HEDL-7598

THE RELEASE OF FISSION PRODUCTS FROM IRRADIATED SRP FUELS AT ELEVATED TEMPERATURE

DATA REPORT ON THE FIRST STAGE OF THE SRP SOURCE TERM STUDY

This document is
PUBLICLY RELEASABLE
B. Steels
Authorizing Official
Date: *9-20-06*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

HANFORD ENGINEERING DEVELOPMENT LABORATORY — Operated by Westinghouse Hanford Company, P.O. Box 1970, Richland, WA, a Subsidiary of Westinghouse Electric Corporation, Prepared for Savannah River Laboratory under Contract No. DE-AC06-76FF02170, B&R No. 83-04-04.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The Release of Fission Products from Irradiated
SRP Fuels at Elevated Temperatures

Data Report on the First Stage of the SRP
Source Term Study

Report Written By:

R. E. Woodley

Work Performed By:

D. L. Baldwin
F. E. Holt
R. E. Woodley
D. V. Archer
R. T. Steele

CONTENTS

Acknowledgments	iii
Figures	iv
Tables	vi
I. Introduction	1
II. Experimental Procedures	4
A. Fuel Specimens	4
B. Apparatus	5
1. Experimental System for Source Term Measurements	5
2. Equipment for Gamma Scanning the Thermal Gradient Tubes	9
C. Procedures	10
1. Source Term Measurement	10
2. Gamma Spectrometry	12
a. Fuel Specimens	12
b. Apparatus Components	13
3. Iodine Analyses	13
a. Fuel Specimens	13
b. Thermal Gradient Tube Sections and Apparatus Components	15
c. Charcoal and Filters	16
III. Experimental Results and Discussion	17
A. Analysis of Fuels Prior to Source Term Measurements	17
1. Gamma Spectrometry	17
a. MK-16 Fuel	17
b. OX-2 Fuel	17
c. Comparison of Measured and Calculated Activities	19
2. Iodine Analyses	19
3. Krypton-85 by Calculation	22

B.	Analysis of Fuels Following Source Term Measurements	23
1.	Gamma Spectrometry	23
a.	MK-16 Fuel	23
b.	OX-2 Fuel	25
2.	Iodine Analyses	28
C.	Cesium Release	31
1.	Thermal Gradient Tube Results	31
2.	Cesium Deposition on Other System Components	32
D.	Iodine Release	37
1.	Thermal Gradient Tube Results	37
2.	Activation Analysis of Charcoal and Filters	40
3.	Iodine on Other Apparatus Components	43
E.	Krypton-85 Release	46
IV.	Conclusions	49
V.	Future Measurements	51
VI.	References	52
VII.	Appendix: Fission Product Deposition Model	54

Acknowledgments

The author wishes to acknowledge many valuable discussions throughout the course of this study with P. G. Whitkop of the Savannah River Laboratory, who also contributed the description and application of his fission product deposition model, which is presented in the Appendix of this report.

D. L. Baldwin and F. E. Holt provided descriptions of analytical procedures and figures depicting the experimental system for use in this report.

The skill and patience of Lisa S. Cline in the preparation of this report is also gratefully acknowledged.

Funding for this study was provided by the Savannah River Plant, which is operated for the United States Department of Energy by E. I. duPont de Nemours & Company, Inc.

FIGURES

<u>Figure</u>	<u>Page</u>
1. Source Term Apparatus	60
2. Furnace Tube Details	61
3. Filter/Charcoal Trap Components	62
4. Typical Furnace Tube Temperature Distribution	63
5. Release of Cs-137 from MK-16 Fuel as a Function of Temperature	64
6. Cs-137 Deposition in the Thermal Gradient Tube - Run 2: MK-16 Fuel in Argon	65
7. Cs-137 Deposition in the Thermal Gradient Tube - Run 5: MK-16 Fuel in Argon	66
8. Cs-137 Deposition in the Thermal Gradient Tube - Run 1: MK-16 Fuel in Argon	67
9. Cs-137 Deposition in the Thermal Gradient Tube - Run 7: MK-16 Fuel in Argon	68
10. Cs-137 Deposition in the Thermal Gradient Tube - Run 4: MK-16 Fuel in Air	69
11. Cs-137 Deposition in the Thermal Gradient Tube - Run 6: MK-16 Fuel in Air	70
12. Cs-137 Deposition in the Thermal Gradient Tube - Run 3: MK-16 Fuel in Air	71
13. Cs-137 Deposition in the Thermal Gradient Tube - Run 8: MK-16 Fuel in Air	72
14. Cs-137 Deposition in the Thermal Gradient Tube - Run 18: MK-16 Fuel in Steam/Argon	73
15. Cs-137 Deposition in the Thermal Gradient Tube - Run 20: MK-16 Fuel in Steam/Argon	74
16. Cs-137 Deposition in the Thermal Gradient Tube - Run 21: MK-16 Fuel in Steam/Argon	75
17. Cs-137 Deposition in the Thermal Gradient Tube - Run 23: MK-16 Fuel in Steam/Argon	76
18. Cs-137 Deposition in the Thermal Gradient Tube - Run 9: OX-2 Fuel in Argon	77

<u>Figure</u>		<u>Page</u>
19.	Cs-137 Deposition in the Thermal Gradient Tube - Run 11: OX-2 Fuel in Argon	78
20.	Cs-137 Deposition in the Thermal Gradient Tube - Run 12: OX-2 Fuel in Argon	79
21.	Cs-137 Deposition in the Thermal Gradient Tube - Run 13: OX-2 Fuel in Argon	80
22.	Cs-137 Deposition in the Thermal Gradient Tube - Run 15: OX-2 Fuel in Argon	81
23.	Cs-137 Deposition in the Thermal Gradient Tube - Run 10: OX-2 Fuel in Air	82
24.	Cs-137 Deposition in the Thermal Gradient Tube - Run 14: OX-2 Fuel in Air	83
25.	Cs-137 Deposition in the Thermal Gradient Tube - Run 16: OX-2 Fuel in Air	84
26.	Cs-137 Deposition in the Thermal Gradient Tube - Run 17: OX-2 Fuel in Steam/Argon	85
27.	Cs-137 Deposition in the Thermal Gradient Tube - Run 19: OX-2 Fuel in Steam/Argon	86
28.	Cs-137 Deposition in the Thermal Gradient Tube - Run 22: OX-2 Fuel in Steam/Argon	87
29.	Cs-137 Deposition in the Thermal Gradient Tube - Run 24: OX-2 Fuel in Steam/Argon	88
30.	I-129 Deposition in the Thermal Gradient Tube - Run 19: OX-2 Fuel in Steam/Argon	89
31.	I-129 Deposition in the Thermal Gradient Tube - Run 6: MK-16 Fuel in Air	90
32.	Release of Kr-85 as a Function of Cs-137 Release	91
33.	Comparison of Kr-85 Release during Run 19 to Kr-85 Release during a Calibration Measurement	92
A-1.	Comparison of Calculated and Experimental Cs-137 Deposition Profiles for Run 8	93
A-2.	Calculated Cs-137 Deposition Profile for Run 17.	94
A-3.	Calculated Cs-137 Deposition Profile for Run 21.	95

TABLES

<u>Table</u>		<u>Page</u>
1	Test Matrix for the SRP Source Term Study	3
2	Fuel Specimens for the SRP Source Term Study	4
3	Pre-Run Gamma Activity Measurements	18
4	Comparison of Measured and Calculated Activities	20
5	Pre-Run Iodine-129 Activity Measurements	21
6	Post-Run Gamma Activity Measurements - MK-16 Fuel	24
7	Fractional Releases and Release Rate Constants for Cs-137	26
8	Post-Run Gamma Activity Measurements - OX-2 Fuel	27
9	Post-Run Iodine-129 Activities in MK-16 Fuel	29
10	Post-Run Iodine-129 Activities in OX-2 Fuel	30
11	Total Cesium Activity in the Thermal Gradient Tubes - MK-16 Fuel	33
12	Total Cesium Activity in the Thermal Gradient Tubes - OX-2 Fuel	34
13	Post-Run Cesium-137 Measurements - MK-16 Fuel	35
14	Deposition of Cesium-137 on Filters and Charcoal in the Initial Eight Runs with MK-16 Fuel	36
15	Iodine Deposition in the Thermal Gradient Tubes - MK-16 Fuel	38
16	Iodine Deposition in the Thermal Gradient Tubes - OX-2 Fuel	39
17	Iodine-129 Adsorbed on Charcoal	41
18	Iodine Deposition on Other Apparatus Components - MK-16 Fuel	44
19	Comparison of the Estimated Iodine-129 Content of the Experimental System with the Fuel Specimen Iodine-129 Inventory	45
20	Krypton-85 Release	47

I. Introduction

For a sound evaluation of the consequences of a hypothetical nuclear reactor accident, a knowledge of the extent of fission product release from the fuel at anticipated temperatures and atmosphere conditions is required. Measurements of fission product release have been performed with a variety of nuclear fuels under various conditions of temperature and atmosphere. While the use of data obtained on fuels similar to the fuel of interest may provide a reasonable estimate of release fractions, precise information of this nature can only be obtained from measurements employing specimens of the actual fuels used in the nuclear reactor under consideration. The two fuels of interest in the present study are an alloy, a dispersion of UAl_4 in an aluminum matrix, and a cermet, a dispersion of U_3O_8 in an aluminum matrix. Both fuels are clad in aluminum.

Uranium-aluminum alloys clad in aluminum have been commonly employed as nuclear fuels and, consequently, several studies have examined fission product release from these materials. An early study⁽¹⁾ of the evolution of radiokrypton from a 20w/o U-Al alloy determined that no release occurred below the 640°C eutectic temperature, whereas above this temperature, the rate of gas emission suggested a mechanism involving diffusion from spherical particles.

In another investigation⁽²⁾ where alloy fuels with uranium contents averaging ca. 37w/o were heated, krypton emission commenced when the solidus temperature of the aluminum cladding was exceeded and was essentially complete at 670°C. The release of cesium was also noted, but the quantity was not determined.

Parker and his coworkers at ORNL⁽³⁾ extended the fission product release measurements on uranium-aluminum alloy fuels to conditions more typical of accident situations than those employed in the aforementioned studies, where the fuel was heated in a vacuum to relatively low temperatures. In the ORNL measurements, temperatures to 1145°C and atmospheres of helium, air, or steam plus air were utilized. Further-

more, they studied the release of other volatile fission products in addition to the fission gases. As expected, all release fractions were found to increase with temperature but were also affected by the atmosphere into which release occurred. Release fractions also increased with burnup, but this dependence saturated at a relatively low burnup level.

Shibata et al.⁽⁴⁾ heated a uranium-aluminum alloy fuel in helium to a maximum temperature of 700°C and determined that fission product release commenced at a temperature where blisters formed on their fuel specimens but below the cladding solidus temperature. Additional releases occurred at the solidus temperature and when the 640°C eutectic temperature was exceeded. Their results suggested that up to 70% of the fission gas resides in the aluminum matrix and is available for release when the cladding melts.

The emission of fission gas from a U_3O_8 -Al cermet fuel into a vacuum at temperatures to 670°C was found to be somewhat slower than release from U-Al alloy fuels⁽²⁾. Much of the U_3O_8 had reacted during irradiation to form UAl_3 or UAl_4 plus Al_2O_3 . These reaction products surrounded the remaining U_3O_8 particles and acted as a diffusion barrier to gas release.

In a study⁽⁵⁾ in which U_3O_8 -Al cermet fuel was heated at temperatures ranging from 500°C to 700°C in flowing helium, radiokrypton emission commenced with blister formation on the fuel at 550°C, but the largest release occurred at 650°C. The release of cesium isotopes was also noted but could not be quantified because of their reaction with the quartz furnace tube.

In the present study, a particular effort was made to construct the experimental system from materials which would not readily interact chemically with the emitted radionuclides in order to gain a better understanding of their chemical nature. Moreover, to provide reliable source term information for Savannah River Plant (SRP) fuels, irradiated specimens of the actual fuels were subjected to temperatures and

atmospheres encompassing credible accident conditions. Thus, the measurements performed included both alloy and cermet fuels, two fuel temperatures, and three different atmospheres. A matrix of the 24 experimental measurements is presented in Table 1. This report presents the results of the first stage of the investigation. A second stage comprising 24 additional measurements at two intermediate temperatures is underway.

TABLE 1
Test Matrix for the SRP Source Term Study

<u>Fuel Type*</u>	<u>Fuel Temperature = 700°C</u>			<u>Fuel Temperatures = 1100°C</u>		
	<u>Argon</u>	<u>Air</u>	<u>Steam</u>	<u>Argon</u>	<u>Air</u>	<u>Steam</u>
MK-16 Alloy	2	2	2	2	2	2
OX-2 Cermet	2	2	2	2	2	2

* Additional information on the fuel specimens is presented in Section II.A.

II. Experimental Procedures

A. Fuel Specimens

Thirteen specimens of each of two types of SRP fuel were provided for the source term measurements. MK-16 fuel, a uranium-aluminum alloy fuel, is essentially a dispersion of UAl_4 in an aluminum matrix. OX-2 fuel consists of a dispersion of U_3O_8 particles in an aluminum matrix. Both fuel types are aluminum clad.

It was originally intended that all of the fuel specimens would be punched from the irradiated elements, but it was subsequently found that only the OX-2 fuel specimens could be prepared in this manner. Specimens of MK-16 fuel were removed from the fuel element by sawing. Consequently, they were less uniform than the 0.5 inch diameter OX-2 specimens and their weights displayed a greater variation, as may be seen in Table 2, where other data on both fuel types are included.

TABLE 2

Fuel Specimens for the SRP Source Term Study

	MK-16 Fuel (U-Al Alloy)	OX-2 Fuel (U_3O_8 -Al Cermet)
Fuel Thickness (mil)	75	40
Cladding Thickness (mil)	30	20
Specimen weight (g):		
Maximum	1.7170	0.863
Minimum	1.0878	0.841
Composition (w/o U)	33.6	28.7
Burnup (atom %)	ca. 52	ca. 52

When the fuel specimens were punched or cut from the fuel elements, a record of their positions within the element was maintained and they were packaged for shipment in a definite order. This order was preserved for the MK-16 fuel specimens, but unfortunately was lost in the case of the OX-2 specimens. The latter were packaged in a plastic container which melted during shipping because the decay heat of the fuel could not be dissipated. Their packaging order was consequently lost in separating the fuel specimens from the remains of the plastic container.

It was necessary to remove residual plastic from the OX-2 fuel specimens prior to their use, and it was decided to accomplish this by oxidation. The use of a solvent was rejected because of concern that dissolved plastic might find its way into any open porosity that existed in the specimens. Oxidation was performed in flowing air at 400°C and removed all but a thin black film of pyrolyzed plastic which remained on the cladding. The black film was removed by light abrasion. In an initial run to test this procedure, the final specimen weight was within 0.001 gram of the average weight of all OX-2 specimens prior to shipping. A measurement of the vaporization of Cs-137 from the specimen during this test indicated a maximum loss of < 0.005%, an insignificant fraction of the Cs-137 inventory. All remaining OX-2 fuel specimens were therefore cleaned by the oxidation procedure.

B. Apparatus

1. Experimental System for Source Term Measurements

Although this experimental apparatus has been described in a previous report⁽⁶⁾, certain minor changes were made and, for completeness, it will be described here. Much of the following description was taken from Reference 6, to which the reader is referred for additional details.

The apparatus, which is pictured schematically in Figure 1, includes a controlled atmosphere source, a means of heating the fuel specimen rapidly to the desired temperature, and a thermal gradient tube which provides an inert surface whose temperature decreases approximately exponentially from that of the fuel specimen to a temperature somewhat above the boiling point of water. A trap containing a series of three filters plus three one-gram quantities of activated charcoal is positioned downstream from the thermal gradient tube exit to collect those fission product entities which escape deposition in the thermal gradient tube, with the exception, of course, of the fission gases, krypton and xenon, which continue out of the cell to the NaI detector. Here, Kr-85 detection is enhanced by loops of copper tubing packed with activated charcoal and positioned adjacent to the detector. Beyond this point, the gases are passed back into the cell where they are vented.

During the first source term measurement, radiocesium in the form of an aerosol passed through the filter/charcoal trap to the NaI detector. The detector was swamped and the desired measurement of Kr-85 was consequently lost. Thereafter, two aerosol traps were added to the line between the filter/charcoal trap and the NaI detector to prevent any recurrence of cesium radioisotopes escaping the hot cell.

Of two primary differences from other experimental systems, the first is simply that the furnace tube is continuous. With no necessity for a joint with its associated extraneous materials between the point at which the fuel specimen is heated and the thermal gradient tube entrance, undesirable chemical interactions at this location are prevented. The second and more important difference, alluded to in the Introduction, relates to materials of construction. To avoid the chemical reactions known to occur between cesium and silica⁽⁷⁾ and/or zirconia⁽⁸⁾, high purity alumina was selected for the furnace tube, "dee" tube, specimen boat, and thermocouple insulator. The dee tube (see Figure 2) is a tube with a D-shaped cross section used to support the specimen boat at the midplane of the cylindrical furnace tube and thus center the fuel specimen in the load coil of the induction

thus center the fuel specimen in the load coil of the induction heater. To avoid the reaction of iodine with steel components, the closure at the furnace tube exit was machined from teflon. Additionally, the tubing connecting this end cap to the filter trap housing, the housing itself, and its internal parts are all constructed of teflon, with the exception of the viton o-rings on the edges of the teflon separators (see Figure 3). Furthermore, the three filters are teflon membranes with pores ranging from 0.25 to 10 microns. Thus, neither the fuel specimen nor its fission product emissions ever come into contact with materials with which they readily react chemically, thereby giving a false picture of their mobility.

As indicated in Figure 2, the alumina furnace tube is heated by three separate resistance heaters as well as induction heating. The preheater was added to the system solely to minimize the occurrence of a temperature dip between the fuel specimen and the thermal gradient tube. A drop in temperature at this location might otherwise cause an undesired premature deposition of fission products. The sample zone heater maintains the location of the fuel specimen at a temperature near the ultimate specimen temperature. This heater is provided with longitudinal windings to avert interaction with the RF field of the induction heater. The nichrome windings are wrapped on an alumina core whose thickness was reduced to minimize the overall diameter of the heater, thereby allowing a reduction in the load coil diameter for better coupling with the fuel specimen. Additionally, the load coil was formed in two layers to enhance coupling and minimize the heatup time of the fuel specimen.

As its name implies, the thermal gradient heater provides a temperature gradient along a 12-inch section of the furnace tube which is lined with 5 mil thick platinum foil. Deposition of fission-product compounds along the foil is governed by their vapor pressure as a function of temperature and, following the course of an experiment, the Pt foil is removed and analyzed to determine fission product locations.

Because of the short duration of a given run, 2 minutes at the maximum fuel temperature, the three resistance heaters are controlled by means of variable transformers which offer adequate short-term stability. On the other hand, the induction heater is controlled by a Data-Trak programmer in conjunction with a Thermac temperature controller. This control system, which includes a chromel-alumel thermocouple in contact with the fuel specimen as sensor, allows the rapid heatup of the fuel to its ultimate temperature with minor overshoot, control at temperature, and cutoff of the induction heater following the 2 minute run. Concurrent with the startup of the induction heater, the alumina boat containing the fuel specimen is pushed into the sample zone of the furnace tube by means of the alumina thermocouple insulator, which also serves as a push rod. Similarly, when induction heating is terminated, the alumina boat is withdrawn to an unheated location in the furnace tube, well upstream of the preheater. The thermocouple insulator, which actually contains two identical thermocouples with a common bead, the one mentioned above plus another to record the fuel temperature, enters the furnace tube through a septum in the inlet end fitting. The use of a septum prevents any contamination of the run atmosphere. Also, the holes surrounding the thermocouple wires at the outer end of the insulator were filled with black wax to prevent any loss of the run atmosphere at this location.

A typical temperature distribution measured along the length of the three furnaces is shown in Figure 4. The absence of induction heating during the distribution measurement allowed the sample zone temperature to remain slightly below the desired 1100°C specimen temperature. During an actual run, when the specimen temperature is controlled, the sample zone temperature usually more closely matches the temperature at the thermal gradient tube inlet.

The gas flow rate past the heated fuel specimen is controlled by a needle valve in the inlet gas line and measured on mass flow meters both upstream and downstream from the furnace tube. A gas flow of 100 cm³/min or 35 cm/min was desired and the flow, as read on the inlet

flow meter, was set accordingly. Unfortunately, calibration of the flow meters was not performed until midway through the series of 24 runs. At that time, it was discovered that a reading of 100 cm³/min on the inlet flow meter corresponded to 106.5 cm³/min of argon but only 74.4 cm³/min of air. Rather than increase the air flow in the remaining runs involving air, the same value was maintained so that flow conditions in all air runs would at least be the same, if low. In their measurements of fission product release from uranium-molybdenum alloy and metallic uranium fuels, Castleman and Tang found that a twofold flow variation had no appreciable effect on iodine deposition⁽⁹⁾. It seems likely that a similar result will prevail in the present study.

Of the gas atmospheres employed in the measurements, argon was supplied from a cylinder and air by a small pump connected to the inlet line. When a steam-argon atmosphere was used, 20 cm³ of argon/min. were diverted through a thermostatted water source. The water temperature which yields the required 4:1 steam/argon ratio, i.e. 80 cm³ of steam/min., was determined by a trial and error process. The water temperature is controlled and measured by a thermocouple positioned in a well in the steam generator. In the runs involving steam, the lines between the steam generator and the inlet of the furnace tube and between the outlet of the furnace tube and the moisture trap were wrapped with heating tapes to prevent any premature condensation of the steam. The moisture trap consisted of a tube containing anhydrous magnesium perchlorate.

2. Equipment for Gamma Scanning the Thermal Gradient Tubes

A primary goal of the source term measurements is to determine the distribution of those radionuclides vaporized from the fuel and deposited along the surface of the platinum thermal gradient tubes. Because the profile of deposition as a function of temperature can provide an indication of the chemical nature of the mobile fission product species, a unique counting system was assembled to obtain these data.

Following a given source term measurement, the platinum liner is removed from the alumina furnace tube and inserted into a clean, single-use aluminum counting tube with welded bottom and open top. The top closure includes a hook by which the counting tube can be suspended from the arm of a Zymate laboratory robot. The robot is mounted on a lead brick cave containing a GeLi detector, and the suspended counting tube is positioned in front of an opening into the detector enclosure. Suitable tungsten collimators are situated between the detector and the counting tube.

The robot is used as a programmable positioning device, interfaced to a multichannel gamma analyzer through the robot's input/output unit. It is programmed to count the platinum thermal gradient tubes in 24 half-inch increments. Software initializes the robotic arm at the starting position. The gamma analyzer is adjusted to count for a specified period and, after each counting period, directs the robot to reposition the counting tube. During the repositioning, which is performed with a reproducibility of ca. ± 1 mm, the gamma spectrum is downloaded to a PDP-11 computer, the peaks calculated, and the data both stored on a floppy disk and printed out. Then, under software control, the gamma analyzer is rezeroed and the count at the next position started. This process continues until the entire platinum tube has been counted. This apparatus operates unattended and, consequently, not only reduces personnel exposure but provides all of the required data in final form following an overnight or weekend count.

C. Procedures

1. Source Term Measurement

To initiate a source term measurement, the experimental system is totally assembled with the exception of the closure for the inlet end of the furnace tube and its associated components, which include the specimen boat, the fuel specimen, and the thermocouple/pushrod. It should be noted that, in each run, all alumina components (the furnace

tube, specimen boat, and thermocouple insulator) as well as the platinum thermal gradient tube are new, thereby precluding any possibility of cross-contamination between runs. The preheater, sample zone heater, and thermal gradient heater are stabilized at their respective operating temperatures, as are the steam generator (when used) and heating tapes on those gas lines where steam condensation is to be prevented. At this point, the temperature variation along the Pt thermal gradient tube is determined at eight or nine positions by means of a chromel-alumel thermocouple and digital temperature readout. The thermocouple is enclosed in a 24-inch long alumina insulator which is marked at one inch intervals so that it can be positioned accurately with manipulators at locations along the tube where temperatures are to be measured. Usually, about 5 or 6 minutes are allowed for the thermocouple to equilibrate with its surroundings at each position before a reading is taken. Because the thermocouple output is also recorded, thermal equilibration can also be followed visually. Temperatures at locations where measurements are not performed are obtained by interpolation of the measured values.

When the system temperatures have been determined to be satisfactory, the fuel specimen is inserted into the sample boat and the associated thermocouples bent so that their common bead firmly contacts the fuel surface, thereby holding the fuel specimen in the boat which is attached to the thermocouple insulator by a small quantity of a Sauereisen refractory cement. The inlet end closure is then installed on the furnace tube with the specimen boat positioned well out in the cool portion of the tube. The thermocouple leads are connected to the control system and temperature readout/recorder, respectively. After establishing the gas flow rate, a five minute period is allowed to purge the system, which is then in readiness for the measurement.

The run is initiated by starting the programmed induction heating cycle. Concurrent with the commencement of induction heating, the fuel specimen is pushed into the sample zone of the furnace tube where it generally attains its ultimate temperature within the allowed 30 second time period. Following two minutes at temperature, the induction

heater is programmed off, the fuel specimen is returned to the cool region of the furnace tube, and all heaters are allowed to cool. Gas flow is continued during cooldown and, when the system has cooled, it is disassembled.

Of the various system components, the platinum liner is removed to a counting tube for gamma scanning, as described in Section II.B.2 above, the fuel specimen plus boat are placed in a labelled vial for subsequent gamma spectrometry and iodine analysis, and the various filters and charcoal portions are placed in labelled vials for later analysis if desired. In the first eight source term runs, the alumina furnace tube and dee tube as well as all teflon trap components, end fittings, and connecting lines were washed and the washings analyzed, as described in Section II.C.2.b below. For the most part, these washings and analyses revealed minimal fission product deposition and thus were later discontinued because of the time and expense involved in their performance.

2. Gamma Spectrometry

a. Fuel Specimens

The fuel specimens were analyzed for gamma-active radionuclides both before and after heating. In the pre-run measurements, the specimen was placed on edge in a counting vial with one of its flat surfaces (faces) against the side of the vial. In the post-run measurements, the alumina specimen boat was often included with the fuel specimen in the counting vial and the combination was oriented as in the pre-run measurement. Thus, the post-run activities of the fuel specimen and alumina boat are included together as the activity of the fuel. The counting vial was, in turn, placed in a shielded container with a one-inch hole drilled through one side. The fuel specimen was oriented toward the hole which faced the spectrometer detector. The shielded container was usually located at a position approximately 36 feet from the detector, although its position could be varied to accommodate any activity level. The duration of counting ranged from

one to ten hours to obtain sufficiently precise measurements of the less abundant gamma emitters in the fuel. The instrument was calibrated at all distances from the detector at which the specimens were counted using a Eu-154 source traceable to the National Bureau of Standards.

b. Apparatus Components

As mentioned above, almost all components of the source term apparatus were surveyed for volatile fission products in the first eight runs. Each filter and each portion of charcoal were analyzed separately for gamma-active radionuclides. They were counted directly in their own separate vials. Larger components of the system which could not be counted directly were washed with a solution consisting of 1M H_2SO_4 , 1 mg/ml of iodine as KI, and 0.1M Na_2SO_3 . Initially, the washings from each apparatus component were diluted to a volume of 50 ml in a volumetric flask using the rinse solution. A 2 ml aliquot was then removed for gamma analysis. Later, the washings were diluted to only 25 ml. Then, the 2 ml aliquot contained twice the activity, which improved the counting accuracy. However, more often than not, these apparatus components held an insignificant fraction of the inventory of a given radionuclide. Consequently, this practice was discontinued because of the time required and the expense, and only an occasional filter or charcoal portion was counted in subsequent runs.

3. Iodine Analyses

a. Fuel Specimens

One pre-run specimen of each fuel type was analyzed for its total I-129 inventory. Fourteen post-run fuel specimens, at least one from each pair of duplicate runs plus its boat, were analyzed for their residual I-129 content. The nine OX-2 specimens analyzed were dissolved in 100 ml of 8M HNO_3 , which maintained the contained iodine in its elemental state. After adding 20 mg. of iodine as KI to the HNO_3 solutions to act as a carrier for the radioiodine, distillation of the

solutions was performed under an air sparge and the iodine collected in a trap containing 20 ml of 0.3 M NaOH. Despite the use of a distillation procedure, small quantities of radiocesium occasionally found their way into the distillate. However, it was found that when the iodine in a 1 ml aliquot of the trap solution was precipitated as AgI and removed by filtration, the cesium remained in solution. The filter paper plus precipitate was then carefully dried and weighed to 0.01 mg. Because essentially all of the iodine present was combined in the known quantity of carrier, the fractional recovery of iodine could be readily determined from the weight of the precipitate and used to correct the measured activities of iodine-129. The fractional recoveries generally ranged from about 63 to 99%, although one value near 10% occurred and is believed due to a loss of elemental iodine from the caustic trap. Iodine-129 activities were obtained by inserting the filter paper plus precipitate into a counting vial and counting the radioiodine in a GeLi well detector. These results were then compared to measurements on I-129 standards to obtain absolute values for the activity of residual radioiodine in the OX-2 fuel specimens. The iodine standards were treated in a manner identical to that employed with the iodine trapped during the distillations.

In the case of the MK-16 fuel, the first three specimens were dissolved in 100 ml of 3M HCl, to which were added 20 mg. of carrier iodine and then 1 ml of 30% H₂O₂ plus 0.5 ml of 0.5M (NH₄)₂MoO₄ as catalyst to oxidize the iodine to its elemental state. Thereafter, distillation was conducted in the same manner as with the OX-2 fuel, but Sb-125, probably as the chloride, distilled over with the iodine. Consequently, the caustic trap solution was acidified with 60 ml of 8M HNO₃, additional iodine carrier added, and the iodine oxidized with 5 ml of 1M NaNO₂. Redistillation of the resulting solution thereby effected a separation of the iodine and antimony, and the iodine was subsequently precipitated and counted as was done with the OX-2 fuel.

To avoid further problems with antimony, an attempt was made to dissolve the next MK-16 fuel specimen in 100 ml. of 1.8 M H₂SO₄. While only insignificant fuel dissolution occurred, a small quantity of

iodine was collected. To effect complete dissolution, the H_2SO_4 was replaced with a mixture of 100 ml of 6N HCl plus 25 ml of 8M HNO_3 to which were added 20 mg. of iodine as KI, 1 ml of 30% H_2O_2 and 0.5 ml of 0.5 M $(\text{NH}_4)_2\text{MoO}_4$. Distillation proceeded as before and, when complete, the iodine was precipitated as AgI from the caustic trap solution and counted. The remaining fuel specimens analyzed for residual iodine were also treated in this same manner, but, in the last few distillations, 2 ml of 1M Na_2SO_3 were added to the trap solution to ensure the reduction of trapped iodine to iodide, thereby precluding any iodine loss and enhancing the fractional recoveries. The fractional recoveries of iodine from the MK-16 fuel ranged from 47.2% to 89.6% for specimens dissolved in HCl and from 51.4% to 64.9% for the specimens dissolved in HCl/ HNO_3 .

b. Thermal Gradient Tube Sections and Apparatus Components

The washings from the various apparatus components (See Section II.C.2.b) as well as from sections of the platinum thermal gradient tubes were analyzed for iodine-129. In the case of the platinum tubes, each tube was cut into one-inch lengths after its cesium deposition profile had been determined, and selected pieces were then washed with the same solution used for the apparatus components. Selection of the sections to be washed, usually from 3 to 5 pieces from each tube, was based on the cesium distribution. These washings, like those of the other system components, were diluted with the wash solution to a volume of 25 ml. To remove all radiocesium, which would otherwise totally mask the iodine-129, aliquots of the wash solutions were subjected to an ion-exchange separation followed by solvent extraction. A 1 ml aliquot of the cesium-free solution was then analyzed for I-129 by liquid scintillation counting. Calibration of this counting procedure was performed using a National Bureau of Standards I-129 standard with an activity of about 60 nCi/ml.

c. Charcoal and Filters

The charcoal portions, which were situated in the trap in the upstream position in each run, were analyzed for I-129 by neutron activation analysis. Additionally, one charcoal portion that had been immediately downstream from charcoal exhibiting a high I-129 concentration, as well as one filter from each of two runs, were also analyzed in this manner.

For these analyses, the charcoal or filter was placed in a clean counting vial which was, in turn, inserted into a so-called "rabbit". The "rabbit" is a plastic container capable of holding five vials of the size employed in the present study. Ordinarily, two standards were included with three samples, although occasionally a blank was included. The standards consisted of 0.8 gram of charcoal onto which from 0.02 to 0.05 ml of the National Bureau of Standards I-129 standard was pipetted. The "rabbits" were irradiated in an N-Reactor pneumatic facility for one or two hours to produce adequate I-130 for counting. Each sample and standard was counted for from 0.5 to 1.5 hours depending upon their activity level. Sometimes they were counted again the following day to obtain an accurate decay factor.

The quantity of I-129 in the samples was then based on the known quantity of I-129 in the standards and the results of their respective counting.

III. Experimental Results and Discussion

A. Analysis of Fuels Prior to Source Term Measurements

1. Gamma Spectrometry

a. MK-16 Fuel

The results of the spectrometric analysis of MK-16 fuel are tabulated in Table 3. In general, the activities measured for the six radionuclides of interest are reasonably consistent for a given fuel specimen or from specimen to specimen from the same side of the fuel element. This is indicated by the standard deviations which show a variation in the activities of usually less than ca. 5%. Thus, it is believed that the pre-measurement activities are well established.

When comparing activities of specimens from opposite sides of the fuel element, it is noted that the activities of Eu-154 and Cs-134 are significantly higher on one side than the other. Neither of these radionuclides are formed directly as fission products but result from (n, γ) processes in Eu-153 and Cs-133, respectively. It therefore appears that the specimens removed from "Side 1" of the fuel element received a somewhat higher neutron exposure than those from "Side 2", i.e., "Side 1" of the fuel element was oriented more toward the center of the reactor than "Side 2" during their residence therein. While this difference has no effect on the source term measurement, the correct initial value must be employed in the calculation of release fractions. There is no apparent significant variation in the activities along that length of the fuel element from which fuel specimens were removed.

b. OX-2 Fuel

The gamma spectrometric analysis of OX-2 fuel prior to use was far more limited in extent than that of the MK-16 fuel. Nevertheless, as may be seen in Table 3, the activities determined for the two specimens

TABLE 3
Pre-Run Gamma Activity Measurements

Fuel Specimen No.	Activity (Ci/g of sample)						
	Eu-154 $\times 10^3$	Ce-144	Sb-125 $\times 10^3$	Ru/Rh-106	Cs-134	Cs-137	Zr-95
<u>MK-16 Fuel, Side 1</u>							
B-1-1	3.79	3.69	7.22	0.244	0.142	0.148	7.86
C-1-2	3.83	3.62	7.03	0.241	0.141	0.146	7.77
C-1-3	3.78	3.69	7.28	0.246	0.142	0.148	8.08
D-1-2	3.85	3.74	7.20	0.252	0.147	0.153	7.94
Side 1 Avg.	3.81 ± 0.03	3.68 ± 0.05	7.18 ± 0.11	0.246 ± 0.005	0.143 ± 0.003	0.149 ± 0.003	7.91 ± 0.13
<u>MK-16 Fuel, Side 2</u>							
B-2-1	3.67	3.75	7.30	0.248	0.137	0.152	8.20
C-2-1	3.38	3.65	7.04	0.239	0.130	0.146	7.82
D-2-2	3.39	3.53	6.90	0.230	0.128	0.143	7.66
Side 2 Avg.	3.48 ± 0.16	3.64 ± 0.11	7.08 ± 0.20	0.239 ± 0.009	0.132 ± 0.005	0.147 ± 0.005	7.89 ± 0.28
<u>OX-2 Fuel</u>							
Unknown	4.34	4.35	8.13	0.313	0.163	0.180	9.36
Unknown	4.45	4.28	8.91	0.309	0.162	0.175	9.55
Average	4.40 ± 0.08	4.32 ± 0.05	8.52 ± 0.55	0.311 ± 0.003	0.162 ± 0.001	0.178 ± 0.004	9.46 ± 0.13

measured exhibit reasonable agreement and provide adequate initial values for this fuel type. With only two specimens having been measured and their original positions in the fuel element unknown, nothing can be said about any activity variation which may occur across or along the fuel element.

c. Comparison of Measured and Calculated Activities

The measured activities presented in Table 3 are compared with calculated activities provided by the Savannah River Laboratory in Table 4. In general, agreement between the two sets of activities is reasonable, particularly considering the complexity of the calculation. While the average ratios of measured to calculated activities are 0.853 ± 0.180 and 0.835 ± 0.166 for MK-16 and OX-2 fuels, respectively, ratios for individual radionuclides range from a high of 1.153 to a low of 0.610. Consequently, in instances where initial activities were not measured, e.g. Kr-85, the use of calculated values may lead to release fractions that are somewhat in error.

2. Iodine Analyses

One specimen of each fuel type was analyzed for its inventory of I-129. The results of these analyses, as activities, are presented in Table 5, where they are compared to the SRL calculated values. The measured and calculated activities for MK-16 fuel agree very well, whereas the measured activity for OX-2 fuel is somewhat lower than the calculated value, although not unreasonably so. The measured activities were used to convert all post-run activities to release fractions. Hopefully, they are representative of the actual iodine inventories in all of the fuel specimens employed in the source term measurements. It would have been very worthwhile to have had additional fuel specimens for the initial analyses that require destruction of the specimens. To correct this deficiency, additional measurements of the I-129 inventory will be performed on specimens of both fuel types that were employed in tensile tests. The improved inventory values may then be used to correct the iodine release fractions presented in this report.

TABLE 4

Comparison of Measured and Calculated Activities

Fission Product	MK-16 Fuel			OX-2 Fuel		
	Measured* Activity (Ci/g)	Calculated** Activity (Ci/g)	Ratio	Measured* Activity (Ci/g)	Calculated** Activity (Ci/g)	Ratio
Eu-154	3.81×10^{-3}	5.99×10^{-3}	0.636	4.40×10^{-3}	7.21×10^{-3}	0.610
Ce-144	3.68	4.65	0.791	4.32	5.57	0.776
Sb-125	7.18×10^{-3}	7.07×10^{-3}	1.016	8.52×10^{-3}	8.68×10^{-3}	0.982
Ru/Rh-106	0.246	0.295	0.834	0.311	0.371	0.838
Cs-134	0.143	0.124	1.153	0.162	0.147	1.102
Cs-137	0.149	0.175	0.851	0.178	0.212	0.840
Zr-95	7.91	11.44	0.691	9.46	13.50	0.700

* Measured activities are corrected to end of irradiation.
For MK-16 fuel, Side 1 values are used.

** For MK-16 fuel, weight of one piece = 1.371 g.
For OX-2 fuel, weight of one piece = 0.856 g.

TABLE 5

Pre-Run Iodine-129 Activity Measurements

<u>Fuel Type</u>	<u>Measured Activity (nCi/g of sample)</u>	<u>Calculated Activity (nCi/g of sample)</u>	<u>Ratio</u>
MK-16	38.1	35.9	1.061
	36.2		1.008
OX-2	30.6	43.7	0.700

3. Krypton-85 by Calculation

Without a special program to develop an accurate measurement procedure for the Kr-85 inventory in the two SRP fuels, it was necessary to employ calculated values for the quantities of Kr-85 present. Calculations of the fission product inventories of both fuels at the end of irradiation (EOI) and for various decay periods thereafter were performed at SRL and supplied to HEDL. The calculated activities at EOI for MK-16 and OX-2 fuels amounted to 2.947×10^{-2} Ci/piece and 2.221×10^{-2} Ci/piece, respectively. These values were converted to the more usable quantities 2.15×10^{-2} Ci/g for MK-16 fuel and 2.59×10^{-2} Ci/g for OX-2 fuel using the weights 1.371 g/piece for MK-16 fuel and 0.856 g/piece for OX-2 fuel. The former weight is a calculated value based on the composition and dimensions of an MK-16 fuel specimen, the dimensions being those of a specimen punched from a fuel element. The weight for OX-2 fuel is the average weight/piece of the 13 specimens of OX-2 fuel supplied for the study. The EOI inventory values were corrected to the dates of the various source term measurements using a Kr-85 decay constant abstracted from the SRL calculations, $\lambda = 1.769 \times 10^{-4} \text{ day}^{-1}$, plus the number of days since the EOI, which occurred on October 25, 1982. As was noted in Section III.A.1.c, the use of these calculated Kr-85 inventories may lead to release fractions that are somewhat in error.

B. Analysis of Fuels Following Source Term Measurements

1. Gamma Spectrometry

a. MK-16 Fuel

The activities of MK-16 fuel specimens subsequent to their use in the source term measurements may be found in Table 6. Because it was often more convenient to measure the fuel and the alumina boat together, any activity associated with the boat is assumed to remain with the fuel specimen. The premeasurement values, when given for comparison, are averages of all of the initial measurements on a given specimen. Within the precision of the measurements, only the two cesium isotopes exhibit any significant decrease as a consequence of the heat treatment received during the source term measurements. Activities of the other fission products measured remain essentially constant, indicating little if any volatilization from the fuel specimens at the temperatures employed in the runs.

As anticipated, the release of cesium from the molten alloy increases with increasing temperature but displays only a limited dependence on the gas atmosphere into which release occurs. These results are apparent in Figure 5, Arrhenius plots for the release of Cs-137 into the three atmospheres used in this study. To obtain values of the release rate constant, k , it was assumed that release occurs by a first order process, as is often done with LWR fuels.^(10, 11) Thus, the rate at which the amount, M , of Cs-137 remaining in the fuel decreases with time is given by

$$-\frac{dM}{dt} = kM \quad (1)$$

After integration over the time of heating, t ,

$$\ln \left(\frac{M}{M_0} \right) = -kt \quad (2)$$

TABLE 6

Post-Run Gamma Activity Measurements - MK-16 Fuel

Fuel Specimen & Run	Activity (Ci/g of sample)						
	Eu-154 $\times 10^3$	Ce-144	Sb-125 $\times 10^3$	Ru/Rh-106	Cs-134	Cs-137	Zr-95
<u>Side 1</u>							
B-1-1 (4)	3.88	3.61	6.85	0.238	0.127	0.132	7.65
B-1-2 (2)	3.69	3.56	6.99	0.241	0.121	0.127	7.61
C-1-1 (23)	3.43	3.57	6.10	0.239	0.0391	0.0407	N.D.
C-1-2 (6)	3.56	3.38	6.66	0.227	0.105	0.109	7.24
C-1-3 (5)	3.87	3.73	7.20	0.249	0.117	0.122	8.05
D-1-1 (1)	3.64	3.67	7.06	0.252	0.0301	0.0315	8.00
D-1-2 (8)	3.93	3.80	7.52	0.256	0.105	0.109	8.28
Side 1 Avg.	3.71 ± 0.19	3.62 ± 0.14	6.91 ± 0.45	0.243 ± 0.010	-----	-----	7.80 ± 0.38
<u>Side 2</u>							
B-2-1 (7)	3.57	3.83	7.07	0.257	0.0278	0.0309	8.10
B-2-2 (18)	3.64	3.70	7.15	0.245	0.110	0.122	N.D.
C-2-2 (20)	3.67	3.82	7.35	0.251	0.105	0.116	N.D.
D-2-1 (21)	3.30	3.70	6.10	0.243	0.0504	0.0560	N.D.
D-2-2 (3)	3.39	3.81	6.50	0.255	0.0507	0.0564	8.15
Side 2 Avg.	3.51 ± 0.16	3.77 ± 0.07	6.53 ± 0.88	0.250 ± 0.006	-----	-----	8.12 ± 0.04

where M_0 is the initial quantity of Cs-137 in the fuel. The fraction of Cs-137 released is $F = 1 - \frac{M}{M_0}$, and so Equation 2 can be written

$$\frac{1}{t} \ln\left(\frac{1}{1-F}\right) = k \quad (3)$$

to obtain the rate constant.

When possible, the fractional releases, F , were calculated from pre- and post-heating measurements on the same fuel specimen. When the initial measurements were not performed on a given specimen, those from an adjacent specimen were used. The time used in Equation 3 was, in all cases, 2.5 minutes, an arbitrary interval over which the specimen temperatures were averaged. Averaging was performed by graphical integration of the recorder tracings of the specimen temperature. Fractional releases, release rate constants, and the average temperatures may be found in Table 7.

With one point excepted, the Arrhenius plots yield reasonably straight lines with slopes corresponding to an average apparent activation energy of ca. 13 kcal/mole. This energy is presumably associated with diffusion of cesium atoms through the molten alloy and any surface layer resulting from chemical interaction of the fuel with the surrounding atmosphere. The presence of an oxide layer on the fuel surface may explain the lower fractional releases of cesium into flowing air.⁽¹²⁾ For this same reason, it is surprising that release fractions are higher in steam than in argon.

b. OX-2 Fuel

As was the case for MK-16 fuel, only the two cesium isotopes were released from OX-2 fuel in significant quantities. This may be seen in Table 8, where activities associated with the alumina boat are again assumed to remain with the fuel specimen. Because of the extremely friable nature of the OX-2 fuel specimens following heating, in a few instances a portion of the fuel was lost during its removal from the

TABLE 7

Fractional Releases and Release Rate Constants for Cs-137

Nominal Conditions	MK-16 Fuel				OX-2 Fuel			
	Run	T (°C)*	F	k (min. ⁻¹)	Run	T (°C)	F**	k (min. ⁻¹)
Ar, 700°C	2	657	0.146	0.0632	9	(707)	0	0
	5	689	0.179	0.0788	11	683	0.202	0.0902
					12	668	0.081	0.0338
Ar, 1100°C	1	(1095)	0.794	0.632	13	1018	0.774	0.594
	7	(1090)	0.797	0.638	15	1104	0.597	0.363
Air, 700°C	4	695	0.108	0.0459	10	765	0	0
	6	703	0.255	0.118				
Air, 1100°C	3	1079	0.606	0.372	14	1029	0.635	0.404
	8	892	0.287	0.136	16	1055	0.690	0.469
Steam, 700°C	18	(665)	0.199	0.0887	17	742	0.206	0.0921
	20	688	0.206	0.0920	19	683	0.018	0.0074
Steam, 1100°C	21	954	0.608	0.375	22	756	0.086	0.0362
	23	1018	0.722	0.512	24	(620)	0.001	0.0005

* Temperatures in parentheses are approximate.

** Fractional releases for OX-2 fuel have been normalized to account for handling losses

TABLE 8

Post-Run Gamma Activity Measurements - OX-2 Fuel

Run	Activity (Ci/g of sample)						
	Eu-154 $\times 10^3$	Ce-144	Sb-125 $\times 10^3$	Ru/Rh-106	Cs-134	Cs-137	Zr-95
9	0.672	0.642	1.27	0.046	0.0256	0.0276	1.42
10	4.45	4.45	9.07	0.319	0.165	0.181	9.48
11	4.57	4.40	8.24	0.309	0.129	0.140	9.22
12	4.59	4.52	9.22	0.322	0.157	0.168	9.43
13	4.52	4.40	9.11	0.321	0.0365	0.0409	9.43
14	4.40	4.25	8.49	0.299	0.0559	0.0625	8.87
15	4.69	4.40	8.57	0.315	0.0667	0.0718	9.12
16	4.22	4.20	8.64	0.307	0.0480	0.0530	8.89
17	4.79	4.35	9.18	0.323	0.135	0.146	9.65
19	4.67	4.34	8.53	0.310	0.162	0.174	N.D.
22	3.61	2.87	6.40	0.249	0.110	0.121	N.D.
24	4.10	3.80	7.20	0.273	0.142	0.154	N.D.
Average*	4.52 ± 0.17	4.36 ± 0.09	8.74 ± 0.38	0.313 ± 0.007	-----	-----	9.30 ± 0.27

* Averages exclude values from Runs 9, 22, and 24 in which some fuel loss occurred.

experimental system following the run. This is particularly noticeable in the case of the Run 9 specimen. Nevertheless, the constancy of the fractions of radionuclides remaining in the fuel specimen indicates that little or no volatilization occurred in Run 9. Other instances of fuel loss, more minor in extent, occurred in Runs 22 and 24.

For the most part, cesium-137 release fractions are of the same order of magnitude as those found for MK-16 fuel, but even when normalized to account for fuel losses due to handling, the results are more scattered and do not yield linear plots like those of Figure 5. While the reason for this is not known, it may arise, in part, from a variation in the cesium inventory with location in the fuel element, as was noted in the case of MK-16 fuel. In any event, it appears likely that the behavior of the gamma-active nuclides in the two fuel types is essentially the same. Fractional releases, release rate constants, and average run temperatures for this fuel material may also be found in Table 7.

2. Iodine Analyses

Although the analysis of residual iodine in the post-run fuel specimens was accomplished by various procedures (Section II.C.3.a), because fractional recoveries were always determined from the weights of precipitated AgI, any effects of procedural differences should have been minimized. The residual activities and release fractions of iodine-129 in MK-16 and OX-2 fuels are presented in Tables 9 and 10, respectively.

While iodine release is enhanced at the higher temperatures, as expected, the present results are somewhat scattered and it is not possible to obtain an accurate value of the activation energy for the release process nor to decide with certainty if the release is affected by the atmosphere surrounding the heated fuel. The activation energy is probably of similar magnitude to that observed in the release of cesium from MK-16 fuel, although, in general, iodine appears to be more

TABLE 9

Post-Run Iodine-129 Activities in MK-16 Fuel

Run	Nominal Conditions	<u>Residual Activity</u>		<u>Release Fraction</u> (%)
		<u>(nCi/g)</u>	<u>(%)</u>	
5	Ar, 700°C	20.5	55.2	44.8
		21.0	56.5	43.5
7	Ar, 1100°C	0.78	2.10	97.9
		0.89	2.40	97.6
4	Air, 700°C	10.9	29.3	70.7
		12.1	32.6	67.4
3	Air, 1100°C	4.91	13.2	86.8
20	Steam, 700°C	28.2	75.9	24.1
		27.9	75.1	24.9
23	Steam, 1100°C	1.64	4.43	95.6

TABLE 10

Post-Run Iodine-129 Activities in OX-2 Fuel

Run	Nominal Conditions	Measured Activity (nCi/g)	Normalized Residual Activity		Normalized Release Fraction (%)
			(nCi/g)	(%)	
11	Ar, 700°C	16.1	16.3	53.3	46.7
12	Ar, 700°C	23.2	22.5	73.5	26.5
		19.0	18.4	60.1	39.9
15	Ar, 1100°C	1.7	1.7	5.6	94.4
		3.3	3.3	10.8	89.2
10	Air, 700°C	23.8	23.4	76.5	23.5
		15.1	14.9	48.7	51.3
16	Air, 1100°C	0.81	0.84	2.7	97.3
		1.4	1.5	4.9	95.1
19	Steam, 700°C	9.7	9.7	31.7	68.3
		12.4	12.4	40.5	59.5
22	Steam, 1100°C	2.25	3.0	9.9	90.1
		1.48	2.0	6.5	93.5
24	Steam, 1100°C	22.1	25.4	83.0	17.0
		29.3	33.7	100.0	0

readily vaporized from the two fuels than is cesium. For MK-16 fuel, this observation is in accord with the results of Parker et al.⁽³⁾ in their study of fission product release from aluminum-uranium alloys.

C. Cesium Release

1. Thermal Gradient Tube Results

Cesium deposition profiles measured on the platinum thermal gradient tubes are shown in Figures 6 through 29. Only the measurements of Cs-137 are presented, because the Cs-134 results are qualitatively identical. The temperature distributions along the thermal gradient tubes are also included in each figure. For a more ready comparison of deposition patterns, the figures are grouped by fuel type and nominal run conditions rather than in chronological sequence.

For the most part, the deposition patterns are consistent for given atmospheres and temperature distributions and do not exhibit any particular differences for the two types of fuel. Emission of cesium into an argon atmosphere generally led to deposition over a narrow band of temperatures, usually commencing below 700°C. Occasionally, a secondary peak occurred in the deposition profile (Run 11, Figure 19). A model of the behavior of volatile fission product species within the thermal gradient tube suggests that the chemical species responsible for the primary peak in the deposition profile is elemental cesium. This observation is in accord with expectations for cesium volatilized from metallic or essentially metallic fuels into an inert atmosphere. The fission product deposition model is based primarily on Fickian diffusion but includes certain properties of potential chemical species which determine the location of the peak along the temperature gradient. (See the Appendix for mathematical details of the model).

When the atmosphere surrounding the heated fuel specimen was air, deposition profiles similar to those observed in argon were obtained. Again, there was usually a single peak, although occasionally a

secondary peak (Run 4, Figure 10) or a shoulder on the primary peak (Run 3, Figure 12) occurred. In one instance (Run 16, Figure 25), the major peak displayed two maxima but the primary component of the deposit still appears to be elemental cesium. The identity of those chemical species giving rise to the small secondary peaks or shoulders is seldom known.

While the presence of steam at times led to significant peaks arising from CsOH (Run 21, Figure 16 and Run 22, Figure 28), the deposition profiles were still dominated by larger peaks due to elemental cesium. Like the cesium peaks, the identity of the CsOH peaks was suggested by the deposition model.

Each of the cesium deposition profiles was integrated graphically to determine the total activity of each cesium isotope present. The results of these calculations are given in Tables 11 and 12 both as activities per unit weight of fuel specimen and as percentages of the specimen's cesium inventory. Although it was shown in Section II.A.1 that the release of cesium increased with temperature, deposition in the thermal gradient tubes increased with temperature only when the deposits consisted primarily of elemental cesium, i.e. only in runs where cesium was released into argon or air. In runs involving steam, essentially no variation with temperature is apparent. Unfortunately, in these runs, with minor exceptions, system components beyond the thermal gradient tube were not analyzed for cesium and hence the final location of much of the released cesium is unknown.

2. Cesium Deposition on Other System Components

In the first eight runs which involved heating MK-16 fuel in either argon or air, the extent of cesium deposition was determined on several system components in addition to the thermal gradient tube. The results of Cs-137 measurements are presented in Table 13, and Table 14 indicates the extent to which deposition of Cs-137 occurred on the individual filters and charcoal portions in the initial eight runs. Measurements of Cs-134 activities yielded results qualitatively

TABLE 11

Total Cesium Activity in the Thermal Gradient Tubes - MK-16 Fuel

Run	Nominal Conditions	Cs-137 Activity		Cs-134 Activity	
		Ci/g	%	Ci/g	%
1	Ar, 1100°C	5.47×10^{-2}	35.7	5.25×10^{-2}	35.8
2	Ar, 700°C	5.40×10^{-3}	3.64	4.80×10^{-3}	3.38
3	Air, 1100°C	3.86×10^{-2}	27.0	3.37×10^{-2}	26.3
4	Air, 700°C	2.07×10^{-3}	1.39	1.91×10^{-3}	1.34
5	Ar, 700°C	8.70×10^{-3}	5.87	8.19×10^{-3}	5.76
6	Air, 700°C	6.23×10^{-3}	4.25	5.69×10^{-3}	4.05
7	Ar, 1100°C	6.15×10^{-2}	40.4	5.44×10^{-2}	39.7
8	Air, 1100°C	2.43×10^{-2}	15.9	2.19×10^{-2}	14.9
18	Steam, 700°C	3.85×10^{-3}	2.53	3.41×10^{-3}	2.49
20	Steam, 700°C	7.95×10^{-3}	5.45	6.87×10^{-3}	5.28
21	Steam, 1100°C	2.32×10^{-3}	1.62	2.01×10^{-3}	1.57
23	Steam, 1100°C	5.30×10^{-3}	3.62	4.84×10^{-3}	3.44

TABLE 12

Total Cesium Activity in the Thermal Gradient Tubes - OX-2 Fuel

Run	Nominal Conditions	Cs-137 Activity		Cs-134 Activity	
		Ci/g	%	Ci/g	%
9	Ar, 700°C	3.26×10^{-4}	0.18	2.99×10^{-4}	0.18
10	Air, 700°C	4.89×10^{-4}	0.27	4.53×10^{-4}	0.28
11	Ar, 700°C	3.93×10^{-3}	2.21	3.68×10^{-3}	2.27
12	Ar, 700°C	4.43×10^{-3}	2.49	3.98×10^{-3}	2.46
13	Ar, 1100°C	3.65×10^{-2}	20.5	3.15×10^{-2}	19.4
14	Air, 1100°C	5.92×10^{-2}	33.3	5.24×10^{-2}	32.3
15	Ar, 1100°C	2.84×10^{-2}	16.0	2.54×10^{-2}	15.7
16	Air, 1100°C	7.32×10^{-2}	41.1	6.42×10^{-2}	39.6
17	Steam, 700°C	3.15×10^{-4}	0.18	2.91×10^{-4}	0.18
19	Steam, 700°C	1.80×10^{-3}	1.01	1.58×10^{-3}	0.98
22	Steam, 1100°C	1.39×10^{-3}	0.78	1.19×10^{-3}	0.73
24	Steam, 1100°C	3.19×10^{-3}	1.79	2.87×10^{-3}	1.77

TABLE 13

Post-Run Cesium-137 Measurements - MK-16 Fuel

Fuel Specimen & Run	Nominal Conditions	Per Cent of Initial Inventory						
		Fuel + Boat	Pt Tubes	Filters *	Charcoal *	Furnace Tube	Fittings	Trap Parts
B-1-2 (2)	Ar, 700°C	85.38	3.64	1.08	0.01	4.99	0.53	0.10
C-1-3 (5)	Ar, 700°C	82.12	5.87	1.31	0.01	4.41	0.49	0.88
D-1-1 (1)	Ar, 1100°C	20.58	35.73	15.02	0.04	0.60	7.18	2.00
B-2-1 (7)	Ar, 1100°C	20.29	40.38	11.82	0.93	1.76	4.41	2.60
B-1-1 (4)	Air, 700°C	89.15	1.39	0.20	0.04	0.64	0.08	0.07
C-1-2 (6)	Air, 700°C	74.54	4.25	1.12	0.10	3.71	0.61	0.30
D-2-2 (3)	Air, 1100°C	39.44	26.99	0.41	0.003	16.78	0.63	0.52
D-1-2 (8)	Air, 1100°C	71.26	15.94	0.80	0.26	1.70	0.46	0.40
B-2-2 (18)	Steam, 700°C	80.11	2.53	N.D.	0.03(1)	N.D.	N.D.	N.D.
C-2-2 (20)	Steam, 700°C	79.45	5.45	0.58(1)	0.07(1)	N.D.	N.D.	N.D.
D-2-1 (21)	Steam, 1100°C	39.16	1.62	N.D.	0.003(1)	N.D.	N.D.	N.D.
C-1-1 (23)	Steam, 1100°C	27.78	3.62	N.D.	0.10(1)	N.D.	N.D.	N.D.

* (1) indicates that only Filter #1 or Charcoal #1 was analyzed.

N.D. = not determined.

TABLE 14

Deposition of Cesium-137 on Filters and Charcoal
in the Initial Eight Runs with MK-16 Fuel

Run	Nominal Conditions	% of Initial Inventory on Filters			% of Initial Inventory on Charcoal		
		1	2	3	1	2	3
2	Ar, 700°C	0.40	7.4×10^{-3}	0.67	4.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}
5	Ar, 700°C	0.38	0.93	1.6×10^{-5}	3.0×10^{-3}	2.6×10^{-3}	1.8×10^{-3}
1	Ar, 1100°C	8.16	4.11	2.73	1.4×10^{-2}	1.5×10^{-2}	1.2×10^{-2}
7	Ar, 1100°C	10.37	1.43	-----	0.55	0.38	-----
4	Air, 700°C	5.3×10^{-2}	0.15	4.3×10^{-4}	8.8×10^{-3}	2.0×10^{-2}	1.6×10^{-2}
6	Air, 700°C	1.10	1.8×10^{-2}	-----	6.1×10^{-2}	3.9×10^{-2}	-----
3	Air, 1100°C	6.7×10^{-3}	0.40	2.5×10^{-3}	1.8×10^{-3}	7.7×10^{-4}	2.0×10^{-4}
8	Air, 1100°C	0.73	7.3×10^{-2}	-----	0.13	0.12	-----

identical to those for Cs-137 and therefore will not be presented. In the lower temperature runs, the bulk of the cesium remained with the fuel, whereas when the measurements were conducted at a higher temperature, a substantial fraction of the cesium reached the thermal gradient tube and adjacent alumina furnace tube (See Section III.B.1.a). Solely in the high temperature runs involving an inert atmosphere did a significant quantity of cesium deposit on the filters, trap parts, and in the line and fittings connecting the alumina furnace tube with the trap. It appears that, not only can cesium escape the molten fuel more easily into argon than into air (Section III.B.1.a), the formation of an aerosol which can readily attain these downstream locations may be enhanced in an inert atmosphere. The higher gas flow in the runs employing argon may have contributed to this difference. Only minor amounts of cesium were retained by the charcoal in any of the runs, but cesium was known to penetrate beyond the charcoal trap. This was particularly noticeable in Run 1, prior to installation of the two aerosol traps when cesium swamped the detector intended for Kr-85 determination. Over 80% of the released cesium was accounted for in each of the eight initial runs. Because the two cesium radionuclides are so easily detected, the remainder in the form of an aerosol must have passed beyond the filter and charcoal trap to the aerosol traps. The construction of these traps does not allow cesium removal, and consequently no effort was made to determine the amount of cesium collected by the aerosol traps during individual runs.

D. Iodine Release

1. Thermal Gradient Tube Results

Complete profiles of iodine deposition in the thermal gradient tubes were not determined, as was done for cesium, but the selected analyses that were performed (Tables 15 and 16) indicate that iodine deposition often tended to conform qualitatively to the cesium profiles. An example of this coincidence is shown in Figure 30. This result suggests that iodine vaporized from the fuel specimens reacts with cesium deposited on the platinum surface. Equilibrium thermodynamics

TABLE 15

Iodine Deposition in the Thermal Gradient Tubes - MK-16 Fuel

Run	Nominal Conditions	Thermal Gradient Tube Section*				
		2	4	5	6	10
2	Ar, 700°C	0.065(0.18)	0.12(0.32)	0.13(0.35)	0.33(0.89)	0.10(0.27)
5	Ar, 700°C	0.079(0.21)	0.27(0.73)	0.32(0.86)	0.097(0.26)	
1	Ar, 1100°C	0.74(1.99)	5.0(13.5)	2.56(6.89)	1.94(5.22)	0.92(2.48)
7	Ar, 1100°C	0.71(1.91)	1.51(4.06)	0.99(2.66)	0.48(1.29)	0.31(0.83)
4	Air, 700°C	0.068(0.18)	0.118(0.32)	0.068(0.18)	0.169(0.45)	
6	Air, 700°C	0.097(0.26)	0.16(0.43)	0.11(0.30)	0.62(1.67)	
3	Air, 1100°C	0.043(0.12)	0.87(2.34)	1.55(4.17)	1.55(4.17)	1.27(3.42)
8	Air, 1100°C	0.108(0.29)	0.159(0.43)	0.213(0.57)	0.348(0.94)	
18	Steam, 700°C	0.23(0.62)				
20	Steam, 700°C	0.70(1.88)	0.50(1.35)	0.19(0.51)	0.59(1.59)	0.69(1.86)
21	Steam, 1100°C	No measurements.				
23	Steam, 1100°C	0.16(0.43)	0.32(0.86)	0.16(0.43)		

* The first number for each section is the I-129 activity in nCi/g of sample.

The number in parentheses is the percentage of the initial I-129 inventory.

TABLE 16

Iodine Deposition in the Thermal Gradient Tubes -- OX-2 Fuel

Run	Nominal Conditions	Thermal Gradient Tube Section *				
		1	3	5	6	9
9	Ar, 700°C	0.088(0.29)	0.053(0.17)	0.034(0.11)	0.107(0.35)	0.975(3.19)
11	Ar, 700°C	0.19(0.62)	0.08(0.26)	0.47(1.54)	0.51(1.67)	0.27(0.88)
12	Ar, 700°C	1.20(3.92)	1.46(4.77)	0.53(1.73)		
13	Ar, 1100°C	1.66(5.42)	6.62(21.6)	4.00(13.1)	0.55(1.80)	0.82(2.68)
15	Ar, 1100°C	1.87(6.11)	5.63(18.4)	0.53(1.73)	0.65(2.12)	0.52(1.70)
10	Air, 700°C	0.25(0.82)	0.21(0.69)	0.29(0.95)		
14	Air, 1100°C	1.17(3.82)	3.96(12.9)	1.83(5.98)	1.12(3.66)	0.70(2.29)
16	Air, 1100°C	3.73(12.2)	1.07(3.50)	0.26(0.85)		
17	Steam, 700°C	0.94(3.07)	0.88(2.88)	0.82(2.65)	1.37(4.48)	0.34(1.11)
19	Steam, 700°C	0.26(0.85)	1.71(5.59)	1.98(6.47)	0.81(2.65)	0.18(0.59)
22	Steam, 1100°C	0.28(0.92)	0.16(0.52)	0.23(0.76)		
24	Steam, 1100°C	No Measurements				

* The first number for each section is the I-129 activity in nCi/g of sample.
The number in parentheses is the percentage of the initial I-129 inventory.

calculations indicate that about half of the released iodine should be in the molecular state at 1100°C and a larger fraction at lower temperatures. Unlike the gas-phase reaction between cesium and iodine atoms which requires a third body to remove the excess energy released, the reaction of cesium with molecular iodine in the gas phase is readily possible. However, if a significant amount of CsI had formed in the gas phase, it would have deposited at a substantially higher temperature than that at which the iodine deposits were generally found. Consequently, it would appear that the formation of CsI in the gas phase may be too slow to deposit significant quantities of iodine at the inlet to the thermal gradient tube, although small peaks observed in that region may have arisen in this manner. Also, some deposition could have occurred over the short distance between the fuel specimen and the platinum surface, a distance of ca. 0.5 inch.

The occurrence of apparent iodine peaks downstream from the primary cesium peak suggests the possible deposition of an iodine compound which does not involve cesium. Figure 31 presents a deposition pattern of this nature. A compound such as AlI_3 , with a boiling point of 360°C, could conceivably contribute to such a peak. On the other hand, the quantity of cesium at the location of the peak is just adequate to accommodate all of the iodine as CsI. Because only cesium and iodine have been identified on the thermal gradient tubes, any interpretation involving other elements is purely speculative.

2. Activation Analysis of Charcoal and Filters

The results of the activation analysis of the first (upstream) charcoal portions from each of the 24 source term measurements as well as filters from two of the runs are presented in Table 17. In argon and in air, the fraction of iodine adsorbed on the charcoal increases appreciably with increasing fuel temperature, reflecting the greater extent of release by the fuel. In the steam/argon atmosphere on the other hand, while release from the fuel increases with temperature, iodine adsorption on the charcoal tends to decrease. It thus appears that, in steam, the higher fuel temperatures may promote the formation

TABLE 17

Iodine-129 Adsorbed on Charcoal

Nominal Conditions	MK-16 Fuel			OX-2 Fuel		
	Run	nCi/g*	%	Run	nCi/g*	%
Ar, 700°C	2	0.08	0.22	9	0.52	1.70
	5	0.02	0.05	11	0.07	0.23
				12	0.068	0.22
Ar, 1100°C	1	4.2	11.3	13	3.7	12.1
	7	0.62	1.67	15	1.71	5.59
Air, 700°C	4	0.34	0.92	10	0.57	1.86
	6	0.84	2.26			
Air, 1100°C	3	28.0(1)	75.4	14	10.1	33.0
	3	0.02(2)	0.05	16	24.8	81.0
	8	5.7	15.3			
Steam, 700°C	18	3.3	8.88	17	1.3	4.25
	20	2.0	5.38	19	1.3	4.25
	20	0.07(F)	0.19	19	0.07(F)	0.23
Steam, 1100°C	21	0.16	0.43	22	0.40	1.31
	23	0.01	0.03	24	1.54	4.15

* Activities for Run 3 are for the first and second charcoal portions in the trap.

Activities for Runs 19 and 20 followed by (F) are for the first (upstream) filter in the trap.

of an iodine compound which is less readily adsorbed on the charcoal. A probable candidate is HI, which is formed primarily by the reaction of atomic iodine with molecular hydrogen.⁽¹³⁾ The source of the H_2 is the reaction of steam with the molten fuel, more H_2 being formed at the higher temperatures.

Another atmospheric effect apparent from the results in Table 17 is that more iodine is adsorbed on the charcoal in air than in argon. The presence of oxygen tends to maintain iodine in its elemental state, thereby enhancing its passage to and adsorption by the charcoal. Similar iodine behavior was noted by Lorenz et al. in their study of fission product release from LWR fuel.⁽⁷⁾

Elemental iodine is strongly adsorbed by activated charcoal. In Run 3 in which both the first and second charcoal portions were analyzed for iodine, the first or upstream portion contained 75% of the iodine inventory and yet the adjacent downstream charcoal portion contained only 0.05% of the inventory. For this reason, only the first portions were analyzed for iodine in subsequent runs. Again, this same behavior was observed by Lorenz et al.⁽⁷⁾

Very little iodine was found on the two filters analyzed. Iodine that reaches this component of the system is very likely elemental, unless it has reacted with hydrogen to form HI. Consequently, it passes through the filters as a gas and either becomes adsorbed on the first charcoal portion immediately downstream or continues out of the system. Only if it is associated with cesium aerosol particles would it remain on the filters. Apparently, the amount of iodine combined in this manner is very small.

3. Iodine on Other Apparatus Components

As was indicated in Sections II.C.2.b and II.C.3.b, in the first eight source term runs, all involving MK-16 fuel specimens, essentially all system components were analyzed for iodine-129. The results of the analyses on the alumina furnace tubes, fittings (i.e. components which connect the furnace tube to the trap), and trap parts other than filters or charcoal may be found in Table 18. The quantity of iodine found on these system components was ordinarily small, at most only about 5% of the iodine-129 inventory. The one exception is the trap parts from Run 8. Here, the analysis was repeated to confirm the relatively large amount of iodine-129 found, about 16% of the total inventory. In every instance but this one, more than enough cesium was also present on the respective components to combine with all of the iodine found. In Run 8, elemental iodine apparently remained on the trap parts, because the amount of cesium present could only combine with about 40% of the iodine.

With the exception of iodine on certain sections of the platinum thermal gradient tubes, the filters, and the charcoal portions downstream from the first portion, the post-run iodine-129 content of the system is known and can be compared to the specimen inventory. It was found (Table 17) that only an insignificant amount of iodine was present on the two filters and one downstream charcoal portion analyzed, and it is assumed that this holds true in all instances. On those sections of the thermal gradient tubes that were not analyzed for iodine, the quantity of cesium present is known, and its assumed combination with iodine as CsI provides an estimate of the maximum amount of iodine that might be present. If another iodine compound is also present, the estimate naturally would be low but, in reality, it is probably somewhat high. The total iodine content of the system estimated in this manner is given in Table 19 for the four runs where all of the required data are available. In three of the four runs, it is seen that the estimated iodine content equals or exceeds the fuel specimen inventory, i.e. all of the iodine can be accounted for. In Run 4, the estimate is low. Based on the quantity of cesium retained

TABLE 18

Iodine Deposition on Other Apparatus Components -- MK-16 Fuel

Run	Nominal Conditions	Iodine-129 Activity (nCi/g of Sample)		
		<u>Furnace Tube</u>	<u>Fittings</u>	<u>Trap Parts</u>
2	Ar, 700°C	0.19 (0.51)*	0.037 (0.10)	0.10 (0.27)
5	Ar, 700°C	1.71 (4.60)	0.70 (1.88)	0.35 (0.94)
1	Ar, 1100°C	0.09 (0.24)	1.10 (2.96)	1.84 (4.95)
7	Ar, 1100°C	1.28 (3.45)	1.81 (4.87)	1.61 (4.33)
4	Air, 700°C	0.25 (0.67)	0.12 (0.32)	0.30 (0.81)
6	Air, 700°C	0.25 (0.67)	0.12 (0.32)	1.60 (4.31)
3	Air, 1100°C	1.58 (4.25)	1.42 (3.82)	1.05 (2.83)
8	Air, 1100°C	1.06 (2.85)	0.23 (0.62)	5.90 (15.9) 6.20 (16.7)**

* Numbers in parentheses are percentages of the initial I-129 inventory.

** Replicate analysis.

TABLE 19

Comparison of the Estimated Iodine-129 Content of
the Experimental System with the Fuel Specimen Iodine-129 Inventory

Run	Iodine-129 Content (%)					Total **
	Fuel	Thermal Gradient Tube (Analyzed)	Thermal Gradient Tube (Calculated)*	Charcoal	Other Components	
5	56.0	2.06	34.8	0.05	7.42	100.3
7	2.26	10.8	89.9	1.67	12.65	117.3
4	31.0	1.14	6.29	0.92	1.80	41.2
3	13.2	14.2	46.2	75.4	10.9	159.9

* Based on the total cesium present in those sections not analyzed for iodine.

** Percent of available iodine inventory.

by the fuel specimen in Run 4, the amount of retained iodine seems low. Also, the calculated amount of iodine remaining in the thermal gradient tube appears low in comparison to the other tabulated values. The actual reason for the low estimate in Run 4 must remain unknown, however, unless explained by additional measurements. Hopefully, future measurements will provide more accurate values for the fraction of iodine-129 released by the fuel.

E. Krypton-85 Release

The release of Kr-85 from the heated fuel specimens resulted in the measured activities listed in Table 20 and plotted against cesium release in Figure 32. While considerable scatter in the data is evident, it is likely that krypton release is total in those runs where cesium release exceeds ca. 15 or 20%. The reason for the scatter is not entirely clear, but it may well involve some aspect of instrument calibration. For example, it was found that the detector sensitivity for krypton is dependent on the flow rate of the carrier gas, the apparent yield increasing with decreasing flow. Thus, if the flow rates during the measurements and the subsequent calibrations were somewhat different, the apparent yield of krypton was probably affected. In all future source term measurements, calibration of the detector will be performed either immediately before or after the run.

With two exceptions, both involving OX-2 fuel (Runs 9 and 10), both fuel types released a major fraction, if not the entire inventory, of their krypton into all three atmospheres at both experimental temperatures. The small releases of Runs 9 and 10 are apparently real, however, because the quantity of cesium emitted in both runs was also unusually low, even though the fuel temperature followed the normal programmed path. In calculating the fractional releases given in Table 20, it was tacitly assumed that the calculated krypton-85 inventory values are correct. As was noted previously in this report (Section III.A.1.c), these values could very well be less than the

TABLE 20
Krypton-85 Release

Run	Nominal Conditions	Measured Kr-85		Calculated Kr-85
		Ci/g	%	Ci/g
<u>MK-16 Fuel</u>				
1	Ar, 1100°C	N.D.	N.D.	1.87×10^{-2}
2	Ar, 700°C	2.10×10^{-2}	112.4	1.87×10^{-2}
3	Air, 1100°C	1.60×10^{-2}	86.1	1.86×10^{-2}
4	Air, 700°C	N.D.	N.D.	1.86×10^{-2}
5	Ar, 700°C	1.88×10^{-2}	101.5	1.85×10^{-2}
6	Air, 700°C	1.43×10^{-2}	77.4	1.85×10^{-2}
7	Ar, 1100°C	1.60×10^{-2}	86.6	1.85×10^{-2}
8	Air, 1100°C	2.11×10^{-2}	114.6	1.84×10^{-2}
18	Steam, 700°C	2.23×10^{-2}	123.9	1.80×10^{-2}
20	Steam, 700°C	1.54×10^{-2}	85.6	1.80×10^{-2}
21	Steam, 1100°C	2.60×10^{-2}	144.7	1.80×10^{-2}
23	Steam, 1100°C	N.D.	N.D.	1.79×10^{-2}
<u>QX-2 Fuel</u>				
9	Ar, 700°C	2.13×10^{-3}	9.66	2.21×10^{-2}
10	Air, 700°C	1.57×10^{-3}	7.08	2.21×10^{-2}
11	Ar, 700°C	2.46×10^{-2}	111.7	2.20×10^{-2}
12	Ar, 700°C	2.37×10^{-2}	107.9	2.20×10^{-2}
13	Ar, 1100°C	2.51×10^{-2}	114.2	2.20×10^{-2}
14	Air, 1100°C	2.91×10^{-2}	132.3	2.20×10^{-2}
15	Ar, 1100°C	2.32×10^{-2}	106.1	2.19×10^{-2}
16	Air, 1100°C	2.32×10^{-2}	106.2	2.18×10^{-2}
17	Steam, 700°C	2.66×10^{-2}	122.2	2.18×10^{-2}
19	Steam, 700°C	3.60×10^{-2}	166.0	2.17×10^{-2}
22	Steam, 1100°C	1.54×10^{-2}	71.4	2.16×10^{-2}
24	Steam, 1100°C	1.51×10^{-2}	70.2	2.15×10^{-2}

actual inventory values. Accordingly, the release fractions presented may be high, perhaps accounting for at least some of the releases in excess of 100%.

An example of the temporal variation in krypton release is shown in Figure 33. The curves were drawn to coincide at the respective times in the measurement and the calibration when the NaI detector first sensed released krypton. This was done because, when krypton is injected into the carrier gas stream for a calibration measurement, the point of injection is well upstream from the location of the heated fuel specimen during a source term measurement. Consequently, additional time is required for the krypton to reach the detector location. The percentages on the ordinate of Figure 33 relate to the quantity of krypton released, not necessarily to the total inventory of krypton present in the fuel.

From the point of time when detection first occurs, the krypton released during an actual measurement achieved much of its final activity well before that injected during a calibration measurement. The injection of the 50 cm³ of krypton employed for calibration required approximately 45 seconds, and yet it required on the order of 1000 seconds for this total volume to reach the detector. The bulk of the krypton released during Run 19 (Figure 33) arrived at the detector in about half this time, but the last few percent extended the total time of detection to about 1000 seconds. On the basis of these measurements, it is not possible to decide with any accuracy at what rate krypton is released by the molten fuel. It does appear, however, that it is released in a shorter time than that required for krypton injection into the system during calibration measurements. A better comparison will be possible when a Kr-85 calibration gas with a higher activity per unit volume becomes available.

IV. Conclusions

Specimens of irradiated SRP fuels, both MK-16 U-Al alloy and OX-2 U_3O_8 -Al cermet, were exposed to temperatures and atmospheres encompassing credible accident conditions to obtain relevant source term information on these specific fuel materials.

The experimental system in which the measurements were performed was constructed of materials which do not readily react chemically with the fission product species emitted by the heated fuels. Consequently, transport of the volatile fission products was controlled primarily by atmospheric and thermal conditions and was unaffected by unwanted chemical interactions with system components.

The measured inventories of gamma-active radionuclides tended to be somewhat smaller than calculated values but agreement was nevertheless reasonable. The inventories displayed little variation along the fuel element, but those radioisotopes, Cs-134 and Eu-154, whose formation depends directly on neutron absorption by stable fission products, exhibited a variation across the fuel element. Measured initial activities of I-129 also agreed reasonably well with calculated values. Calculated values were employed for initial Kr-85 inventories.

Of the gamma-active radionuclides, only the cesium isotopes were released from the fuels in significant quantities. Release from MK-16 fuel followed a first-order process with an activation energy of ca. 13 kcal/mol. Only a small effect of the atmosphere was noted. Results for OX-2 fuel were more scattered, but it appears likely that its behavior with regard to cesium release is similar to that of MK-16 fuel. Both fuels appear to release both iodine and krypton more readily than cesium.

Cesium deposited on the thermal gradient tubes was primarily elemental, although a smaller amount of CsOH was also deposited when a steam/argon atmosphere was present. When the majority of apparatus

components were analyzed for cesium, over 80% of the initial inventory was found. The remainder is believed to have passed beyond the filter/charcoal trap as an aerosol.

The deposition of iodine in the thermal gradient tubes often tended to coincide with cesium deposition, suggesting the reaction of iodine with cesium deposits. However, small amounts of CsI formed in the gas phase may have deposited in and just upstream from the inlet to the thermal gradient tubes. Apparent iodine peaks downstream from the primary cesium peak indicate the possible deposition of an iodine compound which does not involve cesium.

Iodine released into air tends to remain elemental and, consequently, more of it is adsorbed in the charcoal trap than is iodine released into argon. In a steam/argon atmosphere, it appears that the decreased adsorption of iodine in the charcoal trap at the higher fuel temperatures may result from the enhanced formation of HI. Iodine deposition on other apparatus components is generally small, and it is not always possible to account for all of the iodine released by the fuel.

In spite of considerable scatter in the data, it appears that krypton release is total when cesium release exceeds ca. 15 to 20%, irrespective of the fuel temperature or the surrounding atmosphere.

V. Future Measurements

A second series of 24 source term measurements, complementary to the first, has been initiated. The two SRP fuels, MK-16 and OX-2, and three atmospheres, argon, air, and steam/argon, will remain the same, but the two fuel temperatures to be utilized will be intermediate to those employed in the first set of measurements. The fuel temperatures will be 850°C and 1000°C and, in conjunction with the present results, should afford a more exact knowledge of the effect of temperature on the release of volatile fission products from the two SRP fuels.

Another aspect of fission product release, the movement of aerosols, was not included in the first set of measurements. In the second set, an electron microprobe examination of aerosol particles on the first filter downstream from the thermal gradient tube will provide particle sizes and a qualitative analysis of their composition, information useful in estimating the release of fission products by an aerosol mechanism. The microprobe examinations will be carried out on filters from at least one of each pair of duplicate source term measurements.

Lastly, in the first series, only one unheated specimen of each fuel type was available for initial inventory measurements. This was of no consequence in the case of gamma-active radionuclides such as Cs-137, for which a number of fuel specimens could be measured prior to heating without compromising their fission product contents. However, when a destructive measurement was required, as in the determination of the initial quantity of I-129, it would have been highly desirable to have more than one specimen for the establishment of an accurate inventory value. This deficiency will be rectified during the second series of measurements by analyzing pieces of a few specimens that were employed in tensile tests. These specimens of each fuel type were removed from the same fuel elements as the source term specimens and thus should contain essentially identical fission product inventories.

VI. References

1. M. B. Reynolds, "Fission Gas Behavior in the Uranium-Aluminum System," Nucl. Sci. Eng. 3, 428 (1958).
2. M. J. Graber, M. Zukor, and G. W. Gibson, "Fission Gas Release from Fuel Plate Meltdown," in "Annual Progress Report on Reactor Fuels and Materials Development for FY 1966," W. C. Francis and R. A. Moen, Eds., IDO-17218, November 1966.
3. G. W. Parker, C. J. Barton, G. E. Creek, W. J. Martin, and R. A. Lorenz, "Out-of-Pile Studies of Fission-Product Release from Overheated Reactor Fuels at ORNL, 1955-1965," ORNL-3981, July 1967.
4. T. Shibata, T. Tamai, M. Hayashi, J. C. Posey, and J. L. Snelgrove, "Release of Fission Products from Irradiated Aluminide Fuel at High Temperatures," Nucl. Sci. Eng. 87, 405 (1984).
5. J. C. Posey, "Release of Fission Products from Miniature Fuel Plates at Elevated Temperature," ANL/RERTR/TM-4, November 1982.
6. R. E. Woodley and D. L. Baldwin, "A Preliminary Report on the SRP Source Term Study," HEDL-7507, September 1984.
7. 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, February 1980.
8. 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, December 1982.
9. A. W. Castleman, Jr. and I. N. Tang, "Vaporization of Fission Products from Irradiated Uranium - II. Some Observations on the Chemical Behavior of Fission Products Iodine and Cesium," J. Inorg. Nucl. Chem. 32, 1057 (1970).
10. J. L. Kelly, A. B. Reynolds, and M. E. McGown, "Temperature Dependence of Fission Product Release Rates," Nucl. Sci. Eng. 88, 184 (1984).
11. H. Albrecht and H. Wild, "Investigation of Fission Product Release by Annealing and Melting of LWR Fuel Pins in Air and Steam," Proc. Topical Meeting Reactor Safety Aspects of Fuel Behavior, Sun Valley, ID, August 2-6, 1981.
12. S. Tachimori and H. Amano, "Preliminary Study on Production of Xenon-133 from Neutron-Irradiated Uranium Metal and Oxides by Oxidation," J. Nucl. Sci. Tech. 11, 488 (1974).

13. A. W. Castleman, Jr., I. N. Tang, and H. R. Munkelwitz, "The Chemical States of Fission-Product Iodine Emanating into a High Temperature Aqueous Environment," J. Inorg. Nucl. Chem. 30, 5 (1968).

VII. Appendix

Fission Product Deposition Model

(Contributed by P. G. Whitkop, Savannah River Laboratory)

In order to characterize the chemical form of the cesium species deposited on the thermal gradient tubes, a model for fission product deposition was derived. Parametric studies of deposition profiles predicted with this model are useful in determining which parameters (position of maximum deposition, full width at half maximum or position at which deposition begins) provide the best means of fission product identification. The ability of the model to predict the deposition profile from independently measured physical parameters is also useful in the identification of fission product species.

The deposition model is derived in cylindrical coordinates, with r_0 representing the cross sectional radius and x the direction of the tube axis. The point $x=0$ represents the entrance of the tube near the heated fuel specimen, c is the gas phase concentration of fission product, c_0 the gas phase concentration at $x=0$, v the linear velocity of the carrier gas and t the time. The time rate of change of gas phase fission product concentration is then:

$$\frac{\partial c}{\partial t} = D(x) \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] - k(x) D(x) \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] + \quad (1)$$
$$\frac{\partial}{\partial x} \left[D(x) \frac{\partial c}{\partial x} \right] - v \frac{\partial c}{\partial x}$$

The first term on the right hand side of Equation 1 represents diffusion to the tube wall, while the second term represents evaporation from the wall. The latter was taken as equal to the rate of diffusion to the wall multiplied by a factor $k(x)$, which is less than one and indicates that some of the atoms or molecules that strike the wall are deposited there. The fraction of atoms or molecules striking the wall that are returned to the gas phase can be determined by means of the Clausius-Clapeyron equation, assuming thermal equilibrium between carrier gas and wall. This fraction is expressed as:

$$k = \exp [H_V/R (1/T_b - 1/T)] \quad (2)$$

where H_V is the heat of vaporization of the fission product chemical species and T_b is its boiling point. T is the temperature of the wall at the position of interest. The third term in Equation 1 represents diffusion along the length of the tube. For present purposes, it is considered negligible compared to the fourth term which represents flow down the tube.

Equation 1 is solved for the steady state with the boundary conditions:

$$c = 0 \text{ at } r = r_0 \text{ for } 0 \leq x \leq d, \text{ where } d = \text{length of tube, and}$$

$$c = c_0 \text{ at } x = 0 \text{ for } 0 \leq r \leq r_0, t > 0.$$

The average gas phase concentration of fission product is determined from the relation:

$$\bar{c} = \frac{2}{r_0^2} \int_0^{r_0} c(r,x) r dr \quad (3)$$

The amount of fission product deposited on the wall is obtained from the mass balance consideration

$$\bar{c}_{\text{wall}} = c_0 - \bar{c} \quad (4)$$

The amount of fission product deposited along the wall is then

$$\bar{c}_{\text{wall}} = c_0 \left\{ 1 - 4 \sum_{l=1}^{\infty} \left(\frac{1}{n_l^2} \right) \exp \left[- \frac{n_l^2}{r_0^2 v} \int_{x_0}^x D_e(x) dx \right] \right\} \quad (5)$$

where n_l is the l 'th root of the equation of $J_0(x) = 0$, $J_0(x)$ is a Bessel function of zero order, and $D_e(x)$ is the effective diffusion coefficient given by

$$D_e(x) = D(x) [1 - k(x)] \quad (6)$$

Sufficient accuracy for Equation 5 is obtained by truncating the series after thirty terms. The binary diffusion coefficients are calculated from standard equations derived from the kinetic theory of gases, while diffusion coefficients for multi-component mixtures are calculated according to the method of Reference A1. The fission product deposition profile is obtained by taking the first derivative of Equation 5. The derivative is evaluated by the Savitsky-Golay method (A2) and the integral by means of Simpson's rule.

The cesium deposition profile in Figure A1 (Run 8) was used to test the validity of the deposition model. The profile was selected because it consists of a single peak whose baseline is not severely skewed. These characteristics are useful for unambiguous comparison with the calculated deposition profile. Superposition of the measured and calculated curves simplifies the comparison between their peak maxima and peak widths. Because experimental peak positions varied approximately 11%, the model cannot accurately predict peak position for individual experiments. The peak position of the model is set by the boiling point of the fission product species chosen for a particular calculation.

For calculational purposes, the cesium deposit was considered to be elemental cesium and the following parameters used: $T_b = 670$ C, $H_v = 16.2$ kcal/mole, $MW = 137$ g/mole, and Van der Waals radius = 2.62 Angstroms. Interpolation of temperatures along the tube was accomplished by fitting the thermal gradient to an exponentially decaying function. A comparison between the calculated and experimental deposition profile is shown in Figure A1, with the calculated values scaled to correspond in magnitude to the experimental values. Agreement appears quite reasonable in spite of the approximations made in deriving the model.

Parametric peak shape studies using this model reveal that the position of the peak maximum and full width at half maximum are not reliable parameters on which to base fission product identification. Both parameters depend upon carrier gas flow rate and composition and

cannot be easily related to any known physical parameter. The temperature at which the leading edge of the peak intersects the corrected baseline is a measure of the fission product boiling point.

Performing this evaluation for all major peaks yields an average boiling point of 659 ± 37 degrees centigrade. This is, within experimental error, equivalent to the boiling point of elemental cesium (678°C). The error in these measurements is slightly larger than that reported in Reference A3. The fact that the profile of the major peak is well approximated by parameters for elemental cesium taken from independent measurements reported in the literature is an indication that the deposit is elemental cesium.

In one instance (Run 17, Figure 26) where the thermal gradient temperatures were somewhat lower than normal, cesium deposited in and probably upstream from the thermal gradient tube entrance and also formed a small secondary peak downstream from the point of maximum temperature. This behavior is predicted by the model and is shown in the calculated profile presented in Figure A2. Ordinarily, the higher temperatures at the thermal gradient tube inlet prevent deposition of elemental cesium until a location well into the tube is reached.

In Run 21 in which a steam-argon atmosphere was employed, the model suggests that the two peaks located at temperatures above the cesium boiling point (678°C) resulted from the deposition of CsOH (See Figure 16). One peak is located at the thermal gradient tube inlet and the other is the small peak just upstream from the primary peak, which is due to elemental cesium. The deposit at the thermal gradient tube entrance apparently resulted when gaseous CsOH encountered a temperature below its boiling point (980°C). The deposition rate was minimized at the location of the temperature maximum, but then the remaining CsOH in the gas phase deposited when the temperature again decreased to the CsOH boiling point, yielding the small peak. The deposition profile shown in Figure A3 was calculated by means of the model and is qualitatively identical to the experimental profile given in Figure 16.

Appendix References

- A1. E. J. Hellund, Phys. Rev. 57 (1940) 319.
- A2. A. Savitsky and M.J.E. Golay, Anal. Chem. 36 (1964) 1627.
- A3. A. W. Castleman, Jr. and I. N. Tang, J. Inorg. Nucl. Chem. 32 (1970) 1057.

HEDL 8512-057.7

FIGURE 1. Source Term Apparatus

HEDL 8512-057.6

FIGURE 2. Furnace Tube Details

HEDL 8512-057.5

FIGURE 3. Filter/Charcoal Trap Components

HEDL 8512-057.2

FIGURE 4. Typical Furnace Tube Temperature Distribution

FIGURE 5. Release of Cs-137 from MK-16 Fuel as a Function of Temperature

HEDL 8511-054.2

FIGURE 6. Cs-137 Deposition in the Thermal Gradient Tube -
Run 2: MK-16 Fuel in Argon

FIGURE 7. Cs-137 Deposition in the Thermal Gradient Tube -
Run 5: MK-16 Fuel in Argon

HEDL 8511-054.1

FIGURE 8. Cs-137 Deposition in the Thermal Gradient Tube -
Run 1: MK-16 Fuel in Argon

FIGURE 9. Cs-137 Deposition in the Thermal Gradient Tube -
Run 7: MK-16 Fuel in Argon

FIGURE 10. Cs-137 Deposition in the Thermal Gradient Tube -
Run 4: MK-16 Fuel in Air

FIGURE 11. Cs-137 Deposition in the Thermal Gradient Tube -
Run 6: MK-16 Fuel in Air

HEDL 8511-054.3

FIGURE 12. Cs-137 Deposition in the Thermal Gradient Tube -
Run 3: MK-16 Fuel in Air

FIGURE 13. Cs-137 Deposition in the Thermal Gradient Tube -
Run 8: MK-16 Fuel in Air

FIGURE 14. Cs-137 Deposition in the Thermal Gradient Tube -
Run 18: MK-16 Fuel in Steam/Argon

HEDL 8511-054.20

FIGURE 15. Cs-137 Deposition in the Thermal Gradient Tube -
Run 20: MK-16 Fuel in Steam/Argon

FIGURE 16. Cs-137 Deposition in the Thermal Gradient Tube -
Run-21: MK-16 Fuel in Steam/Argon

HEDL 8511-054.23

FIGURE 17. Cs-137 Deposition in the Thermal Gradient Tube -
Run 23: MK-16 Fuel in Steam/Argon

HEDL 8511-054.9

FIGURE 18. Cs-137 Deposition in the Thermal Gradient Tube -
Run 9: OX-2 Fuel in Argon

HEDL 8511-054.11

FIGURE 19. Cs-137 Deposition in the Thermal Gradient Tube -
Run 11: OX-2 Fuel in Argon

FIGURE 20. Cs-137 Deposition in the Thermal Gradient Tube -
Run 12: OX-2 Fuel in Argon

HEDL 8511-054.13

FIGURE 21. Cs-137 Deposition in the Thermal Gradient Tube -
Run 13: OX-2 Fuel in Argon

HEDL 8511-054.15

FIGURE 22. Cs-137 Deposition in the Thermal Gradient Tube -
Run 15: OX-2 Fuel in Argon

FIGURE 23. Cs-137 Deposition in the Thermal Gradient Tube -
Run 10: OX-2 Fuel in Air

FIGURE 24. Cs-137 Deposition in the Thermal Gradient Tube -
Run 14: OX-2 Fuel in Air

FIGURE 25. Cs-137 Deposition in the Thermal Gradient Tube -
Run 16: OX-2 Fuel in Air

FIGURE 26. Cs-137 Deposition in the Thermal Gradient Tube -
Run 17: OX-2 Fuel in Steam/Argon

FIGURE 27. Cs-137 Deposition in the Thermal Gradient Tube -
Run 19: OX-2 Fuel in Steam/Argon

FIGURE 28. Cs-137 Deposition in the Thermal Gradient Tube -
Run 22: OX-2 Fuel in Steam/Argon

FIGURE 29. Cs-137 Deposition in the Thermal Gradient Tube -
Run 24: OX-2 Fuel in Steam/Argon

FIGURE 30. I-129 Deposition in the Thermal Gradient Tube -
Run 19: OX-2 Fuel in Steam/Argon

HEDL 8603-079.1

FIGURE 31. I-129 Deposition in the Thermal Gradient Tube -
Run 6: MK-16 Fuel in Air

HEDL 8603-079.3

FIGURE 32. Release of Kr-85 as a Function of Cs-137 Release

FIGURE 33. Comparison of Kr-85 Release during Run 19 to Kr-85 Release during a Calibration Measurement

HEDL 8512-057.1

HEDL 8512-057.9

A-1. Comparison of Calculated and Experimental Cs-137 Deposition Profiles for Run 8

HEDL 8512-057.10

A-2. Calculated Cs-137 Deposition Profile for Run 17

HEDL 8512-057.8

A-3. Calculated Cs-137 Deposition Profile for Run 21

HEDL-7598

Distribution

DOE/RL (4)

K. R. Absher
R. D. Filbert
J. M. Hennig
K. H. Rising

Savannah River Laboratory (15)

R. G. Whitkop (15)

HEDL (16)

D. L. Baldwin	(2)	W/C-33
C. A. Hinman		W/C-95
F. E. Holt		W/C-33
M. K. Korenko		W/C-90
J. J. McCown		W/C-33
L. A. Pember		W/A-59
O. D. Slagle		W/C-31
E. T. Weber		W/C-94
R. E. Woodley	(3)	W/C-31
Central Files		W/C-110
Documentation	(3)	W/C-123