

NUREG/CR-3930  
ORNL/TM-9316

OAK RIDGE  
NATIONAL  
LABORATORY

MARTIN MARIETTA



Observed Behavior of Cesium, Iodine,  
and Tellurium in the ORNL  
Fission Product Release Program

J. L. Collins  
M. F. Osborne  
R. A. Lorenz  
K. S. Norwood  
J. R. Travis  
C. S. Webster

Prepared for the  
U.S. Nuclear Regulatory Commission  
Office of Nuclear Regulatory Research  
Under Interagency Agreement DOE 40-551-75

OPERATED BY  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY



NUREG/CR-3930  
ORNL/TM-9316  
Dist. Category R3

Chemical Technology Division

OBSERVED BEHAVIOR OF CESIUM, IODINE, AND TELLURIUM IN THE ORNL  
FISSION PRODUCT RELEASE PROGRAM

J. L. Collins  
M. F. Osborne  
R. A. Lorenz  
K. S. Norwood  
J. R. Travis  
C. S. Webster

Manuscript Completed — July 1984  
Date of Issue — February 1985.

**NOTICE** This document contains information of a preliminary nature.  
It is subject to revision or correction and therefore does not represent a  
final report.

Prepared for the  
U.S. Nuclear Regulatory Commission  
Office of Nuclear Regulatory Research  
Washington, DC 20555  
under Interagency Agreement DOE 40-551-75

NRC FIN No. B0127

Prepared by the  
OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
for the  
U.S. DEPARTMENT OF ENERGY  
under Contract No. DC-AC05-84OR21400



## ABSTRACT

A total of 26 commercial LWR fuel tests have been conducted at ORNL to investigate fission product release and behavior under accident conditions. About 30 supplementary tests have used fission product tracers to obtain additional information. This report presents the results of two recent control tests using radioactively tagged fission product species and compares these results with the behavior of the same species in previous fuel tests.

The purpose of these control tests was to study the behavior of CsI, CsOH, and Te metal in the collection system -- a thermal gradient tube and a filter package -- used in current fuel tests. The deposition profiles of these species were obtained in both platinum and stainless steel tubes with thermal gradients varying from 850°C at the inlet to 150°C at the outlet; the test atmospheres were mixtures of helium, steam, and hydrogen. In good agreement with fuel tests, the CsI deposition peak occurred at ~450°C in both tubes, and there was little evidence of decomposition. Cesium hydroxide was observed to be very reactive with the ZrO<sub>2</sub> furnace liner in the temperature range 800 to 1000°C. Also, evidence of a CsOH/Te reaction to form CsTe was found in the platinum thermal gradient tube. The materials that passed through the thermal gradient tubes were collected on the filters.

The tests of irradiated fuel (Zircaloy-clad UO<sub>2</sub>) were conducted at temperatures of 500 to 2000°C in three different atmospheres. In steam-helium tests, cesium and iodine behaved like CsOH and CsI; in dry air, like Cs<sub>2</sub>O and I<sub>2</sub>; and in purified helium, like Cs<sub>2</sub>O and CsI. Most of the cesium in steam-helium (apparently CsOH) was highly reactive with apparatus materials: with quartz at <1000°C, with ZrO<sub>2</sub> at 800 to 1200°C, and with stainless steel at 600 to 900°C. In one recent test, a large fraction (~50%) of the tellurium was released; analyses indicated that it was collected as a telluride.



## CONTENTS

|  | <u>Page</u> |
|--|-------------|
| ABSTRACT .....   | iii         |
| FOREWORD .....   | vii         |
| ACKNOWLEDGMENTS .....  | ix          |
| LIST OF FIGURES .....  | xi          |
| LIST OF TABLES .....   | xiii        |
| 1. EXECUTIVE SUMMARY .....   | 1           |
| 2. INTRODUCTION .....  | 2           |
| 3. SUMMARY AND CONCLUSIONS .....   | 3           |
| 3.1 COMPARISON WITH PREVIOUS RESULTS (SECTION 7) .....   | 4           |
| 4. EXPERIMENTAL APPARATUS .....  | 5           |
| 5. PREPARATION OF TEST SPECIMENS .....   | 7           |
| 6. TEST C-7 .....  | 8           |
| 6.1 GENERAL RESULTS AND TEST DESCRIPTION .....   | 8           |
| 6.2 THERMAL GRADIENT TUBE RESULTS .....  | 12          |
| 6.2.1 Leachability of Cesium, Iodine, and Tellurium<br>Deposits in the Platinum Thermal Gradient Tube<br>Liner .....                           | 12          |
| 6.2.2 Analysis of the Thermal Gradient Tube Deposits by<br>SEM/EDX and SSMS .....  | 16          |
| 6.2.3 Tellurium Behavior .....   | 23          |
| 6.2.4 Iodine Behavior .....  | 25          |
| 6.2.5 Cesium Behavior .....  | 26          |
| 6.3 COMPARISON OF COLLECTED MATERIAL IN THE THERMAL GRADIENT<br>TUBE BY WEIGHING AND BY ANALYTICAL METHODS .....                               | 26          |
| 7. TEST C-8 .....  | 27          |
| 7.1 GENERAL RESULTS AND TEST DESCRIPTION .....   | 27          |
| 7.2 THERMAL GRADIENT TUBE RESULTS .....  | 33          |
| 7.2.1 Leachability of Cesium, Iodine, and Tellurium<br>Deposits in the Inconel--Stainless Steel Thermal<br>Gradient Tube .....                 | 33          |
| 7.2.2 Tellurium Behavior .....   | 38          |
| 7.2.3 Iodine Behavior .....  | 38          |
| 7.2.4 Cesium Behavior .....  | 38          |
| 8. COMPARISON AND ANALYSIS OF THE RESULTS OBTAINED IN TESTS C-7<br>AND C-8 WITH THOSE OBTAINED IN PREVIOUS TESTS WITH IRRADIATED<br>FUEL ..... | 39          |
| 8.1 INTRODUCTION .....   | 39          |
| 8.2 REACTION OF CESIUM WITH ZIRCONIA .....   | 39          |
| 8.3 IODINE BEHAVIOR .....  | 42          |
| 8.4 CESIUM BEHAVIOR .....  | 47          |
| 8.5 TELLURIUM BEHAVIOR .....   | 55          |
| 9. REFERENCES .....  | 58          |



## FOREWORD

This document is the sixth in a series of reports describing the conduct and results of fission product release testing of commercial LWR fuel. The other reports are:

1. M. F. Osborne, R. A. Lorenz, J. R. Travis, and C. S. Webster, Data Summary Report for Fission Product Release Test HI-1, NUREG/CR-2928 (ORNL/TM-8500), December 1982.
2. M. F. Osborne, R. A. Lorenz, J. R. Travis, C. S. Webster, and K. S. Norwood, Data Summary Report for Fission Product Release Test HI-2, NUREG/CR-3171 (ORNL/TM-8667), February 1984.
3. M. F. Osborne, R. A. Lorenz, K. S. Norwood, J. R. Travis, and C. S. Webster, Data Summary Report for Fission Product Release Test HI-3, NUREG/CR-3335 (ORNL/TM-8793), April 1984.
4. M. F. Osborne, J. L. Collins, R. A. Lorenz, K. S. Norwood, J. R. Travis, and C. S. Webster, Data Summary Report for Fission Product Release Test HI-4, NUREG/CR-3600 (ORNL/TM-9011), June 1984.
5. M. F. Osborne, J. L. Collins, R. A. Lorenz, J. R. Travis, and C. S. Webster, Design, Construction, and Testing of a 2000°C Furnace and Fission Product Collection System, NUREG/CR-3715 (ORNL/TM-9135), in publication.



#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the significant contributions of several colleagues in conducting this work: C. A. Culpepper of the Operations Division for SEM/EDX analyses; L. Landau of the Analytical Chemistry Division for spark-source mass spectrometric analyses; R. L. Fellows of the Chemical Technology Division and H. W. Dunn of the Analytical Chemistry Division for x-ray diffraction analyses; E. C. Beahm of the Chemical Technology Division for technical consultation; B. C. Drake for preparation of the manuscript; and D. R. Reichle for editing.



## LIST OF FIGURES

| <u>Number</u> |  | <u>Page</u> |
|---------------|--|-------------|
| 1             | Diagram of experimental apparatus .....  | 6           |
| 2.            | Collection of cesium, iodine, and tellurium in the TGT in test C-7 as functions of time and specimen temperatures ...  | 9           |
| 3             | Cesium, iodine, and tellurium profiles (mg/cm) along the platinum thermal gradient tube in test C-7 .....  | 13          |
| 4             | This figure shows the locations where sections were cut from the TGT used in test C-7 for analytical (1, 3, 5, and 7) and leaching (2, 4, 6, and 8) purposes .....           | 14          |
| 5             | Comparison of tellurium concentration profiles in the TGT liner before and after leaching in test C-7 .....  | 17          |
| 6             | An SEM view (2280×) of an agglomerate of whitish particles that deposited in the 880 to 800°C temperature region in the TGT during test C-7 .....                            | 19          |
| 7             | General SEM view (228×) of a section of TGT surface deposit from the 880 to 800°C peak region (test C-7) .....   | 20          |
| 8             | General SEM view (228×) of a surface deposit on a section of TGT liner from the 400 to 300°C peak region (test C-7) .  | 24          |
| 9             | Collection of cesium, iodine, and tellurium in the TGT in test C-8 as functions of time and specimen temperatures ...  | 28          |
| 10            | Deposition of tellurium on the nickel tube .....   | 32          |
| 11            | Distribution of cesium ( <sup>137</sup> Cs tagged) along the zirconia furnace tube liner after test C-8 .....  | 34          |
| 12            | Distribution profiles for cesium, iodine, and tellurium in the TGT liner used in test C-8 .....  | 35          |
| 13            | This figure shows the locations in the TGT liner where sections were cut for analytical (1, 3, and 5) and leaching (2, 4, and 6) purposes .....                              | 36          |
| 14            | Estimated temperature gradients along the zirconia "collimators" which were positioned within and at the end of the zirconia furnace tube liners in the HI test series ..... | 41          |
| 15            | Deposition behavior of iodine in the TGT platinum liners in tests HI-1 through HI-5 .....  | 45          |

| <u>Number</u> |   | <u>Page</u> |
|---------------|---|-------------|
| 16.           | Deposition profiles for iodine and cesium in the TGT in Control Test 10 .....         | 48          |
| 17            | Deposition profiles for iodine and cesium in the TGT in Implant Test 11 .....         | 49          |
| 18            | Deposition profiles for iodine and cesium in the TGT in test HT-2 .....               | 50          |
| 19            | Deposition profiles for iodine and cesium in the TGT in test HI-5 .....               | 51          |
| 20            | Concentration profile of $^{134}\text{Cs}$ in apparatus components in test HT-1 ..... | 53          |
| 21            | Deposition profile for cesium in the TGT in test HI-2 ....                            | 56          |

LIST OF TABLES

| <u>Number</u> |  | <u>Page</u> |
|---------------|--|-------------|
| 1             | Data showing the masses of test specimens used in tests C-7 and C-8 as compared with fission product equivalents in segments used in tests HI-1 and HI-4 .....   | 7           |
| 2             | Specific activities calculated for the elements used in tests C-7 and C-8 .....  | 8           |
| 3             | Posttest distribution of tellurium, cesium, and iodine in test C-7 .....   | 11          |
| 4             | Effectiveness of basic and acidic leaches in removing cesium, iodine, and tellurium materials from selected sections of the platinum TGT liner used in test C-7 .....                                  | 15          |
| 5             | Elemental deposit in TGT at 880 to 800°C in test C-7 .....   | 18          |
| 6             | Elemental deposit in TGT at 750 to 700°C in test C-7 .....   | 21          |
| 7             | Elemental deposit in TGT at 500 to 400°C in test C-7 .....   | 22          |
| 8             | Elemental deposit in TGT at 400 to 300°C in test C-7 .....   | 25          |
| 9             | Mass of fission product elements in the platinum TGT liner after test C-7 .....  | 27          |
| 10            | Chemical composition of Inconel-600 and stainless steel 304-L .....  | 30          |
| 11            | Posttest distribution of tellurium, cesium, and iodine in test C-8 .....   | 31          |
| 12            | Effectiveness of basic and acidic leaches in removing cesium, iodine, and tellurium from selected sections of the TGT liner in test C-8 .....  | 37          |
| 13            | Masses of <sup>137</sup> Cs found on the zirconia "collimators" used in the HI test series, and the percentage of the released <sup>137</sup> Cs that was found on the "collimators" in each test .... | 42          |
| 14            | Summary of iodine release species in fission product release tests .....   | 44          |
| 15            | Temperatures at which maximum iodine TGT peak concentrations occurred in tests (control and irradiated fuel) where significant amounts of iodine were deposited .....                                  | 46          |
| 16            | Summary showing the percentages of the released cesium that were retained by the quartz liners and found in the collection trains .....  | 54          |



OBSERVED BEHAVIOR OF CESIUM, IODINE, AND TELLURIUM IN THE ORNL  
FISSION PRODUCT RELEASE PROGRAM

|               |               |
|---------------|---------------|
| J. L. Collins | K. S. Norwood |
| M. F. Osborne | J. R. Travis  |
| R. A. Lorenz  | C. S. Webster |

1. EXECUTIVE SUMMARY

The purpose of this report is twofold, to document and discuss two control tests (C-7 and C-8) that were conducted to examine the collection behavior of CsOH, CsI, and Te (collectively) in the experimental apparatus and to compare, analyze, and draw conclusions about the behavior of cesium, iodine, and tellurium that has been observed in present and past fission product release tests at ORNL. A total of 26 commercial LWR fuel tests (fuels with burnups ranging from 1- to 40-MWd/kg U) and about 30 supplementary tests, which made use of simulated fission products that were traced, have been conducted.

In control test C-7, reported in Sect. 5, the traced CsI, CsOH, and Te species were vaporized and transported by a steam-helium-hydrogen carrier gas through a zirconia liner (maximum 800°C) to the collection system. There was little tendency for the CsI to be decomposed; it was primarily found in a peak deposit in the platinum thermal gradient tube (TGT). Only ~0.06% was found as molecular iodine on the impregnated charcoal. A large fraction (~80%) of the tellurium reacted with CsOH in the gas phase and was found in a peak deposit in the TGT at 700°C. The mol ratio of cesium to tellurium in the peak was 1:1.

Test C-8 (Sect. 6) differed in two ways: (1) a stainless steel rather than a platinum TGT was used, and (2) the hot zone in the zirconia liner was maintained at ~1000°C rather than ~800°C. (A 5-cm-long section of the TGT at the inlet end was actually made of Inconel 600.) As in test C-7, there was little CsI decomposition; only 0.003% of the iodine associated with the vaporized CsI was found on the charcoal as molecular iodine. The largest portion of the CsOH reacted with and was retained by the hot zirconia liner, probably as cesium zirconate (Cs<sub>2</sub>ZrO<sub>3</sub>). Most of the tellurium that transported to the collection train was found to be retained by the Inconel at the hot (inlet) end of the TGT, probably as NiTe.

The most important behavioral results in these two tests were that CsI remained stable, that CsOH reacted with tellurium in the gas phase to form CsTe, and that CsOH rapidly reacted with and was retained by zirconia at temperatures >800°C.

The conclusions discussed in Sect. 7 were based upon all test results.

1. In the gap purge tests of high-burnup fuel in purified helium, the cesium and iodine behaved as cesium oxide ( $\text{Cs}_2\text{O}$ ) and  $\text{CsI}$ , rather than as the elements.
2. In dry air tests of similar fuel sections heated at 500 and 700°C, iodine and cesium were collected as molecular iodine and  $\text{Cs}_2\text{O}$ .
3. In steam-helium tests where significant masses of iodine were released ( $>17 \mu\text{g}$ ), the iodine collection behavior was that of  $\text{CsI}$ . Collectively, where  $\sim 43 \text{ mg}$  of iodine has been released in all the steam tests, only  $\sim 0.38\%$  of this iodine was determined to be molecular iodine.
4. In the steam tests, released cesium behaved as  $\text{CsOH}$ . It reacted vigorously with and was retained by quartz surfaces at temperatures  $<1000^\circ\text{C}$ , probably forming cesium silicate. It reacted with and was retained by zirconia ceramics at temperatures between 800 and  $1200^\circ\text{C}$ . It also reacted with oxidized stainless steel at temperatures  $>600$ .
5. Our results indicate that tellurium is retained by the Zircaloy cladding. Significant tellurium release was measured (by SSMS) in only one test. In that test, unlike the other steam tests, the cladding was totally oxidized, and the fractional release of tellurium was estimated to have been similar to that of  $\text{Kr}$ ,  $\text{Cs}$ , and  $\text{I}$ . Its collection behavior was that of telluride rather than elemental tellurium. Interestingly, significant quantities of tin (a component of the Zircaloy cladding) were also found associated with the deposited tellurium throughout the collection system, possibly having transported there as  $\text{SnTe}$ .

## 2. INTRODUCTION

The objectives of the current Fission Product Release from LWR Fuel Project at Oak Ridge National Laboratory (ORNL) are to measure and characterize the material released from specimens of commercial, high-burnup fuel under accident conditions. Six tests of irradiated fuel have been conducted at temperatures of 1400 to  $2000^\circ\text{C}$ , and the results have been reported elsewhere.<sup>1-4</sup> In addition, tests of simulated high-burnup fuel and of unirradiated fuel with radioactively traced structural material have been carried out to provide supplementary release data.

This report discusses the results of two tests, designated C-7 and C-8, which were performed to aid in the interpretation of data from fuel tests; the deposition behavior of specific fission product forms in the thermal gradient tube (TGT) was of particular interest. Therefore, tests C-7 and C-8 were designed to clarify the deposition behavior of three known species —  $\text{CsI}$ ,  $\text{CsOH}$ , and  $\text{Te}$  (elemental) — in both platinum and stainless steel TGT liners. The elements  $\text{Cs}$ ,  $\text{I}$ , and  $\text{Te}$  are high-yield fission products of relatively high volatility, and other experiments

have indicated that the forms CsI, CsOH, and Te<sub>2</sub> should predominate in steam atmosphere of the fission product release tests with LWR fuel.<sup>5-7</sup> Because of its chemical inertness, platinum has been used as the TGT liner in most of the release tests. Stainless steel, the most common surface in LWR coolant systems, has been used as the TGT liner in a few tests to provide data for this more typical (and more reactive) material. As a simplification, fuel specimens were not used in these tests. Instead, pure CsI, CsOH, and metallic tellurium, appropriately traced with <sup>134</sup>Cs, <sup>131</sup>I, <sup>137</sup>Cs, and <sup>129m</sup>Te, were injected by vaporization into a flow steam-helium-hydrogen at the furnace inlet. The results of these two control tests are presented independently. These results, as well as results obtained in present and past fission product release programs, were compared and analyzed and are described in Sect. 7 of this report.

### 3. SUMMARY AND CONCLUSIONS

In each control test, CsI proved to be very stable; there was little evidence of decomposition. On the other hand, CsOH and Te were observed to be very reactive with regard to surfaces in the apparatus and each other. Cesium hydroxide was found to react with zirconia components in the furnace tube in the temperature range >800 and <1000°C, probably forming cesium metazirconate (Cs<sub>2</sub>ZrO<sub>3</sub>). In test C-7, a fraction of the CsOH reacted with the quartz furnace tube and the quartz TGT housing tube to form a compound that was less volatile, probably cesium silicate. There was also evidence in test C-8 that some of the CsOH reacted with the surface of the stainless steel TGT which was heated in the temperature range 700 to 600°C. A large fraction of the tellurium in test C-7 reacted with CsOH in the gas phase to form the telluride, CsTe, which deposited by condensation at ~700°C in the platinum TGT. Tellurium that did not form tellurides with cesium in each of the tests was gettered by nickel and platinum surfaces in the apparatus, probably forming nickel and platinum tellurides.

In each of the tests, most of the iodine (predominantly as CsI) that entered the TGT deposited by vapor condensation in the temperature range 600 to 300°C. (This deposition behavior was also characteristic of iodine in the TGT in the recently conducted HI tests as well as in all the previously conducted irradiated fuel tests.) Cesium hydroxide was also found deposited in the same general region as the CsI, between 550 and 300°C. The species CsI and CsOH·H<sub>2</sub>O were identified by x-ray diffraction as the only constituents present in samples taken from the peak deposits.

In the HI test series and other series of tests conducted with irradiated fuel segments, the iodine (<sup>129</sup>I) that was released had to be quantified by neutron activation analyses of leach samples. In each of those tests, components were leached with basic and acid leaches to remove the iodine. In this study, sections of the TGTs from test C-7 and C-8 were also leached in the same manner. The results are given in the text.

### 3.1 COMPARISON WITH PREVIOUS RESULTS (SECTION 7)

The chemical behavior of a fission product in LWR fuel rods under accident conditions depends on its chemical form. The chemical form is important because it dictates whether or not the fission product will interact with the fuel, cladding, other fission products, and materials outside the fuel rods. More importantly, it dictates the extent of the release. In Sect. 7 a detailed discussion is given of the observed behavior of Cs, I, and Te in the fission product release tests conducted at ORNL. The following conclusions were indicated by the experimental results:

1. In the purified helium tests, iodine and cesium were released from both BWR and PWR fuel segments as cesium iodide and cesium oxide (probably  $\text{Cs}_2\text{O}$ ). The segments were heated to a maximum temperature of  $1200^\circ\text{C}$ , and the releases were primarily the pellet-cladding gap inventories of cesium and iodine. In the BWR test, the "gap" releases were significant —  $\sim 12\%$  of the total segment inventories.
2. In dry air atmosphere tests (maximum temperature was  $700^\circ\text{C}$ ), cesium was released as cesium oxide, and iodine as molecular iodine.
3. In the steam-helium atmosphere tests, iodine was released primarily as CsI in tests where the mass released was  $\geq 17 \mu\text{g}$ . Considering all the tests conducted in steam, only 0.38% of the total iodine released was collected as molecular iodine. This included a test where  $\sim 53\%$  of the fuel rod segment inventory of iodine was released.
4. The release behavior of cesium (excluding CsI) in steam was that of CsOH.
5. A significant release of tellurium was measured in only one test (in steam). Its collection behavior was that of telluride. Because of a paucity of data, the release form of tellurium in steam is not certain.
6. Tellurium, like cesium and iodine, is a very reactive element. In test C-7, it reacted with CsOH in the gas phase (at  $\sim 800^\circ\text{C}$ ) and formed cesium telluride ( $\text{CsTe}$ ). In both control tests C-7 and C-8, it was also observed to be very reactive with nickel, platinum, Inconel-600, and 304-stainless steel surfaces.
7. Cesium released from the irradiated fuel significantly reacted with zirconia ceramics at temperatures between  $800$  and  $1200^\circ\text{C}$ , probably forming cesium metazirconate ( $\text{Cs}_2\text{ZrO}_3$ ). By comparison, in control test C-8, CsOH was also observed to rapidly react with zirconia at temperatures  $> 800^\circ\text{C}$  (maximum temperature was  $1000^\circ\text{C}$ ).
8. In steam tests where quartz furnace tube liners were used, the released cesium (excluding CsI) reacted quickly and vigorously with the quartz surface at temperatures  $< 1000^\circ\text{C}$ . This behavior was similar to that observed for the CsOH quartz reaction in control tests.

9. There was no evidence of CsI reaction in steam with zirconia in either irradiated fuel or control tests. Also, in the control tests, CsI remained stable when exposed to Inconel-500 and 304-stainless steel.

#### 4. EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus that was used in tests C-7 and C-8 is shown in Fig. 1. The apparatus was composed of a furnace assembly and a collection train.

Two independently controlled resistance heaters were used to heat the furnace assembly, one to vaporize the simulant fission product specimens (CsI, CsOH, and Te), and the other to provide a hot zone for the gaseous species to pass through before entering the collection train. Since CsI and CsOH were known to react with quartz, and Te with Pt and Ni, they had to be isolated in the vaporization chamber. As is shown in Fig. 1, the CsOH and CsI specimens were put into separate platinum boats that were placed in a nickel tube, and the tellurium specimen was put into a quartz boat that was placed inside a zirconia tube. These tubes were positioned parallel to each other within a zirconia liner which was housed in a quartz furnace vessel. To minimize contact of the species with the quartz furnace vessel, a zirconia "collimator" was used at the outlet end of the zirconia liner to channel the gaseous species into the collection train. Neither Zircaloy nor  $UO_2$  were used in these tests.

The collection train was composed of a TGT and a filter package. The TGT used in these tests was actually a liner that was placed in a quartz tube which was connected to the end of the quartz vessel. For the remainder of the text, the TGT liner will be referred to as the TGT. In tests C-7 and C-8, they were made of platinum and stainless steel, respectively. In test C-7, the platinum TGT was inserted into the collimator opening. This could not be done with the stainless steel TGT in test C-8 because the diameter was too large. (Thermal gradient tube dimensions are given in Sects. 4.1 and 5.1.) During a test, vaporized species were transported from the furnace to the TGT by a flowing carrier gas mixture of steam and helium; the helium contained 9.6% hydrogen. The TGT was heated to provide a temperature gradient from  $\sim 850^\circ\text{C}$  at the inlet to  $\sim 150^\circ\text{C}$  at the outlet. Temperature was measured along the TGT with calibrated chromel vs alumel thermocouples. A specie entering the TGT either condensed (if the dew point was  $>150^\circ\text{C}$ ), reacted, or was carried on through to the filter package.

The filter package contained a glass wool prefilter, two HEPA filters, and cartridges containing impregnated charcoal to collect the more volatile and penetrating species (e.g., elemental iodine, methyl iodide, and hydrogen iodide).

An ice-bath-cooled condenser and a dry-ice-cooled freeze trap ( $-78^\circ\text{C}$ ), located further downstream, were used to remove the steam for measurement.

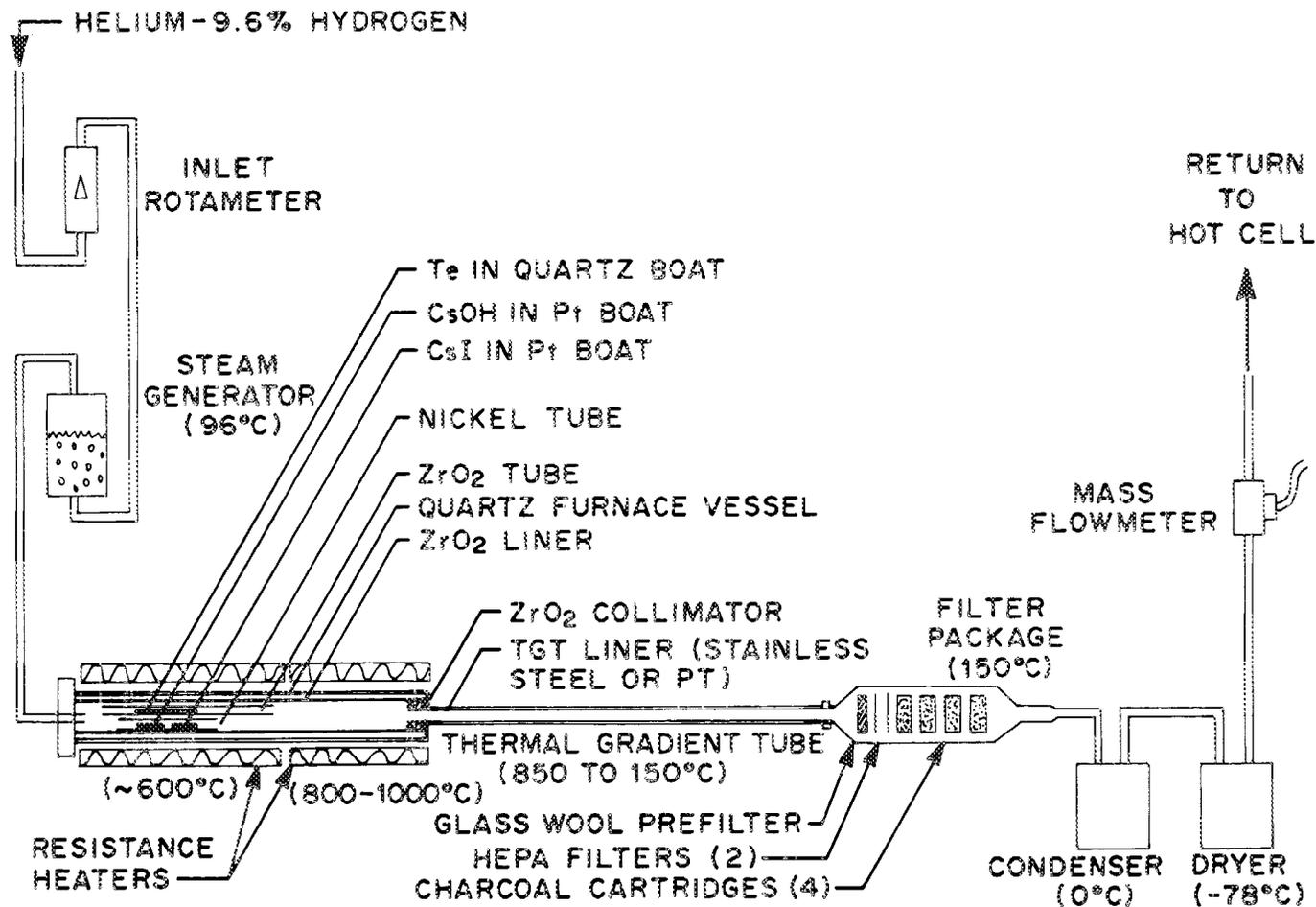


Fig. 1. Diagram of experimental apparatus.

During a test, the radioactively tagged species that deposited in the TGT and filter package were continuously monitored by NaI(Tl) detectors which were connected to multichannel analyzers. A data acquisition system was used to record the data at 1 min intervals. Several individual chart recorders were used to continuously record temperature and flow rates.

#### 5. PREPARATION OF TEST SPECIMENS

The quantities of Cs, I, and Te used in tests C-7 and C-8 were similar to the calculated inventories for these elements that were contained in segments of highly irradiated LWR fuel that were used in the fission product release experiments in the HI test series.<sup>1-4</sup> These data, along with mass ratios of these elements and the masses of the chemical forms used, are given in Table 1.

Table 1. Data showing the masses of test specimens used in tests C-7 and C-8 as compared with fission product equivalents in the segments used in tests HI-1 and HI-4

|               | Mass available   |                  |                                     |                                     |
|---------------|------------------|------------------|-------------------------------------|-------------------------------------|
|               | Test C-7<br>(mg) | Test C-8<br>(mg) | Peach Bottom-2 <sup>a</sup><br>(mg) | H. B. Robinson <sup>b</sup><br>(mg) |
| Element       |                  |                  |                                     |                                     |
| Cs            | 225.5            | 286.6            | 205.8                               | 252.5                               |
| I             | 19.6             | 21.3             | 20.0                                | 25.2                                |
| Te            | 37.9             | 38.3             | 39.0                                | 50.9                                |
| Chemical form |                  |                  |                                     |                                     |
| CsOH          | 231.2            | 298.1            |                                     |                                     |
| CsI           | 40.1             | 41.1             |                                     |                                     |
| Te            | 37.9             | 38.3             |                                     |                                     |
| Mass ratio    |                  |                  |                                     |                                     |
| Cs/I          | 11.5             | 13.5             | 10.3                                | 10.0                                |
| Cs/Te         | 5.9              | 7.5              | 5.3                                 | 5.0                                 |
| Te/I          | 1.9              | 1.8              | 2.0                                 | 2.0                                 |

<sup>a</sup>Segment used in test HI-4 (calculated inventories).

<sup>b</sup>Segment used in test HI-1 (calculated inventories).

One or both of two methods were employed to radioactively tag the test specimens: neutron activation and radioactive isotope addition. In the preparation of the tellurium specimens, two metallic samples that were enriched to 98.2% in the isotope <sup>128</sup>Te were encapsulated in quartz ampuls and irradiated in the High Flux Isotope Reactor (HFIR). The

tellurium isotope  $^{129m}\text{Te}$ , which has a half-life of 33.6 d, was produced. Upon being removed from the reactor, it was discovered that a large portion of the tellurium had fused to the walls of each of the ampuls (apparently by vapor deposition or reaction). Since there was not enough unaffected tellurium to do the tests, the ampuls were broken into smaller pieces and also placed in the test boats.

The CsOH specimens were prepared by adding predetermined amounts of  $^{137}\text{CsCl}$  to solutions containing known amounts of CsOH and evaporating them to dryness in platinum boats. Only about 3-ppm chlorine was introduced as a contaminant by the  $^{137}\text{CsCl}$  addition. Since CsOH is known to react rapidly with  $\text{CO}_2$  to form cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ), the preparation was done in a glove box under a flowing helium atmosphere.

Cesium iodide specimens were first tagged with  $^{134}\text{Cs}$  by neutron activation in the Oak Ridge Research Reactor (ORR), and subsequently tagged with  $^{131}\text{I}$  by addition of  $\text{Na}^{131}\text{I}$ . To obtain good isotopic mixing of the iodine, each irradiated CsI specimen was dissolved and thoroughly mixed in a small volume of water that contained the  $\text{Na}^{131}\text{I}$ . Afterward, the solutions were evaporated to dryness in platinum boats.

In each of the preparations, emphasis was given to minimizing introduction of contaminant materials and to obtaining accurate weights and activity measurements. The calculated specific activities for the elemental species are given in Table 2.

Table 2. Specific activities calculated for the elements used in tests C-7 and C-8

| Element | Tracer             | Half life | Chemical form | Specific activities<br>$\mu\text{Ci (tracer)}/\text{mg (element)}$ |                       |
|---------|--------------------|-----------|---------------|--|-----------------------|
|         |                    |           |               | Test C-7 <sup>a</sup>  | Test C-8 <sup>b</sup> |
| Cs      | $^{134}\text{Cs}$  | 2.06 y    | CsI           | 5.44   | 5.50                  |
| I       | $^{131}\text{I}$   | 8.04 d    | CsI           | 408.6  | 156.7                 |
| Cs      | $^{137}\text{Cs}$  | 30.17 y   | CsOH          | 0.92   | 0.85                  |
| Te      | $^{129m}\text{Te}$ | 33.6 d    | Te            | 1407.5   | 864.6                 |

<sup>a</sup> September 19, 1983, at 8:00 am.

<sup>b</sup> October 11, 1983, at 8:00 am.

## 6. TEST C-7

### 6.1 GENERAL RESULTS AND TEST DESCRIPTION

In this test, the specimens were heated as shown in Fig. 2. The vaporized species were carried to the collection system by a flowing steam (0.156 L/min at STP) and helium-9.6% hydrogen (0.147 L/min at STP)

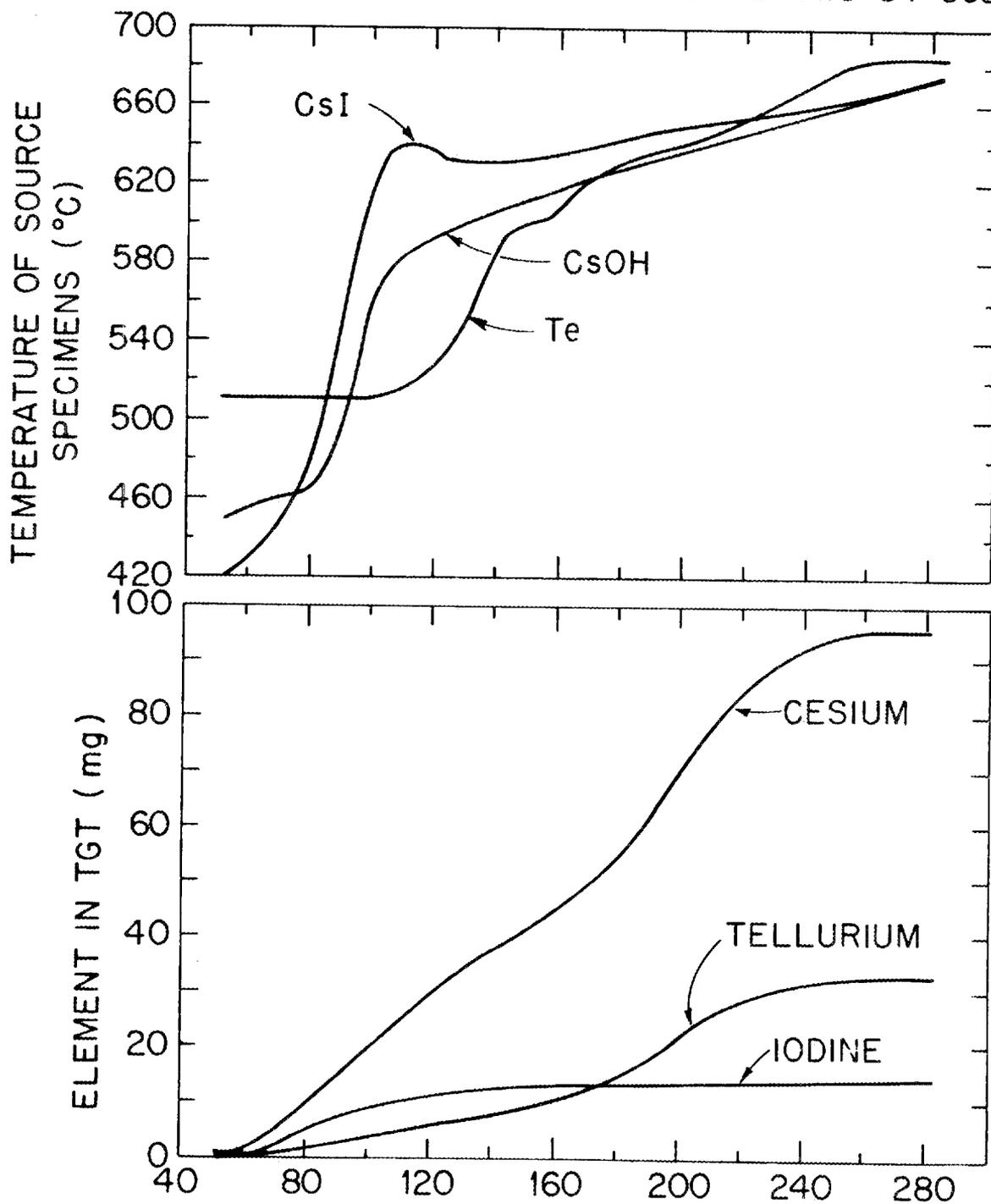


Fig. 2. Collection of cesium, iodine, and tellurium in the TGT in test C-7 as functions of time and specimen temperatures.

atmosphere. Before entering the platinum TGT, the gaseous species had to pass through a hot zone in the zirconia liner that was maintained at  $\sim 800^\circ\text{C}$  during the test (see Fig. 1). There were three reasons for having the hot zone; (1) to keep the species from condensing, (2) to supply a preheated reaction zone for the species prior to their entering the TGT, and (3) to help determine the temperature range where CsOH reacts with zirconia to form cesium metazirconate ( $\text{Cs}_2\text{ZrO}_3$ ). The latter reason is of interest because large percentages of the released cesium (25-50%) in the HI series tests were retained, by the zirconia ceramic components at the outlet end of the furnace, which were heated in the temperature range  $\sim 900$  to  $\sim 1800^\circ\text{C}$  (see Sect. 6.1).

Table 3 summarizes the posttest distribution of Cs, I, and Te as determined by gamma spectrometry. As shown,  $\sim 9.4\%$  of the cesium and  $\sim 2.7\%$  of the iodine were found on the surfaces of the zirconia liner and collimator. Most of the iodine and an almost equal amount of  $^{134}\text{Cs}$  (see masses) were found in the cooler upstream half of the zirconia liner; this was probably condensed CsI. Conversely, the largest portion of the cesium that was tagged with  $^{137}\text{Cs}$  (CsOH) was found on the hotter, downstream half of the liner and fairly uniformly deposited. This suggests that there was some tendency for the CsOH to react with the zirconia liner.

It can also be seen in Table 3 that all the CsI and 83% of the CsOH were vaporized and transported from the nickel tube during the test, and that 94% of the tellurium escaped from the smaller diameter zirconia tube. Of the fractions vaporized, 88.2% of the CsI (based on  $^{131}\text{I}$  only), 88% of the tellurium, and 47% of the cesium that was tagged with  $^{137}\text{Cs}$  (mostly CsOH) were carried out of the furnace to the TGT and filter package.

Cesium iodide and CsOH were initially tagged with  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ , respectively (see Sect. 4). While being transported in the gaseous phase some isotopic exchange occurred, but it was not as extensive as was expected. For this reason, the results have been more meaningful. (In Sect. 5.2.4, it is shown that CsI remained a stable specie during the test.) Notice that 14.2 mg iodine and 9.6 mg cesium, which was tagged with  $^{134}\text{Cs}$ , deposited in the TGT. If no isotopic exchange had occurred, 14.9 mg cesium tagged with  $^{134}\text{Cs}$  would have deposited in the TGT. Of course, in this case, the missing CsI cesium was tagged with  $^{137}\text{Cs}$ . Therefore, it appears that  $\sim 36\%$  of the cesium originally associated with iodine as CsI exchanged with the CsOH cesium during the test.

The largest portions of the CsOH ( $^{137}\text{Cs}$  tagged) that remained in the furnace assembly was found on surfaces of the quartz furnace vessel and quartz TGT housing, mainly within  $\sim 4$  cm of the TGT entrance. Most of the iodine (8%) was found downstream in the quartz TGT housing at a temperature  $< 500^\circ\text{C}$ . The CsOH probably reacted with the quartz to form  $\text{Cs}_2\text{SiO}_3$ , and the iodine as CsI passed down the gap between the platinum TGT liner and the quartz TGT until it condensed at a characteristic temperature.

Only a trace amount of tellurium was found in the filter package. In contrast to this,  $\sim 17\%$  of the iodine deposited there; however, only a

Table 3. Posttest distribution of tellurium, cesium, and iodine in test C-7

| Location                                 | Temperature<br>(°C) | Amount and percentage of Te, Cs, and I found in each location |                      |                   |       |                   |       |                 |       |                        |       |
|--|---------------------|---|----------------------|-------------------|-------|-------------------|-------|-----------------|-------|------------------------|-------|
|  |                     | <sup>129m</sup> Te  |                      | <sup>137</sup> Cs |       | <sup>134</sup> Cs |       | Cs <sup>a</sup> |       | <sup>131</sup> I       |       |
|  |                     | (mg)  | (%) <sup>b</sup>     | (mg)              | (%)   | (mg)              | (%)   | (mg)            | (%)   | (mg)                   | (%)   |
| Furnace components                       |                     |   |                      |                   |       |                   |       |                 |       |                        |       |
| Quartz furnace vessel                    | 600-800             | 0.927   | 2.32                 | 55.78             | 23.98 | 4.65              | 23.25 | 60.43           | 23.92 | 1.61                   | 8.06  |
| Quartz spacer                            | 600                 | 0.072   | 0.18                 | 0.028             | 0.01  | 0.0               | 0.0   | 0.03            | 0.01  | 0.084                  | 0.42  |
| Quartz holder                            | 600-800             | 0.003   | 0.01                 | 5.37              | 2.31  | 0.757             | 3.79  | 6.13            | 2.43  | 0.001                  | 0.005 |
| Zirconia furnace tube liner              | 600-800             | 2.18  | 5.44                 | 14.85             | 6.38  | 0.771             | 3.85  | 15.61           | 6.18  | 0.516                  | 2.58  |
| Zirconia outlet plug                     | 785                 | 0.053   | 0.13                 | 7.46              | 3.21  | 0.581             | 2.91  | 8.04            | 3.18  | 0.018                  | 0.09  |
| Zirconia tube (Te specimen) <sup>c</sup> | 600-755             | 2.35  | 5.86                 | 0.0               | 0.0   | 0.0               | 0.0   | 0.0             | 0.0   | 0.0                    | 0.0   |
| Nickel tube (CsOH and CsI specimens)     | 625-675             | 1.20  | 3.00                 | 27.01             | 11.61 | 0.130             | 0.65  | 27.14           | 10.74 | 0.118                  | 0.59  |
| Platinum boat (CsOH)                     | ~635                | 0.036   | 0.09                 | 13.52             | 5.81  | 0.068             | 0.34  | 13.59           | 5.38  | 0.0                    | 0.0   |
| Platinum boat (CsI)                      | ~650                | 0.003   | 0.01                 | 0.133             | 0.06  | 0.004             | 0.02  | 0.14            | 0.06  | 0.001                  | 0.005 |
| Total                                    |                     | 6.824   | 17.04                | 124.15            | 53.37 | 6.961             | 34.81 | 131.11          | 51.90 | 2.35                   | 11.76 |
| Thermal gradient tube                    | 900-150             | 32.56   | 81.31                | 87.78             | 37.74 | 9.63              | 48.15 | 97.41           | 38.56 | 14.20                  | 71.12 |
| Filter pack components                   |                     |   |                      |                   |       |                   |       |                 |       |                        |       |
|  | 180                 |   |                      |                   |       |                   |       |                 |       |                        |       |
| Entrance tube                            |                     | 0.07  | 0.18                 | 1.30              | 0.56  | 0.186             | 0.93  | 1.49            | 0.59  | 0.242                  | 1.21  |
| Entrance cone                            |                     | 0.001   | 0.002                | 0.024             | 0.01  | 0.003             | 0.015 | 0.03            | 0.01  | 0.031                  | 0.16  |
| Glass wool prefilter                     |                     | 0.586   | 1.46                 | 17.46             | 7.51  | 2.873             | 14.37 | 20.33           | 8.05  | 2.93                   | 14.67 |
| First HEPA filter                        |                     | 5 × 10 <sup>-5</sup>  | 1 × 10 <sup>-4</sup> | 1.86              | 0.80  | 0.346             | 1.73  | 2.21            | 0.87  | 0.199                  | 1.00  |
| Second HEPA filter                       |                     | 0.002   | 0.005                | 0.0               | 0.0   | 0.0               | 0.0   | 0.0             | 0.0   | 3.2 × 10 <sup>-4</sup> | 0.002 |
| First charcoal                           |                     | 0.0   | 0.0                  | 0.0               | 0.0   | 0.0               | 0.0   | 0.0             | 0.0   | 0.015                  | 0.07  |
| Second charcoal                          |                     | 0.0   | 0.0                  | 0.0               | 0.0   | 0.0               | 0.0   | 0.0             | 0.0   | 0.001                  | 0.005 |
| Miscellaneous parts                      |                     | 0.0   | 0.0                  | 0.042             | 0.02  | 0.001             | 0.005 | 0.04            | 0.02  | 1.2 × 10 <sup>-4</sup> | 0.001 |
| Total                                    |                     | 0.66  | 1.65                 | 20.69             | 8.89  | 3.41              | 17.04 | 24.10           | 9.54  | 3.42                   | 17.12 |
| Condenser                                | 0                   | 0.0   | 0.0                  | 0.0               | 0.0   | 0.0               | 0.0   | 0.0             | 0.0   | 0.0                    | 0.0   |
| Total all components <sup>d</sup>        |                     | 40.04   | 100.0                | 232.62            | 100.0 | 20.00             | 100.0 | 252.62          | 100.0 | 19.97                  | 100.0 |

<sup>a</sup>Sum of <sup>137</sup> Cs and <sup>134</sup> Cs.

<sup>b</sup>Percentage of total mass found.

<sup>c</sup>Tellurium sample was about 630 ± 50°C.

<sup>d</sup>The initial specimen weights were 19.6 mg iodine (<sup>131</sup>I tagged), 37.9 mg tellurium (<sup>129m</sup>Te tagged), 205 mg cesium (<sup>137</sup>Cs tagged), and 20.5 mg cesium (<sup>134</sup>Cs tagged).

small fraction (0.07%) of the iodine was detected on the charcoal. (As was pointed out previously, only the more volatile, or penetrating, forms of iodine, like  $I_2$ ,  $CH_3I$ , and  $HI$ , should penetrate the filters and be found on the charcoal.) The largest fraction of iodine (14%) in the filter package was on the glass wool prefilter. Interestingly, the same amount of cesium that was tagged with  $^{134}Cs$  was also found there. About 9.5% of the total cesium was found in the filter package.

Table 3 gives the initial masses of the specimens and the posttest values for mass balance considerations. The values for  $^{134}Cs$  and  $^{131}I$  were within  $\pm 3\%$ , and the values for  $^{129m}Te$  and  $^{137}Cs$  were high by 5.7 and 13.4%. Considering the uncertainties in counting statistics and in attenuation factors, in both pretest and posttest measurements, we feel that these values represent good agreement.

## 6.2 THERMAL GRADIENT TUBE RESULTS

Posttest TGT deposition profiles for Cs, I, and Te are shown in Fig. 3. The behavior of each specimen is discussed in the following subsections.

The first two centimeters of the platinum TGT was positioned in the zirconia collimator (Fig. 1) during the test. The TGT liner was 38.3 cm long with an ID of 0.38 cm.

### 6.2.1 Leachability of Cesium, Iodine, and Tellurium Deposits in the Platinum Thermal Gradient Tube Liner

The primary objective of the leaching study was to examine the leach behavior of known simulant fission product species from platinum (test C-7) and stainless steel (test C-8) TGT surfaces in hopes of better understanding the leach behavior of the fission products that were collected in similar TGTs in the HI tests.

Sections 2, 4, 6, and 8 were cut from the four main peak regions (see Fig. 4) of the platinum TGT used in test C-7 for leaching purposes. Adjoining sections 1, 3, 5, and 7 were also sampled for analyses (SSMS, SEM/EDX, and x-ray diffraction).

The leaching method used was the same as was employed in the HI test series. First, the sections were individually leached two or three times (2 h each) with a basic solution composed of concentrated  $NH_4OH$  and 30%  $H_2O_2$  (2:1), and finally, they were individually leached with an acid solution, 4 M  $HNO_3$  and 0.25 M  $HF$ , for half an hour.

The leach results are tabulated in Table 4. These data show that all the cesium and iodine (>99%) were removed from each of the sections by the first basic leach. Analytical results (see Sect. 6.2.2) suggested that the likely species of cesium and iodine that were collected in the TGT were  $CsOH \cdot H_2O$ ,  $CsI$ ,  $CsTe$ , and  $Cs_2SiO_3$  (see Sect. 6.2.2), all of which are known to be soluble in aqueous solutions.

ORNL DWG 84-290

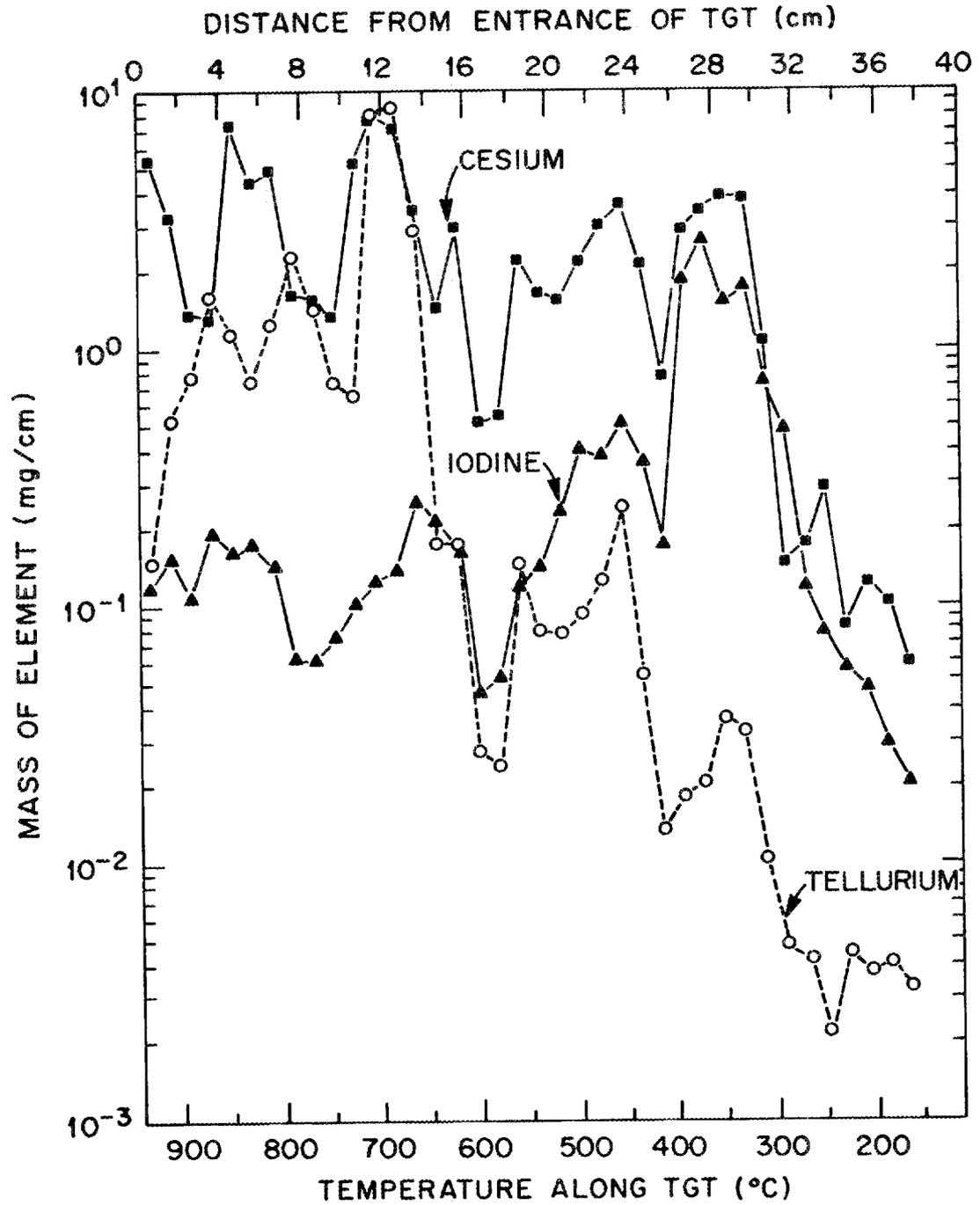


Fig. 3. Cesium, iodine, and tellurium profiles (mg/cm) along the platinum thermal gradient tube in test C-7.

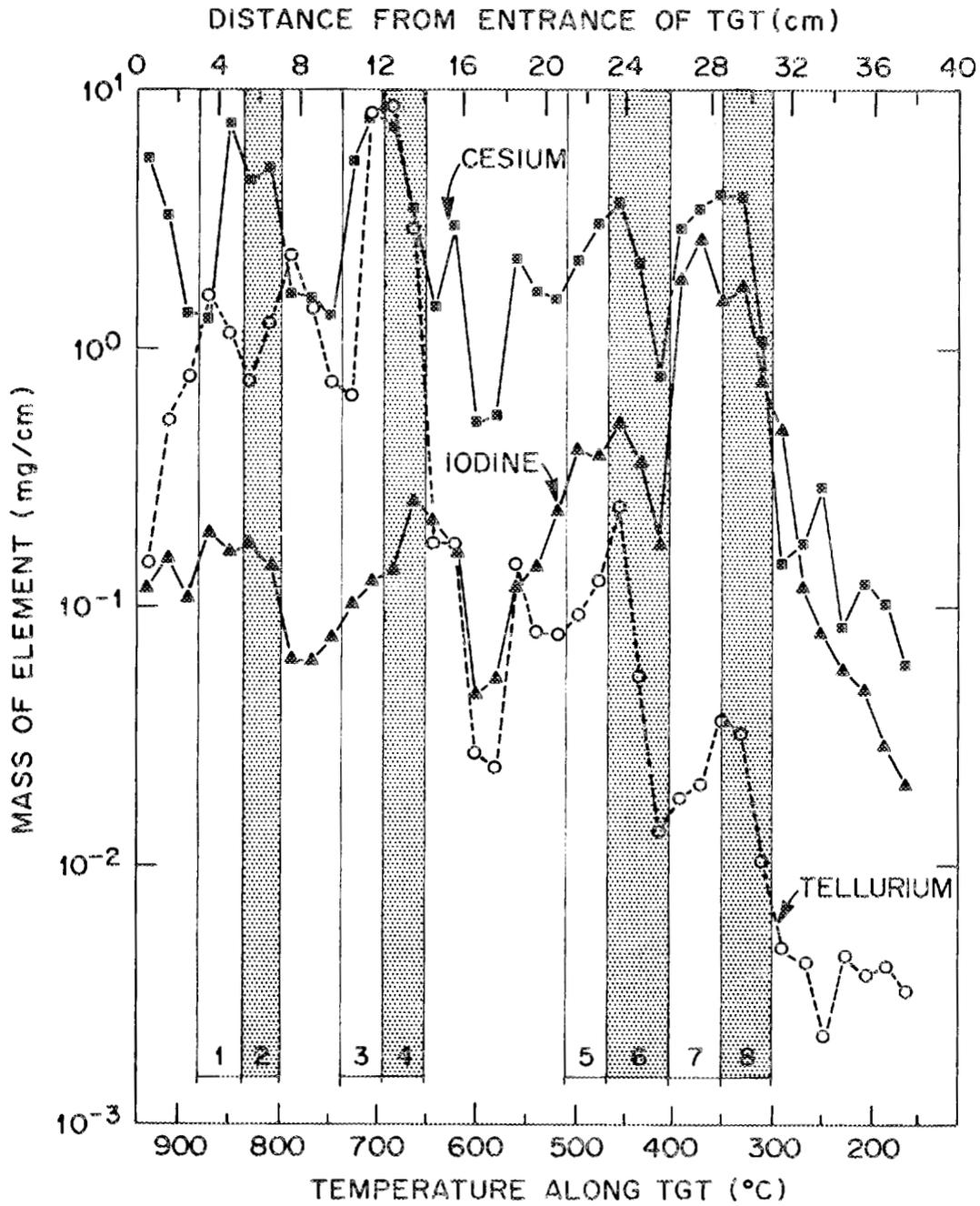


Fig. 4. This figure shows the locations where sections were cut from the TGT used in test C-7 for analytical (1, 3, 5, and 7) and leaching (2, 4, 6, and 8) purposes.

Table 4. Effectiveness of basic and acidic leaches<sup>a</sup> in removing cesium, iodine, and tellurium materials from selected sections of the thermal gradient tube liner used in test C-7

| Tagged <sup>b</sup><br>element              | Initial<br>mass<br>(mg) | Cumulative percent removed |                             |                     |
|---|-------------------------|----------------------------|-----------------------------|---------------------|
|   |                         | After first<br>basic leach | After second<br>basic leach | After<br>acid leach |
| <u>Section 2 (835 to 800°C)<sup>c</sup></u> |                         |                            |                             |                     |
| <sup>129</sup> Te                           | 1.63                    | 57.8                       | 59                          | 59                  |
| <sup>131</sup> I                            | 0.033                   | 100                        | 100                         | 100                 |
| <sup>134</sup> Cs                           | 0.381                   | 100                        | 100                         | 100                 |
| <sup>137</sup> Cs                           | 4.96                    | 100                        | 100                         | 100                 |
| <u>Section 4 (695 to 650°C)<sup>c</sup></u> |                         |                            |                             |                     |
| <sup>129</sup> Te                           | 3.20                    | 91.8                       | 94.6                        | 95                  |
| <sup>131</sup> I                            | 0.316                   | 100                        | 100                         | 100                 |
| <sup>134</sup> Cs                           | 0.380                   | 99.3                       | 100                         | 100                 |
| <sup>137</sup> Cs                           | 4.01                    | 99.1                       | 98.7                        | 100                 |
| <u>Section 6 (468 to 405°C)<sup>c</sup></u> |                         |                            |                             |                     |
| <sup>129</sup> Te                           | 0.118                   | 83.6                       | 86.3                        | 87                  |
| <sup>131</sup> I                            | 0.809                   | 100                        | 100                         | 100                 |
| <sup>134</sup> Cs                           | 0.697                   | 99.6                       | 100                         | 100                 |
| <sup>137</sup> Cs                           | 3.98                    | 99.5                       | 99.9                        | 100                 |
| <u>Section 8 (355 to 300°C)<sup>c</sup></u> |                         |                            |                             |                     |
| <sup>129m</sup> Te                          | 0.033                   | 93.9                       | 94.5                        | 95                  |
| <sup>131</sup> I                            | 2.21                    | 99.9                       | 100                         | 100                 |
| <sup>134</sup> Cs                           | 0.607                   | 99.8                       | 100                         | 100                 |
| <sup>137</sup> Cs                           | 3.05                    | 99.7                       | 99.8                        | 100                 |

<sup>a</sup>The basic leach solution was a 2:1 mixture of  $\text{NH}_4\text{OH}$  (concentrated) and  $\text{H}_2\text{O}_2$  (30%). The acid leach was a solution of 4 M  $\text{HNO}_3$  and 0.25 M  $\text{HF}$ .

<sup>b</sup>The initial starting materials were  $\text{CsI}$ ,  $\text{CsOH}$ , and elemental  $\text{Te}$ . Cesium iodide was tagged with  $^{134}\text{Cs}$  and  $^{131}\text{I}$ ;  $\text{CsOH}$  was tagged with  $^{137}\text{Cs}$ .

<sup>c</sup>The temperature of the section during the test (see Fig. 3).

The leach behavior for tellurium was different. Table 4 shows that ~59% of the tellurium on section 2 was very soluble in basic leach. On the other hand, the unaffected, remaining fraction could not be removed by the second basic leach or the follow up acid leach, indicating that it was probably dissolved in or reacted with the platinum.

Section 4 of the TGT contained a portion of the CsTe deposit found at ~700°C (see Sect. 6.2.2). The two basic leaches removed 95% of the tellurium and all the cesium; in fact, both were removed by the first basic leach. The remaining 5% of the tellurium could not be removed by the acid leach.

Tellurium deposits on TGT sections 6 and 8, where the two minor downstream tellurium peaks occurred, were easily removed by the first basic leach solutions. Only 13 and 5%, respectively, could not be removed by the acid leaches.

Figure 5 compares the TGT concentration profiles for tellurium (mg/cm) before and after leaching. These data show that ~14% of the tellurium that deposited in the TGT was dissolved in or reacted with the platinum surface, and that the surface concentration of this tellurium decreased exponentially from the inlet to the outlet end. This is the behavior that would be expected for gaseous elemental tellurium or possibly a tellurium specie that was less stable than PtTe.<sup>8</sup> In previous fission product release tests, <sup>125</sup>Sb has been found deposited in a similar pattern.

#### 6.2.2 Analysis of the Thermal Gradient Tube Deposits by SEM/EDX and SSMS

Two of the analytical methods employed in this research program to identify fission products and contaminant elements have been scanning electron microscopy with an energy dispersive x-ray system (SEM/EDX) and spark-source mass spectrometry (SSMS). The SSMS analyzes the total collected sample while EDX is effective in determining elemental compositions to a depth of 1 to 5 μm, depending on sample density and operating condition.

Elements with atomic numbers less than 11 (sodium) cannot be detected by EDX; however, none of these elements except oxygen should have been present in these two tests. The SSMS, on the other hand, is sensitive to all elements except C, N, O, Be, He, and H.

For test C-7, pieces of TGT that contained typical deposit materials were taken from the four peak regions (see Fig. 4). Table 5 gives the elemental compositions for three particles that were located on a small section of platinum TGT from the peak region 880 to 800°C, and for a general view of a larger fraction of the deposit. For comparison, it also gives the results obtained by SSMS for a sample taken from the same region. Cesium was assigned the value 100 atoms. Figure 6 is an SEM view (2280×) of an agglomerate of whitish particles that was located in the general view picture of Fig. 7. The major elements present in two of

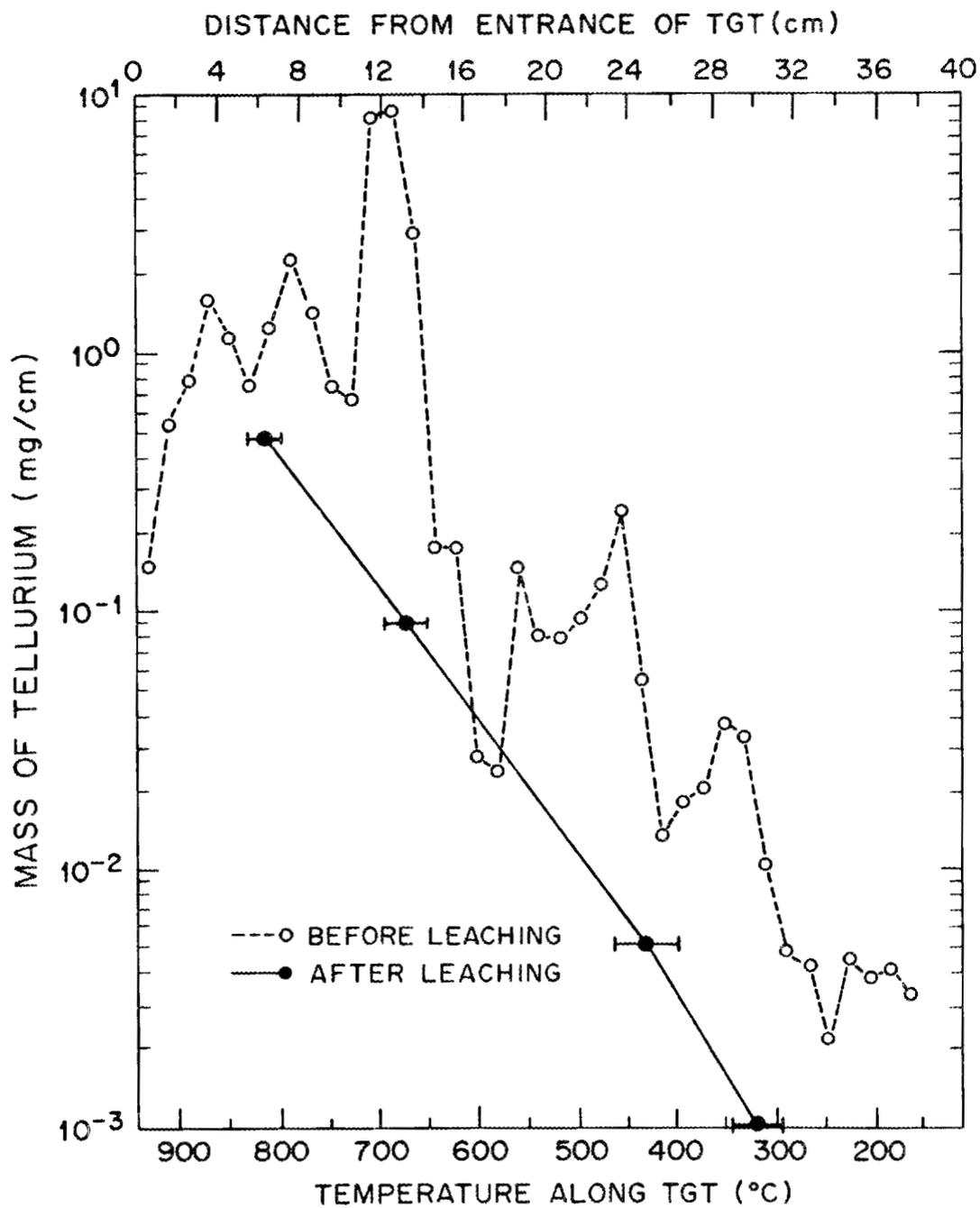


Fig. 5. Comparison of tellurium concentration profiles in the TGT liner before and after leaching in test C-7.

Table 5. Elemental deposit in TGT at 880 to 800°C  
in test C-7

| Sample         | Atom composition <sup>a</sup> |    |     |     |
|----------------|-------------------------------|----|-----|-----|
|                | Cs                            | Te | Si  | Fe  |
| A              | 100                           | 29 | 45  |     |
| B <sup>b</sup> | 100                           | 51 | 71  | 8   |
| C <sup>b</sup> | 100                           |    | 167 |     |
| D <sup>c</sup> | 100                           | 35 | 127 |     |
| E <sup>d</sup> | 100                           | 5  | 36  | 0.3 |

<sup>a</sup>Values normalized to 100 cesium atoms.

<sup>b</sup>Particle analyzed by EDX.

<sup>c</sup>Large surface area analyzed by EDX.

<sup>d</sup>Sample analyzed by SSMS.

ORNL PHOTO 3696-84



Fig. 6. An SEM view (2280 $\times$ ) of an agglomerate of whitish particles that deposited in the 880 to 800 $^{\circ}$ C temperature region in the TGT during test C-7.

ORNL PHOTO 3698-84

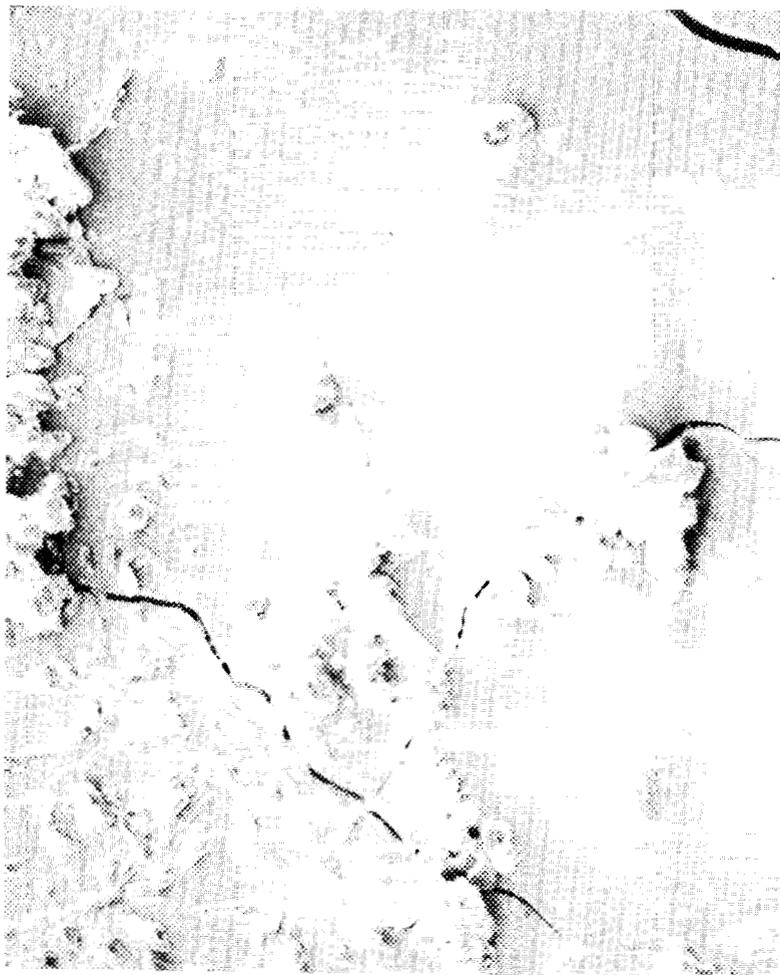


Fig. 7. General SEM view (228 $\times$ ) of a section of TGT surface deposit from the 880 to 800 $^{\circ}$ C peak region (test C-7).

these particles (A and B) that were analyzed by EDX were Ce, Te, and Si. A small amount of iron was also detected in B. A stray particle (C), not associated with the agglomerate, contained no tellurium, but contained more silicon. For a large area of the sample surface in the Fig. 7 view that was also examined by EDX, the ratio of Te:Cs atoms for this sample is similar to those obtained for particles A and B; however, the Si:Cs ratio is considerably higher. The values obtained by SSMS (see specimen E in Table 5) for a similar deposit sample show that the tellurium content was lower. This was expected because a large fraction of the tellurium was alloyed with the platinum and could not be removed by the sampling method for SSMS. The silicon value, on the other hand, was similar to the values obtained for particles A and B.

These data offer an explanation for the cesium peaks near the hot inlet end of the TGT liner (see Fig. 3); apparently small quartz particles from the tellurium specimen tube were transported to the liner (see Sect. 5). Cesium was probably retained in this location because CsOH reacts readily with quartz to form cesium silicates, which are stable at higher temperatures (<1000°C).

Analysis of the deposit on the section of liner located in the temperature region 750 to 650°C (see Fig. 4) revealed a cesium to tellurium atom ratio of 1:1. Table 6 gives both the EDX and the SSMS results.

Table 6. Elemental deposit in TGT at 750 to 700°C  
in test C-7

| Sample         | Atom composition <sup>a</sup> |     |   |    |
|----------------|-------------------------------|-----|---|----|
|                | Cs                            | Te  | I | Si |
| A <sup>b</sup> | 100                           | 99  |   |    |
| B <sup>b</sup> | 100                           | 96  |   |    |
| C <sup>b</sup> | 100                           | 96  |   |    |
| D <sup>c</sup> | 100                           | 115 |   |    |
| E <sup>c</sup> | 100                           | 83  |   |    |
| F <sup>d</sup> | 100                           | 95  | 1 | 6  |

<sup>a</sup> Values normalized to 100 cesium atoms.

<sup>b</sup> Particle analyzed by EDX.

<sup>c</sup> Large surface area analyzed by EDX.

<sup>d</sup> Sample analyzed by SSMS.

Traces of iodine and silicon were also detected by SSMS. These values also compare well with the values obtained by gamma spectrometry for the atom composition (Cs = 100, Te = 104, I = 1.6). Since only a small fraction of the tellurium (5%) was reacted with the platinum in this section of liner, and since there were only trace amounts of contaminant materials

present in the surface deposit, it is likely that the primary deposited species was cesium telluride (CsTe).

A section of TGT that was located in the temperature region 500 to 400°C (see Fig. 4) during the test had two different appearing deposits, one whitish and the other grayish colored. Each was examined and analyzed by SEM/EDX. Based on the EDX results shown in Table 7, there was not a significant difference in atom composition of particles from the deposits. No tellurium was detected in particle samples E and F or silicon in particle samples A and D. The atom composition of a similar sample deposit was obtained by SSMS as indicated by sample L; it compares favorably with the results obtained by gamma spectrometry.

Table 7. Elemental deposit in TGT at 500 to 400°C in test C-7

| Sample <sup>c</sup> | Atom composition <sup>a</sup> |                |    |    |
|---------------------|-------------------------------|----------------|----|----|
|                     | Cs                            | I <sup>b</sup> | Te | Si |
| A <sup>d</sup>      | 100                           | 16             | 14 |    |
| B <sup>d</sup>      | 100                           | 22             | 17 | 3  |
| C <sup>d</sup>      | 100                           | 11             | 15 | 3  |
| D <sup>d</sup>      | 100                           | 89             | 10 |    |
| E <sup>d</sup>      | 100                           | 55             |    | 12 |
| F <sup>d</sup>      | 100                           | 39             |    | 40 |
| G <sup>d</sup>      | 100                           | 21             | 18 | 56 |
| H <sup>e</sup>      | 100                           | 18             | 19 | 19 |
| I <sup>d</sup>      | 100                           | 73             | 22 | 6  |
| J <sup>d</sup>      | 100                           | 55             | 31 | 5  |
| K <sup>e</sup>      | 100                           | 52             | 24 | 26 |
| L <sup>f</sup>      | 100                           | 9              | 1  | 5  |

<sup>a</sup>Values normalized to 100 cesium atoms.

<sup>b</sup>Iodine was corrected for EDX sensitivity differences based on EDX analysis of pure CsI samples. The iodine values were increased by the factor 1.22.

<sup>c</sup>Samples A through H were sample examples of the whitish deposit; samples I through J were sample examples of the gray deposit.

<sup>d</sup>Particle analyzed by EDX.

<sup>e</sup>Large surface area analyzed by EDX.

<sup>f</sup>Sample analyzed by SSMS.

Samples were examined by x-ray diffraction and  $\text{CsOH}\cdot\text{H}_2\text{O}$  and  $\text{CsI}$  were identified as the major species. There were also some weak unidentified lines that were not those of  $\text{Cs}_2\text{CO}_3$  or elemental tellurium. Since silicon was present, these possibly could have been  $\text{Cs}_2\text{SiO}_3$  lines.

Figure 4 shows that the major iodine peak in the TGT occurred in the temperature region 400 to 325°C. There was also a major cesium peak associated with it, which suggested a  $\text{CsI}$  deposit. Samples of the white crystalline deposit were identified by x-ray diffraction as  $\text{CsI}$ , but there were also some less intense lines for  $\text{CsOH}\cdot\text{H}_2\text{O}$  and very faint lines that appeared to be  $\text{Cs}_2\text{CO}_3$ .

Figure 8 shows a typical SEM view (228×) of the deposit on a sample section of liner from the region. Six particles were picked at random and analyzed by EDX; five of them had a mean atom composition of ~100 iodine atoms per 100 cesium atoms (see Table 8). Sample particle F contained no I, only Te and Si. Analysis of a larger area, which encompassed many particles, showed 50 iodine atoms and 14 silicon atoms per 100 cesium atoms. Analysis of a deposit sample by SSMS showed the number of iodine atoms as being similar to the numbers determined by EDX. The SSMS analysis also showed that tellurium and silicon were present.

### 6.2.3 Tellurium Behavior

Tellurium is thought to vaporize in a steam-hydrogen atmosphere as the dimer,  $\text{Te}_2$ . If it had remained in that form, it would have reacted irreversibly with the surface of the hot platinum TGT, and the posttest surface concentration profile would have decreased exponentially with distance from the inlet to the outlet.<sup>8</sup> Obviously, as can be seen in Fig. 3, that did not happen; the tellurium profile was irregular, having five peak regions. It was determined by leaching (see Sect. 6.2.1), that only ~14% of the tellurium in the TGT was alloyed (or reacted) with the platinum.

Significant and almost identical tellurium and cesium peaks occurred at 700°C. Analyses of deposited material by SSMS and SEM/EDX showed that Ce, Te, and I were the only elements present, and the amount of I was negligible; furthermore, as gamma spectrometry also indicated, the atom ratio of Cs:Te was 1:1. The leach study (Sect. 6.2.1) showed that both the cesium and the tellurium were readily soluble in basic leach; alkali tellurides are soluble in aqueous solutions. From these data, it appears that  $\text{CsTe}$  was the deposited specie.

When the TGT was opened in the posttest examination, a 4-cm-long black deposit was observed at the Cs-Te peak location; the temperature range covered was between 740 and 650°C (see Fig. 3). Closer examination showed that there was white crystalline material on the surface of the black deposit. When a section of the deposit was dried for 2 h in a flowing helium atmosphere, the deposited material appeared to be somewhat yellowish green.

ORNL PHOTO 3697-84

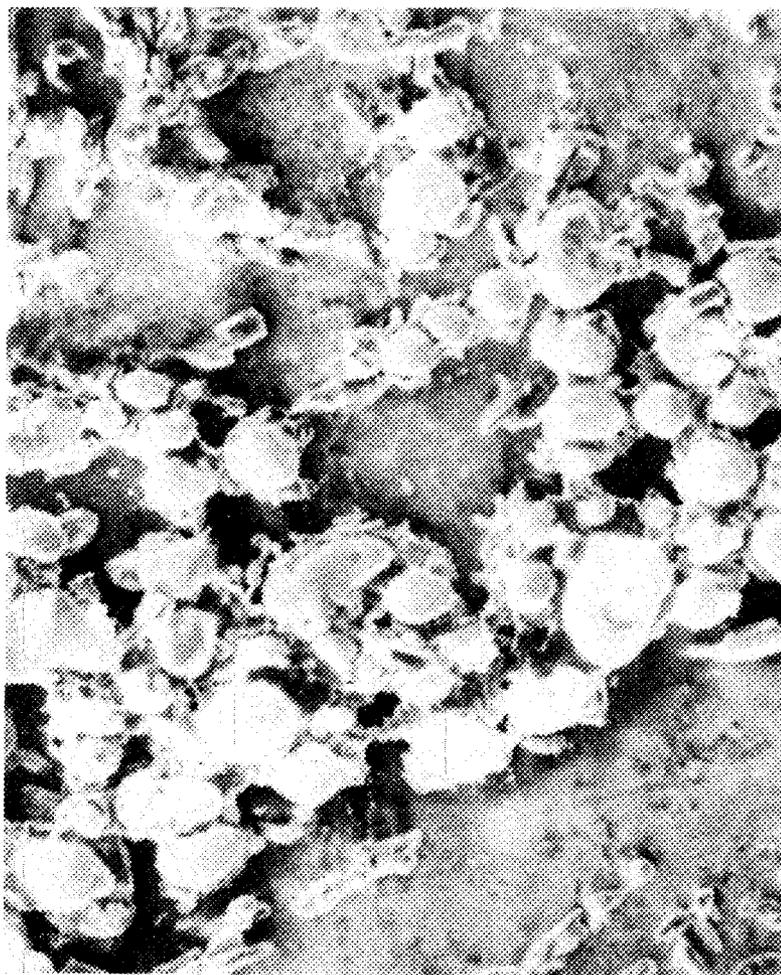


Fig. 8. General SEM view (228 $\times$ ) of a surface deposit on a section of TGT liner from the 400 to 300 $^{\circ}$ C peak region (test C-7).

Table 8. Elemental deposit in TGT at 400 to 300°C  
in test C-7

| Sample         | Atom composition <sup>a</sup> |                |    |    |
|----------------|-------------------------------|----------------|----|----|
|                | Cs                            | I <sup>b</sup> | Te | Si |
| A <sup>c</sup> | 100                           | 96             |    |    |
| B <sup>c</sup> | 100                           | 98             |    |    |
| C <sup>c</sup> | 100                           | 107            |    |    |
| D <sup>c</sup> | 100                           | 84             |    |    |
| E <sup>c</sup> | 100                           | 115            |    |    |
| F <sup>d</sup> | 100                           |                | 18 | 65 |
| G <sup>e</sup> | 100                           | 50             |    | 14 |
| J              | 100                           | 74             | 1  | 11 |

<sup>a</sup>Values normalized to 100 cesium atoms.

<sup>b</sup>Iodine was corrected for EDX sensitivity differences based on EDX analyses of pure CsI samples. The iodine values were increased by the values 1.22.

<sup>c</sup>Particle analyzed by EDX.

<sup>d</sup>Large surface area analyzed by EDX.

<sup>e</sup>Sample analyzed by SSMS.

Samples of deposited material from all the peak regions were examined by x-ray diffraction. There were no lines in the film for tellurium species; apparently, the crystals were too small for identification.

#### 6.2.4 Iodine Behavior

During the test, most of the CsI specimen (99.4%) was vaporized and transported from the nickel tube (see Fig. 1). About 71% of the CsI was found in the TGT (Table 3); furthermore, most of that deposited in a peak that occurred in the temperature range 400 to 300°C, as seen in Fig. 3. Samples taken from this peak were analyzed by x-ray diffraction. Cesium iodide and CsOH·H<sub>2</sub>O were identified as the major species. Also, in the adjacent peak region between 500 and 400°C, CsOH·H<sub>2</sub>O and CsI were identified as the major species there.

In the posttest examination of the TGT, a whitish deposit was observed in the cesium-iodine peak region, which was found to be very soluble in aqueous leaches. The color and leach behavior characteristics of both CsI and CsOH·H<sub>2</sub>O.

All the evidence in this test indicates that CsI remained a stable specie; there was little evidence of any dissociation. Only 0.005% of

the iodine was found on the charcoal in the filter package. Volatile forms of iodine, like elemental iodine, methyl iodide, and hydrogen iodide are trapped and collected by the charcoal.

#### 6.2.5 Cesium Behavior

Cesium was initially present as CsOH and CsI; there were 10 times more moles of CsOH than CsI. Since the behavior of CsI was discussed in the previous subsection, only CsOH behavior in the TGT will be discussed here.

During the test, ~83% of the CsOH was vaporized and transported out of the nickel specimen tube. Of that, only 56% entered the collection train. The fraction that stayed in the furnace (17%) was reacted with the quartz furnace vessel and quartz TGT housing, mostly on surfaces near the inlet end of the TGT, even though very little quartz surface was exposed to the flowing gas. Cesium hydroxide reacts readily with quartz to form cesium silicates, which are stable at temperatures  $\leq 1000^\circ\text{C}$ .<sup>9,10</sup>

About 81% of the CsOH that was found in the collection train deposited in the platinum TGT liner. The deposition profile for cesium in Fig. 3 is very complex. The cesium peak that occurred in the temperature zone 850 to 800°C during the test was apparently caused by quartz particles that transported there from the tellurium specimen tube. Silicon was identified by SEM/EDX and SSMS analyses as being the only contaminant in the deposit samples and primarily at this location.

As was discussed in Sect. 5.2.3, a significant fraction of the CsOH apparently reacted in the gas phase with tellurium to form CsTe and deposited at ~700°C in the TGT. The constituents in the two cesium peaks that occurred in the temperature range 500 to 300°C were identified by x-ray diffraction analyses as CsOH·H<sub>2</sub>O and CsI.

### 6.3 COMPARISON OF COLLECTED MATERIAL IN THE THERMAL GRADIENT TUBE BY WEIGHING AND BY ANALYTICAL METHODS

One of the techniques used in the HI test series<sup>1-4</sup> to help understand the transport and chemical behavior of released fission products was to compare the mass value obtained by weighing the TGT with the value obtained by making use of gamma spectrometry, SSMS, and neutron activation data. Considering the masses that were involved ( $\leq 100$  mg), the values were in good agreement. For example, in test HI-4 the mass by weighing was 35 mg compared to ~40 mg by analytical analyses.

This type of comparison was also done for test C-7. After the TGT liner was counted and scanned by gamma spectrometry, it was dried in a tube furnace at ~150°C for 2 h in a flowing helium atmosphere and subsequently cooled and weighed. (This procedure had to be done because CsOH is hygroscopic and can react with the CO<sub>2</sub> in air to form Cs<sub>2</sub>CO<sub>3</sub>.) The weight gain during the test was 166 mg.

A value of 159 mg was obtained analytically (with some judgment). To obtain this value, certain assumptions had to be made based on several analytical methods — gamma spectrometry, SSMS, SEM/EDX, and x-ray diffraction. The masses for Cs, I, and Te were determined by gamma spectrometry; the total was 144 mg. Contaminant material was identified and semiquantified by examining samples of deposits taken at key locations along the TGT by SSMS and SEM/EDX. Silicon was the only significant contaminant identified. Some of the chemical species in the peak deposits were identified by x-ray diffraction; others were inferred by results from the leach study (see Sect. 6.2.1) and analytical evidence (see Sects. 6.2.2 and 4.2). Table 9 gives the estimated weights of the different deposited species.

Table 9. Mass of fission product elements in the platinum TGT liner after test C-7

| Element | Chemical form                    | Mass (mg) |
|---------|----------------------------------|-----------|
| Te      | Alloyed with platinum            | 4.5       |
| Te      | Surface deposit (CsTe)           | 57.3      |
| I       | CsI                              | 29.1      |
| Cs      | CsOH·H <sub>2</sub> O            | 29.9      |
| Cs      | Cs <sub>2</sub> SiO <sub>3</sub> | 38.1      |
| Total   |                                  | 158.9     |

## 7. TEST C-8

### 7.1 GENERAL RESULTS AND TEST DESCRIPTION

Unlike in test C-7, which was run for a long period of time, the specimens in this test were heated at 715°C for 26.3 min (see Fig. 9) in a flowing steam (0.136 L/min at STP) and helium-9.6% hydrogen (0.147 L/min at STP) atmosphere. (During the heatup and cooldown periods, they were also at temperatures above 650°C for 29 min.) Figure 9 illustrates the collection behavior of Cs, I, and Te as a function of time and specimen temperature. Compared with test C-7, there were two experimental variants; a stainless steel rather than a platinum TGT was used, and the hot zone in the zirconia liner was maintained at ~1000 rather than ~800°C (see Fig. 1).

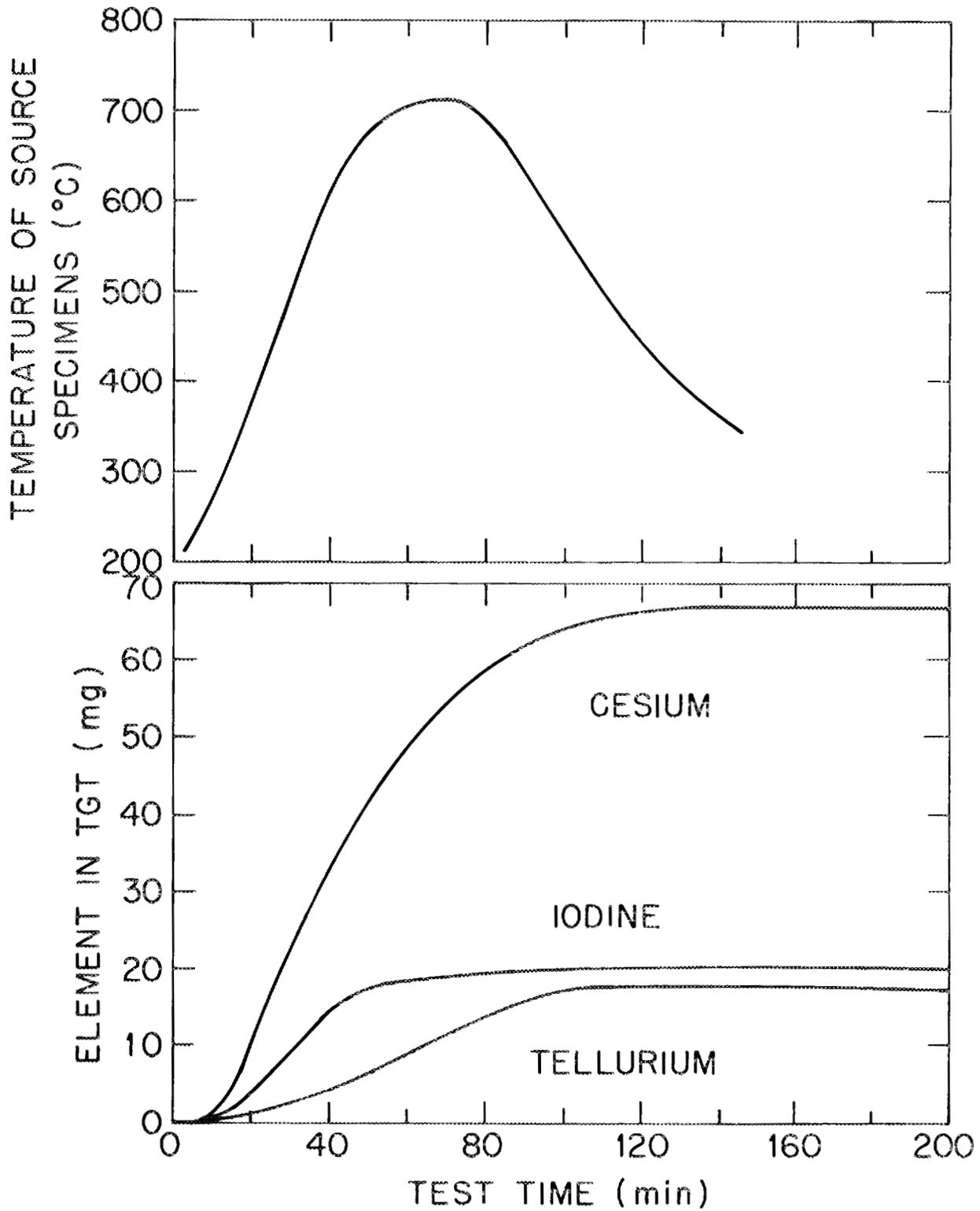


Fig. 9. Collection of cesium, iodine, and tellurium in the TGT in test C-8 as functions of time and specimen temperatures.

The TGT was 38.3 cm long and made of three interlocking sections. The first section, the one at the inlet end, was made of Inconel-600. It was 5.1 cm long with an ID of 0.457 cm; the wall thickness was 0.089 cm. The other two tube sections were each 16.6 cm long and made of 304-L stainless steel with the same ID and wall thickness. Table 10 gives the chemical composition of the two materials. Inconel-600 was used at the hot entrance end (925-800°C) because of uncertainty about the rate of oxidation of stainless steel at those temperatures. There was concern that the expansion caused by oxidation when coupled with thermal expansion might cause the quartz tube in which the TGT was housed to break.

A summary of the posttest distribution of Cs, I, and Te is given in Table 11. These data show that all of the CsI was vaporized from the platinum boat and that 91% of the iodine was found in the TGT and 5.1% in the filter package. Furthermore, only 0.003% of the iodine penetrated the collection system to the activated charcoal. This suggests, as was also the case in test C-7, that there was little tendency for CsI to decompose under the test conditions. (There had been pretest concerns that CsI reaction with stainless steel might free elemental iodine.)

Table 11 shows that ~90% of the tellurium specimen was vaporized and transported from the zirconia tube. About 47% of the total tellurium passed through the furnace to the collection train and deposited mainly in the Inconel section of the TGT. Most of the tellurium that remained in the furnace was found reacted with the nickel tube and the platinum boats. For this to have happened, a limited flow restriction had to have occurred in the zirconia tube causing vapor to diffuse out the inlet end. It probably was caused by pieces of broken quartz ampul that were placed in the tube along with the tellurium specimen (see Sect. 5). Figure 10 illustrates the deposition behavior of tellurium on the nickel tube. The concentration is shown to decrease exponentially along the tube. This suggests that tellurium rapidly reacted with the nickel. The tube was at a temperature <700°C during the test.

Interpretation of the cesium deposited in the TGT was complicated by isotopic exchange that apparently occurred as the gaseous species were transported through the hot zone of the furnace. The CsI and CsOH were initially tagged with  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ , respectively. The best evidence of isotopic exchange is seen in examining the behavior of CsI in the TGT. First, it must be pointed out that 91% of the iodine deposited in the TGT, that all the analytical results (including x-ray diffraction) suggested that iodine deposited there as CsI (see Sect. 6.2.2), and that posttest values in Table 11 were determined by using the pretest specific activities for the individual elements. Notice that there was 22.3 mg iodine compared with only 15.9 mg cesium, which was tagged with  $^{134}\text{Cs}$  in the TGT. If no isotopic exchange had occurred, the  $^{134}\text{Cs}$ -tagged cesium mass would have been ~23.4 mg. This means that ~32% (or 7.5 mg) of the cesium in the CsI was associated with  $^{137}\text{Cs}$  instead. On the other hand, isotopic exchange had little influence on the interpretation of CsOH behavior because there was 12 times more cesium associated with CsOH than with CsI.

Table 10. Chemical composition of Inconel-600 and stainless steel 304-L

| Composition (%) |         |          |         |           |         |         |        |        |        |            |
|-----------------|---------|----------|---------|-----------|---------|---------|--------|--------|--------|------------|
| Material        | Nickel  | Chromium | Iron    | Manganese | Silicon | Niobium | Carbon | Sulfur | Copper | Phosphorus |
| Inconel-600     | 73.55   | 16       | 7.55    | 0.2       | 0.3     | 2.30    | 0.04   | 0.005  | 0.03   |            |
| S.S. 304-L      | 8 to 10 | 18 to 20 | Balance | 2.0       | 1.0     |         | 0.03   | 0.03   |        | 0.045      |

Table 11. Posttest distribution of tellurium, cesium, and iodine in test C-8

| Location                             | Temperature<br>(°C)  | Amount and percentage of Te, Cs, and I found in each location <sup>a</sup> |                        |                  |       |                  |       |                 |                    |                        |                        |
|--------------------------------------|----------------------|--|------------------------|------------------|-------|------------------|-------|-----------------|--------------------|------------------------|------------------------|
|                                      |                      | 129m traced<br>Te  |                        | 137 traced<br>Cs |       | 134 traced<br>Cs |       | Cs <sup>b</sup> |                    | 131 traced I           |                        |
|                                      |                      | (mg)   | (%) <sup>c</sup>       | (mg)             | (%)   | (mg)             | (%)   | (mg)            | (%)                | (mg)                   | (%)                    |
| Furnace components                   |                      |  |                        |                  |       |                  |       |                 |                    |                        |                        |
| Quartz furnace tube                  | 600-1000             | 0.037  | 0.09                   | 3.579            | 1.50  | 0.332            | 1.56  | 3.91            | 1.51               | 0.020                  | 0.09                   |
| Quartz spacer                        | 600                  | 0.001  | $3 \times 10^{-1}$     | 0.012            | 0.005 | 0.001            | 0.005 | 0.013           | $5 \times 10^{-3}$ | 0.0                    | 0.0                    |
| Quartz holder                        | 600-1000             | 0.035  | 0.09                   | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | 0.0                    | 0.0                    |
| Zirconia furnace tube liner          | 600-1000             | 0.655  | 1.65                   | 171              | 71.73 | 2.49             | 11.67 | 173.49          | 66.80              | 0.861                  | 3.85                   |
| Zirconia outlet plug                 | 980                  | 0.035  | 0.09                   | 10.01            | 4.20  | 1.99             | 9.32  | 12.0            | 4.62               | 0.001                  | 0.004                  |
| Zirconia tube (Te specimen)          | 635-850 <sup>d</sup> | 4.09   | 10.31                  | 0.378            | 0.16  | 0.0              | 0.0   | 0.378           | 0.15               | 0.0                    | 0.0                    |
| Nickel tube (CsOH and CsI specimens) | 635-750              | 4.9  | 12.34                  | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | 0.001                  | 0.004                  |
| Platinum boat (CsOH)                 | ~715                 | 0.042  | 0.11                   | 0.367            | 0.15  | 0.008            | 0.04  | 0.375           | 0.14               | 0.0                    | 0.0                    |
| Platinum boat (CsI)                  | ~715                 | 11.35  | 28.60                  | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | 0.0                    | 0.0                    |
| Total                                |                      | 21.15  | 53.26                  | 185.34           | 77.75 | 4.82             | 22.59 | 190.16          | 73.22              | 0.883                  | 3.95                   |
| Thermal gradient tube                | 950-150              | 18.45  | 46.46                  | 50.97            | 21.38 | 15.91            | 74.57 | 66.88           | 25.75              | 20.33                  | 90.95                  |
| Filter pack components               |                      |  |                        |                  |       |                  |       |                 |                    |                        |                        |
|                                      | 145                  |  |                        |                  |       |                  |       |                 |                    |                        |                        |
| Entrance tube                        |                      | 0.004  | 0.01                   | 0.040            | 0.02  | 0.011            | 0.05  | 0.051           | 0.02               | 0.023                  | 0.10                   |
| Entrance cone                        |                      | 0.002  | 0.005                  | 0.009            | 0.004 | 0.002            | 0.01  | 0.011           | $4 \times 10^{-3}$ | 0.002                  | 0.01                   |
| Glass wool prefilter                 |                      | 0.099  | 0.25                   | 1.90             | 0.80  | 0.559            | 2.62  | 2.45            | 0.95               | 1.065                  | 4.77                   |
| First HEPA filter                    |                      | 0.003  | 0.008                  | 0.103            | 0.04  | 0.034            | 0.16  | 0.137           | 0.05               | 0.048                  | 0.22                   |
| Second HEPA filter                   |                      | 0.0  | 0.0                    | 0.026            | 0.01  | 0.001            | 0.005 | 0.027           | 0.01               | $(4.6 \times 10^{-5})$ | $(2.0 \times 10^{-4})$ |
| First charcoal                       |                      | $(4.5 \times 10^{-5})$   | $(1.0 \times 10^{-4})$ | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | $(6.6 \times 10^{-4})$ | 0.003                  |
| Second charcoal                      |                      | 0.0  | 0.0                    | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | $(4.9 \times 10^{-6})$ | $(2.0 \times 10^{-5})$ |
| Miscellaneous parts                  |                      | 0.001  | $3 \times 10^{-3}$     | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | $(6.0 \times 10^{-4})$ | 0.001                  |
| Total                                |                      | 0.109  | 0.28                   | 2.08             | 0.87  | 0.607            | 2.84  | 2.68            | 1.03               | 1.139                  | 5.10                   |
| Condenser                            | 0                    | 0.0  | 0.0                    | 0.0              | 0.0   | 0.0              | 0.0   | 0.0             | 0.0                | 0.0                    | 0.0                    |
| Total all components <sup>e</sup>    |                      | 39.70  | 100.0                  | 238.38           | 100.0 | 21.34            | 100.0 | 259.72          | 100.0              | 22.35                  | 100.0                  |

<sup>a</sup>All these values were based on the initial specific activities.

<sup>b</sup>Sum of 137 traced Cs and 134 traced Cs.

<sup>c</sup>Percentage of total mass found.

<sup>d</sup>Tellurium sample was at ~715°C.

<sup>e</sup>The initial specimen weights were 38.3 mg tellurium (<sup>129m</sup>Te tagged), 21.3 mg iodine (<sup>131</sup>I tagged), 264.3 mg cesium (<sup>137</sup>Cs tagged), and 22.3 mg cesium (<sup>134</sup>Cs tagged).

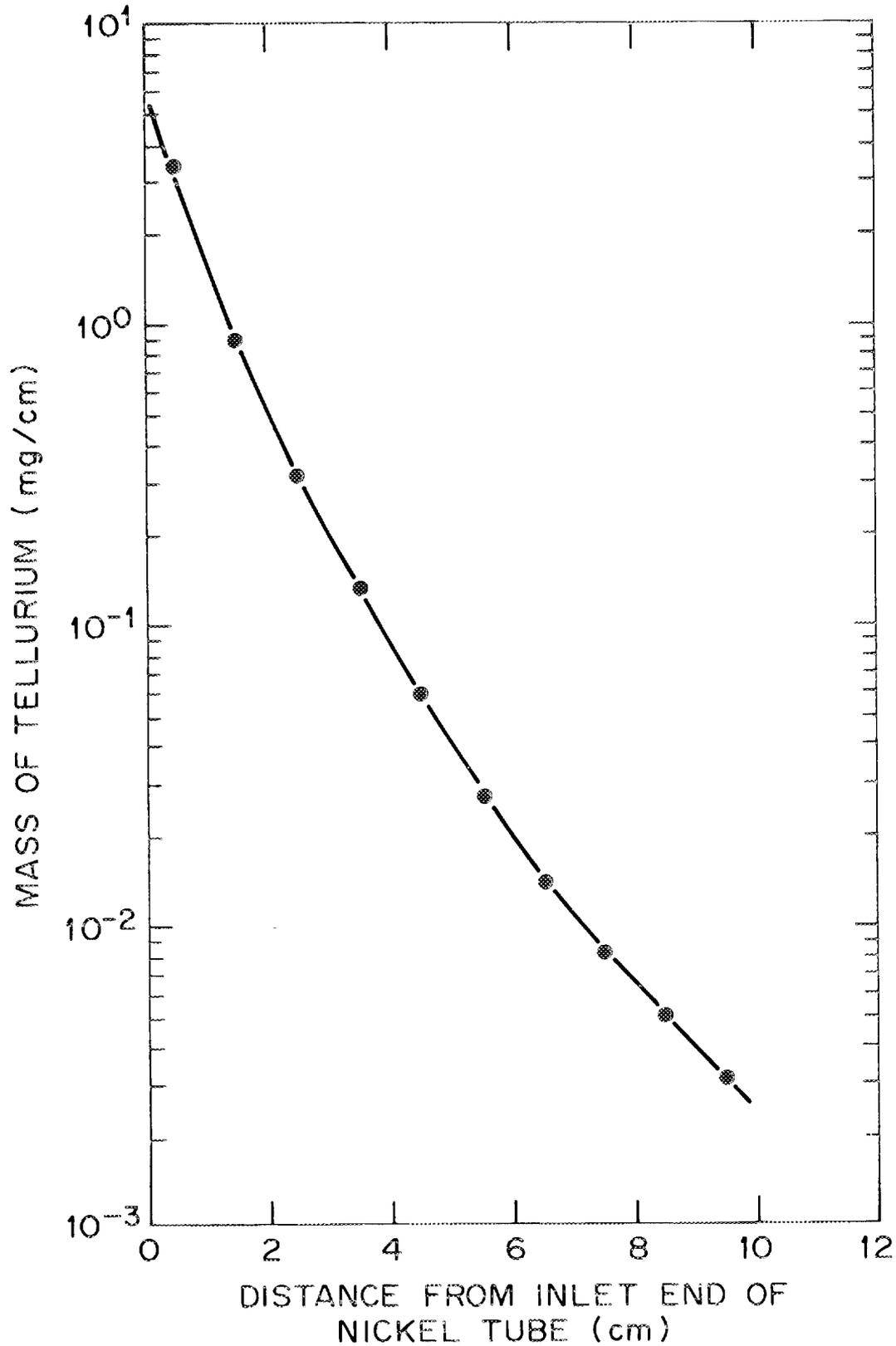


Fig. 10. Deposition of tellurium on the nickel tube.

Like CsI, essentially all of the CsOH was vaporized from the nickel tube; however, unlike CsI, only 22% was transported to the collection train. Most of the CsOH that was retained in the furnace was found in the zirconia furnace tube liner and the zirconia collimator. Figure 11 illustrates how the cesium (mostly  $^{137}\text{Cs}$  tagged) was distributed along the zirconia liner. (The deposit in the  $\text{ZrO}_2$  collimator is also included.) The largest concentration occurred between 800 and 900°C, immediately downstream from the outlet end of the nickel tube. These data show that CsOH reacted with zirconia to form a less volatile compound, probably cesium metazirconate ( $\text{Cs}_2\text{ZrO}_3$ ).<sup>11,12</sup> Based on the results in these tests and the results in the HI test series, zirconia can react with or getter cesium, especially CsOH, in the temperature range 800 to 1200°C.

Table 11 gives the initial and posttest values for the tagged specimens. The mass balances for each were fairly good. All were within  $\pm 5\%$ , except for the  $^{137}\text{Cs}$  tagged cesium, which was 10% low.

## 7.2 THERMAL GRADIENT TUBE RESULTS

Figure 12 gives the posttest deposition profiles for Cs, I, and Te in the TGT liner used in test C-8, as determined by gamma spectrometry. During the test, 91.0% of the I, 46.5% of the Te, and 25.8% of the Cs deposited in the TGT liner. Figure 9 gives the collection rate in the TGT liner as functions of time and specimen temperature (in boats).

### 7.2.1 Leachability of Cesium, Iodine, and Tellurium Deposits in the Inconel-Stainless Steel Thermal Gradient Tube

One of the main objectives in the Fission Product Release Program is to quantify and characterize iodine release. Prior to conducting test HI-6, only platinum and gold TGTs had been used. Control test C-8 was conducted using a stainless steel TGT to see if iodine might behave differently, and to see if it was leachable by the standard leaching method (see Sect. 6.2). This information was needed because of the indirect method (neutron activation analysis) for measuring iodine in the tests with irradiated fuel. Test C-8 showed that there was no tendency for CsI to react with the stainless steel or Inconel surfaces. Furthermore, the iodine, as CsI, was easily removed from the surfaces by the standard leaching method. In fact, most of it was removed by only one basic leach, thereby facilitating mass balance determinations.

Figure 13 shows that there were three major peak regions where the test specimens deposited in the TGT during the test. The principal tellurium peak occurred in the Inconel 600 section in the 925 to 800°C temperature zone. The other two peaks occurred in the stainless steel sections. One peak formed between 700 to 625°C with cesium and tellurium being the principal constituents; the other formed between 500 to 450°C with cesium and iodine as the major components.

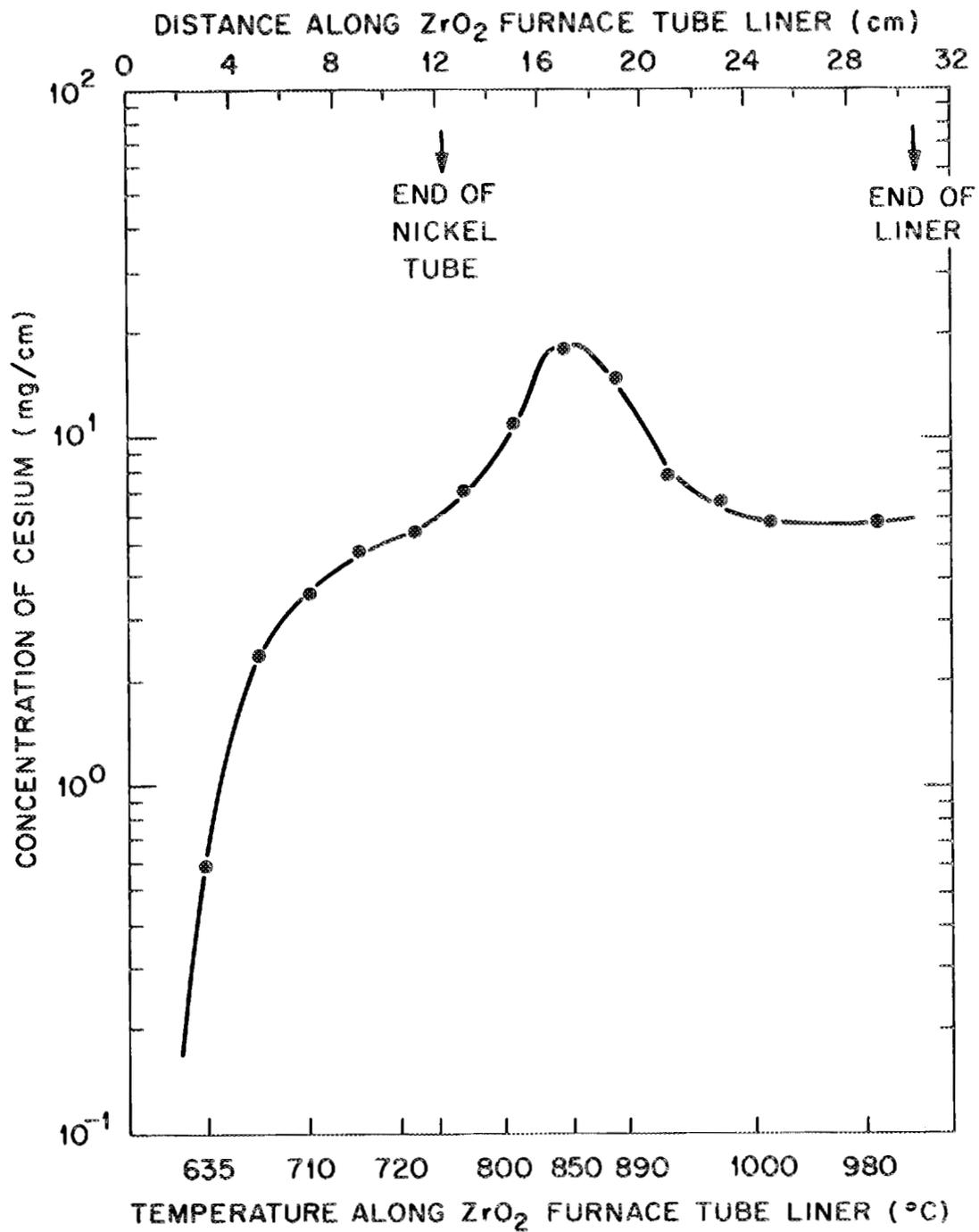


Fig. 11. Distribution of cesium ( $^{137}Cs$  tagged) along the zirconia furnace tube liner after test C-8.

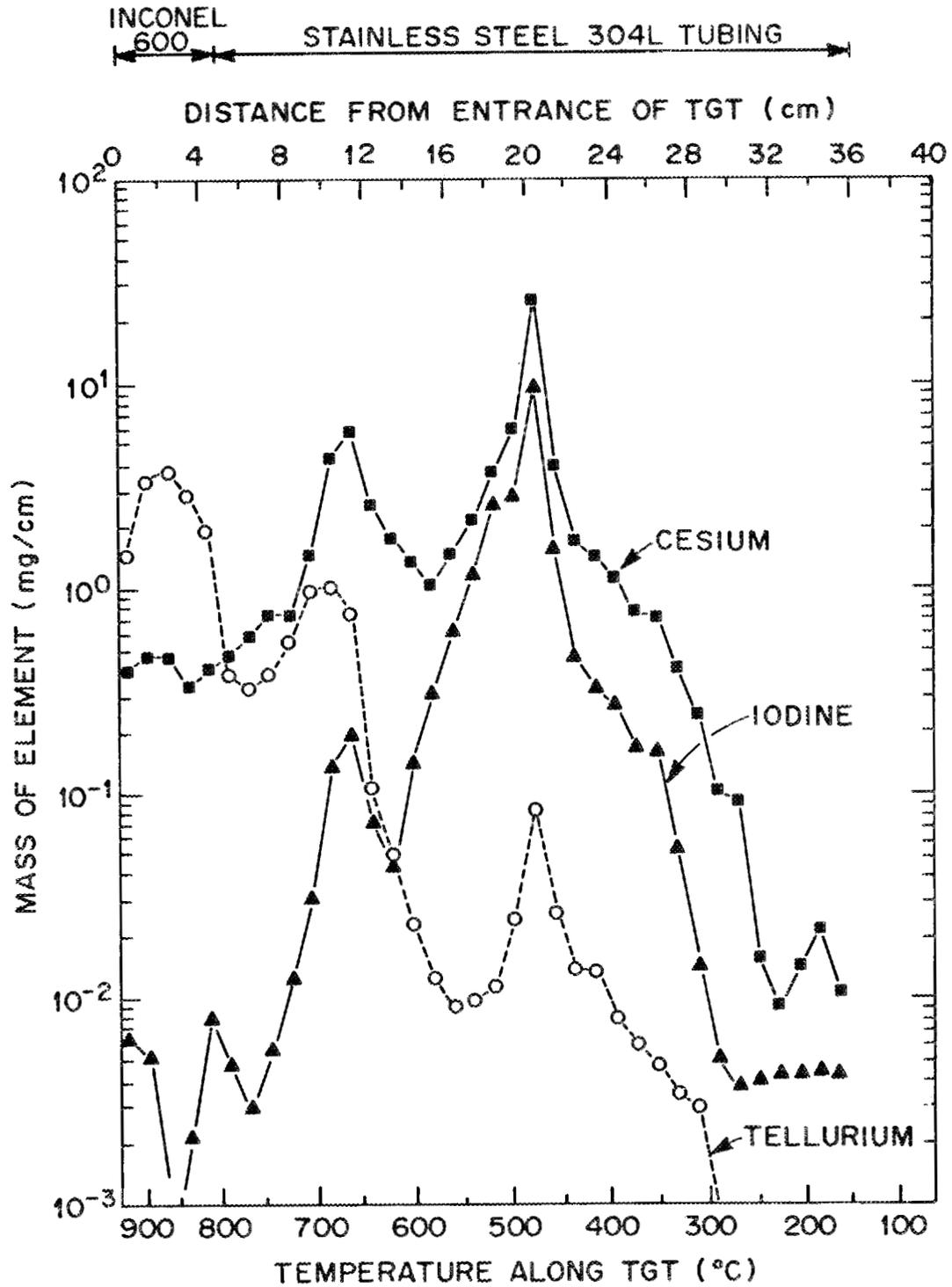


Fig. 12. Distribution profiles for cesium, iodine, and tellurium in the TGT liner used in test C-8.

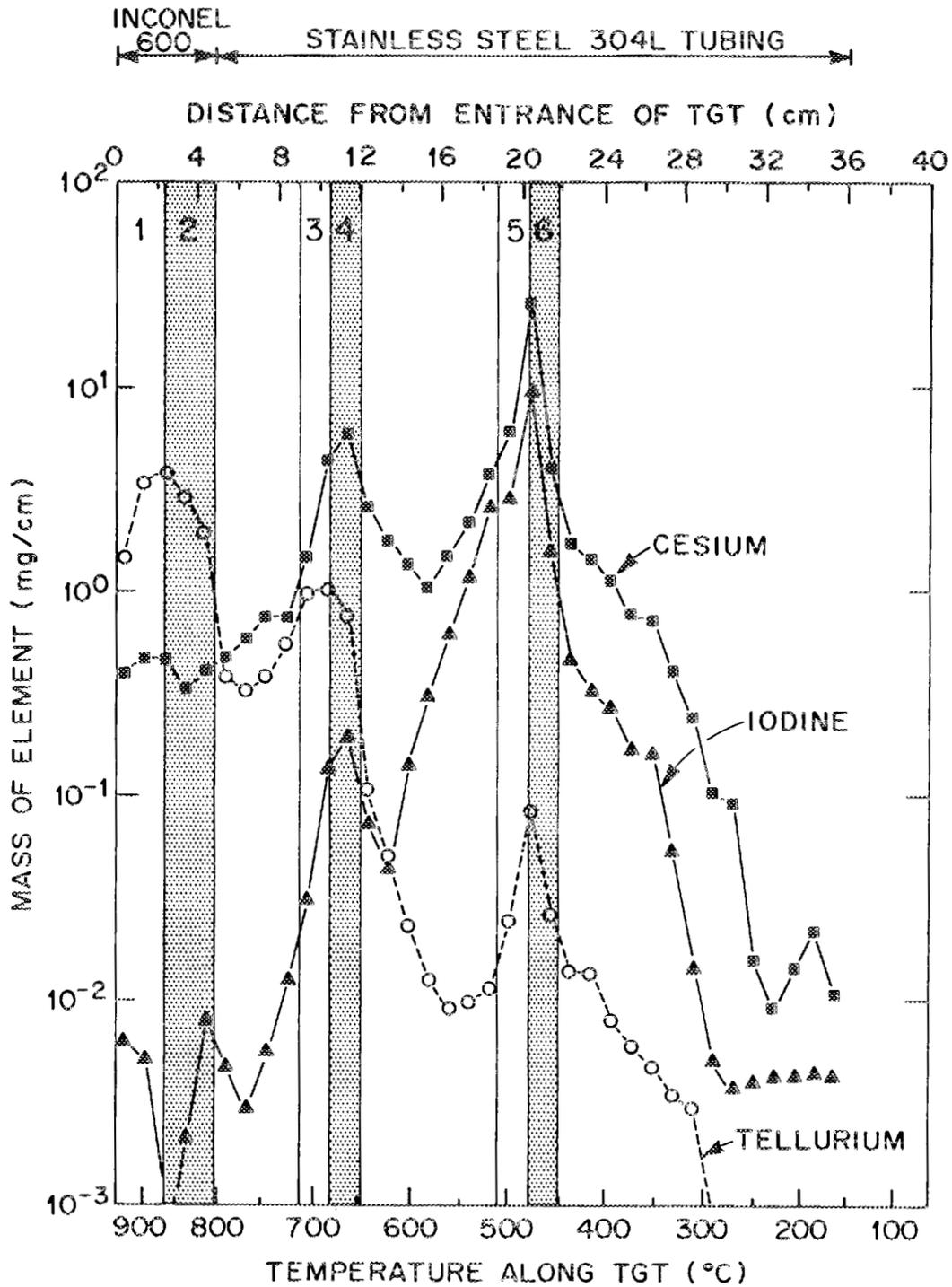


Fig. 13. This figure shows the locations in the TGT liner where sections were cut for analytical (1, 3, and 5) and leaching (2, 4, and 6) purposes.

Figure 13 also shows how the TGT was cut to obtain sections for the leach study and for analyses by SSMS, SEM/EDX, and x-ray diffraction. Sections 2, 4, and 6 were leached.

The leaching results are given in Table 12. Iodine was effectively removed from each of the sections by the first basic leach, with >98.5% being removed. However, the leaching behavior observed for tellurium was different, with approximately half of the tellurium being removed from each of the sections by the first basic leach. Very little of the

Table 12. Effectiveness of basic and acidic leaches<sup>a</sup> in removing cesium, iodine, and tellurium from selected sections of the TGT liner in test C-8

| Tagged <sup>b</sup><br>element                          | Initial<br>mass<br>(mg) | Cumulative percent removed |                             |                            |                     |
|---|-------------------------|----------------------------|-----------------------------|----------------------------|---------------------|
|   |                         | After first<br>basic leach | After second<br>basic leach | After third<br>basic leach | After<br>acid leach |
| <u>Section 2<sup>e</sup> (860 to 800°C)<sup>d</sup></u> |                         |                            |                             |                            |                     |
| <sup>129m</sup> Te                                      | 6.33                    | 52.8                       | 85.5                        | 96.5                       | 100                 |
| <sup>131</sup> I  | 0.011                   | 100                        | 100                         | 100                        | 100                 |
| <sup>134</sup> Cs                                       | 0.172                   | 92.0                       | 92.9                        | 95.4                       | 100                 |
| <sup>137</sup> Cs                                       | 1.26                    | 88.0                       | 88.0                        | 90.8                       | 100                 |
| <u>Section 4<sup>e</sup> (780 to 750°C)<sup>d</sup></u> |                         |                            |                             |                            |                     |
| <sup>129m</sup> Te                                      | 1.11                    | 54.2                       | 55.5                        |                            | 100                 |
| <sup>131</sup> I  | 0.266                   | 98.5                       | 98.7                        |                            | 100                 |
| <sup>134</sup> Cs                                       | 1.42                    | 97.7                       | 98.4                        |                            | 100                 |
| <sup>137</sup> Cs                                       | 6.57                    | 96.7                       | 97.8                        |                            | 100                 |
| <u>Section 6<sup>e</sup> (480 to 455°C)<sup>d</sup></u> |                         |                            |                             |                            |                     |
| <sup>129m</sup> Te                                      | 0.042                   | 47.5                       | 53.4                        |                            | 97.9                |
| <sup>131</sup> I  | 3.56                    | 99.7                       | 100                         |                            | 100                 |
| <sup>134</sup> Cs                                       | 2.49                    | 99.6                       | 99.9                        |                            | 100                 |
| <sup>137</sup> Cs                                       | 6.26                    | 99.5                       | 99.8                        |                            | 100                 |

<sup>a</sup>The basic leach solution was a 2:1 mixture of NH<sub>4</sub>OH (concentrated) and H<sub>2</sub>O<sub>2</sub> (30%). The acid leach was a solution of 4 M HNO<sub>3</sub> and 0.25 M HF.

<sup>b</sup>The initial starting materials were CsI, CsOH, and elemental Te. Cesium iodide was tagged with <sup>134</sup>Cs and <sup>131</sup>I; CsOH was tagged with <sup>137</sup>Cs.

<sup>c</sup>Section was made of Inconel 600 (73.6% Ni, 16% Cr, and 7.6% Fe).

<sup>d</sup>Gives the temperature of the section during the test (see Fig. 13).

<sup>e</sup>Sections were made of stainless steel 304-L.

remaining tellurium on stainless steel sections 4 and 6 was removed by the second basic leach but was completely removed by the subsequent acid leach. On the other hand, the second and third basic leaches removed most of the remaining tellurium from section 2, the Inconel section.

### 7.2.2 Tellurium Behavior

Of the tellurium that entered the TGT during the test, ~70% deposited in the 5.1-cm-long Inconel-600 section at the inlet end, which was at 925 to 800°C. Considering the high nickel (~74%) and chromium (~16%) content of the Inconel and the relatively low amount of cesium found, it is likely that nickel telluride ( $\text{NiTe}_{0.7}$  was identified by x-ray diffraction) and chromium telluride ( $\text{CrTe}$ ) were formed.<sup>13-15</sup> This probably means that a larger fraction of tellurium in this test than in test C-7 was able to transport to the TGT as elemental tellurium ( $\text{Te}_2$ ). Since a very large fraction of the  $\text{CsOH}$  reacted with and was retained by the zirconia ceramic components in the furnace vessel (76% vs ~10% in C-7), there was less potential for its reaction with the tellurium to form  $\text{Cs}_2\text{Te}$  or  $\text{CsTe}$ . There was, however, a tellurium peak that occurred at 700°C, which was the same location where  $\text{CsTe}$  deposited in the platinum TGT liner in test C-7. In test C-7, the cesium to tellurium ratio in the peak was 1:1; here, the ratio was 1.5 to 6 times larger (see Fig. 12). Several things could have happened ---  $\text{CsOH}$  could have reacted with the stainless steel to form cesium ferrite ( $\text{CsFeO}_2$ );  $\text{Cs}_2\text{Te}$  or  $\text{CsTe}$  could have condensed; and tellurium could have reacted with the stainless steel components to form tellurides. Further downstream, a minor tellurium peak also occurred at ~480°C.

In the posttest examination of the Inconel section, the inner surface appeared to be black and sprinkled with silvery microspheres when a light was shone through it.

### 7.2.3 Iodine Behavior

The largest fraction of the iodine in the TGT was found in a peak region that occurred in a temperature range 500 to 450°C during the test (see Fig. 12). As can be seen, a cesium peak also occurred there. Samples of the peak deposit were identified by x-ray diffraction as  $\text{CsI}$  and  $\text{CsOH}\cdot\text{H}_2\text{O}$ ; no other lines were detected. A heavy whitish deposit was observed at that location during the posttest examination of the TGT; both  $\text{CsI}$  and  $\text{CsOH}\cdot\text{H}_2\text{O}$  have crystals that are white.

### 7.2.4 Cesium Behavior

As is shown in Table 11 and was discussed in Sect. 7.1, only ~27% of the cesium passed through the furnace to the collection train. Most of this 27% deposited in the TGT liner in two peak regions --- one at ~675°C and the other at ~480°C. Only  $\text{CsI}$  and  $\text{CsOH}\cdot\text{H}_2\text{O}$  lines were detected on the x-ray diffraction film for samples taken from the 480°C peak region. For samples taken from the 675°C peak region, only  $\text{Fe}_3\text{O}_4$  lines were detected. Most of the cesium that deposited at temperatures above 600°C

was tagged with  $^{137}\text{Cs}$ ; this suggests that  $\text{CsOH}$  reaction with stainless steel components at these higher temperatures might have occurred, possibly as a cesium ferrite.<sup>16</sup>

As was also discussed in Sect. 7.1 and the iodine behavior section (Sect. 6.2.4),  $\text{CsI}$  remained a stable species. Approximately 96% of it transported to the collection train and the largest fraction of it (see Table 11) deposited in the 480°C peak.

Black and brown flakes and particles were observed in the leach solutions for sections 2 and 4 and were removed by filtration. Gamma spectrometric analysis of solids and filtrates revealed that only trace amounts of the Cs, I, and Te were associated with the solids. These solids were probably iron oxides. Posttest examination of the TGT showed that the surface was darkened at temperatures  $>600^\circ\text{C}$ , indicating that surface oxidation had occurred. Oxidation was more extensive at higher temperatures. Ferriferrous oxide was identified by x-ray diffraction as being one of the main constituents in a deposit sample taken from section 3, which was at  $\sim 700^\circ\text{C}$  during the test.

## 8. COMPARISON AND ANALYSIS OF THE RESULTS OBTAINED IN TESTS C-7 AND C-8 WITH THOSE OBTAINED IN PREVIOUS TESTS WITH IRRADIATED FUEL

### 8.1 INTRODUCTION

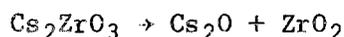
At ORNL 26 experiments have been conducted with irradiated light-water reactor (PWR and BWR) fuel rod segments in the temperature range 500 to 2000°C — 24 with high burnup<sup>1-7</sup> and 2 with low burnup<sup>5</sup> fuels. Three different test atmospheres were examined: dry air, inert (purified helium), and steam-helium. To aid in the interpretation of fission product release behavior, 12 simulant<sup>17</sup> and 18 control experiments<sup>9,18</sup> were also conducted; the behavior of  $\text{CsI}$ ,  $\text{HI}$ ,  $\text{I}_2$ ,  $\text{Cs}_2\text{O}$ ,  $\text{CsOH}$ ,  $\text{Te}$ , and  $\text{TeO}_2$  (individually or in different combinations) was studied. In the following subsections, the evidence is presented and conclusions are drawn about the chemical forms and chemical behavior of the fission products, Cs, I, and Te. The highlights are presented in Sect. 3.2.

### 8.2 REACTION OF CESIUM WITH ZIRCONIA

During a severe LWR accident, cesium most likely would be released into a steam-hydrogen atmosphere as Cs,  $\text{Cs}_2\text{O}$ ,  $\text{CsOH}$ ,  $\text{CsI}$ , and possibly  $\text{Cs}_2\text{Te}$ .<sup>1-7,19-21</sup> One interesting and important reaction that could take place is that of cesium (as Cs,  $\text{Cs}_2\text{O}$ , or  $\text{CsOH}$ ) with zirconia to form cesium metazirconate ( $\text{Cs}_2\text{ZrO}_3$ ).<sup>11</sup> Zirconia, of course, would be formed by the oxidation of the cladding by the steam. Another concern is the question of whether or not  $\text{CsI}$  can react with zirconia with the liberation of elemental iodine. Data obtained in tests C-7 and C-8 and the HI tests have helped considerably in defining the conditions needed for  $\text{Cs}_2\text{ZrO}_3$  formation and decomposition and in describing the behavior of  $\text{CsI}$  in contact with hot zirconia.

As was discussed in Sects. 6.1 and 7.1, there was little reaction (<6%) in test C-7 between CsOH and zirconia components in the furnace vessel, which were heated at temperatures up to a maximum of 800°C. On the other hand, when the zirconia components were heated at temperatures up to 1000°C in test C-8, ~78% of the cesium (mostly CsOH) was retained, with the bulk of it depositing in the temperature range 800 to 900°C. These results indicate that if Cs<sub>2</sub>ZrO<sub>3</sub> were indeed formed, its formation would have been most rapid at temperature >800°C.

Results obtained in the HI tests also helped define this reaction behavior. In each of those tests, two zirconia "collimators" (thick-walled cylinders with an 0.5-cm ID) were positioned within and at the end of the zirconia liner. Figure 14 shows the estimated temperature gradients along the collimators during the tests, while Table 13 gives the mass of <sup>137</sup>Cs found on the individual collimators and the composite percentages of the released <sup>137</sup>Cs found on the collimators in the tests. Of the <sup>137</sup>Cs found on the collimators in test HI-1, the largest fraction, 88%, was found on the upstream collimator (No. 1), which was at a temperature between 1250 and 1130°C. Equally informative, in test HI-4 ~93% of the <sup>137</sup>Cs on collimator II was found on the downstream half, which had a temperature gradient of 1200 to 900°C. When the temperature of the zirconia collimators was >1200°C, there was minimal retention of the cesium. Less than 6% of the <sup>137</sup>Cs on the collimators was found on the upstream collimators in tests HI-2, HI-5, and HI-6, where the temperature exceeded 1200°C (see Table 13 and Fig. 14). This means that at the higher temperatures the reaction product, probably Cs<sub>2</sub>ZrO<sub>3</sub>, was not stable. Thermodynamic calculations<sup>12</sup> indicate that a minimum temperature of 1463 K (1190°C) is needed to cause decomposition as indicated in the following equation. The ΔG for the reaction



at 1473 K (1200°C) is -655 cal/mol. The calculated prediction is in good agreement with the observed behavior.

The percentage of <sup>137</sup>Cs released from the fuel segment that was retained by the zirconia collimators in each test is given in Table 13; these values are significant. The largest retention (42%) occurred in test HI-1 where the fuel specimen was heated for 30 min at 1400°C, and the temperature gradient along the collimators was 1225 to 900°C. The smallest retention (13%) occurred in test HI-2, where the fuel specimen was heated for 20 min at 1700°C.

One factor that possibly could have affected the retention was the rate of carrier gas (steam-He or Ar) flow. In tests HI-3, 4, and 5, the rate was ~0.6 L/min; in tests HI-1 and 2, ~1.5 L/min; and in test HI-6, ~3.6 L/min. Higher rates would be expected to cause lower retention. This is not evident in Table 13.

The percentage retention data suggest that other factors may have been involved. The most obvious one would be the chemical form of the

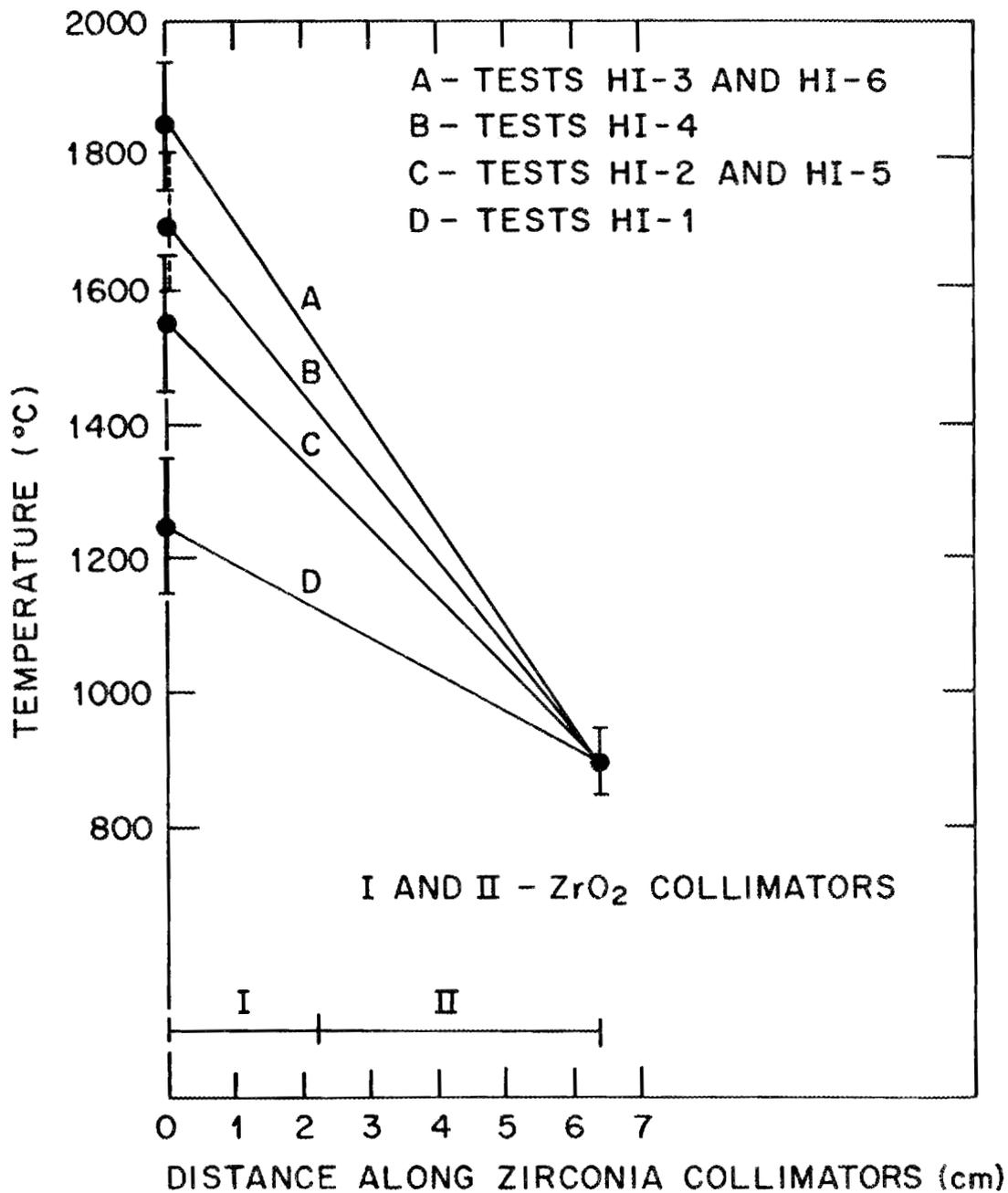


Fig. 14. Estimated temperature gradients along the zirconia "collimators" which were positioned within and at the end of the zirconia furnace tube liners in the HI test series.

Table 13. Masses of  $^{137}\text{Cs}$  found on the zirconia "collimators" used in the HI test series, and the percentage of the released  $^{137}\text{Cs}$  that was found on the "collimators" in each test

| Collimator <sup>a</sup>         | $^{137}\text{Cs}$ (mg) |       |          |                   |      |       |
|---------------------------------|------------------------|-------|----------|-------------------|------|-------|
|                                 | Test                   |       |          |                   |      |       |
|                                 | HI-1                   | HI-2  | HI-3     | HI-4              | HI-5 | HI-6  |
| I                               | 1.63                   | 0.71  | <i>b</i> | <i>b</i>          | 0.12 | 0.72  |
| II                              | 0.21                   | 15.67 | 27.52    | 7.71 <sup>c</sup> | 8.30 | 10.21 |
| Total                           | 1.84                   | 16.39 | 27.52    | 7.71              | 8.42 | 10.93 |
| % of released $^{137}\text{Cs}$ | 42                     | 13    | 20       | 30                | 32   | 22    |

<sup>a</sup> Collimators were thick-walled zirconia cylinders with an 0.5-cm ID which were positioned within and at the end of the zirconia liner. The upstream collimator is designated I.

<sup>b</sup> Information was not obtainable because the collimator (I) could not be removed from the zirconia liner after the test.

<sup>c</sup> A scan of this collimator revealed that ~93% of the cesium was on the downstream half.

cesium and its reactivity. For example, in tests C-7 and C-8 it was observed that CsI did not react with the hot zirconia components in the furnace vessel.

One of the problems encountered in the HI tests<sup>1-4</sup> was that structural material (W, C, Si, and Zr) and impurities (S, Si, and Cl) in the ceramics used in the furnace were transported to the collection train as vapor or particulate. Analyses of deposits by gamma spectrometry, SSMS, and SEM/EDX showed that some of these materials (especially sulfur and chlorine) were always found with the cesium. Reactive species like elemental cesium and CsOH could have reacted with these elements and formed CsCl and Cs<sub>2</sub>S, which would have been less likely to react with the hot zirconia. Variation in the amounts of sulfur and chlorine in the ceramics would have influenced the retention accordingly.

### 8.3 IODINE BEHAVIOR

The iodine behavior observed in HI tests 1-5 was similar to that observed for CsI in tests C-7 and C-8. In all these tests, only trace amounts of iodine were found on the activated charcoal in the filter

package (<0.5% of the total iodine released). Only more volatile (penetrating) forms like HI, CH<sub>3</sub>I, and I<sub>2</sub> would be found there. In each of the HI tests, the iodine was released into a flowing steam-helium-hydrogen atmosphere and was transported through hot zirconia ceramics into a platinum TGT; there was negligible contact with the quartz furnace vessel.

In earlier work,<sup>5-7</sup> the interpretation of iodine behavior was complicated because the released iodine was exposed to quartz which, under certain conditions, could react with CsI to form Cs<sub>2</sub>SiO<sub>3</sub> and I<sub>2</sub>. This effect was noticeable only in tests where the iodine releases were small, <20 µg. (In each of those tests, the fuel specimen was placed on a quartz holder inside a quartz furnace tube.)

Under accident conditions zirconia, not quartz, would be present. The HI tests were conducted under very severe conditions with iodine releases resulting as high as 53%. The behavior of the released iodine was consistent with that of CsI as was observed in the two control tests. It deposited in the TGT like CsI, and little was collected in the filter pack as I<sub>2</sub>.

A summary that lists the percent of evolved iodine found as "presumably CsI," "presumably molecular iodine," and as particulate for each of the earlier tests and for each of the HI tests is given in Table 14. The percentage values were estimated by assuming the iodine that deposited on surfaces at temperatures above 200°C was CsI, the iodine that collected on the charcoal was I<sub>2</sub> (also HI and CH<sub>3</sub>I), and the fraction on the first filter was particulate. With the exclusion of the HI test data, this table was extensively discussed and reviewed in NUREG-0772<sup>21</sup> with conflicting interpretation. Notice that the percentage of molecular iodine was high only in tests in steam where the releases were very low, <71 µg. In fact, in tests where the percentage of molecular iodine was >11%, the mass of iodine released was <17 µg, an amount that could be lost in the percent error in tests where the releases were high (>500 µg iodine). When total iodine release for all the tests is considered, only 0.38% of the iodine was apparently collected as molecular iodine.

Figure 15 illustrates the deposition behavior of iodine in the platinum TGTs used in tests HI-1 through HI-5. There was only one peak in each iodine profile, which indicates only one iodine form. The temperature range where the maximum surface concentration for each of the peaks occurred was between 410 and 575°C. In tests HI-3, 4, and 5, where the maximum surface concentrations were similar (310, 265, and 300 µg/cm<sup>2</sup>, respectively), the temperature range of peaks was quite narrow, 515 ± 20°C. Also, in each of these three tests the steam-helium flow rate was ~0.6 L/min (STP).

Table 15 gives the maximum iodine peak concentrations (best estimate) and the temperatures at which they occurred for several irradiated fuel, implant,<sup>17</sup> and control tests;<sup>9,18</sup> other pertinent data are given as well. The peak deposition behavior for iodine (as CsI) in the control

Table 14. Summary of iodine release species in fission product release tests

| Test No. <sup>a</sup> | Temperature (°C) | Gaseous environment <sup>b</sup> | Test duration (min) | Amount of I released (µg) | % of each form |             |                                  |
|-----------------------|------------------|----------------------------------|---------------------|---------------------------|----------------|-------------|----------------------------------|
|                       |                  |                                  |                     |                           | Presumably CsI | Particulate | Presumably mainly I <sub>2</sub> |
| BWR-4 <sup>c</sup>    | 700-1100         | Helium                           | 300                 | 4800                      | 99.99          | 0.01        | 0.004                            |
| HBU-12 <sup>c</sup>   | 700-1200         | Helium                           | 480                 | 170                       | 91.2           | 8.6         | 0.27                             |
| HBU-1                 | 700              | Steam                            | 300                 | 0.9                       | 18             | 10          | 72                               |
| HBU-2                 | 900              | Steam                            | 120                 | 1.8                       | 14             | 13          | 73                               |
| HBU-4                 | 500              | Steam                            | 1200                | 0.1                       | 40             | 16          | 44                               |
| HBU-11                | 1200             | Steam                            | 27                  | 20                        | 34             | 58          | 8                                |
| HBU-7 <sup>d</sup>    | 900              | Steam                            | 1                   | 11                        | 71             | 25          | 4                                |
| HBU-8 <sup>d</sup>    | 900              | Steam                            | 61                  | 14                        | 4              | 8           | 88                               |
| HBU-9 <sup>d</sup>    | 1000             | Steam                            | 10                  | 17                        | 6              | 6           | 88                               |
| HBU-10 <sup>d</sup>   | 1050             | Steam                            | 11                  | 14                        | 26             | 20          | 53                               |
| BWR-1 <sup>d</sup>    | 960              | Steam                            | 1                   | 490                       | 67             | 33          | 0.4                              |
| BWR-2 <sup>d</sup>    | 850              | Steam                            | 1                   | 1000                      | 79             | 21          | 0.1                              |
| BWR-3                 | 1200             | Steam                            | 25                  | 1200                      | 44             | 56          | 0.7                              |
| HT-1 <sup>e</sup>     | 1300             | Steam                            | 10                  | 71                        | 70             | 20          | 10                               |
| HT-2 <sup>e</sup>     | 1445             | Steam                            | 7                   | 990                       | 90             | 9.9         | 0.1                              |
| HT-3 <sup>e</sup>     | 1610             | Steam                            | 3                   | 5400                      | 86             | 14          | 0.2                              |
| HT-4 <sup>e</sup>     | 1440             | Steam                            | 0.4                 | 750                       | 78             | 22          | 0.3                              |
| HI-1                  | 1400             | Steam                            | 30                  | 514                       | 41.7           | 58.8        | 0.5                              |
| HI-2                  | 1700             | Steam                            | 20                  | 13554                     | 31.85          | 67.8        | 0.4                              |
| HI-3                  | 2000             | Steam                            | 20                  | 7950                      | 36.7           | 62.9        | 0.4                              |
| HI-4                  | 1850             | Steam                            | 20                  | 4929                      | 38.3           | 61.7        | 0.006                            |
| HI-5                  | 1700             | Steam                            | 20                  | 5803                      | 33.5           | 66.4        | 0.07                             |

<sup>a</sup>See refs. 1-8 for details.

<sup>b</sup>The steam environments were actually steam-(helium or argon)-hydrogen; hydrogen resulted from the Zircaloy-steam reaction.

<sup>c</sup>Gap purge tests.

<sup>d</sup>Burst release tests.

<sup>e</sup>Cladding was expanded before the test to provide an enlarged uniform fuel-cladding gap.

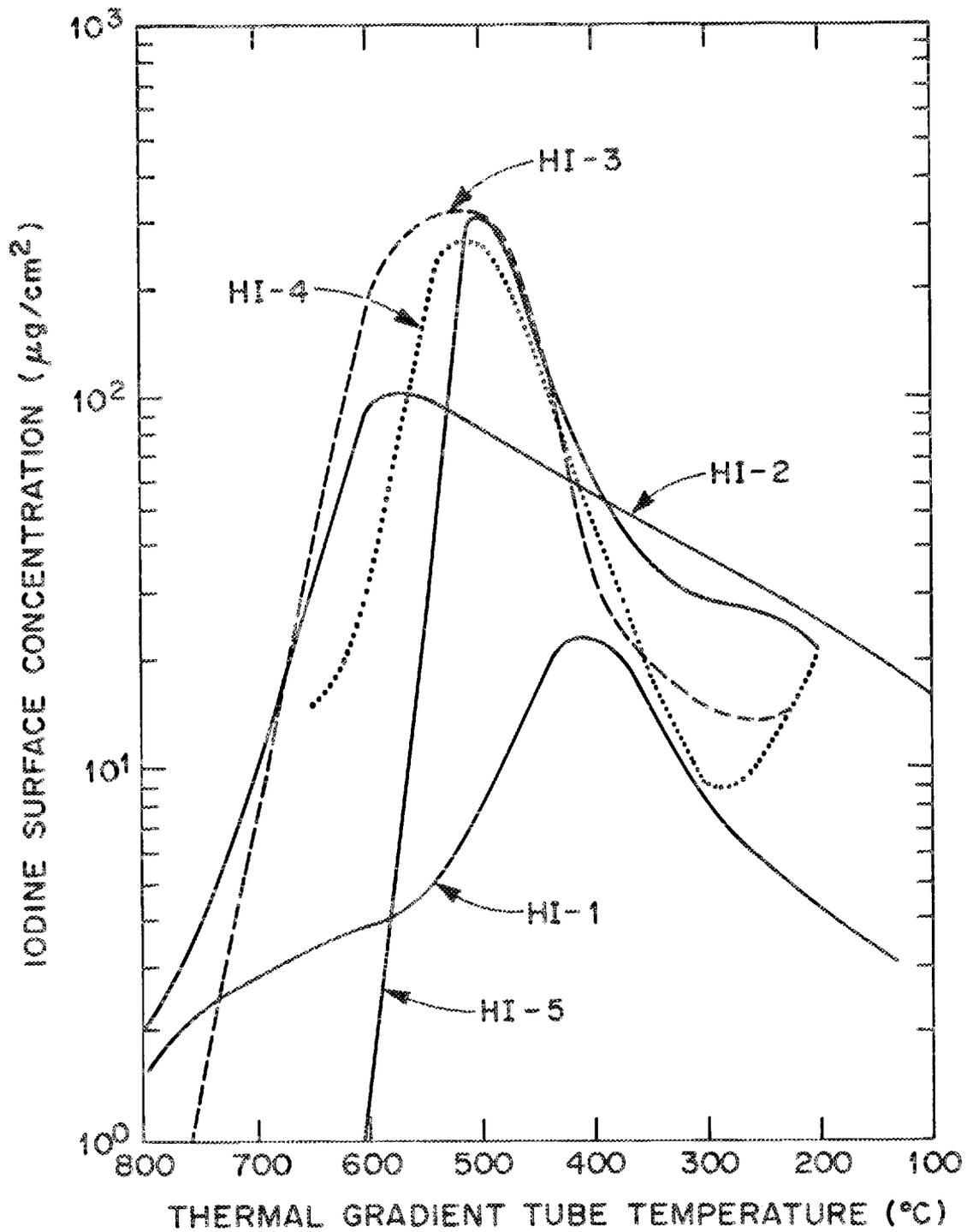


Fig. 15. Deposition behavior of iodine in the TGT platinum liners in tests HI-1 through HI-5.

Table 15. Temperatures at which maximum iodine TGT peak concentrations occurred in tests (control and irradiated fuel) where significant amounts of iodine were deposited

| Test No.           | Test temperature (°C) | Test time <sup>a</sup> (min) | Iodine in TGT (µg) | Flow rate at STP (L/min) |        | Maximum iodine peak concentration (µg/cm <sup>2</sup> ) | Temperature at peak (°C) |
|--------------------|-----------------------|------------------------------|--------------------|--------------------------|--------|---|--------------------------|
|                    |                       |                              |                    | Steam                    | Helium |   |                          |
| HI-1               | 1400                  | 30                           | 210                | 1.0                      | 0.5    | 22  | 410                      |
| HI-2               | 1700                  | 20                           | 2702               | 1.0                      | 0.45   | 103   | 575                      |
| HI-3               | 2000                  | 20                           | 2780               | 0.3                      | 0.3    | 265   | 525                      |
| HI-4               | 1850                  | 20                           | 1712               | 0.32                     | 0.3    | 310   | 510                      |
| HI-5               | 1700                  | 20                           | 1909               | 0.41                     | 0.3    | 300   | 500                      |
| HT-1 <sup>b</sup>  | 1300                  | 10                           | 50                 | 0.72                     | 0.87   | 8   | 360                      |
| HT-2 <sup>b</sup>  | 1445                  | 7                            | 858                | 0.94                     | 0.87   | 110   | 475                      |
| HT-3 <sup>b</sup>  | 1610                  | 3                            | 1716               | 1.02                     | 0.87   | 270   | 470                      |
| BWR-1 <sup>c</sup> | 960                   | 1                            | 104                | 1.8                      |        | 14  | 390                      |
| CT-7               | <i>d</i>              | <i>d</i>                     | 14200              | 0.16                     | 0.15   | 2200  | 477                      |
| CT-8               | 715                   | 26.3                         | 20330              | 0.14                     | 0.15   | 6500  | 383                      |
| CT-10 <sup>e</sup> | 700                   | 60                           | 199                | 0.28                     | 0.05   | 100   | 567                      |
| IT-11 <sup>f</sup> | 1300                  | 11                           | 19                 | 0.31                     | 0.11   | 4   | 470                      |

<sup>a</sup> Only includes time at the test temperature indicated.

<sup>b</sup> R. A. Lorenz, J. L. Collins, A. P. Malinauskas, M. F. Osborne, and R. L. Towns, Fission Product Release from Highly Irradiated LWR Fuel Heated to 1300-1600°C in Steam, NUREG/CR-1386 (ORNL/NUREG/TM-346), November 1980.

<sup>c</sup> R. A. Lorenz, J. L. Collins, M. F. Osborne, R. L. Towns, and A. P. Malinauskas, Fission Product Release from BWR Fuel Under LOCA Conditions, NUREG/CR-1773 (ORNL/NUREG/TM-388), July 1981.

<sup>d</sup> See Fig. 2.

<sup>e</sup> R. A. Lorenz, M. F. Osborne, J. L. Collins, S. R. Manning, and A. P. Malinauskas, Behavior of Iodine, Methyl Iodide, Cesium Oxide, and Cesium Iodide in Steam and Argon, ORNL/NUREG/TM-25, July 1976.

<sup>f</sup> R. A. Lorenz, J. L. Collins, and S. R. Manning, Fission Product Release from Simulated LWR Fuel, NUREG/CR-0274 (ORNL/NUREG/TM-154), October 1978.

tests and in the implant test was similar to that observed for iodine in the irradiated fuel tests. The peak temperature range for all the tests was 360 to 575°C.

Figures 16--19 illustrate the TGT deposition profiles for iodine and cesium in Control Test 10, Implant Test 11, HT-2, and HI-5, respectively. In Control Test 10, CsI was the only species vaporized; peak deposit material was identified by x-ray diffraction as CsI. In test HT-2, almost all the cesium except that associated with iodine was retained by the quartz furnace tube liner that housed the fuel specimen. Considering the fact that almost equal quantities of cesium and iodine were found in the TGT, that both elements deposited in the same peak region, and that the peak location was similar to that which was obtained in the control tests, it is apparent that the cesium and iodine were deposited as CsI. (Identical behavior was also observed in test HT-3.<sup>6</sup>) Figure 19 shows the cesium and iodine TGT profiles for one of the more current tests, HI-5. Again, the behavior of iodine is that of CsI.

Analysis by SSMS of TGT deposits obtained in the HI tests<sup>1-5</sup> showed that the only fission products, other than iodine, that deposited in the temperature range where iodine deposition occurred were Cs, Rb, Br, and Cd. Compared with Cs and I, the amounts of Rb and Br found were considerably less. As Rb and Br are chemical analogs of Cs and I, their presence there was expected. The peak concentrations of cadmium were not found where the peak concentrations of iodine were found but further downstream. This would suggest that the cadmium was not significantly associated with the iodine.

Since the BWR and PWR fuel rod segments that were used in the HI tests were from the same fuel rods as the segments used in previous tests, it is reasonable to assume that these fission products were probably the only ones that deposited in the same temperature region of the TGT in those tests. If so, these results give more credulance to the results obtained in previous tests that indicated that iodine was deposited in the TGT as CsI in steam. Since the largest fractions of the released iodine deposited in the TGT in tests where >17 µg iodine was released, it also means that iodine in those tests was released as CsI.

All the preceding discussions about iodine results and observations in this subsection have led to one point — iodine was consistently released from the tested irradiated fuel specimen in a steam-helium atmosphere as CsI. The experimental evidence obtained in the recently conducted HI tests have made this conclusion more convincing.

#### 8.4 CESIUM BEHAVIOR

The behavior of cesium has been well documented in the fission product release programs at ORNL. Knudsen cell-mass spectrometry studies<sup>22</sup> of mixtures of CsOH-UO<sub>2</sub> and Cs<sub>2</sub>CO<sub>3</sub>-UO<sub>2</sub> showed that when these mixtures were heated in vacuum the cesium species were stabilized by the urania, probably as cesium uranate (Cs<sub>2</sub>UO<sub>4</sub>).<sup>20</sup> The appearance and growth of the

ORNL DWG 84-560

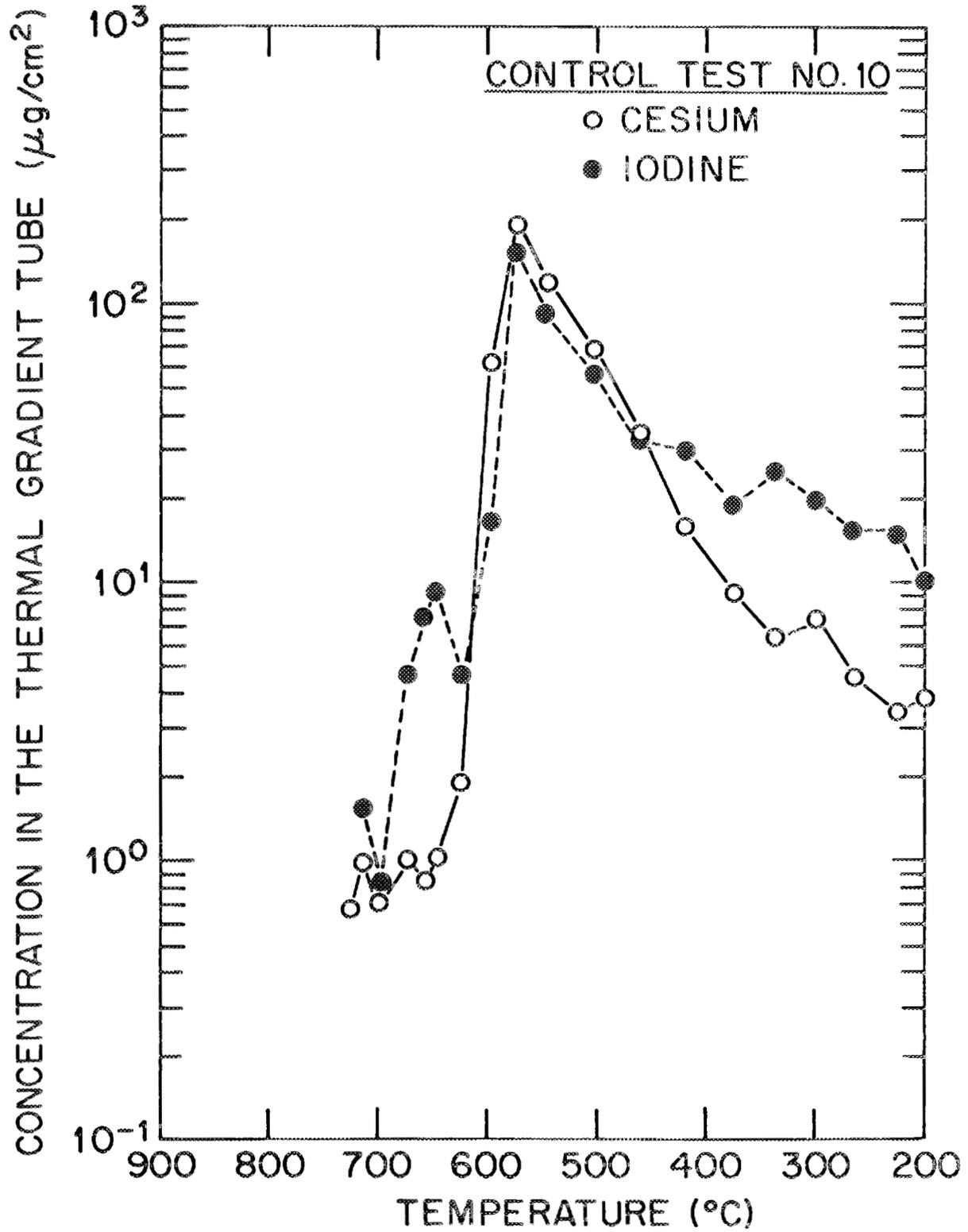


Fig. 16. Deposition profiles for iodine and cesium in the TGT in Control Test 10.

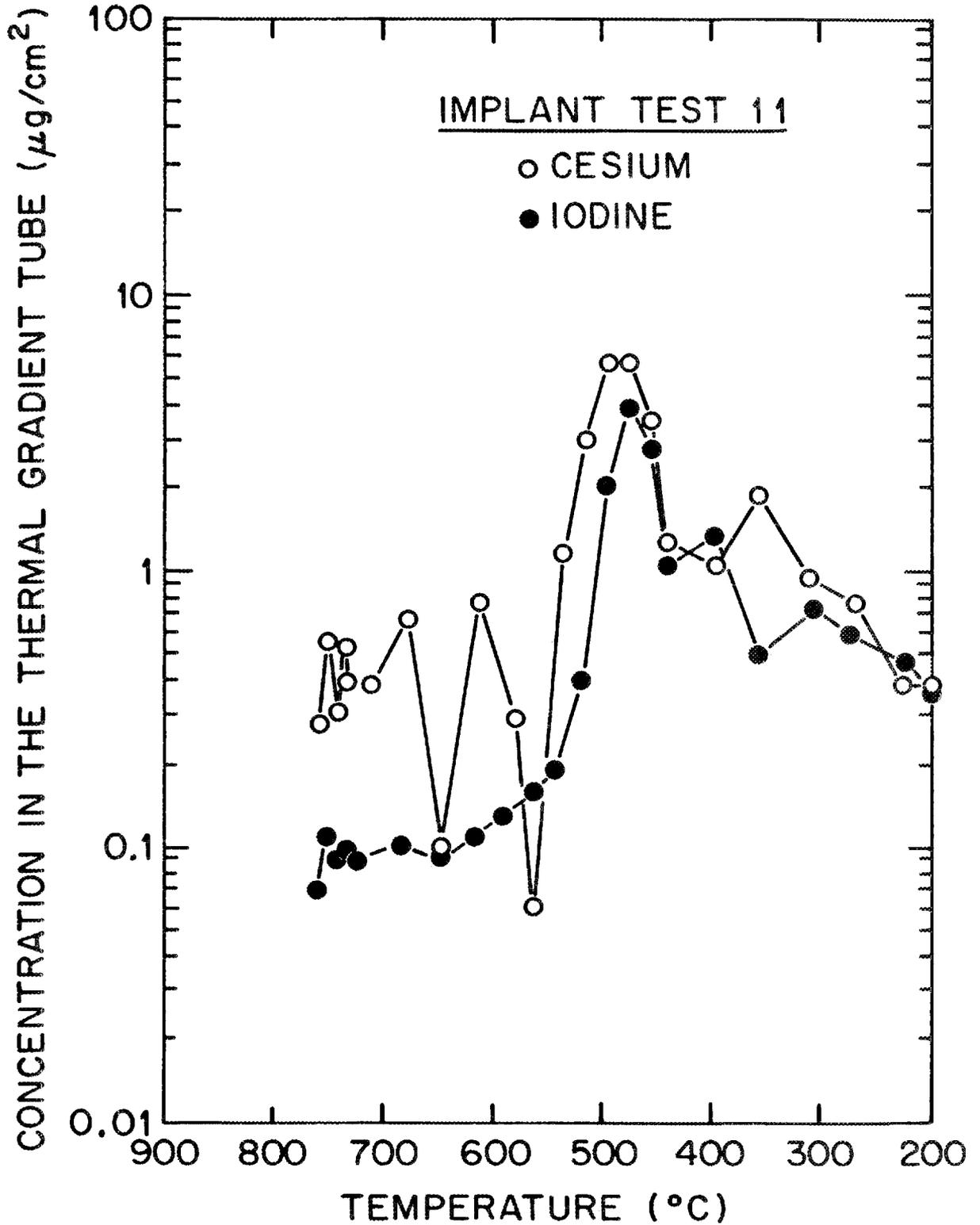


Fig. 17. Deposition profiles for iodine and cesium in the TGT in Implant Test 11.

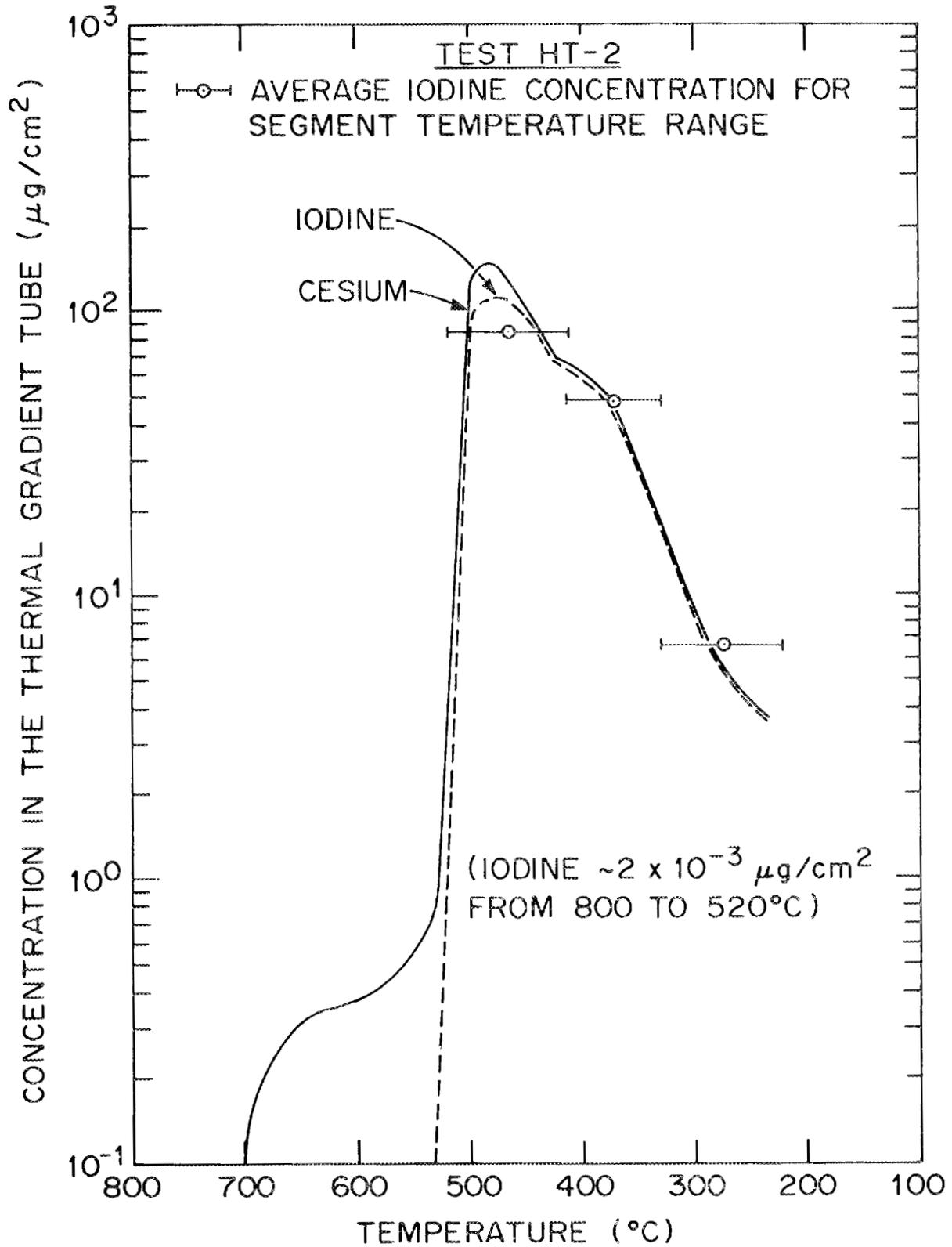


Fig. 18. Deposition profiles for iodine and cesium in the TGT in test HT-2.

ORNL DWG 84-418

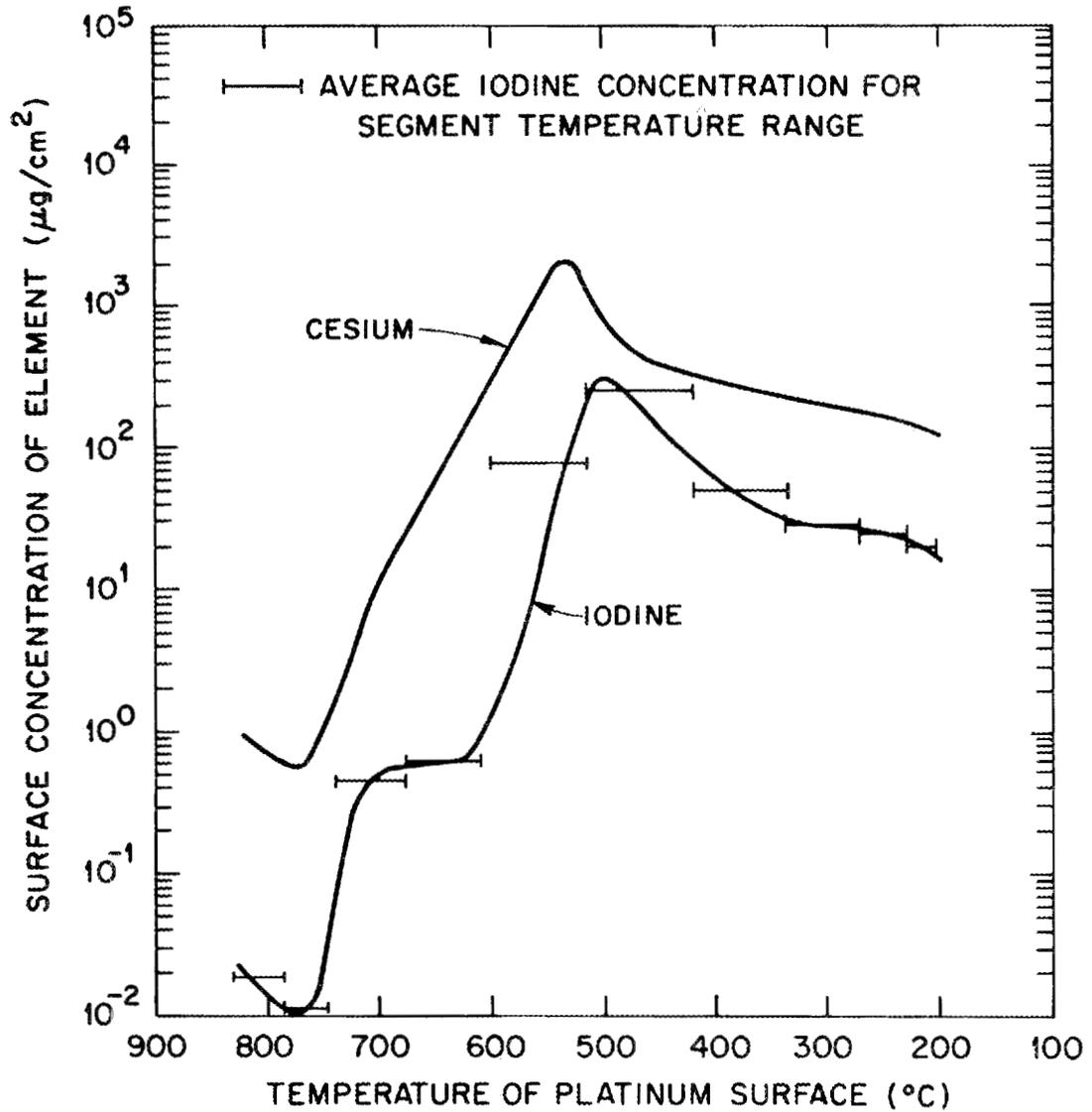


Fig. 19. Deposition profiles for iodine and cesium in the TGT in test HI-5.

cesium peaks in the mass spectra occurred when the temperature of each of the mixtures reached  $\sim 950^{\circ}\text{C}$ . In the gap purge tests,<sup>5,7</sup> H. B. Robinson and Peach Bottom fuel sections were heated in incremental, temperature steps from 500 to  $\sim 1200^{\circ}\text{C}$ . Purified helium pressure was applied to the inlet ends of the sections to purge the volatile fission products out at the outlet ends and directly into platinum TGT liners. The results indicated that cesium deposited as an oxide of cesium (probably  $\text{Cs}_2\text{O}$ ) and as  $\text{CsI}$  rather than as the more volatile elemental species; almost no iodine was found on the charcoal (Table 14).

In tests conducted with irradiated fuel (and simulant fuel), where the fuel specimens were heated in a quartz liner at temperatures not exceeding  $1000^{\circ}\text{C}$  (as was the case where the fuel specimens were induction heated), the most significant fractions of the released cesium (not  $\text{CsI}$ ) were retained by the quartz, probably as cesium silicate ( $\text{Cs}_2\text{SiO}_3$ ). The deposit on the quartz in each of the tests was found only a short distance downstream from the fuel rod segment defect opening (ruptured or drilled). Figure 20 shows the concentration profile for  $^{134}\text{Cs}$  along the quartz liner in test HF-1. The fuel specimen in that test was heated at  $1300^{\circ}\text{C}$  for 10 min in a flowing steam-helium atmosphere. About 92% of the released cesium was retained on the quartz liner as shown. Similar results occurred in ten other tests; the percent values are tabulated in Table 16. A hole (0.159-cm ID) was drilled in the center of the cladding of each fuel specimen used in the HF tests; all the other fuel specimens in the other test series were pressurized and ruptured at  $\sim 700$  or  $\sim 900^{\circ}\text{C}$ . Afterwards, the fuel specimens were heated to the test temperatures. Only in the rupture tests were the fractions of cesium in the collection train larger, 11.7 to 14.5%. This was probably due to the surge of vapor that occurred with rupture. The proximity of the cesium deposits to the defect openings suggests a very rapid cesium-quartz reaction. The intensity of the attack was evident in some of the tests; the quartz surface was severely etched. This behavior is typical for the  $\text{CsOH}$ -quartz reaction,<sup>9</sup> rather than the  $\text{Cs}_2\text{O}$ -quartz reaction.<sup>5</sup> As the  $\text{Cs}_2\text{O}$  was being exposed to steam while being released from the fuel specimens, it was quickly converted to  $\text{CsOH}$ .

The  $\text{Cs}_2\text{O}$ -quartz reaction behavior was observed best in the dry air atmosphere test HBU-6.<sup>5</sup> In that test, the released cesium demonstrated less affinity for the quartz; it initially appeared to passivate the surface of the quartz liner, thus allowing the remaining cesium that was being released to transport to the collection train. In this test, which was conducted at  $700^{\circ}\text{C}$  for 5 h,  $\sim 70\%$  of the released cesium transported to the collection train. An hour had elapsed during the test before any cesium was monitored entering the collection system.

In steam tests, where the quartz liners were heated at temperatures  $>1000^{\circ}\text{C}$ , most of the released cesium transported to the collection train; there was little affinity for the cesium to react with the quartz. The fractions that were retained by the quartz liners were found at the cooler outlet end. As an example,  $\sim 71\%$  of the released cesium in test HBU-11 was carried to the collection train. In that test, the fuel

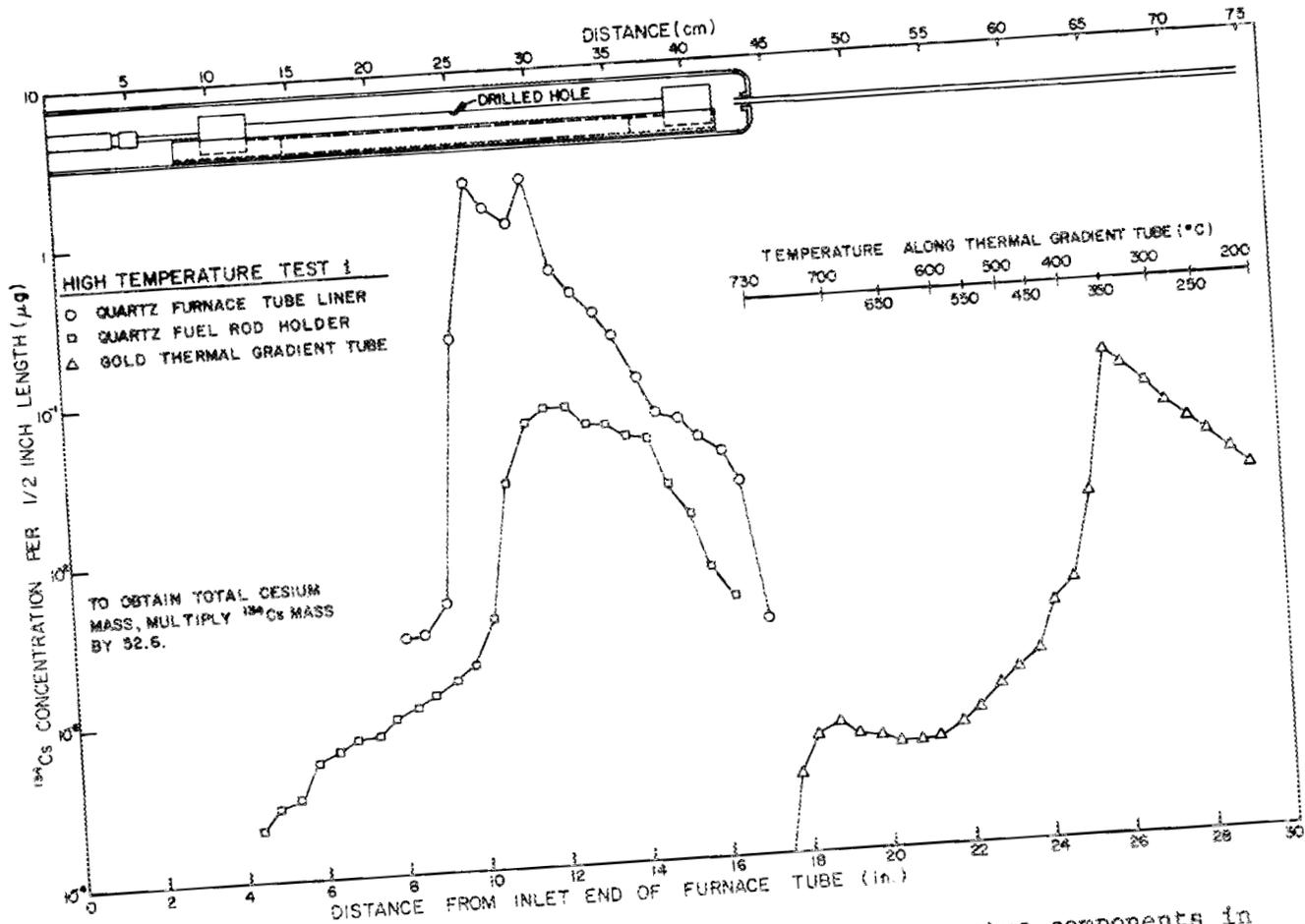


Fig. 20. Concentration profile of Cs in apparatus components in test HT-1.

Table 16. Summary showing the percentages of the released cesium that were retained by the quartz liners and found in the collection trains

| Test No.            | Mass of cesium released ( $\mu\text{g}$ ) | Amount of cesium found reacted with the quartz liner (%) | Amount found in collection train (%) |
|---------------------|---|--|--------------------------------------|
| HT-1 <sup>a</sup>   | 523                                       | 92.0   | 8.0                                  |
| HT-2 <sup>a</sup>   | 22,023                                    | 94.6   | 5.4                                  |
| HT-3 <sup>a</sup>   | 51,311                                    | 96.8   | 3.2                                  |
| HT-4 <sup>a</sup>   | 14,191                                    | 98.4   | 1.6                                  |
| BWR-1 <sup>b</sup>  | 7,146                                     | 95.3   | 4.7                                  |
| BWR-2 <sup>b</sup>  | 6,922                                     | 85.5   | 14.5                                 |
| IT-4 <sup>c</sup>   | 2,320                                     | 95.0   | 5.0                                  |
| IT-11 <sup>c</sup>  | 1,240                                     | 97.2   | 2.8                                  |
| HBU-7 <sup>b</sup>  | 279                                       | 88.3   | 11.7                                 |
| HBU-9 <sup>b</sup>  | 112                                       | 96.5   | 3.5                                  |
| HBU-10 <sup>b</sup> | 131                                       | 86.9   | 13.0                                 |

<sup>a</sup> A small hole was drilled in fuel segment to cause the defect. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, M. F. Osborne, and R. L. Towns, Fission Product Release from Highly Irradiated LWR Fuel Heated to 1300-1600°C in Steam, NUREG/CR-1386 (ORNL/NUREG/TM-346), November 1980.

<sup>b</sup> Fuel segments were pressurized ruptured to cause the defect. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, O. L. Kirkland, and R. L. Towns, Fission Product Release from Highly Irradiated LWR Fuel, NUREG/CR-0722 (ORNL/NUREG/TM-287/R2), February 1980.

R. A. Lorenz, J. L. Collins, M. F. Osborne, R. L. Towns, and A. P. Malinauskas, Fission Product Release from BWR Fuel Under LOCA Conditions, NUREG/CR-1773 (ORNL/NUREG/TM-388), July 1981.

<sup>c</sup> Simulant fuel tests. R. A. Lorenz, J. L. Collins, and S. R. Manning, Fission Product Release from Simulated LWR Fuel, NUREG/CR-0274 (ORNL/NUREG/TM-154), October 1978.

specimen was heated at 1200°C for ~27 min in a flowing steam-helium atmosphere. The fuel specimen was heated by a resistance tube furnace which also heated the quartz liner to the same temperature.

The CsOH-quartz reaction results in the formation of cesium silicates.<sup>10</sup> In control tests,<sup>21</sup> the reaction was observed to occur in the temperature range 125 to 950°C when Cs<sub>2</sub>O was exposed to a flowing steam-helium atmosphere. Cesium silicate was readily formed at temperatures up to 800°C; at temperatures >800°C but <950°C, it formed but not as readily; and at 1200°C it did not form. Cesium silicates are known to decompose at temperatures >1000°C.<sup>10</sup>

The cesium-quartz reaction in steam is interesting, but again, quartz is not a material found in light water reactors. The essence of the above background information is to point out that CsOH was the major species of cesium that was formed after release in a steam-helium atmosphere from the irradiated fuel specimens as Cs<sub>2</sub>O.

The behavior of CsOH in tests C-7 and C-8 was discussed in Sects. 6.2.5 and 7.2.4. Samples of TGT peak deposits from the same region as where the iodine deposited were determined by x-ray diffraction to contain CsOH as well as CsI. The reactive nature of CsOH was also demonstrated; it reacted with tellurium in the gas phase in test C-7, forming CsTe; it reacted with the zirconia liner in test C-8, forming Cs<sub>2</sub>ZrO<sub>3</sub>; it reacted with SiO<sub>2</sub> (quartz furnace) in test C-7, forming cesium silicates; and it reacted with the stainless steel TGT in test C-8, probably forming CsFeO<sub>2</sub>.

The reactive nature of CsOH was also clearly demonstrated in the HI series of tests. The TGT profiles for cesium in several of these tests, like that shown in Fig. 21 for test HI-2, were very complex. The SSMS data showed that structural materials, like W, C, Si, and Zr, and ceramic impurities, like S and Cl, were deposited in the TGT as well as fission products. Cesium hydroxide can react with most of these elements (especially if they were in the oxide form) to form compounds with varying degrees of volatility and stability. For example, these compounds could have possibly formed: Cs<sub>2</sub>WO<sub>4</sub>, Cs<sub>2</sub>MoO<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>SiO<sub>3</sub>, Cs<sub>2</sub>ZrO<sub>3</sub>, Cs<sub>2</sub>SO<sub>4</sub>, Cs<sub>2</sub>S, and CsCl.

## 8.5 TELLURIUM BEHAVIOR

For every 100 atoms of cesium in a high burnup LWR fuel rod, there are ~10 atoms of iodine and ~19 atoms of tellurium. Like Cs and I, Te also has a high potential for being a radiological hazard in a severe accident. Because of current interest in tellurium, an increased effort is being made to understand its behavior.

It is generally thought that tellurium is present in the pellet-cladding gap as Te and Cs<sub>2</sub>Te when not reacted with the cladding as a telluride.<sup>21,23</sup> The reaction with the cladding can take place at temperatures as low as 400°C.<sup>24</sup> The calculated Te<sub>2</sub> vapor pressure over <ZrTe> was determined to be  $7.3 \times 10^{-5}$  MPa (0.55 torr) at 1700°C.<sup>13</sup>

ORNL DWG 82-1486R

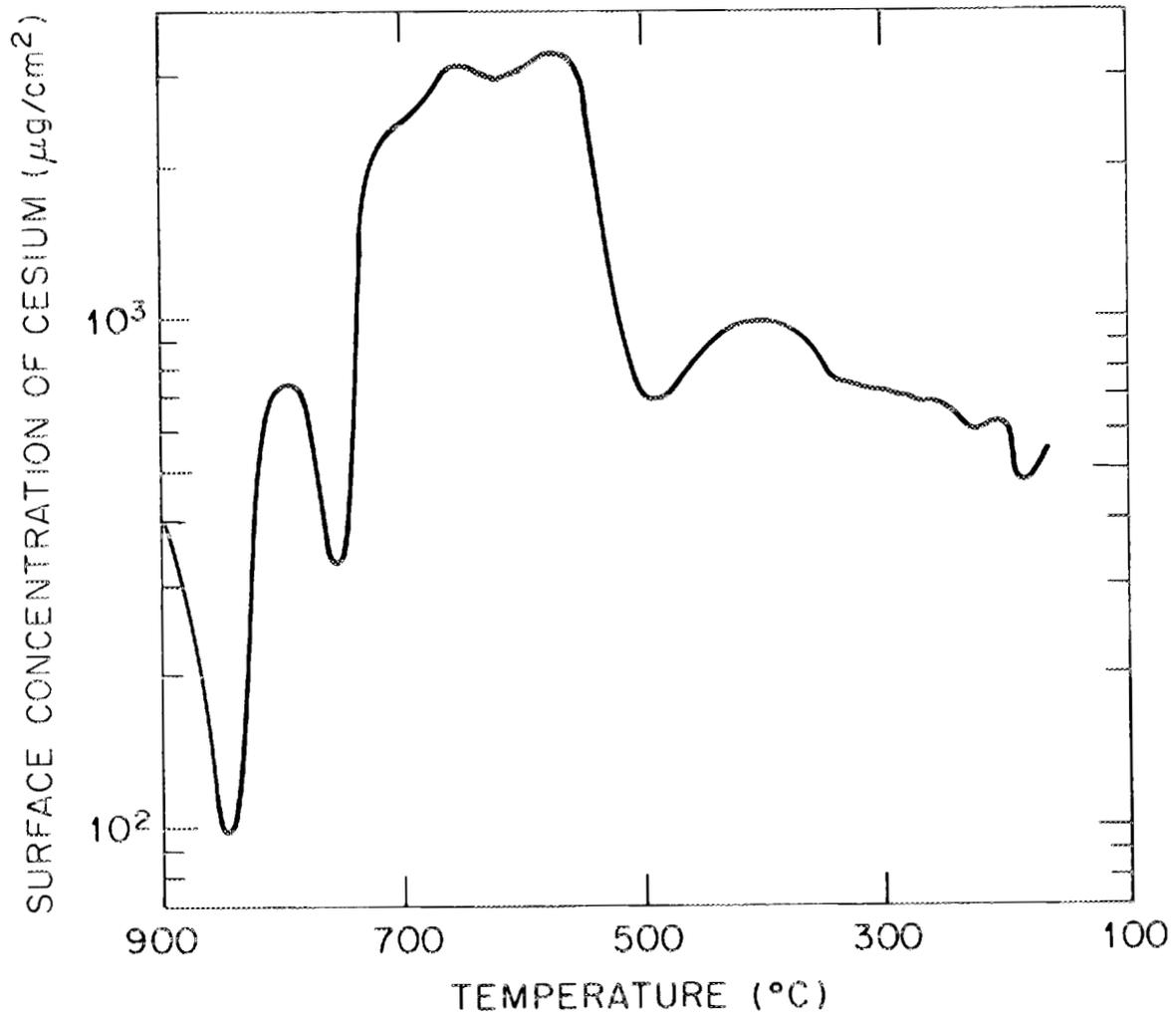


Fig. 21. Deposition profile for cesium in the TGT in test HI-2.

Under accident conditions the cladding becomes oxidized by the steam atmosphere with the rate being temperature dependent. Before the cladding is totally oxidized, the tellurium that finds its way to the gap can react with the available unoxidized zirconium to form relatively stable tellurides. However, once most of the zirconium is converted to  $ZrO_2$ , the tellurium is liberated. Thermodynamic data for  $ZrTe_2$  and  $ZrO_2$  indicate that, at  $1227^\circ C$ , oxygen would replace tellurium in  $ZrTe_2$  at oxygen potentials more positive than  $-171 \text{ kcal/mol } O_2$ .<sup>13</sup>

In test C-7, 88% of the metallic tellurium that was vaporized was transported to the collection train. Of that, 98% deposited in the platinum TGT. Only 14% of the tellurium in the TGT reacted with or dissolved in the platinum. The most significant amount was found in a surface deposit that peaked at  $700^\circ C$ . The ratio of tellurium to cesium in the deposit was 1 to 1, and the deposit was very soluble in basic leach. (Alkali tellurides are soluble in aqueous solution; elemental tellurium and platinum tellurides are not.)

The above data for tellurium suggest that prior to entering the platinum TGT and while passing through the hot zone ( $\sim 800^\circ C$ ), there was considerable gas phase reaction of tellurium with  $CsOH$  to form cesium telluride ( $CsTe$ ). Had this not happened, most of the tellurium would have reacted with the hot platinum liner. Furthermore, the shape of the Cs-Te peaks at  $700^\circ C$  (see Fig. 3) also suggests condensation on the TGT surface.

Additional evidence that lends credibility to the idea of  $CsTe$  being a possible gas phase species was obtained in mass spectrometer experiments that were conducted at Argonne National Laboratory (ANL).<sup>25</sup> Cesium telluride ( $CsTe$ ) was identified in the mass spectra when a small simulated piece of fuel rod was heated to  $1000^\circ C$ . The Zircaloy clad specimen contained  $UO_2$  pellets with simulated fission products.

In test C-8,  $\sim 52\%$  of the metallic tellurium that was vaporized was carried to the collection train. Of that,  $99.4\%$  deposited in the TGT. The Inconel-600 section at the inlet end of the liner, which had a temperature gradient between  $925$  and  $800^\circ C$ , gettered  $\sim 70\%$  of the tellurium. Considering the high nickel ( $\sim 74\%$ ) and chromium ( $\sim 16\%$ ) contents of the Inconel, and the relatively low amount of cesium and iodine found there, it is likely that the tellurium reacted to form the stable nickel and chromium tellurides ( $NiTe$  and  $CrTe$ ).<sup>14,15</sup> There was also a tellurium peak that occurred at  $700^\circ C$  in the stainless steel portion of the TGT, which was the same location where the main Cs-Te peak occurred in test C-7.

In the tests with high-burnup fuel, the detection of tellurium was complicated because there were no measurable gamma photons for tellurium. Samples of surface deposits for SSMS analysis were taken at key locations along the TGT in each of the HI tests and also from deposit material on the glass wool prefilter. Although this analytical method was semiquantitative and only considered tellurium in the surface deposits (tellurium

dissolved in or reacted with the platinum could not be studied by this sampling technique), it did offer some insight into the behavior of tellurium.

The only test in the HI series of tests where considerable tellurium was measured (SSMS) in the collection system was HI-2. In that test, unlike the other HI tests, the Zircaloy cladding was totally oxidized. This implies that steam oxidation of the cladding played an important role in tellurium release. This may be true, but to verify it, the platinum TGT liners will have to be analyzed for tellurium that might have dissolved in or reacted with the platinum. To do this, a method has been developed for isolating tellurium and mixed fission products in a suitable form for neutron activation analysis.<sup>8</sup> The tellurium release behavior in the HI series will be better understood when this work has been performed.

The analyses by SSMS have been used strictly for the determination of surface deposit materials. Based upon these data for test HI-2, it was estimated that 50 to 100% of the tellurium in the fuel specimen was released, an amount equivalent to the amounts of cesium (51%) and iodine (54%) released. Some of the SSMS data were based upon samples taken of the basic leach solutions. The fact that the tellurium was both smearable and leachable suggests that it probably deposited as telluride. Interestingly, significant quantities of tin were also found associated with the deposited tellurium throughout the collection system. This indicates that the tellurium may have transported there as SnTe; tin is a cladding component.

#### 9. REFERENCES

1. M. F. Osborne, R. A. Lorenz, J. R. Travis, and C. S. Webster, Data Summary Report for Fission Product Release Test HI-1, NUREG/CR-2928 (ORNL/TM-8500), December 1982.
2. M. F. Osborne, R. A. Lorenz, J. R. Travis, C. S. Webster, and K. S. Norwood, Data Summary Report for Fission Product Release Test HI-2, NUREG/CR-3171 (ORNL/TM-8667), February 1984.
3. M. F. Osborne, R. A. Lorenz, K. S. Norwood, J. R. Travis, and C. S. Webster, Data Summary Report for Fission Product Release Test HI-3, NUREG/CR-3335 (ORNL/TM-8793), April 1984.
4. M. F. Osborne, J. L. Collins, R. A. Lorenz, K. S. Norwood, J. R. Travis, and C. S. Webster, Data Summary Report for Fission Product Release Test HI-4, NUREG/CR-3600 (ORNL/TM-9011), June 1984.
5. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, O. L. Kirkland, and R. L. Towns, Fission Product Release from Highly Irradiated LWR Fuel, NUREG/CR-0722 (ORNL/NUREG/TM-287/R2), February 1980.

6. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, M. F. Osborne, and R. L. Towns, Fission Product Release from Highly Irradiated LWR Fuel Heated to 1300-1600°C in Steam, NUREG/CR-1386 (ORNL/NUREG/TM-346), November 1980.
7. R. A. Lorenz, J. L. Collins, M. F. Osborne, R. L. Towns, and A. P. Malinauskas, Fission Product Release from BWR Fuel Under LOCA Conditions, NUREG/CR-1773 (ORNL/NUREG/TM-388), July 1981.
8. K. S. Norwood, An Assessment of Thermal Gradient Tube Results from the HI Series of Fission Product Release Tests, NUREG/CR-4105 (ORNL/TM-9506), in publication.
9. R. A. Lorenz, M. F. Osborne, J. L. Collins, S. R. Manning, and A. P. Malinauskas, Behavior of Iodine, Methyl Iodide, Cesium Oxide, and Cesium Iodide in Steam and Argon, ORNL/NUREG/TM-25, July 1976.
10. Z. D. Aleckseeva, "The Cs<sub>2</sub>O-SiO<sub>2</sub> System," Russ. J. Inorg. Chem. 2(5), 626-29 (1966).
11. G. A. Bukhalova, I. V. Mardirosova, I. G. Rabkina, and M. A. Savenkova, "Preparation of Cesium Metazirconate," Izvestiya Akademii Nauk SSSR, Neorancheskie Materialy 15(11), 1990-92 (November 1979).
12. S. A. Kutolin and A. E. Sergeeva, "Thermodynamic Study of Formation of Compounds of the Types M<sub>2</sub>TiO<sub>3</sub> and M<sub>2</sub>ZrO<sub>2</sub> (Titanates and Zirconates)," Russ. J. Phys. Chem. 39(11), 1475-76 (November 1965).
13. R. A. Lorenz, E. C. Beahm, and R. P. Wichner, "Review of Tellurium Release Rates from LWR Fuel Elements Under Accident Conditions," Proceedings of the International Meeting on Light Water Reactor Severe Accident Evaluation, Cambridge, Mass., Aug. 28-Sept. 1, 1983.
14. R. C. Lobb and I. H. Robins, "A Study of the 20% Cr/25% Ni/Nb Stabilized Stainless Steel-Tellurium Reaction," J. Nucl. Mater. 62, 50-62 (1976).
15. O. Götzmann, "A Thermodynamic Model for the Attack Behavior in Stainless Steel Clad Oxide Fuel Pins," J. Nucl. Mater. 84, 39-54, 1979.
16. T. B. Lindemer, T. M. Besmann, and C. E. Johnson, "Thermodynamic Review and Calculations - Alkali-Metal Oxide Systems with Nuclear Fuels, Fission Products, and Structural Materials," J. Nucl. Mater. 100, 178-226 (1981).
17. R. A. Lorenz, J. L. Collins, and S. R. Manning, Fission Product Release from Simulated LWR Fuel, NUREG/CR-0274 (ORNL/NUREG/TM-154), October 1978.

18. M. F. Osborne, J. L. Collins, R. A. Lorenz, J. R. Travis, and C. S. Webster, Design, Construction, and Testing of a 2000°C Furnace and Fission Product Collection System, NUREG/CR-3715 (ORNL/TM-9135), July 1984.
19. R. A. Lorenz, J. L. Collins, and A. P. Malinauskas, Fission Product Source Terms for the LWR Loss-of-Coolant Accident, NUREG/CR-1298 (ORNL/NUREG/TM-321), July 1980.
20. T. M. Besmann and T. B. Lindemer, "Chemical Thermodynamics of the System Cs-U-Zr-H-I-O in the Light Water Reactor Fuel-Cladding Gap," Nucl. Technol. 40, 297-305 (1979).
21. U.S. Nuclear Regulatory Commission, Technical Bases for Estimating Fission Product Behavior During LWR Accidents, NUREG-0772, pp. 4.1-5.3, June 1981.
22. J. L. Collins, M. F. Osborne, A. P. Malinauskas, R. A. Lorenz, and S. R. Manning, Knudsen Cell-Mass Spectrometer Studies of Cesium-Uranium Interactions, ORNL/NUREG/TM-24, June 1976.
23. J. Gittus, Water Reactor Fuel Element Performance Computer Modelling, Applied Science Publishers, London and New York, pp. 32-34, 1983.
24. J. M. Genco, W. E. Berry, H. S. Rosenberg, and D. L. Morrison, Fission Product Deposition and Its Enhancement Under Reactor Accident Conditions: Deposition on Primary-System Surfaces, BMI-1863, 1969.
25. I. Johnson, "Fission Product Release and Transport Experiments," presented at the Joint NRC-ERRI Technical Exchange Meeting at NRC Research Group Headquarters, Silver, Springs, Maryland, Feb. 9-10, 1984.

NUREG/CR-3930  
 ORNL/TM-9316  
 Dist. Category R3

## INTERNAL DISTRIBUTION

- |        |                   |     |   |
|--------|-------------------|-----|---|
| 1.     | R. E. Adams       | 27. | R. D. Spence  |
| 2.     | C. W. Alexander   | 28. | L. M. Toth  |
| 3.     | J. T. Bell        | 29. | R. L. Towns   |
| 4-7.   | J. L. Collins     | 30. | J. R. Travis  |
| 8.     | R. W. Glass       | 31. | V. C. A. Vaughen  |
| 9.     | P. A. Haas        | 32. | C. S. Webster   |
| 10.    | J. R. Hightower   | 33. | S. K. Whatley   |
| 11.    | E. K. Johnson     | 34. | R. P. Wichner   |
| 12.    | T. S. Kress       | 35. | A. L. Wright  |
| 13.    | C. E. Lamb        | 36. | R. G. Wymer   |
| 14.    | R. E. Leuze       | 37. | H. Shaw (Consultant)                                      |
| 15.    | T. B. Lindemer    | 38. | Central Research Library                                  |
| 16-18. | R. A. Lorenz      | 39. | ORNL-Y-12 Technical Library<br>Document Reference Section |
| 19.    | A. P. Malinauskas | 40. | Laboratory Records  |
| 20.    | K. S. Norwood     | 41. | Laboratory Records, ORNL-RC                               |
| 21-24. | M. F. Osborne     | 42. | ORNL Patent Section                                       |
| 25.    | G. W. Parker      |     |   |
| 26.    | D. R. Reichle     |     |   |

## EXTERNAL DISTRIBUTION

43. Office of Assistant Manager for Energy Research and Development, ORO-DOE, P.O. Box E, Oak Ridge, TN 37831
- 44-45. Director, Division of Reactor Safety Research, U.S. Nuclear Regulatory Commission, Washington, DC 20555
- 46-47. Technical Information Center, DOE, Oak Ridge, TN 37831
48. Division of Technical Information and Document Control, U.S. Nuclear Regulatory Commission, Washington, DC 20555
49. L. K. Chan, Fuel Systems Research Branch, Division of Accident Evaluation, U.S. Nuclear Regulatory Commission, Washington, DC 20555
50. M. F. Farahat, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439
- 51-325. Given distribution as shown in Category R3 (NTIS -- 10)



| NRC FORM 335<br>(2-84)<br>NRCM 1102,<br>3201, 3202  |  | U.S. NUCLEAR REGULATORY COMMISSION |                                     | 1. REPORT NUMBER (Assigned by TIOC, add Vol. No., if any)         |  |
|---|--|------------------------------------|-------------------------------------|---|--|
| <b>BIBLIOGRAPHIC DATA SHEET</b>   |  |                                    | NUREG/CR-3930<br>ORNL/TM-9316       |   |  |
| SEE INSTRUCTIONS ON THE REVERSE.  |  |                                    | 3. LEAVE BLANK                      |   |  |
| 2. TITLE AND SUBTITLE   |  |                                    | 4. DATE REPORT COMPLETED            |   |  |
| Observed Behavior of Cesium, Iodine, and Tellurium in<br>The ORNL Fission Product Release Program   |  |                                    | MONTH: July   YEAR: 1984            |   |  |
|   |  |                                    | 5. AUTHOR(S)                        |   |  |
| J. L. Collins, M. F. Osborne, R. A. Lorenz,<br>K. S. Norwood, J. R. Travis, and C. S. Webster   |  |                                    | 6. DATE REPORT ISSUED               |   |  |
|   |  |                                    | MONTH: January   YEAR: 1985         |   |  |
| 7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)  |  |                                    | 8. PROJECT/TASK/WORK UNIT NUMBER    |   |  |
| Oak Ridge National Laboratory<br>Post Office Box X<br>Oak Ridge, TN 37831   |  |                                    | 9. FIN OR GRANT NUMBER              |   |  |
|   |  |                                    | B0127                               |   |  |
| 10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)   |  |                                    | 11a. TYPE OF REPORT                 |   |  |
| Division of Accident Evaluation<br>Office of Nuclear Regulatory Research<br>U.S. Nuclear Regulatory Commission<br>Washington, D.C. 20555  |  |                                    | NUREG/CR and ORNL/TM                |   |  |
|   |  |                                    | b. PERIOD COVERED (Inclusive dates) |   |  |
| 12. SUPPLEMENTARY NOTES   |  |                                    |                                     |   |  |
| 13. ABSTRACT (200 words or less)  |  |                                    |                                     |   |  |
| <p>Two control tests were conducted to study the behavior of CsI, CsOH, and Te in the experimental apparatus used to conduct fission product release tests with highly irradiated LWR fuel at ORNL. In this report the control tests are described, and the results are compared with those obtained for cesium, iodine, and tellurium in 26 tests of irradiated fuel and other tests using tracers.</p> <p>In good agreement with the LWR fuel tests, the CsI behavior in the control tests was similar to that observed for iodine in the fuel tests; iodine was released primarily as CsI rather than highly volatile molecular iodine. Cesium (not associated with CsI) behaved like CsOH in the LWR fuel tests. In both LWR fuel tests and the control tests, cesium hydroxide was observed to react with and be retained by zirconia ceramic surfaces in the temperature range 800 to 1200°C, probably forming cesium metazirconate (Cs<sub>2</sub>ZrO<sub>3</sub>). In one of the control tests, cesium hydroxide reacted with tellurium in the gas phase and was collected as CsTe. Although the results are limited at this time, the indicated collection behavior of tellurium in the LWR fuel tests has been that of a telluride.</p> |  |                                    |                                     |   |  |
| 14. DOCUMENT ANALYSIS -- a. KEYWORDS/DESCRIPTORS  |  |                                    |                                     | 15. AVAILABILITY STATEMENT  |  |
| Fission product chemistry<br>Fission product release<br>Fission product behavior<br>Severe LWR accident   |  |                                    |                                     | 16. SECURITY CLASSIFICATION                                       |  |
|   |  |                                    |                                     | <i>(This page)</i><br><u>Unclassified</u><br><i>(This report)</i> |  |
| b. IDENTIFIERS/OPEN-ENDED TERMS   |  |                                    |                                     | 17. NUMBER OF PAGES   |  |
|   |  |                                    |                                     | 60  |  |
|   |  |                                    |                                     | 18. PRICE   |  |
|   |  |                                    |                                     |   |  |