiodine distribution fractions for Plant 1 . . . . .	14
2	Total coolant concentrations and radioiodine distribution fractions for Plant 2 . . . . .	17
3	Summary of radioiodine spiking data for Plant 2 . . . . .	27
A1	Radioiodine concentrations measured at Plant 1 . . . . .	34
A2	Radioiodine concentrations measured at Plant 2 . . . . .	38
A3	Reactor power level data . . . . .	41
A4	Reactor coolant pressure data . . . . .	42
A5	Reactor coolant temperature data . . . . .	43
A6	Boron concentrations in reactor coolant . . . . .	44
A7	Hydrogen concentrations in reactor coolant . . . . .	45
A8	pH of reactor coolant . . . . .	46

## Part 2

1	Iodine extraction of feed solution at pH 5, 7, and 9 from $\sim 1 \times 10^{-9} \text{ M I}^-$ solutions in $0.2 \text{ M H}_3\text{BO}_3$ . . . . .	51
2	Summary of results from steam generator iodine experiments 285°C, 1000 psi, $0.2 \text{ M}$ borate, $1.0\text{E-}9 \text{ M I}^-$ . . . . .	53
3	Distribution coefficients for the adsorption of iodine on stainless steel pressure vessel walls . . . . .	55

## EXECUTIVE SUMMARY

The evaluation of iodine behavior in steam generator tube rupture (SGTR) accidents in pressurized water reactors (PWRs) requires information on both iodine speciation and on iodine partitioning between aqueous solution and the gas phase. This work was carried out in two experimental programs: (1) Measurements of Iodine Speciation in the Primary Coolant of Two Nuclear Reactor Plants and (2) Studies in a Pressure Vessel to Measure Iodine Partitioning and Iodine Speciation as a Function of pH and Oxygen Environment.

Results of these experimental programs are described in the two parts of this report.

Part 1. Samples of primary coolant at two PWRs in the United States have been collected and analyzed to determine the fraction of the radioiodine present in volatile forms. The volatile species,  $I_2$  and organic iodides, would be available for prompt release following an SGTR accident which overpressurizes the secondary coolant system and causes a venting to the atmosphere. Coolant samples were collected at full power, during power reduction at the start of an outage, and up to 48 h after shutdown at two PWRs.

During temperature reduction and depressurization, the release rates of radioiodines from the plenums of the fuel rods to the coolant are elevated and a spike in the concentration of radioiodine in the coolant is observed. A significant fraction of the radioiodine injected into the coolant from the fuel rod plenums appears to be in the form of elemental iodine. About 20% of the total radioiodine was found to be  $I_2$  in samples of coolant collected near the time of shutdown. Boration (and acidification) of the coolant using boric acid did not cause an increase in the elemental iodine fraction. Volatile iodine fractions of about 30 to 40% were found at later times (about +35 h) at both plants.

Part 2. Measurements of iodine speciation in aqueous solution at 285°C and 1000 psig show a higher percentage as  $I_2$  in solutions at trace concentrations than at higher concentrations. A  $1 \times 10^{-9} \text{ M } I^-$  solution resulted in 2%  $I_2$  whereas a  $1 \times 10^{-4} \text{ M } I^-$  solution had only 0.1%  $I_2$ .

In Part 1 of this report, the maxima in percent iodine as  $I_2$  for  $^{131}I$  at times near shutdown was given as 20.9% at Plant 1 and 16.5% at Plant 2. Using an estimated partition coefficient (PC) for  $I_2$ , we calculate iodine PCs on a concentration basis of  $102 \pm 72$  and  $152 \pm 91$  at the maximum  $I_2$  percentage at Plant 1 and Plant 2, respectively. These calculated values may be compared to a test in the simulated steam generator experiments where 22% as  $I_2$  resulted in a measured PC of 350.

Further calculations indicate that an  $I_2$  percentage of  $<1.25 \pm 0.75$  is necessary if one desires to have an iodine PC, on a concentration basis, of  $>2000$ , which is the minimum allowable limit from document 10 CFR 100.



**PART 1: MEASUREMENTS OF RADIOIODINE SPECIES IN SAMPLES  
OF PRESSURIZED WATER REACTOR COOLANT**

Paul G. Voillequé  
Utility Services Operation  
Science Applications International Corporation  
101 South Park Avenue  
Idaho Falls, Idaho 83402

**1. INTRODUCTION**

One of the design basis accidents for a pressurized water reactor (PWR) is the rupture of a steam generator tube. This failure releases primary coolant at high temperature and pressure and the associated radioactivity into the secondary coolant system. Some activity will be released to the environment via the condenser off-gas system. Larger releases of radioactivity will occur if the secondary system is over-pressurized and the relief valves open. The magnitude of the resulting thyroid dose to persons off-site depends, in part, on the amount of volatile radioiodine in the primary coolant. Iodine present as  $I_2$  or organic iodides is more available for prompt release following initiation of a tube rupture accident. The purpose of this work was to measure the volatile fraction of radioiodine isotopes present in primary coolant of PWRs.

Previous measurement results exhibited variability but indicated that the volatile species fraction (FV, the sum of the concentrations of  $I_2$  and organic iodides divided by total iodine concentration) could be large. Measurements at five nuclear power stations, which were reported by Martucci,<sup>1</sup> showed values of FV ranging from <0.9% at two plants to about 20% at the other three plants. At two plants, the principal volatile iodine species was elemental iodine. Those measurements showed about 70%  $I_2$ ; at the third plant, only 10% was in elemental form. The boron, hydrogen, and lithium concentrations in the coolant were documented at the five plants. The measured concentrations of  $H_2$  ranged from 19 to 45  $cm^3/kg$ ; the values of FV were not correlated with the measured values of  $[H_2]$ . The coolant boron and lithium levels ranged from about 200 to 1000 ppm and 0.09 to 1.8 ppm, respectively; neither variable was correlated with FV. Power levels and operating histories of the plants where measurements were made were not given.

Results of a time sequence of measurements of the volatile radioiodine fraction in coolant samples collected prior to and during the course of a shutdown were reported by Mandler et al.<sup>2</sup> Fourteen samples were collected during a period beginning about 30 h prior to reactor trip and extending to about 50 h after the trip. At about 7 h after shutdown, the volatile iodine fraction was 37% of the total  $^{131}I$  in primary coolant. The increase in FV (from <1% prior to shutdown) appeared to be correlated with additions to the coolant from the borated water storage tank (BWST). The boration process also lowered the pH from 9.1 to 5.8. A second increase in FV from about 2% to nearly 10% followed the addition of hydrogen peroxide to the coolant. Separation

of the volatile fraction into  $I_2$  and organic iodides was performed on only one sample; iodide and iodate fractions were determined for each sample.

Both of the studies cited above support a need for additional measurements. In the first case, there is a need to understand the reason(s) for the order-of-magnitude differences among the measured values of FV at different plants. The second study identified potential changes in FV, apparently due to changes in operation conditions, which could be important in the event of an accident. Oxygenated fluid, like that from the BWST, could be added to the primary system to replace coolant lost due to leakage during a steam generator tube rupture (SGTR) accident.

The measurements reported here were performed to obtain additional data on the forms of radioiodine in coolant at operating PWRs. In addition, collection of other information on the status of the primary system (measurements made by the plant operator) was given priority. Those data provide a basis for assessing the effects of operational changes on the iodine species distributions. The methods used for coolant sample collection and analysis are described in Sect. 2. The results of the coolant radioiodine species measurements are presented in Sect. 3. Also discussed in that section are the data on other plant variables obtained from the participating utilities. Data interpretation and discussion are presented in Sect. 4. Section 5 contains the conclusions drawn from the measurements and analyses. The Appendix contains the radioiodine results and uncertainties, as well as compilations of measurements obtained from plant personnel.

The fractional amounts of the radioiodine forms in coolant samples are described using the following symbols: F1 refers to the iodide form, F2 refers to iodates and periodates, F3 refers to elemental iodine, and F4 refers to the organic iodides. In each case, the fraction is that part of the total  $^{131}I$  (or other iodine isotope) activity present in the specified form at the time of sampling. The procedure used to achieve separation of these four components is described below.

## 2. ANALYTICAL METHODS

Primary coolant samples, obtained by utility personnel using the normal reactor coolant sampling line, were delivered to the radiochemistry laboratory area for processing. Coolant samples were withdrawn from the letdown line upstream of the coolant filtration and ion-exchange beds. Prior to sample collection, the sampling line was flushed to assure that fresh coolant was obtained. The time between collection and the first separation averaged 26 min. Most (72%) of the samples were delivered in 25 min or less. A delay of more than 40 min was experienced for three coolant samples.

After receipt, the samples were subjected to a series of chemical separation steps. First, the carrier-free 50-mL coolant sample was contacted with an equal volume of  $CCl_4$ , in which the volatile species



are soluble. Then, the elemental iodine fraction was back-extracted from the  $\text{CCl}_4$  phase into thiosulfate solution containing iodide carrier. The  $\text{CCl}_4$  phase and the thiosulfate solution were counted to determine the organic iodine (Fraction #4) and elemental iodine (Fraction #3) activities, respectively. The aqueous phase from the first separation was contacted with 50 ml of  $\text{CCl}_4$  containing 3 g/L of dissolved  $\text{I}_2$ . The iodide fraction (Fraction #1) exchanges with the elemental iodine in the  $\text{CCl}_4$ ; the iodate and periodate activity (Fraction #2) remains in the aqueous phase. These fractions were counted to determine the radioiodine activities present in those forms. This chemical separation technique was basically the same as that employed in Refs. 1 and 2 and is based on procedures developed by Castleman et al.<sup>3</sup> and, subsequently, by Lin.<sup>4</sup>

Each of the four separated fractions was counted using a calibrated gamma spectrometry system with a high-resolution solid-state detector. The counting system was transported to each plant and set up near the radiochemical separation work area to provide rapid counting capability for the samples and to assure the detection of short-lived radioiodines ( $^{132}\text{I}$ ,  $^{134}\text{I}$ , and  $^{135}\text{I}$ ).

The detector calibration technique for extended samples was developed by Cline;<sup>5</sup> it employs sources traceable to the National Institute of Standards and Technology. Counting times were necessarily limited to about 1000 s because of the large number of analyses required in a relatively short time. Under these conditions, a typical minimum detection limit was about 0.2 nCi/g (corrected to the time of sampling). However, as shown in Tables A1 and A2 of the Appendix, both lower and higher values were achieved for some individual samples. Corrections were made for radioactive decay between sampling and analysis for all counting results, but were only important for the very short-lived radioiodines.

### 3. RESULTS

Measurements of radioiodine concentrations and chemical forms in coolant were performed at two PWRs in the United States. To understand the results, the radioiodine data must be examined in the context of other plant parameters. The plant operating conditions affect radioiodine levels in the coolant and the potential for subsequent release to the environment. For this reason, the data describing plant conditions are presented in the first subsection and the radioiodine data follow in Sect. 3.2.

#### 3.1 PLANT OPERATING CONDITIONS

Each set of measurements was organized around a scheduled plant shut-down which was defined to occur at  $t = 0$  h. Coolant samples were collected and analyzed according to the protocol described above from about -35 h to +48 h at Plant 1 and from about -19 h to +38 h at Plant 2. During these intervals, the plant staff were also making measurements for their own purposes. Data on the pH of the coolant and the  $\text{H}_2$  and boron concentrations in coolant were obtained from the staff.



Also provided to us were records containing data on thermal power level and primary coolant temperature and pressure at various times during the period of interest. Tabulations of the data collected on plant operating conditions are contained in the Appendix to this report.

Reduction in reactor power level began several hours before shutdown at both plants; the rate of decrease was 10 to 15% per hour (see Fig. 1). Power reduction was preceded by degassing of the primary system, which reduced the  $H_2$  concentration from the normal operating level of about  $35 \text{ cm}^3/\text{kg}$  to  $<10 \text{ cm}^3/\text{kg}$ . Figure 2 shows the concentrations of  $H_2$  measured in reactor coolant at both plants. After shutdown, the coolant temperature was reduced from the normal range of 270 to 290°C to about 90°C by +20 h. Figure 3 shows the coolant temperature and pressure data for Plant 1. The reactor coolant temperature at Plant 1 was held at the operating value until about +10 h. Pressure reduction at Plant 1 was also delayed, although this is not shown in the pressure data provided to GPO. Somewhat more detailed data were obtained for Plant 2 and are presented in Fig. 4. At that plant, pressure reduction began soon after shutdown and was accomplished in two steps. Normal operating pressure was about 15 MPa (2250 psi). At +15 h, the pressure had been reduced to about 12 MPa (1700 psi), and the second reduction to about 1 MPa (150 psi) occurred between +20 h and +22 h.

Boration of the primary coolant was accomplished by addition of boric acid at both plants, but the times of boration differed. Figure 5 shows the boron concentration and pH measurement results for Plant 1. The first measurements of boron concentration and pH after shutdown show that boration was delayed until the pressure and temperature reductions began. Then the concentration was raised from 1 to about 510 ppm. The pH changed from 8.8 to 6.3. At Plant 2, the boric acid addition occurred promptly after shutdown and the boron concentration was increased from about 70 ppm to 750 ppm by +2 h (Fig. 6). The pH decreased from 7.5 during operation to about 6.6 at +22 h.

At Plant 1, hydrogen peroxide was added to the coolant at +41 h. This practice is followed at some PWRs to increase the solubility of radioactive corrosion products in coolant and then to remove them before the clean-up system is shut down.<sup>6</sup> No peroxide was added to the coolant at Plant 2.

### 3.2 DATA FOR RADIOIODINES

The measured concentrations of  $^{131}\text{I}$  in reactor coolant at the two plants are shown in Fig. 7. The maximum concentration at Plant 1 was observed at +21 h. It is likely that an initial peak (before +10 h) was missed. At Plant 2, the concentration peaked at +6 h. Because the concentrations of  $^{131}\text{I}$  in coolant at Plant 1 were rather low, more of the counting results for separated fractions were less than the detection limit. Typical counting uncertainties for  $^{131}\text{I}$  at Plant 1 were 15 to 25% before shutdown and 5 to 10% afterwards. At Plant 2, counting uncertainties for  $^{131}\text{I}$  were 5 to 10% before shutdown and only 2 to 4%

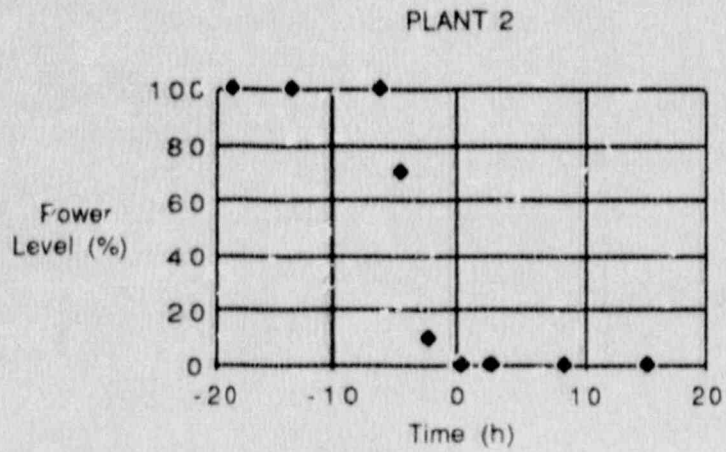
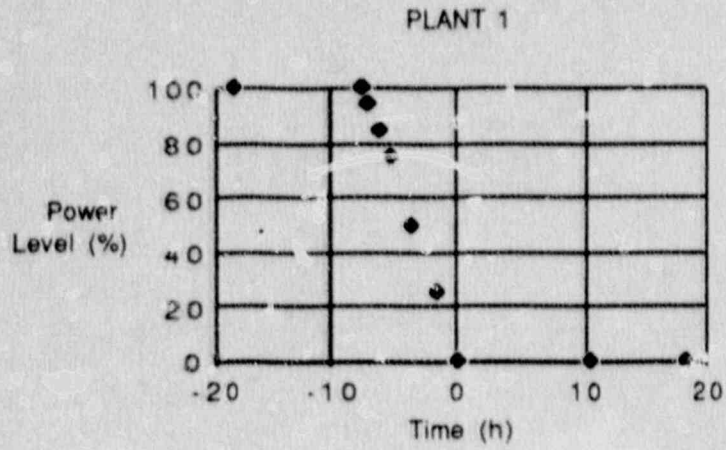


Fig. 1. Power level changes with time near shutdown (time = 0) at the two PWRs studied.

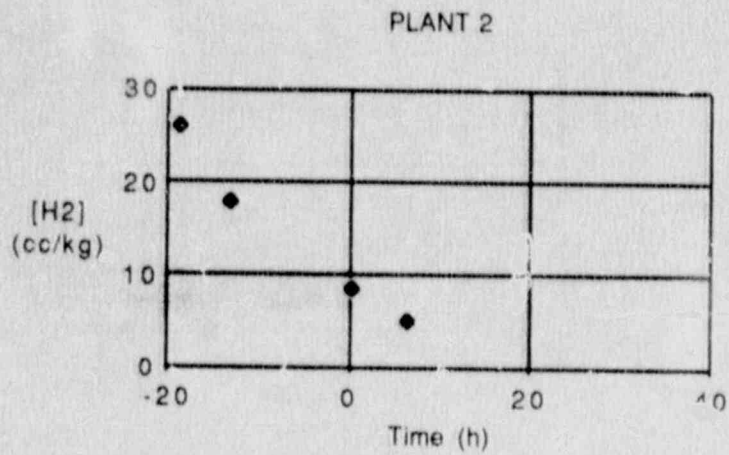
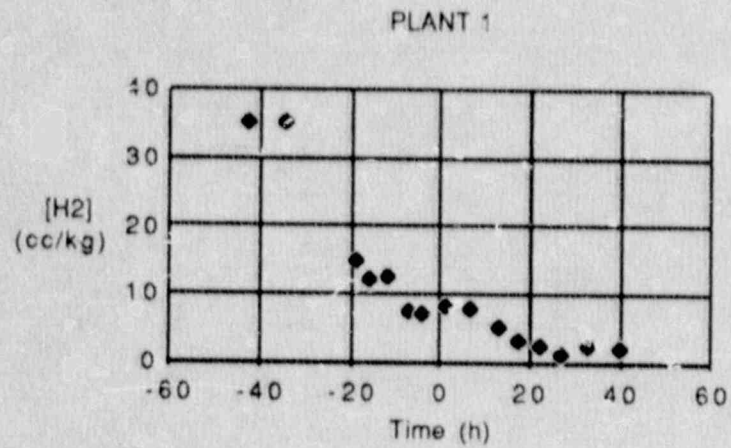


Fig. 2. Changes in hydrogen ( $H_2$ ) concentration in reactor coolant as a function of time near shutdown (time = 0) at the two PWRs.



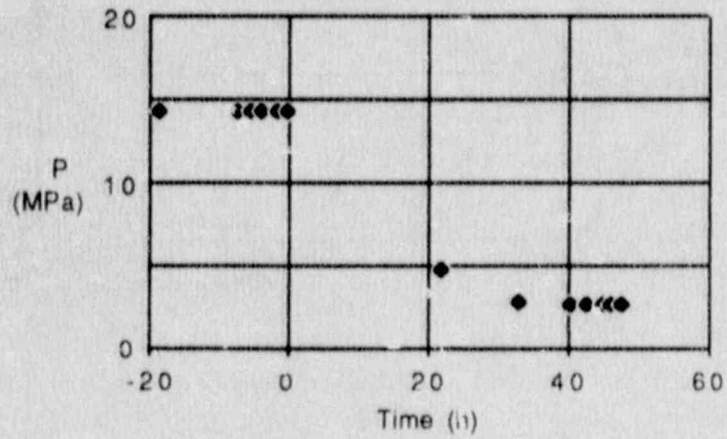
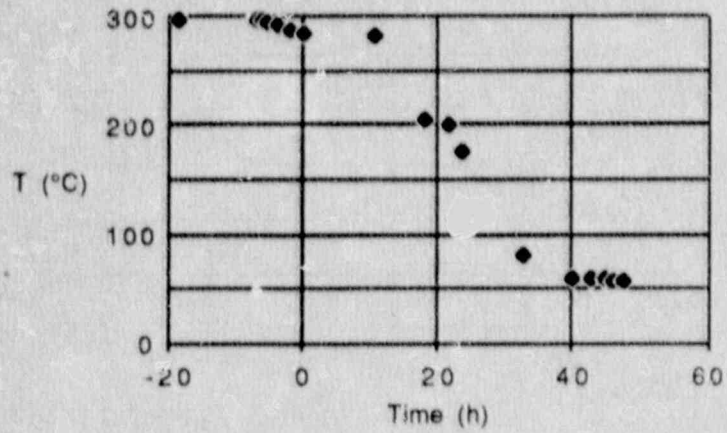


Fig. 3. Changes in reactor coolant temperature and pressure with time near shutdown (time = 0) at Plant 1.

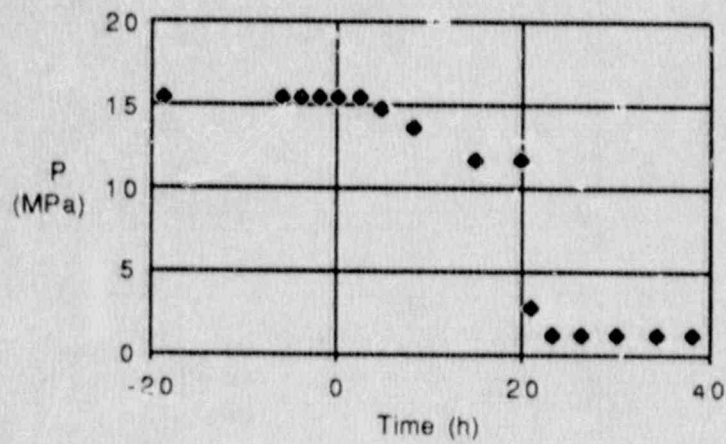
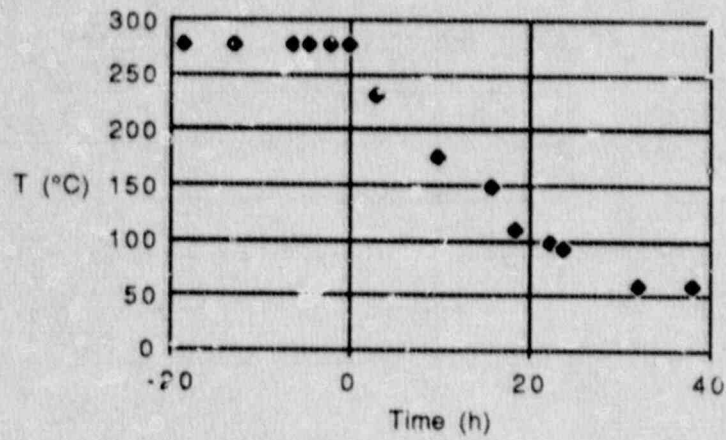


Fig. 4. Changes in reactor coolant temperature and pressure with time near shutdown (time = 0) at Plant 2.

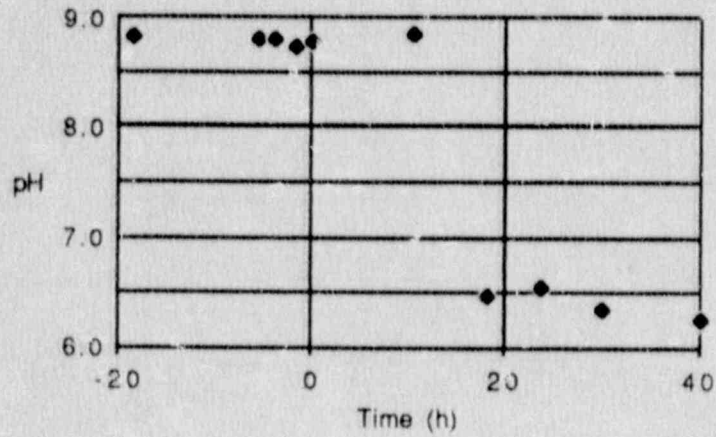
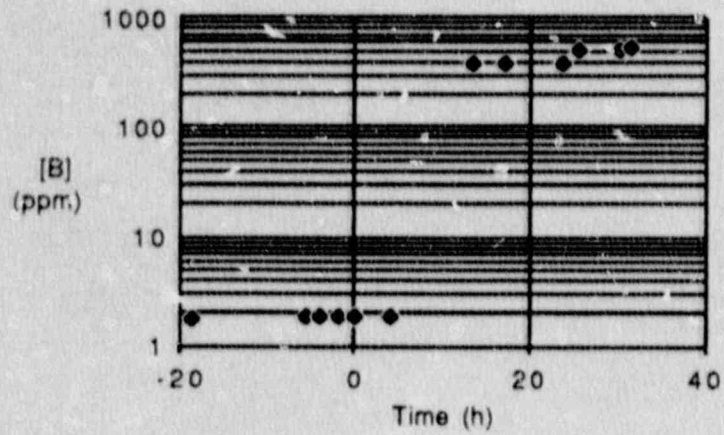


Fig. 5. Changes in boron concentration and pH of the reactor coolant at Plant 1.



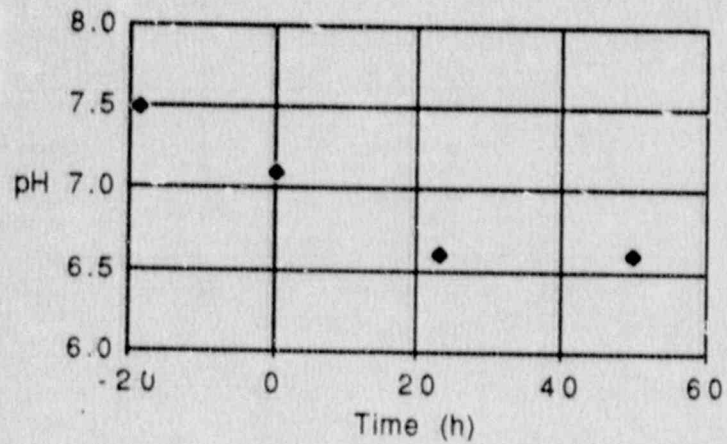
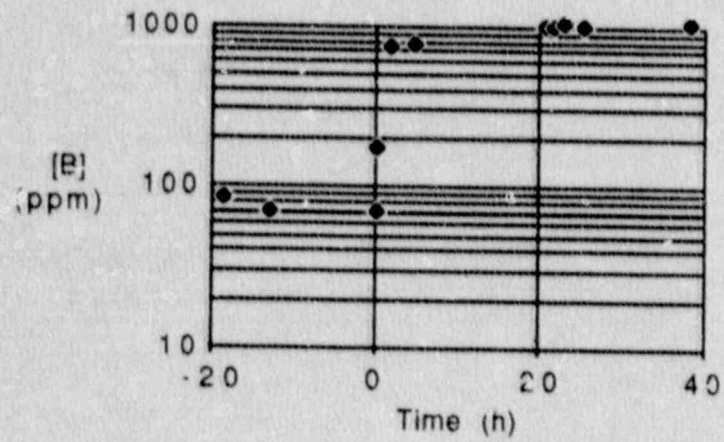


Fig. 6. Changes in boron concentration and pH of the reactor coolant at Plant 2.

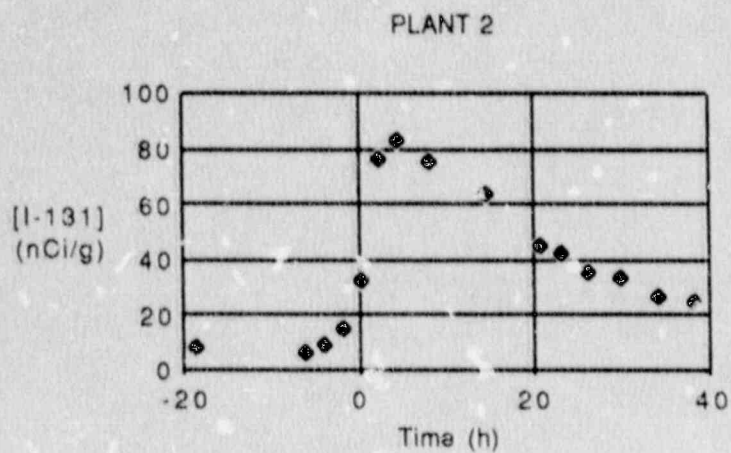
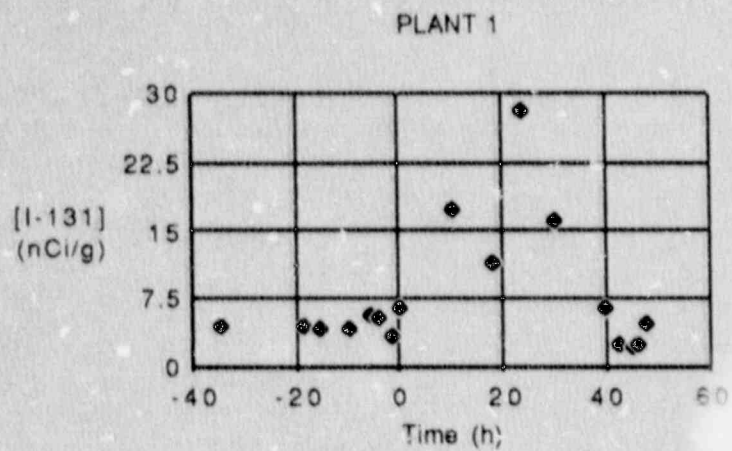


Fig. 7. Measured concentration of  $^{131}\text{I}$  in reactor coolant near the time of shutdown (time = 0) at the two PWRs.

for later samples. Uncertainties for each sample are shown in Tables A1 and A2 in the Appendix.

Figure 8 shows the behavior of the  $^{132}\text{I}$ ,  $^{133}\text{I}$ , and  $^{135}\text{I}$  concentrations in coolant near the time of shutdown of Plant 2. Sharp increases, or "spikes," in the concentration were observed for all three nuclides soon after shutdown. This behavior was not observed for  $^{134}\text{I}$ , whose concentration decreased continuously after power reduction began.

The largest fraction of the radiiodine present in most of the samples was found to be iodide (F1). This is shown in Tables 1 and 2, which contain values of F1 to F4 for the coolant samples collected at Plants 1 and 2, respectively. The fractions were computed using the assumption that the undetectable radiiodine activities were just below the detection limits (i.e., using the maximum iodine concentrations shown in column 2). In some cases, the tabulated values of F1 and F2 are actually lower bounds because activity was not detected in the other subsamples. Values are given to the nearest 0.1% only to show the activity balance. For example, at  $t = -9.6$  h at Plant 1, the tabulated value of F1 is 90.9%, but the true value could be 100%. For subsamples containing detectable amounts of  $^{131}\text{I}$ , typical counting uncertainties were 15 to 25% before shutdown at Plant 1 and 5 to 10% after shutdown. At Plant 2, they were lower: 5 to 10% before shutdown and 2 to 4% afterward (see Appendix).

The elemental iodine fractions (F3) for  $^{131}\text{I}$  measured at the two plants are shown in Fig. 9. Open points indicate that F3 was below the minimum detectable value for the analysis. At both plants, increases in F3 were observed at shutdown and the maximum value was seen at times between +35 and +40 h. Fractional uncertainties for the plotted values of F3 were about 30% at Plant 1 and about 5% at Plant 2. At both plants, the values of F3 for  $^{132}\text{I}$ ,  $^{134}\text{I}$ , and  $^{135}\text{I}$  also increased at shutdown to between 15% and 20%. The behavior of  $^{133}\text{I}$  at Plant 2 was similar. However, at Plant 1 no spike in the total  $^{133}\text{I}$  concentration was observed and the activity in this fraction was generally below the detection limit.

Organic iodide fractions were generally small. Only one positive value was observed for  $^{131}\text{I}$  at Plant 1; F4 was 6.3% at +29 h. The result for  $^{132}\text{I}$  at the same time was 4.5%. At Plant 2, F4 was between 2.3% and 3.9% at +0.3 h for all five radioiodines. The highest values for F4 at Plant 2 were seen at +21 h when results for the four longer-lived isotopes ranged from 4.7% to 6.5%. This occurred soon after the second stage of depressurization and the startup of the shutdown cooling system.

The fractional concentrations of iodates in the coolant at Plant 1 are shown in Fig. 10. The values of F2 were <7%, and many were below the detection limit, until +43 h. At the same time, F2 increased dramatically and remained very high until +48 h. Similarly large values of F2 were observed for  $^{132}\text{I}$  at the same times. Concentrations of F2 were below the detection limits for  $^{133}\text{I}$ ,  $^{134}\text{I}$ , and  $^{135}\text{I}$  at the time. At



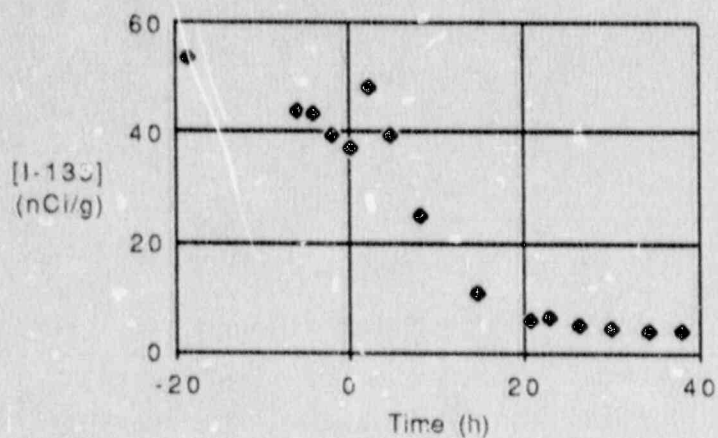
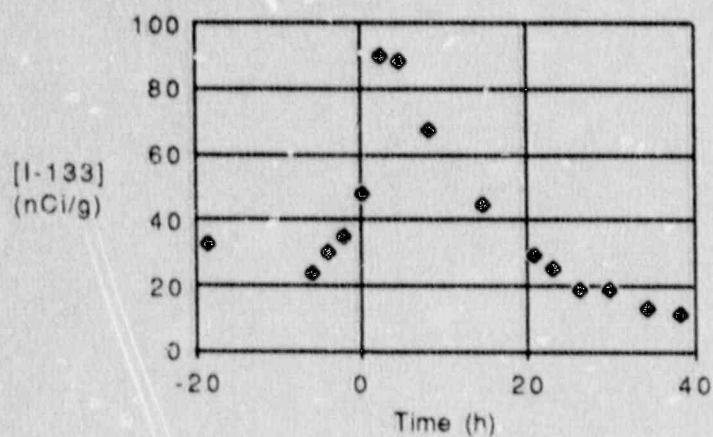
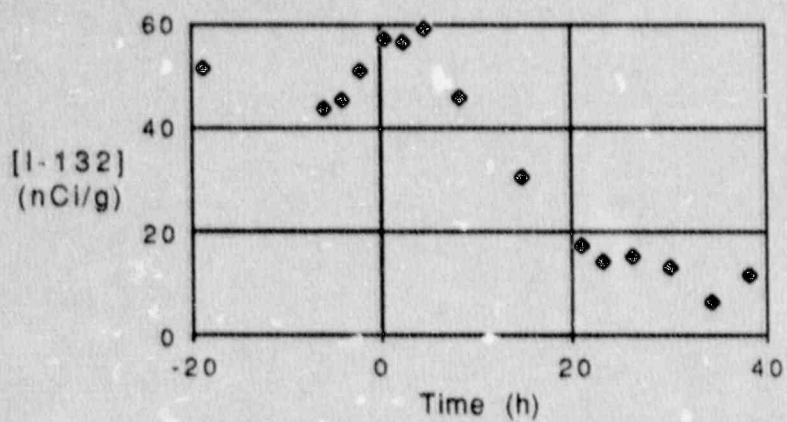


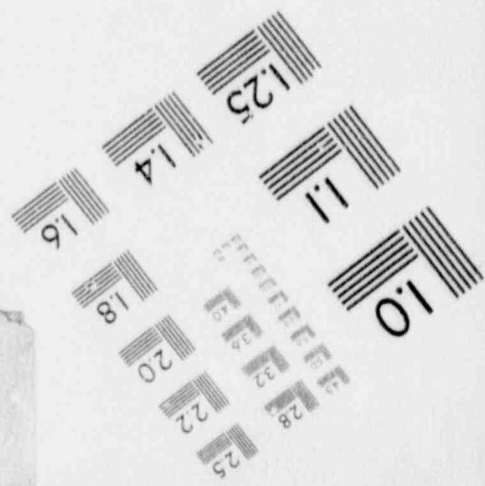
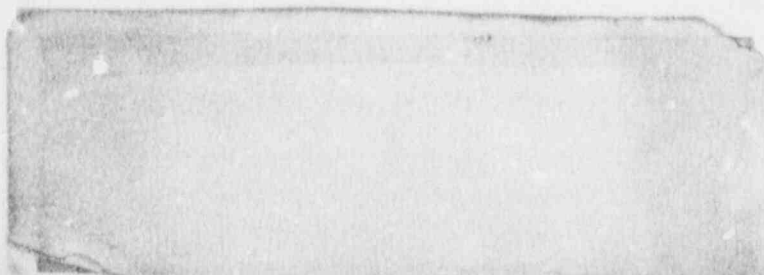
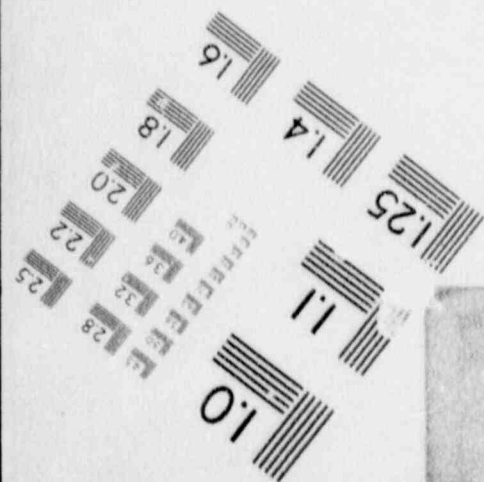
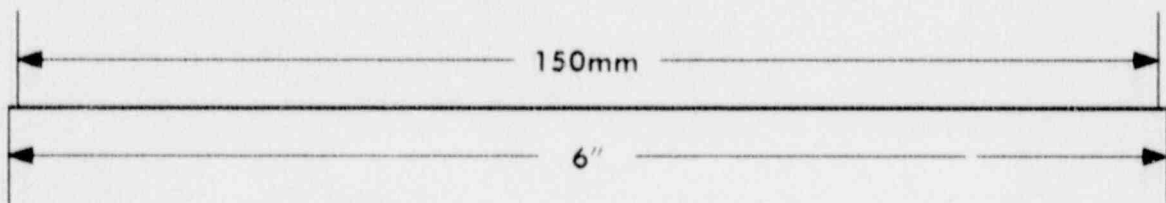
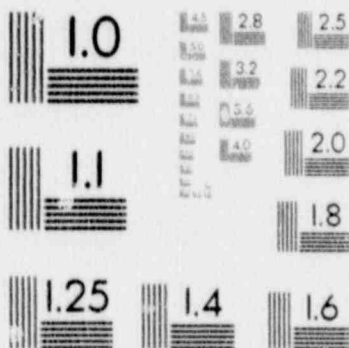
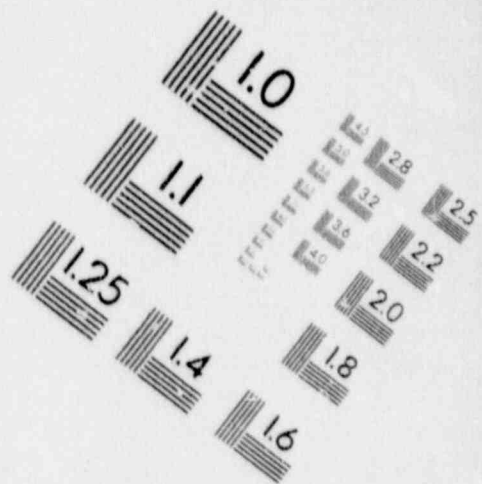
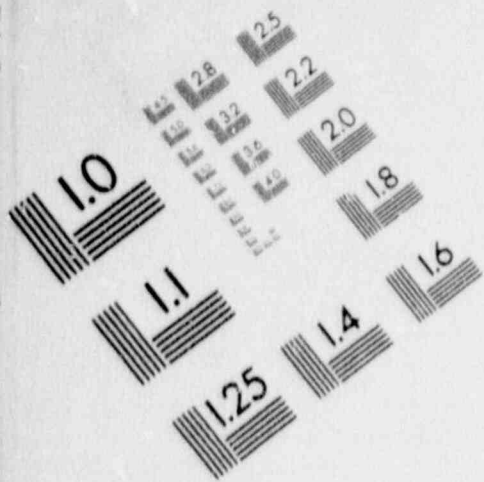
Fig. 8. Measured concentrations of  $^{132}\text{I}$ ,  $^{133}\text{I}$ , and  $^{135}\text{I}$  in reactor coolant near the time of shutdown (time = 0) at Plant 2.

Table 1. Total coolant concentrations and radioiodine distribution fractions for Plant 1

Time (h)	Total coolant concentration (nCi/g)		Radioiodine distribution fractions (%)			
	Maximum <sup>a</sup>	Minimum <sup>b</sup>	F1	F2	F3	F4
Results for <sup>131</sup> I						
-34.5	4.5	4.4	91.8	5.3	<1.4	<1.6
-18.8	4.4	4.3	90.4	7.1	<2.2	<0.3
-15.6	4.2	4.0	91.2	<2.4	4.0	<2.4
- 9.6	4.1	3.7	90.9	<3.9	<2.9	<2.2
- 5.5	5.6	5.2	92.5	<1.4	<2.5	<3.6
- 3.9	5.3	4.9	92.0	<2.8	<3.0	<2.1
- 1.7	3.3	3.1	73.9	<1.8	20.9	<3.3
0.0	6.4	6.2	87.9	<1.6	8.8	<1.7
+10.4	17.4	17.3	96.5	2.1	1.0	<0.4
+18.2	11.3	11.2	88.6	8.9	1.9	<0.7
+23.8	28.2	28.1	95.0	1.9	2.9	<0.2
+30.1	16.2	16.2	85.5	3.2	5.0	6.3
+40.2	6.5	6.5	60.6	3.4	33.9	2.1
+42.7	2.5	2.4	38.9	55.8	<3.0	<2.4
+44.9	2.2	2.1	20.9	73.1	<2.9	<3.1
+46.2	2.4	2.3	22.1	70.9	4.2	<2.8
+47.8	4.7	4.6	81.0	15.2	2.6	<1.2
Results for <sup>132</sup> I						
-34.5	85.2	85.2	98.7	0.4	0.3	0.6
-18.8	77.9	77.9	96.0	1.6	1.0	1.4
-15.6	83.9	83.6	98.7	1.0	<0.2	<0.1
- 9.6	79.1	78.9	98.9	<0.2	0.5	0.3
- 5.5	95.9	95.9	97.2	1.8	0.4	0.5
- 3.9	91.0	91.0	94.2	2.2	2.6	0.9
- 1.7	118.5	118.2	83.9	0.7	15.2	<0.2
0.0	86.9	86.9	89.3	1.2	8.2	1.4
+10.4	83.3	83.3	97.8	1.5	0.4	0.3
+18.2	52.1	49.3	92.9	<2.9	1.8	<2.5
+23.8	54.6	53.3	93.8	1.6	2.3	<2.2
+30.1	30.9	30.9	88.1	3.6	3.8	4.5
+40.2	20.5	17.8	55.6	<9.3	31.1	<4.0
+42.7	11.1	9.9	29.6	59.9	<9.9	<0.5
+44.9	8.1	8.0	22.1	76.0	<1.1	<0.7
+46.2	9.6	9.6	17.0	80.2	<0.6	2.2
+47.8	5.6	5.5	29.2	68.5	<1.4	<0.9

# 1

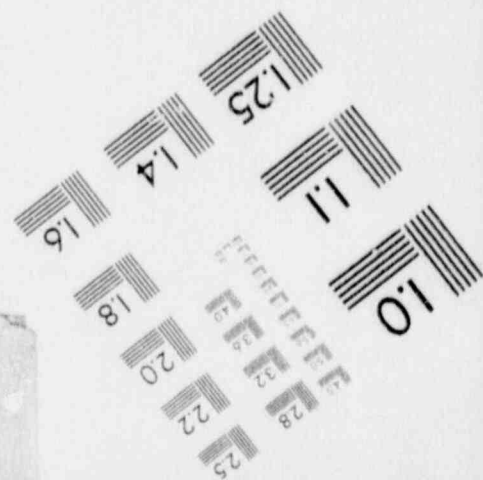
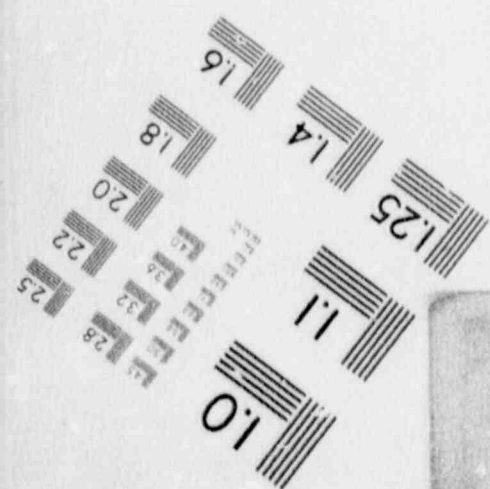
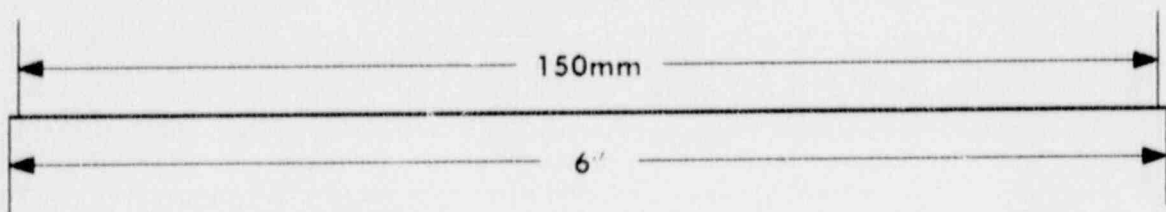
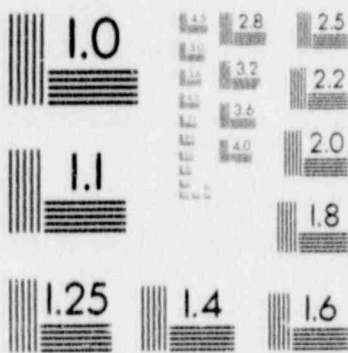
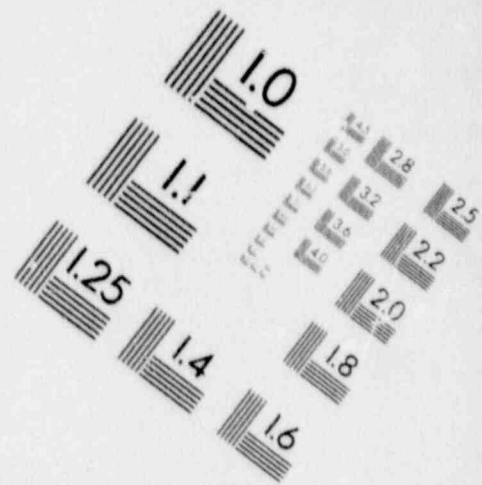
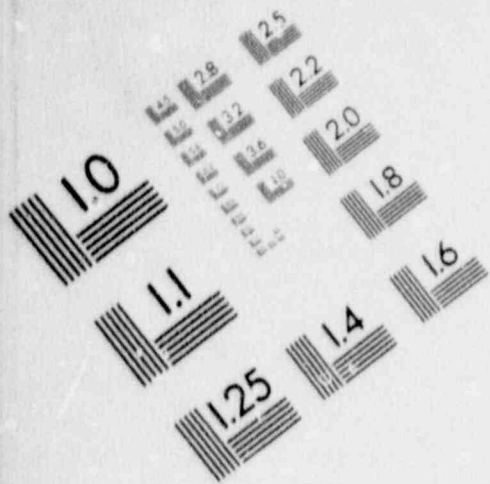
## IMAGE EVALUATION TEST TARGET (MT-3)





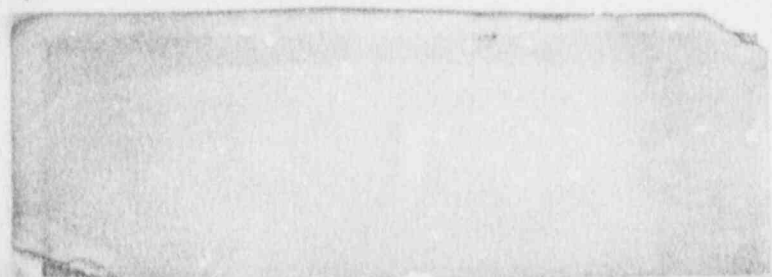
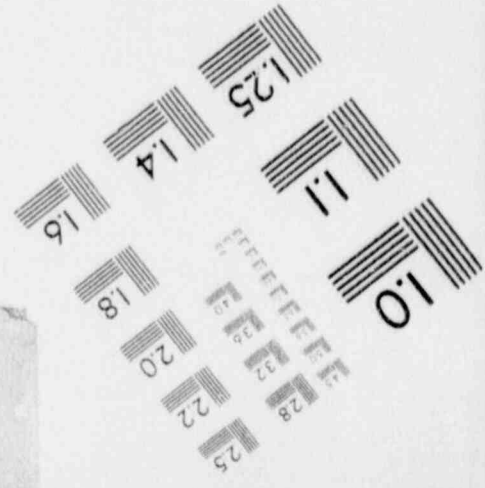
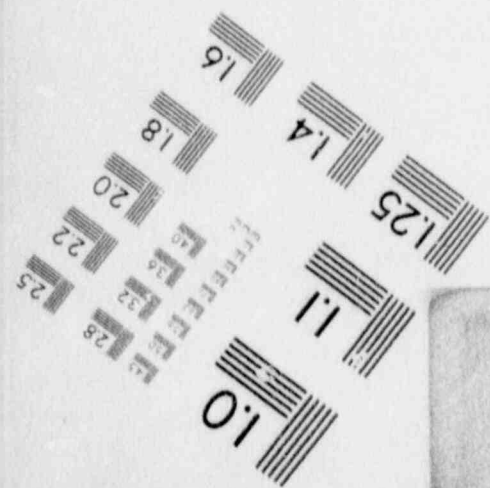
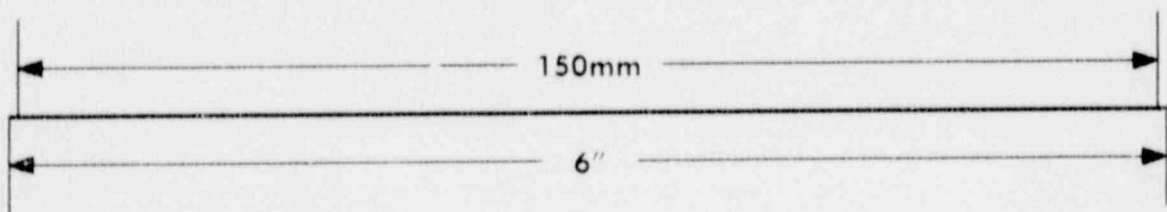
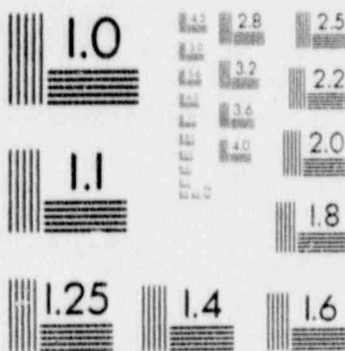
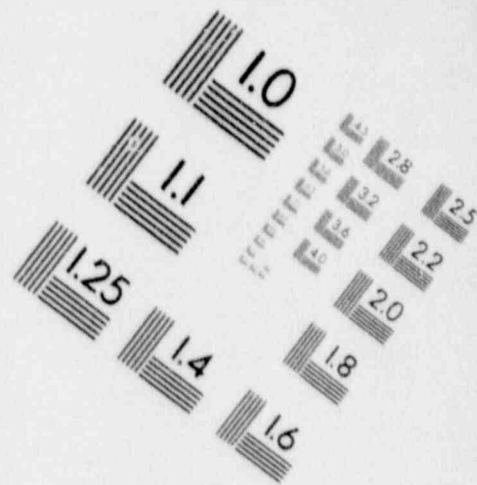
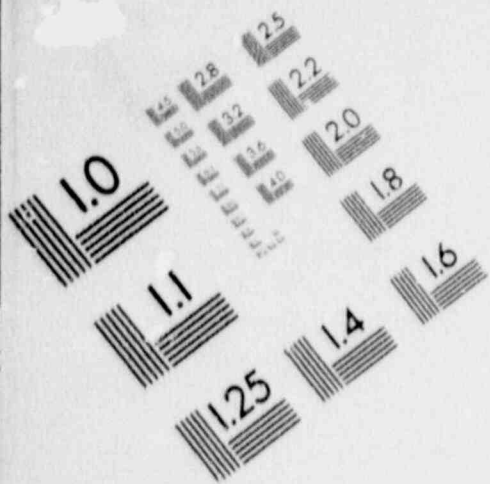
# 1

## IMAGE EVALUATION TEST TARGET (MT-3)



# 1

## IMAGE EVALUATION TEST TARGET (MT-3)



# 1

## IMAGE EVALUATION TEST TARGET (MT-3)

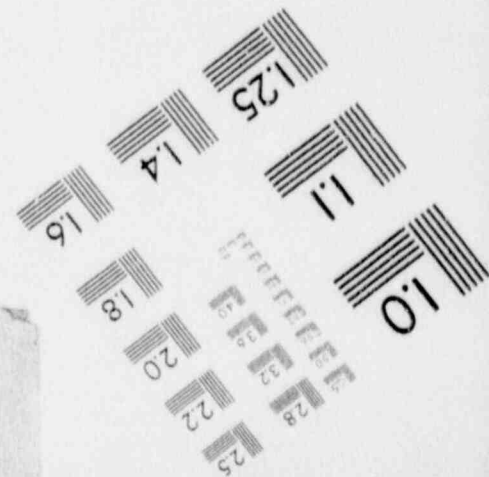
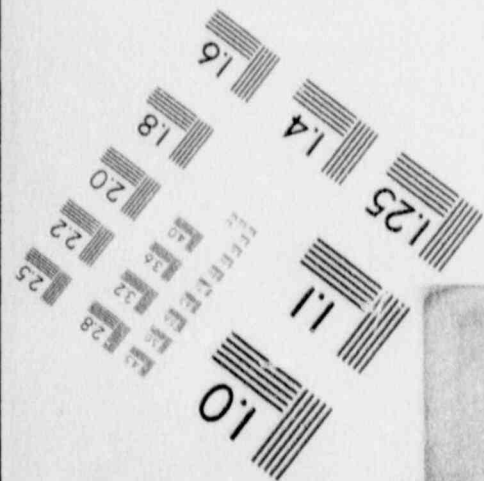
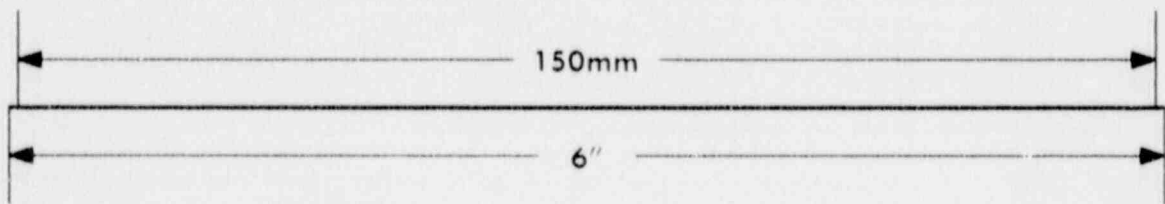
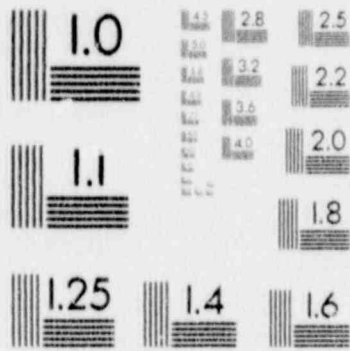
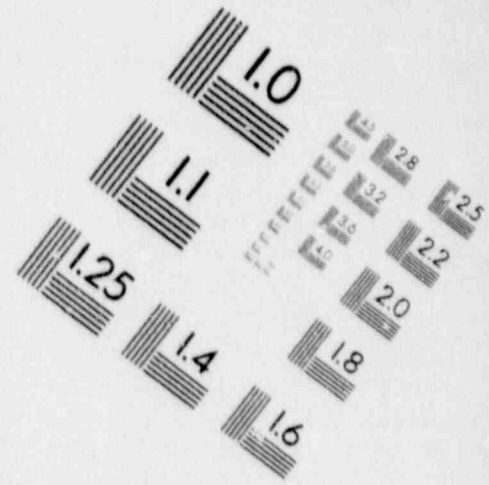
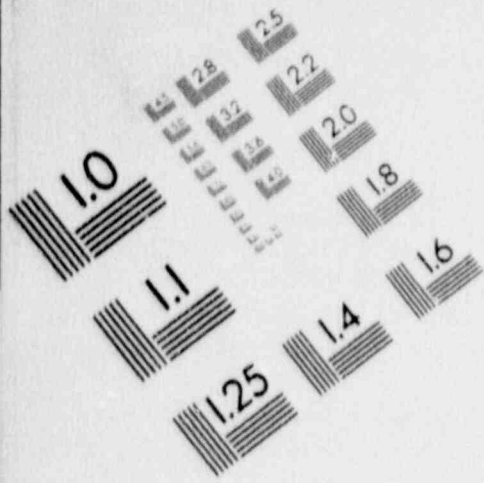




Table 1 (continued)

Time (h)	Total coolant concentration (nCi/g)		Radioiodine distribution fractions (%)			
	Maximum <sup>a</sup>	Minimum <sup>b</sup>	F1	F2	F3	F4
Results for <sup>133</sup> I						
-34.5	36.3	36.1	99.5	<0.1	<0.2	<0.2
-18.8	30.8	30.4	98.6	<0.5	<0.4	<0.5
-15.6	32.2	31.1	96.6	<2.8	<0.2	<0.4
- 9.6	31.9	31.6	96.7	<0.4	<0.3	<2.6
- 5.5	32.2	31.9	99.0	<0.4	<0.3	<0.3
- 3.9	26.2	25.3	96.5	<2.5	<0.5	<0.4
- 1.7	20.7	20.1	97.3	<0.3	<1.7	<0.6
0.0	22.8	21.7	95.3	<2.9	<1.2	<0.6
+10.4	14.8	14.6	97.4	<0.6	0.9	1.1
+18.2	1.6	1.5	84.0	7.5	<4.1	<4.4
+23.8	7.0	6.8	97.0	<1.1	<1.1	<0.8
+30.1	0.72	0.0	c	c	c	c
+40.2	0.55	0.0	c	c	c	c
+42.7	0.38	0.0	c	c	c	c
+44.9	0.37	0.0	c	c	c	c
+46.2	0.36	0.0	c	c	c	c
+47.8	0.28	0.0	c	c	c	c
Results for <sup>134</sup> I						
-34.5	181.9	181.0	99.5	<0.2	<0.1	<0.2
-18.8	163.6	163.6	95.3	1.4	1.1	2.2
-15.6	212.4	212.1	98.4	1.2	0.3	<0.1
- 9.6	134.0	133.9	97.8	1.2	0.9	<0.1
- 5.5	177.9	177.9	97.2	1.8	0.7	0.3
- 3.9	128.8	128.8	93.9	2.4	3.3	0.4
- 1.7	189.9	189.9	83.2	0.6	15.1	1.2
0.0	41.5	41.5	88.2	1.5	8.0	2.3
+10.4	6.1	0.0	d	d	d	d
+18.2	0.54	0.0	d	d	d	d
+23.8	0.51	0.0	d	d	d	d
+30.1	0.46	0.0	d	d	d	d
+40.2	1.5	0.0	d	d	d	d
+42.7	0.48	0.0	d	d	d	d
+44.9	0.41	0.0	d	d	d	d
+46.2	0.46	0.0	d	d	d	d
+47.8	0.37	0.0	d	d	d	d

Table 1 (continued)

Time (h)	Total coolant concentration (nCi/g)		Radioiodine distribution fractions (%)			
	Maximum <sup>a</sup>	Minimum <sup>b</sup>	F1	F2	F3	F4
Results for <sup>135</sup> I						
-34.5	83.8	83.4	99.5	<0.1	<0.2	<0.2
-18.8	75.9	75.9	93.8	2.2	2.3	1.7
-15.6	75.0	74.8	97.5	1.5	0.8	<0.3
- 9.6	87.8	87.8	97.0	1.5	0.8	0.6
- 5.5	85.1	84.8	97.7	1.4	0.6	<0.3
- 3.9	79.7	79.7	92.8	2.7	3.2	1.3
- 1.7	69.4	69.4	81.9	0.8	16.1	1.1
0.0	46.9	46.9	88.3	2.1	9.2	0.4
+10.4	10.9	10.6	97.2	<1.5	<0.5	<0.9
+18.2	3.1	2.9	93.8	<1.8	<2.7	<1.7
+23.8	3.7	3.5	92.5	<2.3	<2.9	<2.3
+30.1	3.9	3.6	92.8	<2.2	<2.8	<2.2
+40.2	0.30	0.0	e	e	e	e
+42.7	0.39	0.0	e	e	e	e
+44.9	0.41	0.0	e	e	e	e
+46.2	0.47	0.0	e	e	e	e
+47.8	0.38	0.0	e	e	e	e

<sup>a</sup>Computed by assuming that undetectable concentrations were equal to the detection limit.

<sup>b</sup>Computed by assuming that undetectable concentrations were zero.

<sup>c</sup>No <sup>133</sup>I was detected in the sample.

<sup>d</sup>No <sup>134</sup>I was detected in the sample.

<sup>e</sup>No <sup>135</sup>I was detected in the sample.

Table 2. Total coolant concentrations and radioiodine distribution fractions for Plant 2

Time (h)	Total coolant concentration (nCi/g)		Radioiodine distribution fractions (%)			
	Maximum <sup>a</sup>	Minimum <sup>b</sup>	F1	F2	F3	F4
Results for <sup>131</sup> I						
-18.6	8.1	7.9	96.6	2.0	<0.6	<0.8
- 6.0	6.2	5.5	88.1	<1.4	<9.2	<1.3
- 4.0	8.8	7.9	90.5	<2.4	<6.4	<0.7
- 2.0	15.2	14.8	94.0	<1.2	<1.0	<3.8
+ 0.3	32.7	32.7	76.0	4.3	16.5	3.2
+ 2.4	75.8	75.7	86.8	<0.2	12.0	1.0
+ 4.7	82.8	82.8	97.1	2.0	0.6	0.3
+ 8.2	75.1	75.1	96.3	2.0	1.2	0.4
+14.8	63.0	63.0	91.9	2.0	5.7	0.3
+20.8	44.8	44.8	88.7	3.6	2.9	4.7
+23.1	41.6	41.6	94.9	3.0	1.3	0.9
+26.3	35.0	34.8	94.0	5.5	<0.3	<0.2
+30.1	33.7	33.7	92.3	5.9	1.0	0.8
+34.4	26.5	26.5	51.6	6.0	40.7	1.8
+38.3	24.1	24.1	85.9	9.0	3.9	1.2
Results for <sup>132</sup> I						
-18.6	51.5	50.6	98.2	<1.4	<0.2	<0.2
- 6.0	44.0	44.0	96.1	2.2	1.5	<0.2
- 4.0	45.1	45.1	94.6	3.2	1.7	0.5
- 2.0	51.2	51.1	98.0	1.6	<0.3	<0.2
+ 0.3	57.1	57.1	77.7	4.0	16.0	2.3
+ 2.4	56.7	56.7	85.7	2.1	11.5	0.7
+ 4.7	59.4	59.3	97.0	2.2	0.6	<0.2
+ 8.2	45.9	45.9	95.1	2.7	1.4	0.8
+14.8	30.4	30.4	92.2	1.8	5.5	0.5
+20.8	17.5	17.1	93.0	<0.9	<0.7	5.5
+23.1	14.1	14.1	94.6	1.4	2.8	1.2
+26.3	15.3	15.3	91.1	6.0	1.6	1.4
+30.1	13.3	13.2	93.1	4.4	1.9	<0.7
+34.4	6.8	6.8	75.3	15.0	6.3	3.4
+38.3	11.5	11.4	83.8	12.6	2.8	<0.8



Table 2 (continued)

Time (h)	Total coolant concentration (nCi/g)		Radioiodine distribution fractions (%)			
	Maximum <sup>a</sup>	Minimum <sup>b</sup>	F1	F2	F3	F4
Results for <sup>133</sup> I						
-18.6	32.4	32.2	97.2	1.5	0.7	<0.6
- 6.0	23.8	23.7	97.0	1.9	0.8	<0.3
- 4.0	30.1	30.1	95.3	2.4	1.6	0.7
2.0	34.9	34.9	96.5	1.9	1.4	<0.2
+ 0.3	48.3	48.3	77.8	3.9	15.1	3.1
+ 2.4	89.9	89.9	85.8	2.0	10.9	1.3
+ 4.7	88.2	88.2	97.1	1.9	0.6	0.4
+ 8.2	67.6	67.6	96.2	2.0	1.3	0.5
+14.8	44.8	44.8	91.9	2.0	5.7	0.5
+20.8	29.3	29.3	87.8	4.6	2.7	4.8
+23.1	25.8	25.8	95.0	2.4	1.5	1.1
+26.3	19.0	19.0	92.8	4.7	1.8	0.7
+30.1	18.5	18.5	91.6	5.9	1.3	1.2
+34.4	13.3	13.1	50.5	6.9	41.2	<1.4
+38.3	11.7	11.7	85.8	8.7	2.7	2.7
Results for <sup>134</sup> I						
-18.6	97.8	97.1	96.4	2.8	<0.4	<0.4
- 6.0	62.4	62.4	96.4	1.9	1.3	0.4
- 4.0	60.3	60.3	94.6	3.0	1.7	0.7
- 2.0	36.0	35.9	96.1	2.6	1.1	<0.2
+ 0.3	12.6	12.5	70.3	6.9	19.2	3.5
+ 2.4	4.8	0.0	c	c	c	c
+ 4.7	1.4	0.0	c	c	c	c
+ 8.2	1.6	0.0	c	c	c	c
+14.8	2.8	0.0	c	c	c	c
+20.8	0.64	0.0	c	c	c	c
+23.1	0.53	0.0	c	c	c	c
+26.3	0.45	0.0	c	c	c	c
+30.1	0.90	0.0	c	c	c	c
+34.4	0.95	0.0	c	c	c	c
+38.3	0.73	0.0	c	c	c	c

Table 2 (continued)

Time (h)	Total coolant concentration (nCi/g)		Radioiodine distribution fractions (%)			
	Maximum <sup>a</sup>	Minimum <sup>b</sup>	F1	F2	F3	F4
Results for <sup>135</sup> I						
-18.6	53.7	53.4	97.5	2.0	<0.2	<0.3
- 6.0	43.9	43.9	95.4	2.5	1.1	0.9
- 4.0	43.6	43.6	93.5	3.4	2.1	0.9
- 2.0	39.3	39.2	95.5	1.8	2.5	<0.3
+ 0.3	37.3	37.3	73.7	4.5	17.9	3.9
+ 2.4	48.3	48.3	84.4	3.0	11.4	1.2
+ 4.7	39.7	39.6	95.8	2.8	1.1	<0.4
+ 8.2	24.8	24.7	95.1	2.8	1.7	<0.4
+14.8	10.8	10.7	89.1	3.6	6.5	<0.8
+20.8	6.0	5.7	89.4	<2.9	<1.2	6.5
+23.1	6.7	6.5	89.5	8.2	<1.2	<1.1
+26.3	5.1	4.9	88.1	8.1	<1.8	<2.0
+30.1	4.8	4.5	93.3	<2.3	<1.8	<2.7
+34.4	4.0	3.9	47.1	<4.3	46.9	<1.7
+38.3	4.0	3.8	81.2	13.4	<2.1	<3.2

<sup>a</sup>Computed by assuming that undetectable concentrations were equal to the detection limit for the analysis.

<sup>b</sup>Computed by assuming that undetectable concentrations were zero.

<sup>c</sup>No <sup>134</sup>I was detected in the sample.

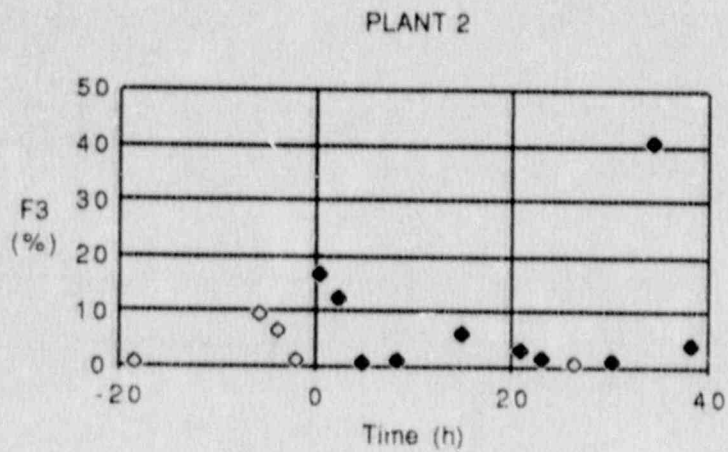
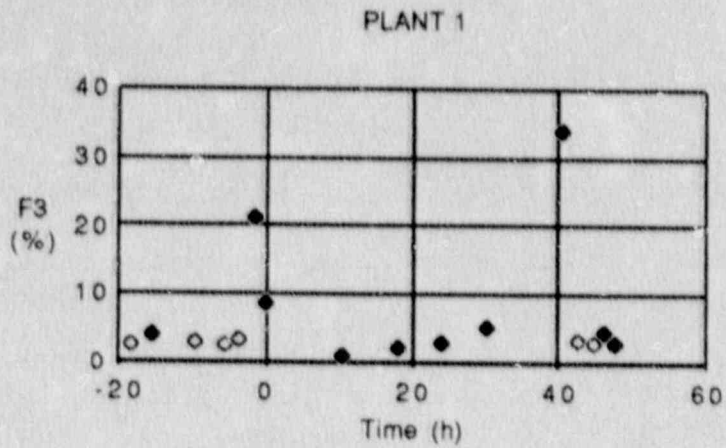


Fig. 9. Measured elemental iodine fractions (F3) for  $^{131}\text{I}$  in reactor coolant near the time of shutdown (time = 0) at the two PWRs (open points indicate values below detection limit).



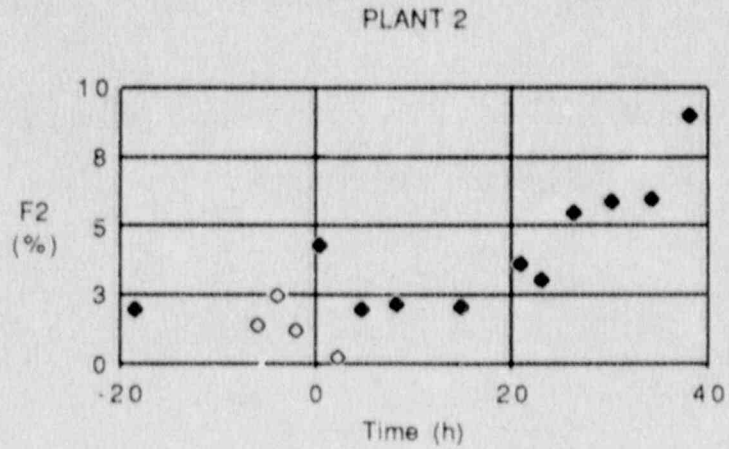
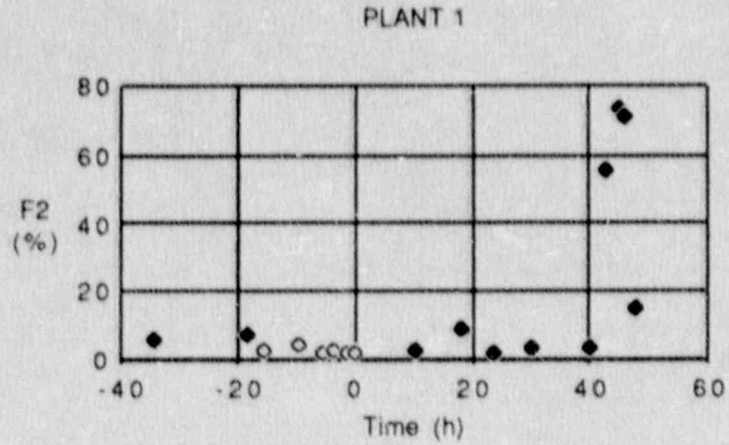


Fig. 10. Measured iodate/periodate fractions (F2) for  $^{131}\text{I}$  in reactor coolant near the time of shutdown (time = 0) at the two PWRs (open points indicate values below detection limit).

Plant 2, a gradual increase in F2 after 20 h and the maximum value for  $^{131}\text{I}$  was only 8.2% (Fig. 10). There were similar increases in F2 for  $^{132}\text{I}$ ,  $^{133}\text{I}$ , and  $^{135}\text{I}$  at Plant 2. The maximum value of F2 was 15% for  $^{132}\text{I}$  at +36 h.

#### 4. DISCUSSION

The data collected at the operating PWRs reflect radioiodine behavior at very low mass concentrations. In addition to the five radioactive isotopes discussed above, the stable isotope  $^{127}\text{I}$  and the very long-lived nuclide  $^{129}\text{I}$  were produced in the fuel. For plants that have operated for several years, these two isotopes comprise about 90% of the mass of iodine in the fuel.<sup>7</sup>

The amounts of the various radioiodine isotopes in the coolant depend on processes governing transport from fuel to coolant, as well as the coolant cleanup rate. Iodine moves from the fuel pellets to the plenum within the fuel rod and subsequently into the coolant via penetrations in the fuel cladding. A simple model (Fig. 11) of the movement of iodine can be used to estimate the mass concentrations of iodine in coolant. The general equations describing the iodine atom inventories for a particular isotope are given below. The same equations apply to each of the isotopes, with appropriate changes in the fission yield and half-life.

$$\frac{dA_F}{dt} = Pf\gamma - (\lambda + \lambda_1) A_F \quad (1)$$

$$\frac{dA_P}{dt} = \lambda_1 A_F - (\lambda + \lambda_2) A_P \quad (2)$$

$$\frac{dA_C}{dt} = \lambda_2 kA_P - (\lambda + \lambda_{Cu}) A_C \quad (3)$$

where

- $A_F$  = inventory (atoms) of the isotope in the fuel,
- $A_P$  = inventory (atoms) of the isotope in the fuel rod plenums,
- $A_C$  = inventory (atoms) of the isotope in the coolant,
- $P$  = reactor power level (MWt),
- $f$  = fission rate per unit power level,
- $\gamma$  = fission yield of the isotope,
- $\lambda_1$  = fuel-to-plenum escape rate constant ( $s^{-1}$ ),
- $\lambda_2$  = plenum-to-coolant transfer rate constant ( $s^{-1}$ ),
- $k$  = fraction of fuel rods that leak,
- $\lambda$  = radioactive decay rate constant ( $s^{-1}$ ),
- $\lambda_{Cu}$  = rate constant ( $s^{-1}$ ) describing removal by the cleanup system, namely  $(F_{Cu}/M_C)\epsilon$ . (In this ratio,  $F_{Cu}$  is the cleanup flow rate (g/s),  $M_C$  is the mass (g) of the reactor coolant, and  $\epsilon$  is the overall efficiency of the cleanup system.)

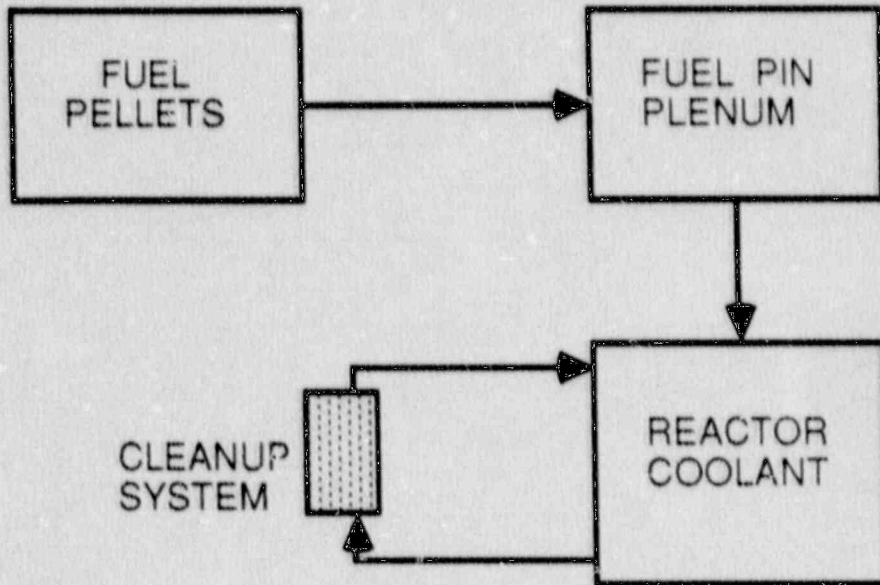


Fig. 11. Simple model of radioiodine transport from fuel pellets to reactor coolant.



For radioiodine,  $\epsilon$  is near unity. Values of  $(F_{Cu}/M_c)$  can be computed from data on the removal of the activation product  $^{24}Na$  from the coolant following shutdown.<sup>8</sup> Values of  $\lambda_{Cu}$  estimated in this way are  $2.8 \times 10^{-5} s^{-1}$  at Plant 1 and  $1.6 \times 10^{-5} s^{-1}$  at Plant 2. The principal reason for the difference is a smaller primary coolant mass at Plant 1.

Under equilibrium conditions, the atom inventory of the isotope in the coolant ( $A_{ce}$ ) can be obtained from Eq. (3)

$$A_{ce} = \frac{k_2 k A_{pe}}{(\lambda + \lambda_{Cu})} \quad (4)$$

where  $A_{pe}$  is the equilibrium inventory in the plenum. Solving Eqs. (1) and (2) at equilibrium and using those results in Eq. (4) yields

$$A_{ce} = \frac{\lambda_2 k \lambda_1 P f \gamma}{(\lambda + \lambda_{Cu})(\lambda + \lambda_2)(\lambda + \lambda_1)} \quad (5)$$

For the isotopes  $^{127}I$  and  $^{129}I$ , radioactive decay can be ignored and Eq. (5) reduces to

$$A_{ce} = \frac{k P f \gamma}{\lambda_{Cu}} \quad (6)$$

The activity inventory of a radioactive iodine isotope in the coolant at equilibrium is  $Q_{ce}$  (nCi):

$$Q_{ce} = \frac{\lambda \lambda_2 k \lambda_1 P f \gamma}{37 (\lambda + \lambda_{Cu})(\lambda + \lambda_2)(\lambda + \lambda_1)} \quad (7)$$

where 37 disintegrations/s nCi is the activity conversion factor.

Beyer et al.<sup>9</sup> have summarized data on PWR coolant activity and fuel rod failures and Beyer\* has developed an approach to the utilization of the data to estimate fuel rod failure. The model employs a correlation between the two rate constants  $\lambda_1$  and  $\lambda_2$  and the observation that the fuel-to-plenum escape ( $\lambda_2$ ) is dependent on  $\lambda$ . The dependence on  $\lambda$  of transport from fuel to coolant has been observed by others.<sup>10</sup> The following relationships were developed by Beyer; a more complex model is given in Ref. 10.

$$\lambda_1 = a \lambda^{0.5} \quad , \quad \text{and} \quad (8)$$

$$a = b + c \lambda_2 \quad (9)$$

\*C. E. Beyer, Estimating Number of Failed Fuel Rods and Defect Size from PWR Coolant and BWR Offgas Activities, Draft EPRI Report, Battelle Pacific Northwest Laboratory (January 1988).

Estimated values of  $\lambda_2$  based on PWR coolant data range from  $6 \times 10^{-7}$  to  $6 \times 10^{-6}$  per second.<sup>10</sup> The observed spread in values of the parameter  $a$  for the PWR data is also about an order of magnitude. Beyer's best-fit values for the parameters in Eq. (9) were  $b = -4.76 \times 10^{-7}$  and  $c = 6.51$ . Deviations of individual observations from the values predicted using Eq. (8) and the best-fit parameters for the entire data set are as great as a factor of 2.5.

The coolant concentration data for four radioiodines at Plant 2 were used with the range of  $\lambda_2$  values cited above to estimate the  $^{129}\text{I}$  and  $^{127}\text{I}$  concentrations in reactor coolant. Equations (9) and (8) were used to estimate  $\lambda_1$  and  $k$  was calculated from Eq. (7). Then,  $k$  was used in Eq. (6) to calculate  $A_{ce}$ , which was converted to the mass concentration of iodine in the coolant. A nominal value of  $\lambda_2$  was taken to be  $1.9 \times 10^{-6} \text{ s}^{-1}$ . This led to estimated mass concentrations of  $3.6 \times 10^{-12}$  to  $1.9 \times 10^{-10} \text{ g } ^{129}\text{I}$  per gram of coolant. This range of mass concentrations arises from the use of the data for  $^{131}\text{I}$ ,  $^{133}\text{I}$ ,  $^{134}\text{I}$ , and  $^{135}\text{I}$  to obtain four separate estimates. The estimates obtained using the  $^{131}\text{I}$  and  $^{133}\text{I}$  data, which should be the most reliable, were  $3.6 \times 10^{-12}$  and  $4.7 \times 10^{-12} \text{ g } ^{129}\text{I}$  per gram of coolant, respectively. The calculated concentration of  $^{127}\text{I}$  is about 10% of that for  $^{129}\text{I}$ .

The model in Fig. 11 is also useful for the analysis and discussion of the measurement results. If it is assumed, as a first approximation, that the input from plenum to coolant is a constant during the time periods between samples, then the coolant concentration data can be used to determine the magnitude of the radioiodine inputs during those periods. The average input of an iodine isotope to the coolant between times  $t_1$  and  $t_2$  ( $I_{c12}$ , nCi/s) is

$$I_{c12} = \lambda_e (Q_{c2} - Q_{c1} \exp [-\lambda_e(t_2 - t_1)]) / (1 - \exp [-\lambda_e(t_2 - t_1)]) \quad (10)$$

In this equation,  $\lambda_e (= \lambda + \lambda_{cu})$  is the effective removal rate constant ( $\text{s}^{-1}$ ) for radioiodine from the coolant and  $Q_{c1}$  and  $Q_{c2}$  are the radioiodine activities (nCi) in coolant at the two times.

At Plant 1, the picture is incomplete because it is likely that the initial peak in coolant activity was not observed. Data for two plants in Ref. 8 show that there was a sharp increase in coolant concentration at shutdown even though the temperature and pressure of the primary system were maintained at the operating level well after shutdown. Because the data are incomplete, radioiodine injection rates were not calculated from the measurements at Plant 1.

Results of the calculations of injection rates for four radioiodines at Plant 2 are shown in Fig. 12 for the time period during which the cleanup system was in operation. The primary injection of activity occurred at shutdown, but there was a second pulse in the injection rate at about +20 h when the second depressurization occurred. The input of  $^{132}\text{I}$  to coolant is the sum of contributions from the decay of  $^{132}\text{Te}$  and plenum-to-coolant transfer does not exhibit the same sharp rise after shutdown.

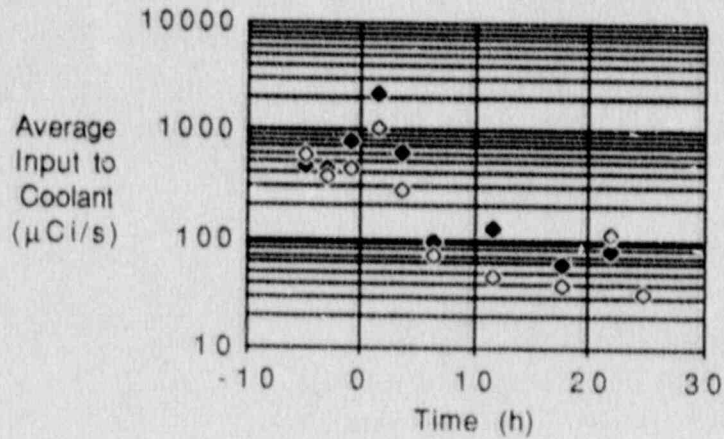
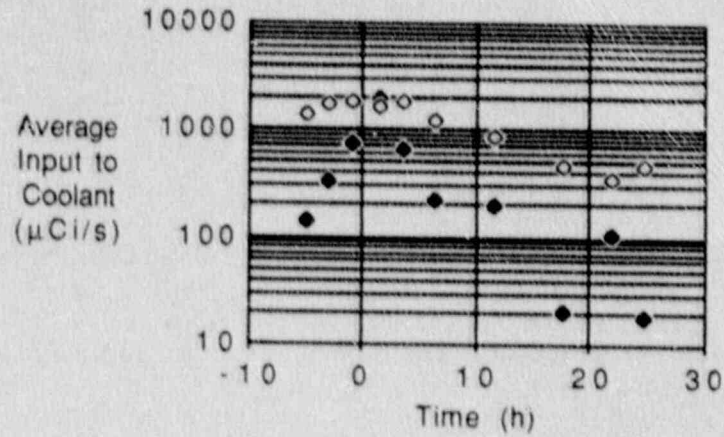


Fig. 12. Calculated average inputs of radioiodine isotopes to reactor coolant at Plant 2. Upper plot contains data for  $^{131}\text{I}$  (solid points) and  $^{132}\text{I}$  (open points); lower plot contains data for  $^{133}\text{I}$  (solid points) and  $^{135}\text{I}$  (open points).



Table 3 summarizes the radioiodine spiking results at Plant 2. The observed ratios of the peak coolant concentrations to the pre-shutdown values are shown for four radioiodines. Also shown are the ratios of the peak injection rates to those required to maintain the concentration measured six hours before shutdown.

Table 3. Summary of radioiodine spiking data for Plant 2

Isotope	Ratios of peak values to preshutdown (-6.0 h) values	
	Coolant concentration	Plenum-to-coolant injection rate
$^{131}\text{I}$	13.0	66.0
$^{132}\text{I}$	1.4	1.4
$^{133}\text{I}$	3.8	12.0
$^{135}\text{I}$	1.1	1.7

The ratios in Table 3 are substantially smaller than those normally assumed in evaluating potential accidents at PWRs. They are, however, larger than the ratios observed when prompt depressurization does not occur. For example, ratios of peak to preshutdown  $^{131}\text{I}$  concentrations reported in Ref. 8 ranged from 6 to 8. In those cases, the effect of depressurization was separated in time from the shutdown.

Examination of the data on the measured elemental iodine fractions at Plant 1 shows that the peak in F3 for  $^{131}\text{I}$  (see Fig. 9) occurred during the last phase of power reduction. The highest values of F3 for  $^{132}\text{I}$ ,  $^{134}\text{I}$ , and  $^{135}\text{I}$  were also found in the sample collected at -1.8 h. Boration did not begin until about +10 h and could not be the reason for the elevated values of F3 at shutdown. The addition of boric acid did not appear to have a marked effect on F3, which remained at 1 to 2% in the samples collected between +9 and +23 h. The foregoing observations suggest that the rise in F3 at the time Plant 2 was shut down was due to the power, temperature, and pressure changes that were occurring, rather than to the addition of boric acid (which also occurred immediately after shutdown).

The largest increase in FV reported in Ref. 2 was attributed to addition of oxygenated fluid from the BWST. However, the data indicate that at about +2.6 h, the boron concentration was already about 800 ppm and no change in species had occurred. Cooldown of the system was in process when the increase in FV occurred. Unfortunately, data on coolant pressure were not given, but it is possible that the Prairie Island data reflect radioiodine injection at the time of depressurization, as was observed in this study.

Increases in F3 at both plants appear to be correlated with injections of radioiodine from the fuel rods into the coolant. This

suggests that the increases in F3 are due to injection of elemental iodine from the fuel rod plenums. Figure 4 shows that  $I_2$  in the coolant does not remain for long; removal half-times of 2.2 to 2.5 h were estimated from the data collected near the time of shutdown. For the data collected at Prairie Island, a half-time of 3.4 h was estimated following the large increase in FV, which was observed at 11 h after shutdown.

At Plant 1, the maximum value of F3 occurred at +40 h, before hydrogen peroxide was added to the coolant. It is believed that this peak was due to the final cooling and depressurization of the coolant. At Plant 2, the highest F3 also occurred late in the shutdown (+34 h). There is no clear correlation of this value with plant operations. Cooldown and depressurization had been completed and the shutdown cooling system had been operating for some time. At both plants, the residence half-time of  $I_2$  in the coolant was shorter (<1.2 h) than that seen following the earlier peak. For the second peak in volatile iodine concentration described in Ref. 2, the half-time was about 2.1 h, also shorter than for the first peak.

The largest organic iodide fractions were also observed well after shutdown. At Plant 2, F4 was about 3% for all radioiodines at shutdown, but the values for all detectable isotopes were between 5 and 6% at about +21 h. At Plant 1, F4 was generally below the detection limit for  $^{131}I$ , but was about 6.3% at +29 h. For  $^{132}I$ , F4 was 3.8% in the same sample. The isotopes  $^{132}I$ ,  $^{134}I$ , and  $^{135}I$  present as organic iodides were detectable in several samples before and near  $t = 0$ , but F4 did not exceed 2.5%. Thus, these results generally agree with the observations of Martucci<sup>1</sup> who reported that the predominant volatile species at two of three plants was elemental iodine.

The principal effect following peroxide addition at +41 h was the conversion of large fractions of the coolant radioiodines to the iodate forms. The results in Fig. 10 show this change in F2 clearly. At Plant 2, where the coolant was oxygenated slowly during operation of the shutdown cooling system, a gradual increase in the iodate fraction was observed. This oxygenation may also have contributed to the late peak in F3 observed at Plant 2. These observations differ from those in Ref. 2. As noted in Sect. 1, an increase in FV to about 10% was reported following peroxide addition. No change in F2 was observed. Coolant pressure was not reported; however, the temperature data suggest that final depressurization took place between 3 and 12 h prior to peroxide addition.

The potential off-site dose from volatile radioiodines depends primarily upon two time-dependent factors. They are the volatile activity concentrations of the five isotopes and the effective coolant release to the environment. Also affecting the calculation of potential dose are the assumed atmospheric dispersion parameter, the exposed individual's breathing rate, and the dose conversion factors for the radioiodines. The driving forces for the release are the pressure and temperature of the primary system. When this is considered, it is clear that the most important volatile iodine measurements are those near the

time of shutdown. Increases in the volatile iodine fraction that occur when the pressure and temperature have been lowered are not important to an assessment of the consequences of SGTR accidents.

The data collected for Plant 2 can be used to approximate the time sequence of volatile radioiodine concentrations following an SGTR. The concentration of volatile radioiodine  $i$  in the coolant is  $CV_i$  (nCi/g),

$$CV_i = C_i (F3_i + F4_i) = C_i FV_i , \quad (11)$$

where  $C_i$  is the total concentration (nCi/g) of isotope  $i$  in the coolant and  $F3_i$  and  $F4_i$  are the elemental iodine and organic iodide fractions, respectively. The contribution of a particular radioiodine to the potential dose and risk from an SGTR accident depends on the thyroid dose conversion factor for that isotope. A thyroid risk-weighted volatile concentration  $CV^*$  (rem/g) can be computed using

$$CV^* = \sum CV_i DCF_i , \quad (12)$$

where  $DCF_i$  (rem/nCi) is the thyroid dose conversion factor for the particular radioiodine. Best estimates of the  $DCF_i$  for the adult thyroid are given in ICRP Publication 30.<sup>11</sup> Those  $DCF_i$  and the time histories of  $C_i$  and  $FV_i$  measured at Plant 2 were used to compute  $CV^*$  as a function of time before and after shutdown. The coolant pressure ratio (PR), defined as the pressure at a particular time divided by the normal operating pressure, was used as a gross indicator of coolant release potential. The product  $(CV^*)(PR)$  was computed for 14 measurement times at Plant 2; the results are shown in Fig. 13. Even though  $CV^*$  at +34 h was comparable to that of +2.4 h, the potential risk at +34 h was lower by more than an order of magnitude.

The amounts of volatile radioiodines actually released depend on the time history of their availability, as well as the primary system temperature and pressure, the magnitude of the primary to secondary leakage, mixing and removal processes of the secondary side, and the set points of the secondary-side relief valves.<sup>12</sup> The effective coolant release to the environment may consist of several pulses. In one case, there were five safety valve openings and discharges during a 2-h period.<sup>13</sup>

The data for Plant 2 show that most of the volatile iodine that was present was elemental iodine, rather than organic iodides. This fact may be considered in detailed evaluations of the iodine transport through the steam generator.<sup>12</sup> Radioiodine in elemental form will deposit on surfaces in the steam generator and the steam dryer, but organic forms will not be removed by this process. Scavenging by secondary-side liquid will also be more effective for elemental iodine. The relative importance of the two forms will depend on the assumptions made about the effectiveness of these processes for removal of elemental iodine.



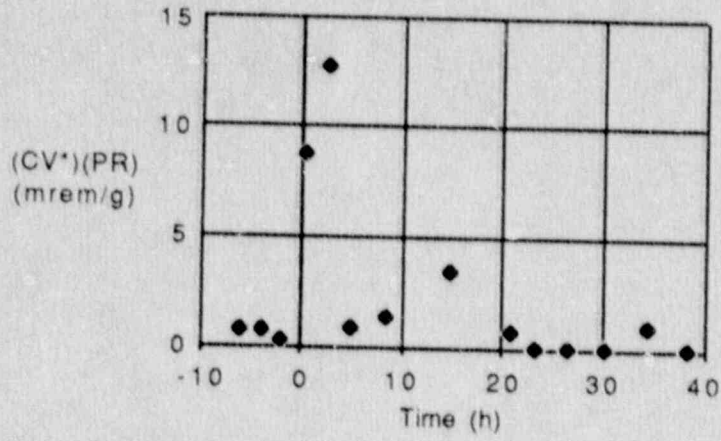


Fig. 13. Product of thyroid risk-weighted radioiodine concentration (CV\*) and coolant pressure ratio (PR) computed using data from Plant 2.

## 5. CONCLUSIONS

During temperature reduction and depressurization, the release rates of radioiodines from the plenums of the fuel rods to the coolant are elevated and a spike in the concentration of radioiodine in the coolant is observed. A significant fraction of the radioiodine injected into the coolant from the fuel rod plenums appears to be in the form of elemental iodine. About 20% of the total radioiodine was found to be  $I_2$  in the samples of coolant collected near the time of shutdown. Boration (and acidification) of the coolant using boric acid did not cause an increase in the elemental iodine fraction. Volatile iodine fractions of about 30 to 40% were found at later times (about +35 h) at both plants. One of the peaks could have resulted from the final depressurization of the coolant, but the operational cause of the other peak is not clear. Contrary to a previous report, measurements showed that addition of hydrogen peroxide to the coolant at one plant did not increase the elemental iodine fraction.

An SGTR accident would cause a shutdown and provide a path for discharge of radionuclides to the environment. The potential off-site dose primarily depends on the volatile iodine species concentrations and the driving force (high pressure and temperature of the primary system) for a release. The initial increase in the volatile iodine fraction and the spike in radioiodine concentration are clearly important to the assessment of off-site dose. However, later increases in the volatile iodine fraction are of less consequence because the driving force for a release to the environment has been substantially reduced.

## 6. ACKNOWLEDGMENT

This work was performed under contract with Oak Ridge National Laboratory. The radiochemistry and counting for this study were performed by the staff of the Rockville Laboratory of SAIC's Utility Services Operation. The contributions of Scott Hay, Bob Lubaszewski (now with Philadelphia Electric Company), and Linnea Coffey are acknowledged and appreciated. Without their dedicated and conscientious efforts, the study would not have been possible.

## 7. REFERENCES

1. J. A. Martucci, Iodine Decontamination Factors During PWR Steam Generation and Steam Venting, Combustion Engineering Report CENPD-67, Combustion Engineering, Windsor, CN (1973).
2. J. W. Mandler et al., In-Plant Source Term Measurements at Prairie Island Nuclear Generation Station, NRC Report NUREG/CR-4397, National Technical Information Service, Springfield, VA (1985).
3. A. W. Castleman, Jr., I. N. Tang, and H. R. Munkelwitz, "The Chemical States of Fission Product Iodine Emanating Into High Temperature Aqueous Environment," J. Inorg. Nucl. Chem. **30**, 5 (1968).

4. C. C. Lin, "Chemical Behavior of Radioiodine in BWR Systems," J. Inorg. Nucl. Chem. 42, 1093 (1980).
5. J. E. Cline, "A Technique of Gamma-Ray Detector Absolute Efficiency Calibration for Extended Sources," in Computers in Activation Analysis and Gamma Ray Spectroscopy, DOE Report CONF-780421, National Technical Information Service, Springfield, VA (1979).
6. J. W. Kormuth, Shutdown Operation Techniques for Radiation Control in PWR Plants, EPRI Report NP-859, Electric Power Research Institute, Palo Alto, CA (1981).
7. D. K. Craig, H. W. Adrian, and D. J. J. C. Boucher, "Effect of Iodine Concentration on the Efficiency of Activated Charcoal Adsorbers," Health Phys. 19, 223 (1970).
8. C. A. Pelletier et al., Sources of Radioiodine at Pressurized Water Reactors, EPRI Report NP-939, Electric Power Research Institute, Palo Alto, CA (1978).
9. C. E. Beyer, E. R. Bradley, and W. D. Bennett, Collection and Formatting of Data on Reactor Coolant Activity and Fuel Rod Failures, EPRI Report NP-4804, Electric Power Research Institute, Palo Alto, CA (1986).
10. B. J. Lewis, C. R. Phillips, and M. J. F. Notley, "A Model for the Release of Radioactive Krypton, Xenon, and Iodine from Defective UO<sub>2</sub> Fuel Elements," Nucl. Technol. 73, 72 (1986).
11. International Commission on Radiological Protection, Limits for Intakes of Radionuclides by Workers, ICRP Publication 30, Supplement to Part 1, Pergamon Press, Oxford (1979).
12. J. Hopenfeld, Radioactivity Transport Following Steam Generator Tube Rupture, NRC Report NUREG-1108, National Technical Information Service, Springfield, VA (1985).
13. T. T. Martin et al., NRC Report on the January 25, 1982 Steam Generator Tube Rupture at R. E. Ginna Nuclear Power Plant, NRC Report NUREG-0909, National Technical Information Service, Springfield, VA (1982).



**APPENDIX A**  
**TABULATION OF PLANT MEASUREMENT DATA**

This Appendix contains the data obtained during the field measurement campaigns at the two PWRs. The radioiodine concentration measurements were performed by SAIC as described in Sect. 2 of the report. Other data on plant operating conditions were obtained from station chemistry logs, printouts of plant operating parameters, and discussions with plant staff. These data are grouped by variable and tabulated in the following sequence.

	<u>Tables</u>
Radioiodine concentrations in coolant	A1, A2
Reactor power level	A3
Reactor coolant pressure	A4
Reactor coolant temperature	A5
Boron concentrations in coolant	A6
Hydrogen concentrations in coolant	A7
pH of coolant	A8

The data are presented in sequence with negative (-) values before and positive (+) values after the time of reactor shutdown. Reactor shutdown (time = 0) is defined to occur at the time the power level reached zero.

Table A1. Radioiodine concentrations measured at Plant 1

1986 Date	Time <sup>b</sup>	Isotope	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>			
			Fraction #1	Fraction #2	Fraction #3	Fraction #4
9-25	1615  (-34.5)	<sup>131</sup> I	4.13±.39	0.24±.05	<0.061	<0.070
		<sup>132</sup> I	84.1±1.2	0.34±.12	0.27±.10	0.48±.10
		<sup>133</sup> I	36.1±1.8	<0.053	<0.068	<0.062
		<sup>134</sup> I	181±3	<0.43	<0.13	<0.30
		<sup>135</sup> I	83.4±4.7	<0.098	<0.16	<0.16
9-26	0800  (-18.8)	<sup>131</sup> I	3.97±.54	0.31±.10	<0.096	<0.14
		<sup>132</sup> I	74.8±1.3	1.25±.30	0.77±.14	1.11±.24
		<sup>133</sup> I	30.4±.8	<0.16	<0.11	<0.15
		<sup>134</sup> I	156±4	2.25±.38	1.77±.25	3.59±.55
		<sup>135</sup> I	71.2±4.7	1.66±.32	1.78±.41	1.27±.24
9-26	1100  (-15.6)	<sup>131</sup> I	3.84±.50	<0.10	0.17±.08	<0.10
		<sup>132</sup> I	82.8±2.5	0.85±.30	<0.14	<0.11
		<sup>133</sup> I	31.1±.7	<0.89	<0.078	<0.12
		<sup>134</sup> I	209±16	2.51±.50	0.72±.16	<0.18
		<sup>135</sup> I	73.1±4.9	1.09±.33	0.57±.18	<0.21
9-26	1700  (-9.8)	<sup>131</sup> I	3.71±.68	<0.16	<0.12	<0.090
		<sup>132</sup> I	78.2±2.6	<0.19	0.43±.15	0.27±.11
		<sup>133</sup> I	31.6±2.6	<0.12	<0.088	<0.86
		<sup>134</sup> I	131±6	1.58±.32	1.25±.41	<0.15
		<sup>135</sup> I	85.2±5.9	1.34±.24	0.73±.21	0.57±.22
9-26	2100  (-5.8)	<sup>131</sup> I	5.16±.72	<0.080	<0.14	<0.20
		<sup>132</sup> I	93.2±3.3	1.76±.16	0.42±.13	0.48±.12
		<sup>133</sup> I	31.9±3.8	<0.13	<0.090	<0.11
		<sup>134</sup> I	173±10	3.15±.47	1.19±.21	0.57±.14
		<sup>135</sup> I	83.1±5.1	1.22±.21	0.47±.19	<0.27

Table A1. Radioiodine concentrations measured at Plant 1 (cont.)

1986 Date	Time <sup>b</sup>	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>				
		Isotope	Fraction #1	Fraction #2	Fraction #3	Fraction #4
9-26	2240  (-3.9)	<sup>131</sup> I	4.85±.64	<0.15	<0.16	<0.11
		<sup>132</sup> I	85.8±2.1	2.03±.19	2.40±.22	0.81±.31
		<sup>133</sup> I	25.3±1.2	<0.66	<0.14	<0.11
		<sup>134</sup> I	121±17	3.13±.31	4.22±.40	0.47±.19
		<sup>135</sup> I	74.0±5.2	2.12±.32	2.58±.33	1.03±.24
9-27	0050  (-1.8)	<sup>131</sup> I	2.44±.61	<0.060	0.69±.18	<0.11
		<sup>132</sup> I	99.4±2.3	0.79±.15	18.0±.6	<0.27
		<sup>133</sup> I	20.1±1.1	<0.068	<0.36	<0.13
		<sup>134</sup> I	158±11	1.10±.28	28.6±2.6	2.22±.57
		<sup>135</sup> I	56.9±2.9	0.57±.11	11.2±.9	0.77±.23
9-27	0235  (0.0)	<sup>131</sup> I	5.59±.56	<0.10	0.56±.15	<0.11
		<sup>132</sup> I	77.6±1.7	1.01±.20	7.09±.53	1.18±.04
		<sup>133</sup> I	21.7±3.1	<0.65	<0.27	<0.14
		<sup>134</sup> I	36.6±5.5	0.64±.17	3.31±.33	0.95±.23
		<sup>135</sup> I	41.4±2.6	1.00±.17	4.32±.62	0.17±.06
9-27	1300  (+10.4)	<sup>131</sup> I	16.8±.6	0.36±.06	0.18±.04	<0.068
		<sup>132</sup> I	81.4±3.2	1.26±.27	0.30±.12	0.29±.09
		<sup>133</sup> I	14.4±1.4	<0.089	0.14±.04	0.16±.04
		<sup>134</sup> I	<1.7	<3.2	<1.0	<0.16
		<sup>135</sup> I	10.6±1.2	<0.16	<0.055	<0.093
9-27	2050  (+18.3)	<sup>131</sup> I	10.0±.5	1.00±.41	0.21±.06	<0.080
		<sup>132</sup> I	48.4±2.4	<1.5	0.92±.31	<1.3
		<sup>133</sup> I	1.34±.39	0.12±.03	<0.066	<0.070
		<sup>134</sup> I	<0.27	<0.093	<0.080	<0.10
		<sup>135</sup> I	2.93±.74	<0.055	<0.084	<0.054



Table A1. Radioiodine concentrations measured at Plant 1 (cont.)

1986 Date	Time <sup>b</sup>	Isotope	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>			
			Fraction #1	Fraction #2	Fraction #3	Fraction #4
9-28	0255  (+24.3)	<sup>131</sup> I	26.8±1.4	0.53±.07	0.82±.08	<0.061
		<sup>132</sup> I	51.2±1.5	0.90±.40	1.26±.23	<1.2
		<sup>133</sup> I	6.76±.45	<0.080	<0.078	<0.053
		<sup>134</sup> I	<0.23	<0.11	<0.091	<0.082
		<sup>135</sup> I	3.46±.70	<0.085	<0.11	<0.086
9-28	0840  (+30.1)	<sup>131</sup> I	13.8±.7	0.52±.07	0.81±.08	1.01±.08
		<sup>132</sup> I	27.2±.8	1.10±.22	1.17±.39	1.40±.23
		<sup>133</sup> I	<0.46	<0.076	<0.093	<0.089
		<sup>134</sup> I	<0.19	<0.11	<0.079	<0.078
		<sup>135</sup> I	3.6±1.0	<0.085	<0.11	<0.086
9-28	1850  (+40.3)	<sup>131</sup> I	3.95±.26	0.22±.05	2.21±.12	0.14±.05
		<sup>132</sup> I	11.4±.6	<1.9	6.39±.30	<0.83
		<sup>133</sup> I	<0.25	<0.055	<0.20	<0.049
		<sup>134</sup> I	<1.2	<0.12	<0.10	<0.076
		<sup>135</sup> I	<0.10	<0.059	<0.059	<0.085
9-28	2115  (+42.7)	<sup>131</sup> I	0.97±.13	1.39±.13	<0.074	<0.059
		<sup>132</sup> I	3.28±.24	6.63±.36	<1.1	<0.054
		<sup>133</sup> I	<0.14	<0.13	<0.070	<0.043
		<sup>134</sup> I	<0.087	<0.18	<0.13	<0.078
		<sup>135</sup> I	<0.088	<0.14	<0.093	<0.070
9-28	2330  (+44.9)	<sup>131</sup> I	0.46±.12	1.61±.14	<0.064	<0.069
		<sup>132</sup> I	1.80±.21	6.18±.35	<0.087	<0.060
		<sup>133</sup> I	<0.14	<0.13	<0.058	<0.043
		<sup>134</sup> I	<0.085	<0.16	<0.080	<0.083
		<sup>135</sup> I	<0.096	<0.14	<0.084	<0.090

Table A1. Radioiodine concentrations measured at Plant 1 (cont.)

1986 Date	Time <sup>b</sup>	Isotope	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>			
			Fraction #1	Fraction #2	Fraction #3	Fraction #4
9-29	0045  (+46.2)	<sup>131</sup> I	0.52±.11	1.67±.15	0.10±.04	<0.065
		<sup>132</sup> I	1.64±.22	7.72±.42	<0.058	0.21±.04
		<sup>133</sup> I	<0.13	<0.14	<0.037	<0.048
		<sup>134</sup> I	<0.078	<0.20	<0.087	<0.095
		<sup>135</sup> I	<0.11	<0.16	<0.098	<0.10
9-29	0220  (+47.8)	<sup>131</sup> I	3.78±.82	0.71±.10	0.12±.05	<0.056
		<sup>132</sup> I	1.64±.32	3.85±.29	<0.081	<0.051
		<sup>133</sup> I	<0.083	<0.096	<0.052	<0.046
		<sup>134</sup> I	<0.078	<0.10	<0.11	<0.080
		<sup>135</sup> I	<0.088	<0.12	<0.10	<0.071

<sup>a</sup>Results are ± 1-sigma uncertainties (or are <2-sigma detection limits) and have been decay-corrected to the time of sampling.

<sup>b</sup>Sampling time, with time (h) before (-) or after (+) shutdown shown in parentheses.

Table A2. Radioiodine concentrations measured at Plant 2

1986 Date	Time <sup>b</sup>	Isotope	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>			
			Fraction #1	Fraction #2	Fraction #3	Fraction #4
10-24	0710  (-18.6)	<sup>131</sup> I	7.78±.35	0.16±.06	<0.047	<0.064
		<sup>132</sup> I	50.6±1.4	<0.70	<0.12	<0.11
		<sup>133</sup> I	31.5±1.0	0.50±.07	0.22±.04	<0.20
		<sup>134</sup> I	94.4±4.9	2.73±.53	<0.39	<0.36
		<sup>135</sup> I	52.4±3.0	1.06±.24	<0.13	<0.16
10-24	1945  (-6.0)	<sup>131</sup> I	5.48±.46	<0.084	<0.57	<0.083
		<sup>132</sup> I	42.3±2.2	0.99±.34	0.66±.09	<0.088
		<sup>133</sup> I	23.1±.5	0.46±.08	0.18±.06	<0.074
		<sup>134</sup> I	60.1±5.5	1.20±.10	0.82±.18	0.23±.10
		<sup>135</sup> I	41.9±2.1	1.11±.25	0.49±.19	0.40±.12
10-24	2145  (-4.0)	<sup>131</sup> I	7.94±.42	<0.21	<0.56	<0.062
		<sup>132</sup> I	42.7±1.2	1.45±.23	0.77±.13	0.21±.08
		<sup>133</sup> I	28.7±.6	0.72±.09	0.47±.06	0.21±.05
		<sup>134</sup> I	57.0±2.6	1.82±.43	1.02±.18	0.42±.12
		<sup>135</sup> I	40.7±2.3	1.49±.21	0.93±.06	0.40±.08
10-24	2345  (-2.0)	<sup>131</sup> I	14.8±.5	<0.19	<0.15	<0.60
		<sup>132</sup> I	50.2±1.7	0.81±.12	<0.15	<0.081
		<sup>133</sup> I	33.7±2.4	0.67±.07	0.50±.07	<0.058
		<sup>134</sup> I	34.6±1.7	0.93±.34	0.40±.15	<0.068
		<sup>135</sup> I	37.5±1.8	0.69±.16	0.97±.17	<0.11
10-24	0200  (+0.3)	<sup>131</sup> I	24.8±.5	1.41±.11	5.38±.20	1.06±.09
		<sup>132</sup> I	44.4±1.3	2.29±.21	9.12±.33	1.31±.21
		<sup>133</sup> I	37.6±2.1	1.89±.11	7.32±.48	1.51±.11
		<sup>134</sup> I	8.8±1.2	0.87±.24	2.41±.39	0.44±.18
		<sup>135</sup> I	27.5±1.3	1.68±.28	6.67±.53	1.44±.25



Table A2. Radioiodine concentrations measured at Plant 2 (cont.)

1986 Date	Time <sup>b</sup>	Isotope	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>			
			Fraction #1	Fraction #2	Fraction #3	Fraction #4
10-25	0410  (+2.4)	<sup>131</sup> I	65.8±1.8	<0.17	9.09±.54	0.79±.04
		<sup>132</sup> I	48.6±1.6	1.17±.16	6.52±.32	0.39±.15
		<sup>133</sup> I	77.1±4.3	1.80±.11	9.80±.22	1.20±.08
		<sup>134</sup> I	<3.4	<0.16	<1.1	<0.096
		<sup>135</sup> I	40.8±1.7	1.46±.23	5.50±.48	0.57±.13
10-25	0625  (+4.7)	<sup>131</sup> I	80.4±2.8	1.62±.11	0.49±.06	0.28±.06
		<sup>132</sup> I	57.6±1.8	1.32±.15	0.34±.09	<0.11
		<sup>133</sup> I	85.6±2.6	1.71±.10	0.54±.06	0.34±.06
		<sup>134</sup> I	<0.73	<0.35	<0.14	<0.19
		<sup>135</sup> I	38.1±1.8	1.10±.22	0.42±.09	<0.15
10-25	0955  (+8.2)	<sup>131</sup> I	72.3±2.5	1.62±.10	0.89±.07	0.27±.06
		<sup>132</sup> I	43.6±1.5	1.26±.13	0.62±.08	0.37±.06
		<sup>133</sup> I	65.0±1.9	1.35±.09	0.90±.06	0.35±.05
		<sup>134</sup> I	<1.1	<0.25	<0.11	<0.10
		<sup>135</sup> I	23.6±1.3	0.69±.12	0.43±.13	<0.099
10-25	1630  (+14.8)	<sup>131</sup> I	57.9±1.4	1.31±.09	3.58±.14	0.19±.06
		<sup>132</sup> I	28.0±.8	0.55±.11	1.67±.19	0.16±.06
		<sup>133</sup> I	41.2±1.2	0.88±.07	2.56±.11	0.21±.04
		<sup>134</sup> I	<0.37	<0.14	<2.2	<0.10
		<sup>135</sup> I	9.6±1.1	0.39±.09	0.70±.11	<0.088
10-25	2130  (+20.8)	<sup>131</sup> I	39.8±.8	1.61±.10	1.32±.08	2.13±.11
		<sup>132</sup> I	16.2±.7	<0.15	<0.12	0.95±.15
		<sup>133</sup> I	25.7±.8	1.36±.08	0.80±.07	1.41±.49
		<sup>134</sup> I	<0.37	<0.11	<0.074	<0.084
		<sup>135</sup> I	5.33±.56	<0.17	<0.074	0.39±.08

Table A2. Radioiodine concentrations measured at Plant 2 (cont.)

1986 Date	Time <sup>b</sup>	Isotope	Concentrations (nCi/g) in primary coolant fractions <sup>a</sup>			
			Fraction #1	Fraction #2	Fraction #3	Fraction #4
10-26	0050  (+23.1)	131I	39.5±.8	1.24±.08	0.53±.06	0.37±.06
		132I	13.3±.5	0.19±.06	0.40±.06	0.17±.06
		133I	24.5±1.3	0.62±.06	0.39±.05	0.29±.04
		134I	<0.28	<0.10	<0.076	<0.073
		135I	5.97±.66	0.55±.10	<0.080	<0.072
10-26	0405  (+26.3)	131I	32.9±1.2	1.92±.11	<0.096	<0.072
		132I	14.0±.9	0.92±.06	0.24±.06	0.21±.05
		133I	17.6±.5	0.89±.08	0.34±.04	0.13±.04
		134I	<0.25	<0.083	<0.067	<0.055
		135I	4.46±.48	0.41±.13	<0.093	<0.099
10-26	0750  (+30.1)	131I	31.1±1.0	1.99±.10	0.33±.06	0.27±.06
		132I	12.4±.7	0.58±.13	0.25±.06	<0.088
		133I	17.0±3.4	1.10±.08	0.24±.04	0.22±.05
		134I	<0.27	<0.30	<0.13	<0.20
		135I	4.49±.64	<0.11	<0.085	<0.13
10-26	1210  (+34.4)	131I	13.7±1.1	1.58±.40	10.8±.5	0.47±.06
		132I	5.13±.41	1.02±.20	0.43±.02	0.23±.06
		133I	6.69±.22	0.91±.07	5.46±.16	<0.19
		134I	<0.43	<0.18	<0.24	<0.10
		135I	1.87±.32	<0.17	1.86±.31	<0.069
10-26	1600  (+38.3)	131I	20.7±.7	2.17±.13	0.93±.06	0.29±.07
		132I	9.6±.8	1.44±.18	0.32±.06	<0.095
		133I	10.0±.3	1.01±.10	0.32±.06	0.32±.06
		134I	<0.37	<0.17	<0.080	<0.11
		135I	3.28±.49	0.54±.11	<0.085	<0.13

<sup>a</sup>Results are  $\pm 1$ -sigma uncertainties (or are  $<2$ -sigma detection limits) and have been decay-corrected to the time of sampling.

<sup>b</sup>Sampling time, with time (h) before (-) or after (+) shutdown shown in parentheses.

Table A3. Reactor power level data

---

<u>Plant 1</u>		<u>Plant 2</u>	
<u>Time (h)<sup>a</sup></u>	<u>Power level</u>	<u>Time (h)<sup>a</sup></u>	<u>Power level</u>
-42.5	100%	-18.6	100%
-18.8	100%	-13.0	100%
- 7.8	100%	- 6.4	100%
- 7.4	95%	- 4.7	70%
- 6.4	85%	- 2.3	10%
- 5.5	75%	0.0	0%
- 4.1	50%		
- 1.7	25%		
0.0	0%		

---

<sup>a</sup>Time (h) before shutdown.

---



Table A4. Reactor coolant pressure data

Plant 1			Plant 2		
Time (h) <sup>a</sup>	Coolant pressure (psig)	(MPa)	Time (h) <sup>a</sup>	Coolant pressure (psig)	(MPa)
-42.5	1990	13.7	-18.6	2250	15.5
-18.8	1990	13.7	- 6.0	2250	15.5
- 7.8	1990	13.7	- 4.0	2250	15.5
- 5.8	1990	13.7	- 2.0	2250	15.5
- 3.9	1990	13.7	+ 0.3	2250	15.5
- 1.8	1985	13.7	+ 2.4	2250	15.5
0.0	1990	13.7	+ 4.7	2150	14.8
+21.9	650	4.5	+ 8.2	1990	13.7
+33.0	400	2.8	+14.8	1700	11.7
+40.3	378	2.6	+19.8	1700	11.7
+42.7	378	2.6	+20.8	400	2.8
+44.9	378	2.6	+23.1	170	1.2
+46.2	378	2.6	+26.3	170	1.2
+47.8	378	2.6	+30.1	170	1.2
			+34.4	170	1.2
			+38.3	170	1.2

<sup>a</sup>Time (h) before (-) or after (+) shutdown.

Table A5. Reactor coolant temperature data

Plant 1			Plant 2		
Time (h) <sup>a</sup>	Coolant temperature		Time (h) <sup>a</sup>	Coolant temperature	
	(°F)	(°C)		(°F)	(°C)
-42.5	575	302	-18.6	532	278
-18.8	565	296	-13.0	532	278
- 7.8	565	296	- 6.4	532	278
- 8.2	565	296	- 4.7	532	278
- 7.4	565	296	- 2.3	532	278
- 5.8	564	296	0.0	532	278
- 3.9	558	292	+ 3.0	450	232
- 1.8	549	287	+ 9.8	350	177
0.0	543	284	+14.8	325	163
+10.4	540	282	+15.8	300	149
+18.3	490	204	+18.5	230	110
+21.9	394	201	+22.3	210	99
+23.8	350	177	+23.7	200	93
+33.0	177	81	+32.3	140	60
+40.3	140	60	+38.3	140	60
+42.7	137	58			
+44.9	137	58			
+46.2	135	59			
+47.8	135	59			

<sup>a</sup>Time (h) before (-) or after (+) shutdown.

Table A6. Boron concentrations in reactor coolant

Plant 1		Plant 2	
Time (h) <sup>a</sup>	[Boron] (ppm)	Time (h) <sup>a</sup>	[Boron] (ppm)
-42.5	1.9	-18.6	85
-18.8	1.8	-13.0	70
- 5.8	1.9	0.0	70
- 3.9	1.9	+ 0.3	173
- 1.8	1.9	+ 1.8	750
0.0	1.9	+ 4.6	783
+ 4.0	1.9	+20.8	1010
+13.6	371	+21.8	998
+17.2	388	+23.1	1057
+23.8	384	+25.3	1000
+25.6	498	+38.3	1067
+30.1	505		
+31.5	519		
+44.9	514		

<sup>a</sup>Time (h) before (-) or after (+) shutdown.



Table A7. Hydrogen concentrations in reactor coolant

Plant 1		Plant 2	
Time (h) <sup>a</sup>	[Hydrogen] (cm <sup>3</sup> /kg)	Time (h) <sup>a</sup>	[Hydrogen] (cm <sup>3</sup> /kg)
-42.5	35.2	-18.6	26.0
-34.5	35.2	-13.0	18.0
-18.8	14.7	+ 0.3	8.4
-15.6	12.2	+ 6.5	4.9
-11.8	12.5		
- 7.2	7.3		
- 3.9	7.0		
+ 1.3	8.1		
+ 6.7	7.9		
+13.2	5.2		
+17.2	3.1		
+21.9	2.5		
+26.8	1.3		
+33.0	2.3		
+40.3	1.8		

<sup>a</sup>Time (h) before (-) or after (+) shutdown.

Table A8. pH of reactor coolant

Plant 1		Plant 2	
Time (h) <sup>a</sup>	pH	Time (h) <sup>a</sup>	pH
-42.5	8.8	-18.6	7.5
-18.8	8.8	+ 0.3	7.1
- 5.8	8.8	+23.1	6.6
- 3.9	8.8	+49.8	6.6
- 1.8	8.7		
0.0	8.8		
+10.4	8.9		
+18.3	6.5		
+23.8	6.5		
+30.0	6.3		
+40.3	6.3		
+42.7	6.4		
+44.9	6.4		
+46.2	6.4		
+47.8	6.3		

<sup>a</sup>Time (h) before (-) or after (+) shutdown.

**PART 2: IODINE PARTITIONING IN PRESSURIZED WATER  
REACTOR STEAM GENERATOR ACCIDENTS**

E. C. Beahm, S. R. Daish, W. E. Shockley, and J. Hopenfeld  
Chemical Technology Division  
Oak Ridge National Laboratory  
Post Office Bx 2008  
Oak Ridge, Tennessee 37831-6221

**1. INTRODUCTION**

**1.1 BACKGROUND**

Pressurized water reactors (PWRs) are designed to withstand certain postulated accidents, called design-basis accidents. The release of radioactive fission products to the environment through a path opened following a rupture of one tube in the steam generator falls into this category of accidents. The release doses depend directly on the concentration levels of fission products in the primary coolant; therefore, these levels are kept below those that could result in exceeding the allowable release doses discussed in the regulatory document 10 CFR 100.<sup>1</sup>

As described by Hopenfeld,<sup>2</sup> the partition coefficient (PC) that expresses the volatility of iodine is a very important factor in dose calculations. A high PC would tend to increase the retention of iodine within the secondary circuit, resulting in relatively small off-site radioactivity releases. Conversely, low PCs would tend to yield high dose releases.

Thermochemical data are not available at temperatures of interest to calculate iodine partitioning. The reducing conditions expected in primary coolant systems would suggest that  $I_2$  will not be stable. However, tests of primary coolant show large variations in  $I_2$  content.<sup>3</sup> It is possible that the results reflect the very low concentrations ( $10^{-9}$  to  $10^{-12}$  M) where anomalous behavior may exist.

Styrikovich,<sup>4</sup> obtained data on iodine volatility attributed to HOI solutions, which show strong pH dependence. However, Martucci's study of iodine species in reactor coolant indicates that iodine volatility does not depend on pH.<sup>3</sup>

Because of these uncertainties and the lack of data, an experimental program was initiated to study iodine behavior under prototypic conditions that represent an accident involving the rupture of a steam generator tube.

This program was carried out in two parts: (1) tests of primary coolant from reactor plants and (2) tests under simulated conditions. The primary coolant tests, carried out by Voillequé, are described in Part 1 of this report.

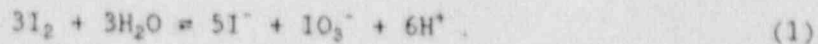


## 1.2 IODINE BEHAVIOR AT LOW AQUEOUS CONCENTRATIONS

It is well known that very low concentrations of many materials exhibit behavior that is unlike the interactions of the same materials at high concentrations.<sup>5</sup> Tracers have been called "a special state of matter" because of the unusual properties they often display. Unusual or tracer behavior is often observed at concentrations from less than  $\sim 10^{-5}$  to  $10^{-6}$  M.<sup>5</sup> In many cases, such interactions can be explained by fundamental chemistry. For example, at very low concentrations, chemical reactions with rates that are dependent on the trace element to greater than first order are not as likely to occur because of the law of mass action. Because reaction paths that are available at high concentrations are sometimes not operable at low concentrations, other interactions that were overwhelmed at high concentrations may become important.

In addition, at very low concentrations, there can be impurities in the system that are often undetectable, which may actually have a greater concentration than the trace element. The concept of "omnipresence concentration" has been introduced by Noddack<sup>6</sup> to illustrate that every element has a borderline concentration at which it can be found virtually everywhere. For example, the omnipresence concentration of such common elements as Si, Mg, Ca, and Fe is approximately  $10^{-3}$  M. The importance of the omnipresence of impurities is that they can interact with the trace element and cause it to exhibit unusual behavior.

Anomalous behavior of low concentrations of radioiodine has been reported since the very earliest studies.<sup>7</sup> Generally, the anomalies consist of unexpected distributions of iodine species and unidentified iodine species.<sup>7-9</sup> The hydrolysis of iodine, given in Eq. (1), provides a clue to this behavior:



In this reaction, iodine appears in three oxidation numbers, and there is little doubt that other oxidation numbers must be involved since the reactant  $\text{I}_2$  has a value of 0 and the products have values of -1 and +5. At trace concentrations, bimolecular reactions of iodine species would not readily occur, and intermediate oxidation states could persist or react by alternative mechanisms.

In the simulated steam generator tests that are reported in this work, the aqueous iodine concentration was  $10^{-9}$  M; the primary coolant in operating PWRs would have iodine concentrations less than or approximately equal to this value.<sup>10</sup> Thus, tracer effects, along with more common processes such as oxidation, hydrolysis, and adsorption, will determine which iodine species will be present in the solution.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 SIMULATED STEAM GENERATOR TESTS

The experimental system, used to study the vapor-liquid partitioning of iodine in a simulated PWR steam generator, consists of a large (152-cm-long, 8.9-cm-diam) stainless steel autoclave, which is heated electrically in three zones along its length and is connected to a separate condenser vessel via an orifice and air-operated valve. A schematic diagram of the system is shown in Fig. 1.

The experimental procedure was as follows. Feed solutions were prepared the day before the experiment. Sufficient orthoboric acid (JMC puratronic grade) to give a concentration of 0.05 to 0.5 M (usually 0.2 M) was dissolved in demineralized-distilled water. If necessary, the pH was adjusted by addition of 1.0 M NaOH, and the volume was adjusted to 1.2 L (some tests were carried out with 1.75 L or 4.0 L of feed solution). Just before the experiment, the  $^{131}\text{I}$  tracer was added. The tracer was received in the form of "carrier free"  $\text{Na}^{131}\text{I}$  in 0.1 M NaOH solution (DuPont); this was diluted and added to the feed solution to give  $\sim 1 \times 10^{-6}$  Ci/mL. This gave a total iodine concentration in each of the experiments of  $1 \times 10^{-9}$  M to  $5 \times 10^{-9}$  M.

If the experiment was to be performed in an argon atmosphere, the feed solution would be sparged with argon for 16 h. A 20-mL sample was taken for iodine analysis, and the solution was loaded into the top of the pressure vessel through a stainless steel funnel. Further argon sparging could take place at this stage; oxygen-free argon was supplied to the bottom of the vessel, and the oxygen content of the exhaust gas was monitored with an oxygen analyzer. The oxygen content was always  $< 2.5 \times 10^{-7}$  atm  $\text{O}_2$  before the test was started, when oxygen-free conditions were required. In order to reduce the amount of inert gas, the chamber was vacuum pumped to 0.2 atm before the start of the test. After all valves to the vessel had been closed, the simulated steam generator was heated to 285°C and 1000 psi pressure.

The use of radioactive tracers at low concentrations in large vessel at high temperature and pressure makes it necessary to ensure that appropriate handling and operating procedures are followed. This involves, among other good practice techniques, thoroughly cleaning the system between runs and also maintaining a temperature profile that eliminates steam condensation at the top of the pressure vessel. Steam reflux in the pressure vessel removes iodine from the vapor phase and results in an erroneously low apparent iodine volatility.

After a period of equilibration at steady temperature and pressure, usually 4 to 6 h after startup, a sample of the vapor phase was taken by opening the air-operated valve for 10 to 20 s and allowing steam to pass through the orifice into the condenser. After waiting a few minutes to allow cooling, the condensate was drawn off from the bottom of the condenser. At this time, a sample of liquid was also taken from the main vessel. Samples were taken in this way periodically

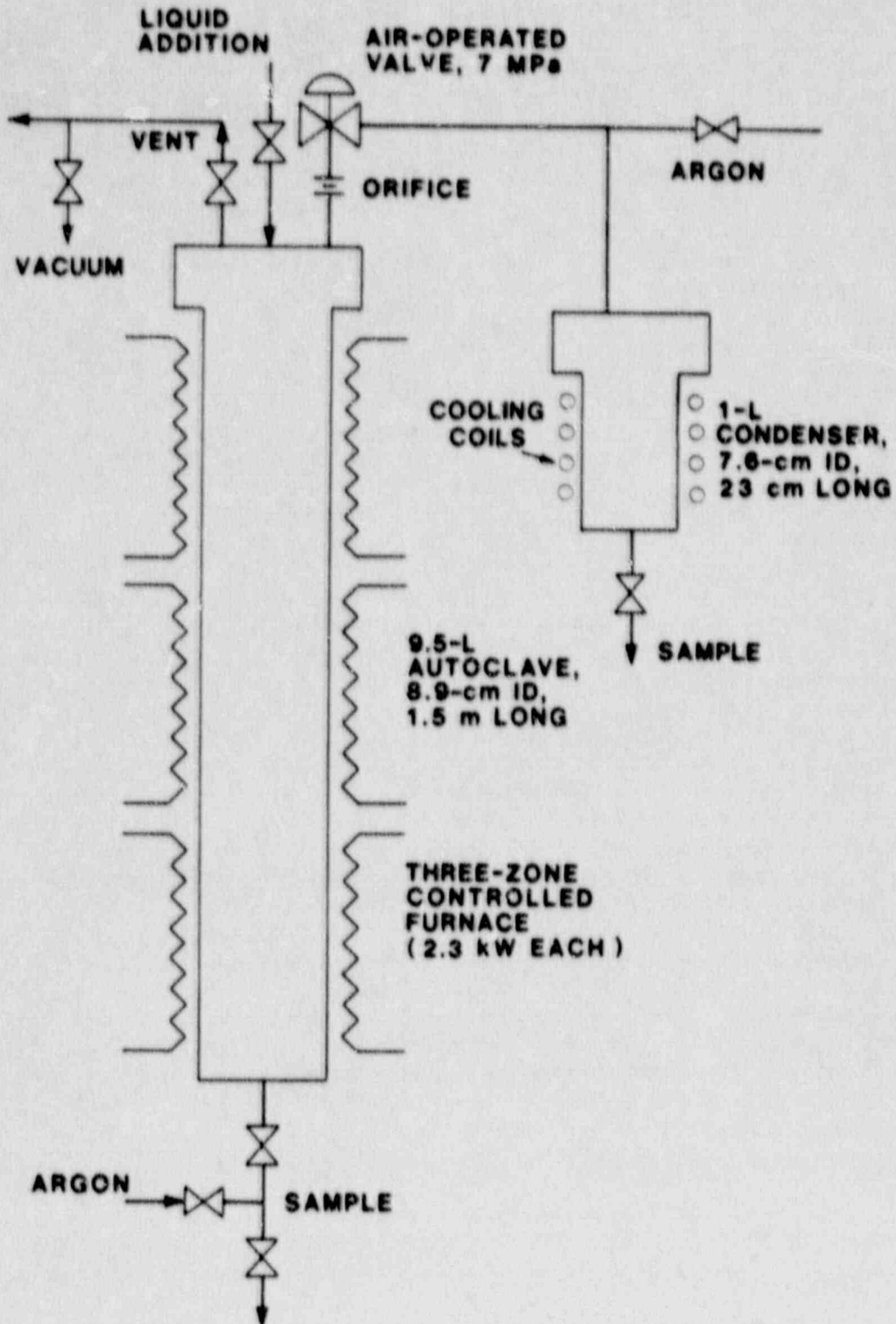


Fig. 1. Experimental system for investigating iodine transport from a simulated steam generator.



throughout the test. Adsorption of iodine from solution onto the vessel walls was determined by comparing the  $^{131}\text{I}$  in the liquid samples with that in the feed solution and correcting for the amount in the gas phase.

The amount of  $^{131}\text{I}$  in the liquid and condensate fractions was determined by counting 1-mL aliquots using a Nuclear Data System 680 with a NaI well detector. The data were corrected for decay, background, and counter efficiency. Samples were counted for between 1 and 16 h, according to their activity; this gave statistical counting errors of between 0.03 and 2.0%.

Iodine speciation in the liquid samples was determined by extracting (with minimum delay time) 10 mL of sample solution into 10-mL of  $\text{CCl}_4$  to remove  $\text{I}_2$  and organic iodides; the phases were separated, and 1 mL of aqueous phase containing the  $\text{I}^-$  and  $\text{IO}_3^-$  fraction was counted as above. The organic phase was then back-extracted with 10 mL of 0.10 M NaOH, using 0.01 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution to convert the  $\text{I}_2$  to  $\text{I}^-$  and extract it back into the aqueous phase - any organic iodides remained in the organic portion. The phases were again separated and counted as before.

It is very difficult to quantitatively evaluate extraction techniques when the material being extracted is present in tracer concentrations. We have tested the extraction technique to determine the recovery of the initial iodine in the pH range of 5 to 9 that was used in the simulated steam generator tests. The extraction tests were done at room temperature on solutions that had not been heated. Table 1 shows the percent recovery of initial iodine,  $\text{I}_2$ , and ( $\text{I}^- + \text{IO}_3^-$ ). The recovery was good throughout the pH range. The percentage of iodine that extracted as  $\text{I}_2$  decreased with increasing pH. This, too, is reasonable behavior for iodine (see Sect. 3.1).

Table 1. Iodine extraction of feed solution at pH 5, 7, and 9 from  $\sim 1 \times 10^{-9}$  M  $\text{I}^-$  solutions in 0.2 M  $\text{H}_2\text{SO}_3$

Sample	$\text{I}_2$ (%)	$\text{I}^- + \text{IO}_3^-$ (%)	Recovery (%)
As made, pH 5	0.3	98.1	98.4
After Ar sparge, pH 5	2.6	98.5	101.4
pH 7 set with NaOH	$2.0 \times 10^{-2}$	97.01	97.03
pH 9 set with NaOH	$7.0 \times 10^{-3}$	98.63	98.64

At the end of the experiment, the heaters were switched off and the system was allowed to cool overnight. The vessel was emptied through a drain at the bottom and was refilled with distilled water to wash off any residue. The rinse water was drained and the process repeated several times to ensure that all chemicals were removed from the inside of the vessel before a new test was begun.

### 3. EXPERIMENTAL RESULTS

#### 3.1 LABORATORY TESTS

##### 3.1.1 Partition Coefficients

Volatility can be conveniently expressed in terms of PCs. They can be given in terms of concentration per unit volume or in terms of mass. In this work, the iodine PC is defined as:

$$PC = \frac{\text{concentration of iodine species in aqueous solution}}{\text{concentration of iodine species in gas}} \quad (2)$$

Because the concentration of iodine species in the gas appears in the denominator of the PC equation, small values of the PC correlate with high volatility, and large values correlate with low volatility. PCs, given on a concentration basis as in Eq. (2), may be converted to PCs on a mass basis by multiplying by the gas-to-aqueous-density ratio:

$$\text{iodine PC (mass basis)} = PC \left( \frac{\text{density of gas}}{\text{density of aqueous}} \right) \quad (3)$$

The PCs given by Eqs. (2) and (3) refer to the concentration or mass of all of the iodine species. For example, the concentration in the aqueous phase may be made up of  $I^-$ ,  $IO_3^-$ ,  $I_2$ , and possibly other chemical species. It is sometimes useful to define a PC in terms of only one species. Since  $I_2$  and organic iodide are expected to be the dominate volatile iodine species in these tests, two additional PCs are defined as follows:

$$PC \text{ of } I_2 = \frac{\text{concentration of } I_2 \text{ in aqueous solution}}{\text{concentration of } I_2 \text{ in gas}} \quad (4)$$

and

$$PC \text{ of } CH_3I = \frac{\text{concentration of } CH_3I \text{ in aqueous solution}}{\text{concentration of } CH_3I \text{ in gas}} \quad (5)$$

Several tests were run at pH 5 to evaluate the effect of the temperature profile in the pressure vessel on the measured PCs. In a test where the aqueous temperature was  $\geq 2^\circ C$  hotter than the top of the steam space, a PC of  $3.7 \times 10^4$  was measured. When the situation was reversed and the top of the steam space was  $\geq 10^\circ C$  higher than the aqueous solution, a PC of  $3.50 \times 10^2$  was measured. All of the PCs reported in this

section were run with a temperature profile such that the top of the pressure vessel near the opening for the steam sample was  $\geq 10^\circ\text{C}$  hotter than the aqueous surface, and there was a smoothly decreasing temperature gradient from the top of the vessel to the aqueous surface. This was done to prevent reflux in the pressure vessel and ensure that the true equilibrium PC was measured.

The matrix for the simulated steam generator tests consisted of experiments performed at pH levels of 5, 7, and 9 (measured at  $25^\circ\text{C}$ ) with an atmosphere of air/steam or argon/steam. Table 2 gives the results of these tests in terms of PC and the percentage of iodine in aqueous solution as  $\text{I}_2$  and organic iodide. Hydrolysis of  $\text{I}_2$  and oxidation of  $\text{I}^-$  are the two processes that may be cited as important in determining the iodine speciation and, thereby, the PCs. In iodine solutions with concentrations above trace levels, hydrolysis of  $\text{I}_2$  depends on pH.<sup>21</sup> This is also probably true of iodine in trace concentrations. The results given in Table 2 show that in either an argon/steam or an air/steam atmosphere, tests run at pH 9 gave a lower  $\text{I}_2$  percentage than those run at pH 5. The PCs at the higher pHs were higher than those at the lower pH and, from the definition of PC given in Eq. (2), this is the behavior that would be expected in solutions with a lower percentage of  $\text{I}_2$ .

Table 2. Summary of results from steam generator iodine experiments  
 $285^\circ\text{C}$ , 1000 psi,  $0.2 \text{ M}$  borate,  $1.0\text{E-}9 \text{ M}$   $\text{I}^-$

Atm	pH at $25^\circ\text{C}$	$\text{I}_2$ in liquid (%)	Organic I in liquid (%)	Partition coefficient, PC
Argon	5	2.04	0.11	6.87E+03
	7	0.44	0.07	5.18E+03
	9	0.02	0.00	4.75E+04
Air	5	22.00	3.95	3.50E+02
	7	1.20	0.15	8.88E+02
	9	0.12	0.01	7.16E+03

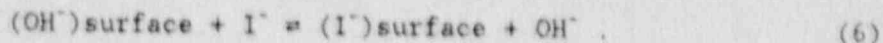
After all of the simulated steam generator tests at low iodine concentrations ( $\sim 10^{-9} \text{ M}$ ) were completed, several tests were run at concentrations near  $10^{-4} \text{ M}$  in order to compare the results with those obtained in tests run at trace concentrations and to obtain data on the aqueous/gas partitioning of  $\text{I}_2$  at  $285^\circ\text{C}$ . A test performed in argon/steam at pH 5 with  $1 \times 10^{-4} \text{ M}$   $\text{I}^-$  gave 0.1%  $\text{I}_2$  in aqueous solution and a PC of  $8 \times 10^3$ . The low percentage of  $\text{I}_2$  and the relatively high PC in this test, compared with results under similar conditions shown in Table 2, indicate that the aqueous iodine behavior is different at trace levels from that observed at concentrations above trace levels. The low percentage of  $\text{I}_2$  in the tests run with  $1 \times 10^{-4} \text{ M}$   $\text{I}^-$  is more consistent



with what might be expected for an iodine solution with a very low oxygen content.

### 3.1.2 Adsorption of Iodine from Solution

Adsorption of trace elements from aqueous solution onto surfaces often depends on pH. Generally, the adsorption of anions is enhanced at low pH, and the adsorption of cations is enhanced at high pH.<sup>5</sup> A somewhat simplified rationale for this behavior is that at high pH, trace anions must compete with OH<sup>-</sup> ions for the available adsorption sites, and at low pH, cations must compete with H<sup>+</sup> ions. For adsorption of I<sup>-</sup>, this interaction can be expressed as



Following the treatment given by Benes and Majer,<sup>5</sup> a distribution coefficient,  $q$ , is defined by

$$q_{\text{I}^-} = \frac{m_s}{m_L} \quad (7)$$

where  $m_s$  and  $m_L$  represent the amounts of I<sup>-</sup> adsorbed on the surface and in solution, respectively. Assuming the equilibrium given in Eq. (6) and a constant number of adsorption sites, it can be shown<sup>5</sup> for anions such as I<sup>-</sup> that

$$\log_{10} q = k - \text{pH}, \quad (8)$$

where the constant  $k$  includes (1) terms for the initial concentration of the tracer, (2) the equilibrium constant for Eq. (6), (3) the number of adsorption sites, and (4) the dissociation constant of water. In any real system, it would be very difficult to evaluate  $k$  by any technique other than empirical measurement.

The present study is consistent with the general expectation of adsorption of I<sup>-</sup>. Tests that were run at a pH of 7 or greater (measured at 25°C) gave little indication of adsorption onto the walls of the container. However, tests run at lower pH levels always had an initial aqueous <sup>131</sup>I count rate greater than that obtained when the sample was in the system at operating conditions.

Table 3 gives values of the distribution coefficient  $q_{\text{I}^-}$  that show less adsorption at the higher pHs. One test run at pH 5 had  $1 \times 10^{-3}$  M NO<sub>3</sub><sup>-</sup> in solution and resulted in a distribution coefficient of 0.53, which is only slightly greater than values obtained at pH 7 or 9. This is consistent with the argument that the extent of adsorption depends on the number of ions competing for adsorption sites.

Table 3. Distribution coefficients for the adsorption of iodine on stainless steel pressure vessel walls

pH	Solution volume (mL)	Distribution coefficient $q_s = m_s/m_L$
4.7-5.2	1200	4.23
5.0	1200	0.53 (NO <sub>3</sub> <sup>-</sup> added)
5.0	1200	1.45 (air)
3.8	1200	1.45 (0.5 M H <sub>3</sub> BO <sub>3</sub> air)
7.0	1200	0.26
7.0	1200	0.33
7.0	1400	0.00
9.0	1200	0.10 (0.5 M H <sub>3</sub> BO <sub>3</sub> air)

#### 4. DISCUSSION

##### 4.1 FORMATION OF I<sub>2</sub> AT TRACE CONCENTRATIONS

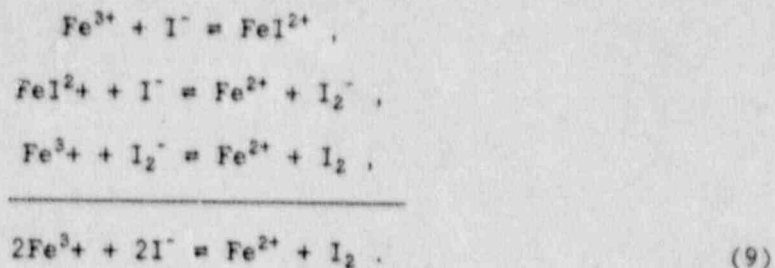
In the simulated steam generator iodine tests, there is clearly some mechanism capable of maintaining a fraction of the aqueous iodine in the form of I<sub>2</sub>. The mechanism is most effective at low pH and with oxygen in the system. Since iodine hydrolysis [Eq. (1)] is faster at high pH and oxidation of I<sup>-</sup> becomes easier with increasing amounts of oxygen in the system, the results of these tests are in line with expectations.

Some additional observations provide insight into the mechanism. First, the mechanism must be capable of maintaining a concentration of I<sub>2</sub> even though hydrolysis is destroying it. We ran a test in argon/steam at pH 5 (under the conditions listed in Table 2), except the initial iodine was in the form of I<sub>2</sub> with a concentration of  $5 \times 10^{-5}$  M ( $1.0 \times 10^{-4}$  gram-atoms I as I<sub>2</sub>/L). The liquid samples taken from the pressure vessel system had only 0.3% I<sub>2</sub>, with the remainder as I<sup>-</sup> and IO<sub>3</sub><sup>-</sup>. Thus, hydrolysis was very effective at removing I<sub>2</sub> at pH 5 (measured at 25°C) when the system temperature was 285°C.

The second observation was that under a given set of conditions, a higher percentage of I<sub>2</sub> can be formed at trace concentrations than at higher concentrations. This indicates a mechanism that is either not effective (i.e., cannot compete with other processes) at higher concentrations or one that is limited in the total amount of iodine that it can maintain as I<sub>2</sub>.

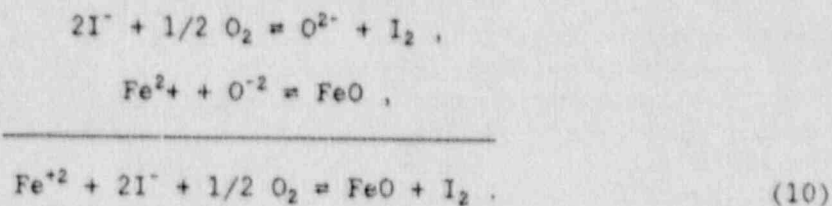
A third observation was that the I<sub>2</sub> fraction decreased when nitrate ions were in the system. A test at trace iodine concentrations (with  $10^{-3}$  M NO<sub>3</sub><sup>-</sup>) gave 0.4% I<sub>2</sub>, rather than 2% without the nitrate. This could indicate that the reaction forming I<sub>2</sub> occurs on the surface,

because the nitrate also resulted in lower adsorption of iodine on the vessel surface (see Table 3). Alternatively, it could indicate that a reaction in solution was inhibited by the excess anion. Fudge and Sykes have studied the effects of nitrate and other anions on the reaction:<sup>12,13</sup>



Their studies were carried out at 20°C. There was some retardation of the reaction rate due to nitrate, but it only amounted to a few percent at  $1 \times 10^{-2} \text{ M NO}_3^-$ , which was the lowest concentration used. However, in their tests, the  $\text{Fe}^{3+}$  and  $\text{I}^-$  concentrations were well above the trace levels of  $1.67 \times 10^{-7} \text{ M}$  and  $5.0 \times 10^{-3} \text{ M}$ , respectively. The retardation was attributed to the formation of  $\text{FeNO}_3^{2+}$ , which lowers the concentration of ferric ions.

We may also propose a surface reaction that directly involves oxygen:



In the tests run in argon/steam, the gaseous oxygen content was  $\leq 2.5 \times 10^{-7} \text{ atm}$ . If we assume the equilibrium at 285°C, then



which corresponds to an aqueous  $\text{O}_2$  concentration of  $\leq 10^{-9} \text{ M}$ . This concentration is of the same magnitude as the aqueous iodine concentration in the simulated steam generator tests.

It does not appear to be possible to choose between the mechanisms given by Eqs. (9) and (10), or perhaps others, based on the present studies.

Additional factors need to be considered in the discussion of the primary coolant tests. First, when a primary coolant sample is taken, it is necessary to depressurize the specimen, and the depressurization is accompanied by the release of hydrogen. Thus, in the process of taking a sample, the conditions of the specimen are altered from what



they were in the primary coolant. However, the test results show that no  $I_2$  was present when the primary coolant initially contained its normal  $H_2$  content. Thus, the primary coolant conditions prior to sampling must have been a determining factor in the percentage of  $I_2$ .

Also, the peak in percentage  $I_2$  observed at shutdown defies explanation by a sampling effect. At both plants, the coolant hydrogen concentration was lowered at least 20 h before shutdown, yet the peak in percent  $I_2$  occurred during the decrease in power just prior to shutdown or at shutdown.

During reactor operation, water radiolysis products such as OH,  $e_{aq}^-$ , H, and  $H_2O_2$  are in the coolant. Hydrogen added to the system suppresses the amount of oxidizing radiolysis products such as OH and  $H_2O_2$ .<sup>14</sup> When a sample is withdrawn from the primary coolant, it is removed from the intense radiation dose rate, and free radicals such as H and OH react very rapidly and thus are dissipated. Some hydrogen peroxide may remain in the sample specimen and this may react with  $I^-$  to form  $I_2$ . Again, this possible sampling effect is counter to the observations of a peak in percent  $I_2$  at shutdown. It is not clear why this mechanism would be favored at shutdown - the dose rate should be reduced and somewhat lower concentrations of water radiolysis products would be expected at shutdown.

#### 4.2 HI AS A SOURCE OF IODINE VOLATILITY

This work has centered on  $I_2$ , with some measurements of organic iodides, as the potential sources of volatile iodine in steam generator accidents. The chemical species HI could also be mentioned as an additional possibility. At the relatively high aqueous temperatures in the primary coolant, the dielectric constant of water is not as great as it is at lower temperatures, and there may be some association of  $H^+$  and  $I^-$  even in such a strong acid as HI.

If we assume the following equilibria,



and



we can calculate a PC due to HI, based on Eq. (13). To do this, we recognize that in aqueous solution the concentration of  $I^- \gg$  concentration of HI; therefore, we define the PC due to HI gas as:

$$PC \text{ (due to HI)} = \frac{\text{concentration of } I^- \text{ aqueous}}{\text{concentration of HI gas}} \quad (14)$$

Assuming ideality, the standard free energy change,  $\Delta G^\circ$ , for the reaction given by Eq. (13) can be written

$$\Delta G^\circ = -RT \ln \frac{P_{\text{HI}}}{\frac{\text{concentration of } \text{I}^- \text{ in aqueous}}{\text{concentration of } \text{H}^+ \text{ in aqueous}}} \quad (15)$$

where T is expressed in Kelvins.

Using the ideal gas law to substitute concentration of HI gas for  $P_{\text{HI}}$  and thermochemical data from Barner and Scheuerman,<sup>15</sup> we find at 285°C (558 K):

$$\text{PC (due to HI)} = \frac{9.6 \times 10^2}{\text{H}^+ \text{ concentration}} \quad (16)$$

From this, it seems that very high hydrogen ion concentrations would be required to make the PC (due to HI) low enough to create a volatility problem. For example, a PC (due to HI) of 2000 would require the extremely high  $\text{H}^+$  concentration of 0.48 M.

This analysis is supported by a test run at pH 5 (measured at 25°C) with an iodine concentration of  $1 \times 10^{-4}$  M. Under the normal operating conditions of argon/steam at 285°C, the measured PC was  $8 \times 10^3$ , and this was at least partially due to the 0.1%  $\text{I}_2$  in the aqueous solution.

#### 4.3 INTERRELATION OF PRIMARY COOLANT TESTS AND SIMULATED TESTS

In the simulated tests, it was possible to measure both the iodine speciation in solution and the iodine PC, whereas only iodine speciation could be measured in the primary coolant tests of Voillequé. The conversion of aqueous iodine speciation data into PCs requires values for the PC of  $\text{I}_2$  and possibly the PC of  $\text{CH}_3\text{I}$ , as defined in Eqs. (4) and (5). Attempts to directly measure the PC of  $\text{I}_2$  in the simulated steam generator pressure vessel were unsuccessful. Samples containing  $\text{I}_2$  above trace concentrations require a low pH to prevent hydrolysis. As described in Sect. 4, a test at pH 5 containing  $5 \times 10^{-5}$  M  $\text{I}_2$  resulted in almost complete hydrolysis of the  $\text{I}_2$ . A similar test at pH 2 produced large quantities of corrosion products from the vessel walls, which obscured attempts to analyze iodine species.

Parsly has evaluated PC values of  $\text{I}_2$  at temperatures up to  $\sim 185^\circ\text{C}$ , the boiling point of iodine.<sup>16</sup> Palmer et al.<sup>17</sup> fit Parsly's data for  $T > 385$  K as:

$$\log_{10} \text{PC of } \text{I}_2 = \frac{5615.4}{T} - 25.179 + 0.02990T \quad (17)$$

While Eq. (16) gives a minimum PC value of  $\text{I}_2$  of 5.45 at  $160^\circ\text{C}$ , extrapolation to temperatures above  $160^\circ\text{C}$  gives increasing values for PCs of  $\text{I}_2$ . At  $285^\circ\text{C}$ , a value of 37 is calculated from Eq. (17). It

should be pointed out that extrapolation far from a minimum value may not be completely justified. It is done here because it is the only value that can be compared with results obtained in the simulant tests.

If it is assumed that the PC values from the simulant tests given in Table 2 were due only to volatility of  $I_2$ , we calculate an average PC of  $I_2$  for those tests of  $23.7 \pm 17.8$ . From this value and the extrapolation using Eq. (17), we estimate the PC of  $I_2$  at  $285^\circ\text{C}$  as  $25 \pm 15$ . In Part 1 of this report, the maxima in percent iodine as  $I_2$  for  $^{131}\text{I}$  at times near shutdown was given as 20.9% at Plant 1 and Plant 2, respectively. The maximum in  $I_2$  percentage at Plant 1 may be compared to a test in the simulated steam generator experiments where 22% as  $I_2$  resulted in a measured PC of 350.

The minimum allowable iodine PCs, in terms of concentration per unit volume, is 2000 (from document 10 CRF 100). Use of the estimated PC for  $I_2$  indicates that an  $I_2$  percentage of  $<1.25 \pm 0.75$  is necessary if one desires to have a PC  $>2000$ . By comparison, a simulant test that showed 1.2% as  $I_2$  gave a PC of 888. In the plant tests, values of ~1% as  $I_2$  were at or near the borderline of detectable concentrations.

In Table 2 the  $I_2$ /organic iodide ratio is ~5 to 20 and this is also true of the plant tests. The volatility of organic iodides varies greatly for different species, with  $\text{CH}_3\text{I}$  being the most volatile. There are no data on the PCs of organic iodides at temperatures near  $285^\circ\text{C}$ . At  $25^\circ\text{C}$ , Nishikawa et al.<sup>16</sup> give a PC for  $\text{CH}_3\text{I}$  of 4.5 to 4.9, and a PC for  $\text{C}_6\text{H}_5\text{I}$  (iodobenzene) of 19.2 to 22.4. These values may be compared with a PC for  $I_2$  of 81 at  $25^\circ\text{C}$  that was calculated from thermochemical data given in Ref. 11. Thus, even though the  $I_2$ /organic iodide ratios are much greater than 1, a significant fraction of gaseous iodine could be in the form of organic iodides.

## 5. CONCLUSIONS

The simulant steam generator tests indicate that iodine at trace concentrations can have a species distribution in solution that is not expected or observed at higher concentrations. This is in agreement with previous experiments on radioiodine, which were conducted at trace concentrations but at lower temperatures.<sup>7-9</sup>

The present work has concentrated on studying iodine at primary coolant conditions. During an accident involving the rupture of a steam generator tube, there may be some mixing of primary and secondary coolants. The extent of this mixing would have to be evaluated in model calculations of such accidents. Secondary coolant generally contains ammonia or morpholine for pH control and hydrazine as a reducing agent. It is clear from the results of our work that high pH and reducing conditions favor low percentage  $I_2$ . Thus, large-scale mixing of primary and secondary coolants should decrease the percentage  $I_2$ . Additional studies to verify this effect and to determine whether volatile iodine species are formed in the reaction of iodine with morpholine degradation products would be useful.



## 6. REFERENCES

1. Code of Federal Regulations, Title 10, Part 100, Reactor Site Criteria.
2. J. Hopenfeld, "Experience and Modeling of Radioactivity Transport Following Steam Generator Tube Rupture," Nucl. Safety **26**, 286 (1985).
3. J. A. Martucci, Iodine Decontamination Factors During PWR Steam Generator and Steam Venting, CENPD-67, Rev. 1, November 1974.
4. M. A. Styrikovich, O. I. Martynova, K. Ya. Katkovskaya, I. Ya. Dubrovskii, and I. M. Smirnova, "Transfer of Iodine from Aqueous Solutions to Saturated Vapor," At. Energ. **17**, (1964).
5. P. Benes and V. Majer, "Trace Chemistry of Aqueous Solutions," Topics in Inorganic and General Chemistry, R. K. H. Clark, ed., Monograph 18, Elsevier Scientific, New York, 1980.
6. I. Noddack, "The Over-All Occurrence of the Chemical Elements," Angew. Chem. **49**, 835 (1936).
7. M. Kahn and A. C. Wahl, "Some Observations on the Chemical Behavior of Iodine at Low Concentrations," J. Chem. Phys. **21**, 1185 (1953).
8. J. Cvorić, "Chemical Forms of Iodine in Carrier Free Preparations of Na <sup>131</sup>I," J. Chromatog. **44**, 349 (1969).
9. J. H. Wolfenden, "Reduction of Aqueous Iodine by Trace Impurities," Anal. Chem. **29**, 1098 (1957).
10. S. D. Clinton and C. M. Simmons, Iodine Partition Coefficient Measurements at Simulated PWR Steam Generator Conditions: Interim Data Report, NUREG/CR-4817 (ORNL/TM-10330), May 1987.
11. J. R. Lemire, J. Paquette, D. F. Torgerson, D. J. Wren, and J. W. Fletcher, Assessment of Iodine Behavior in Reactor Containment Buildings from a Chemical Perspective, ACEL-6812, June 1981.
12. A. J. Fudge and K. W. Sykes, "The Reaction Between Ferric and Iodide Ions. Part 1. Kinetics and Mechanism," J. Chem. Soc. **1952**, 119 (1952).
13. K. W. Sykes, "The Reaction Between Ferric and Iodide Ions. Part II. The Influence of Ionic Association," J. Chem. Soc. **1952**, 124 (1952).
14. A. O. Allen, The Radiation Chemistry of Water and Aqueous Solutions, D. Van Nostrand, New York, 1961.

15. H. E. Barner and R. V. Scheuerman, Handbook of Thermochemical Data for Compounds and Aqueous Species, Wiley-Interscience, New York, 1978.
16. L. H. Parsly, Design Conditions of Reactor Containment - Part IV. Calculations of Iodine-Water Partition Coefficients, ORNL/TM-2412, 1970.
17. D. A. Palmer, R. W. Ramette, and R. E. Mesmer, "The Hydrolysis of Iodine: Equilibria at High Temperatures," J. Nucl. Mater. **130**, 280 (1985).
18. Y. Nishikawa, Y. Kigoshi, S. Oshima, Y. Ozawa, and T. Malkawa, "Vapor-Water Partition Coefficient of Iodine and Organic Iodides," Nippon Genshiryoku Gakkaishi **11**, 205 (1969); ORNL-tr-2255 (1969).

NUREG/CR-5365  
 ORNL/TM-11168  
 Dist. Category R3

## INTERNAL DISTRIBUTION

- |      |                 |        |   |
|------|-----------------|--------|---|
| 1-5. | E. C. Beahm     | 18.    | M. F. Osborne   |
| 6.   | J. T. Bell      | 19.    | G. W. Parker  |
| 7.   | M. L. Brown     | 20-24. | W. E. Shockley  |
| 8.   | D. O. Campbell  | 25.    | M. G. Stewart   |
| 9.   | J. L. Collins   | 26.    | A. L. Wright  |
| 10.  | M. L. Conte     | 27.    | A. Zucker   |
| 11.  | R. K. Genung    | 28.    | Central Research Library                                  |
| 12.  | J. R. Hightower | 29.    | ORNL-Y-12 Technical Library<br>Document Reference Section |
| 13.  | E. K. Johnson   | 30-31. | Laboratory Records  |
| 14.  | T. S. Kress     | 32.    | Laboratory Records, ORNL RC                               |
| 15.  | C. E. Lamb      | 33.    | ORNL Patent Section                                       |
| 16.  | R. A. Lorenz    |        |   |
| 17.  | J. C. Mailen    |        |   |

## EXTERNAL DISTRIBUTION

34. Office of Assistant Manager for Energy Research and Development, ORO-DOE, P.O. Box 2001, Oak Ridge, TN 37831
35. Director, Division of Reactor Safety Research, U.S. Nuclear Regulatory Commission, Washington, DC 20555
- 36-37. Office of Scientific and Technical Information, P.O. Box 2001, Oak Ridge, TN 37831
38. Division of Technical Information and Document Control, U.S. Nuclear Regulatory Commission, Washington, DC 20555
- 39-43. J. Hopenfeld, U.S. Nuclear Regulatory Commission, Division of Reactor System Safety, Washington, DC 20555
- 44-48. P. Voillequé, Utility Services Operation, Science Applications International Corporation, Idaho Falls, ID 83405
49. R. Meyer, U.S. Nuclear Regulatory Commission, Accident Evaluation Branch, Washington, DC 20555
50. T. J. Walker, U.S. Nuclear Regulatory Commission, Accident Evaluation Branch, Washington, DC 20555
51. F. Eltawila, U.S. Nuclear Regulatory Commission, Accident Evaluation Branch, Washington, DC 20555
52. K. Kniel, U.S. Nuclear Regulatory Commission, Washington, DC 20555
53. S. J. Wisbey, B.220, AERE Harwell, Didcot, Oxon OX11 0RA, United Kingdom
54. S. R. Daish, Bldg. 429, AERE Harwell, Didcot, Oxon, OX11 0RA, United Kingdom
55. P. E. Potter, B220, Chemistry Division, AERE Harwell, Didcot, Oxon OX11 0RA, United Kingdom
56. R. Burns, AERE Harwell, Didcot, Oxon OX11, 0RA, United Kingdom



57. T. Yamashita, Nuclear Fuel Chemistry Laboratory, Department of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, 319-11, Japan
58. T. Nakamura, Reactivity Accident Laboratory, Dai-2-Genken-Shinhara-Jutaku-304, 1-23-5, Shinhara, Mito-shi, 310, Japan
59. H. K. Lee, Spent Fuel Storage and Disposal Technology Section, Korea Advanced Energy Research Institute, P.O. Office Box 7, Dae-Danji Choong-Nam, Republic of Korea
60. Y.-C. Tong, Institute of Nuclear Energy Research, P.O. Box 3-6, Lung-Tan, Taiwan, Republic of China
61. M. Jacob, Combustion Engineering, Dept. 9341-0401, 1000 Prospect Hill Road, Windsor, CT 06095
62. J. Bollif, Scientech, P.O. Box 1406, Idaho Falls, ID 83403-1406
63. S. M. Ghiaasiaan, SAIC, 21151 Western Avenue, Torrance, CA 90501-1724
64. S. Pal Kalra, Electric Power Research Institute, 3412 Hillview Avenue, P.O. Box 10412, Palo Alto, CA 94303
- 65-314. Given distribution as shown in Category R3

BIBLIOGRAPHIC DATA SHEET

(See instructions on the reverse)

1. REPORT NUMBER  
(Assigned by NRC. Add Vol., Supp., Rev.,  
and Addendum Numbers, if any.)

NUREG/CR-5365  
ORNL/TM-11168

2. TITLE AND SUBTITLE

Iodine Speciation and Partitioning in PWR Steam  
Generator Accidents

Final Report

3. DATE REPORT PUBLISHED

MONTH YEAR  
October 1989

4. FUNDING OR GRANT NUMBER

B0453

5. AUTHOR(S)

E. C. Beahm, S. R. Daish,<sup>1</sup> J. Hopenfeld,<sup>2</sup> W. E. Shockley, P. Voilleque<sup>3</sup>

6. TYPE OF REPORT

7. PERIOD COVERED (include Dates)

8. PERFORMING ORGANIZATION - NAME AND ADDRESS (If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address. If contractor, provide name and mailing address.)

Oak Ridge National Laboratory  
Oak Ridge, TN 37831

<sup>1</sup>Visiting Scientist From AERE Harwell, England  
<sup>2</sup>U.S. Nuclear Regulatory Commission  
<sup>3</sup>Science Applications International Corporation

9. SPONSORING ORGANIZATION - NAME AND ADDRESS (If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)

Division of Safety Issue Resolution  
Office of Nuclear Regulatory Research  
U.S. Nuclear Regulatory Commission  
Washington, DC 20555

10. SUPPLEMENTARY NOTES

11. ABSTRACT (200 words or less)

Measurements of iodine speciation in aqueous solution at 285°C and 1000 psig show a higher percentage as I<sub>2</sub> in solutions at tracer concentrations than at higher concentrations. A 1 × 10<sup>-8</sup> M I<sup>-</sup> solution resulted in 2% I<sub>2</sub> whereas a 1 × 10<sup>-4</sup> M I<sup>-</sup> solution had only 0.1% I<sub>2</sub>. Tests of primary coolant from operating reactors had a peak in percent I<sub>2</sub> at shutdown, with an increase in volatile species up to 20% of the total iodine. During normal power operation; primary coolant percent I<sub>2</sub> was generally lower than the detection limit.

12. KEY WORDS/DESCRIPTORS (List words or phrases that will assist researchers in locating the report.)

Source terms, design basis accidents, iodine partitioning,  
primary coolant, iodine volatility

13. AVAILABILITY STATEMENT

unlimited

14. SECURITY CLASSIFICATION

(This page)

unclassified

(This report)

unclassified

15. NUMBER OF PAGES

16. PRICE

UNITED STATES  
NUCLEAR REGULATORY COMMISSION  
WASHINGTON, D.C. 20555

OFFICIAL BUSINESS  
PENALTY FOR PRIVATE USE, \$300

SPECIAL FOURTH CLASS RATE  
POSTAGE & FEES PAID  
USNRC  
PERMIT No. G-67

120555139531 1 JAN 83  
US-NRC-OADM  
DIV FOIA R PUBLICATIONS SVCS  
TPS PDR-NUPEG  
P-209  
WASHINGTON DC 20555